Barbara, CA) along with an external pulse/function generator (Model HP 8111 A). Tips were electrochemically etched from Pt/Ir wire (80%/20%, diameter 0.2 mm) in an aqueous solution of 2N KOH and 6N NaCN. Typically, a tunneling current of 0.5 – 1 nA and a bias voltage of 0.2 – 1 V (sample negative) were employed. The STM images were corrected for instrumental drift.

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[14] Our conclusions are based upon approximately 50 STM images for each enantiomer. None of the STM images obtained are in contradiction with the results outlined in the text.
[15] This compound forms two types of monolayer structures. Some domains are completely disordered and contain ringlike structures, individual small lamellae, etc. Other domains are composed of lamellae, but the lamellar width (20 ± 1 Å) and the intralamellar distance between two head groups (8.4 ± 0.2 Å) are much smaller than the values obtained for ISA molecules. The angle between the alkoxy chains and the lamellar axis measures approximately $43 \pm 2°$. No codeposition of solvent molecules was observed. These large deviations are most likely due to the presence of an ether functionality in the alkyl chain and the absence of a stereogenic center. In ISA these stereogenic centers force, probably because of sterical hindrance, the side chains to adapt an extended conformation that is almost perpendicular to the lamellar axis.
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Acetylenic Cyclophanes as Fullerene Precursors: Formation of $C_{60}H_6$ and C_{60} by Laser Desorption Mass Spectrometry of $C_{60}H_6(CO)_{12}$[**]

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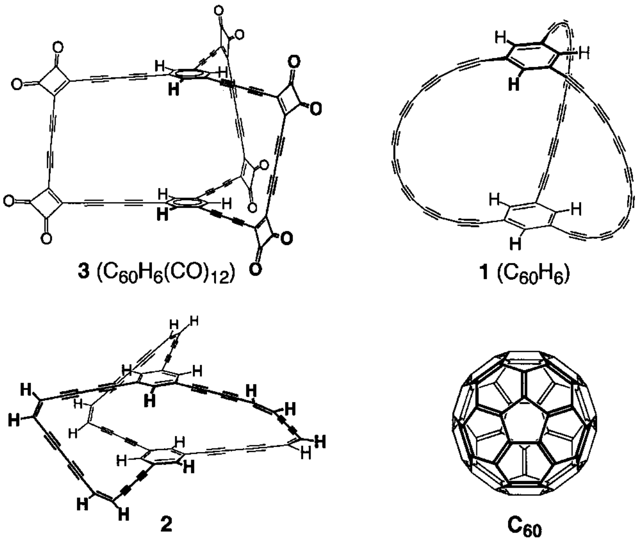
Charles L. Wilkins*

In previous reports[1] we proposed that highly unsaturated macrocyclic cyclophanes such as **1** and **2** may function as precursors of the fullerene C_{60} and its endohedral metal complexes in a process analogous to the coalescence annealing of mono- and polycycles with *sp*-hybridized carbon atoms during the gas-phase formation of fullerenes from evaporated graphite (Scheme 1).[2, 3] Formation of endohedral transition metal complexes by this route is particularly appealing in view of the exceptional physical and chemical properties of C_{60}.[4] Here we report for the first time that the acetylenic macrocycle **3** effectively leads to $C_{60}H_6$ and C_{60} ions in the gas phase in laser desorption mass spectroscopic experiments.[5]



Scheme 1. Structures of the acetylenic macrocycles **1 – 3** and of I_h-C_{60}.

When the thermochemistry of macrocycle **2** was studied by matrix assisted laser desorption ionization Fourier transform (MALDI-FT) and atmospheric pressure chemical ionization

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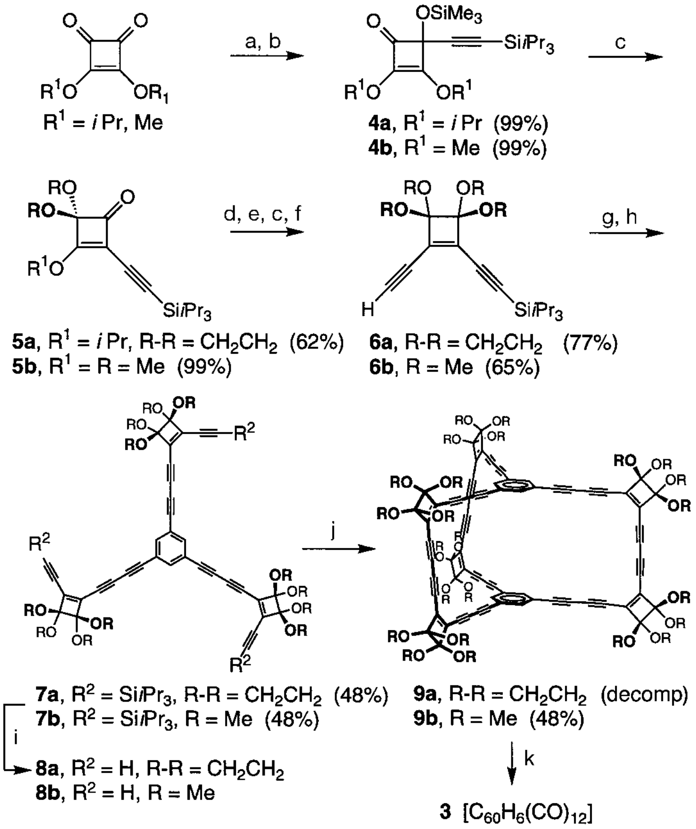
(APCI) negative-ion mass spectrometry, it was found that the parent molecular ion ($C_{60}H_{18}$) showed little propensity to lose hydrogen.[1a] This seemed somewhat surprising in view of the facile Bergman cyclization of enediynes to generate 1,4-benzene diradicals.[1b] Since effective leaving groups should facilitate the formation and consecutive rearrangement of the more highly unsaturated precursor $C_{60}H_6$ (**1**), we decided to embark on the synthesis of the cyclobutenedione **3**. The cyclobutenedione moiety was previously found to release acetylenic bonds very efficiently in the gas phase with concomitant loss of carbon monoxide, for example in the generation of the carbocycles C_{18}, C_{24}, and C_{30} in Fourier transform ion cyclotron resonance laser desorption (FT-ICR LD) mass spectroscopic experiments or in the preparative-scale synthesis of triynes and higher polyynes by flash vacuum pyrolysis.[2a–c, 6]

The preparation of cyclophane **3** proved to be much more challenging than expected. The protected ethylene spiroacetal **7a** was first prepared in analogy to the synthesis of the ethylene acetal precursors of the carbo[*n*]cycles (Scheme 2).[7] However, the deprotected alkyne **8a** could not be cyclized to **9a** under a number of oxidative coupling conditions; the attempts always resulted in rapid polymerizations. It was suggested that the homoconjugated nature of the spiroacetal moieties in **8a** (or **9a**) confers unusual reactivity upon this compound.[8] This was indeed the case: Cyclization of the dimethoxyacetal **8b** by a modified Hay procedure gave macrocycle **9b** as a stable, waxy, yellow solid in good yields (Table 1). For the preparation of acetals **8a** and **8b**, we followed a disconnection similar to the synthesis of macrocycle **2**.[1a] This required the preparation of the half-protected enediynes **6a** and **6b** in gram quantities.[6] Liebeskind's methodology was used most effectively to form siloxy ketones **4a** and **4b**, which were converted into monoacetals **5a** and **5b** in a one-pot reaction.[9] Addition of a second alkyne moiety to **5a** or **5b** and conversion into the stable cyclobutenedione bis(acetal)s **6a** and **6b** was achieved by in situ treatment of the initially formed lithium alkoxides with concentrated H_2SO_4 or 3 M HCl followed by a second acetalization step and selective removal of the trimethylsilyl protecting groups. Both **6a** and **6b** were converted into their yellow copper(I) acetylides and coupled with 1,3,5-tris(bromoethynyl)benzene[1a] in pyridine or THF to give the stable cyclization precursors **7a** and **7b**. These precursors were deprotected just prior to cyclization to the unstable terminal alkynes **8a** or **8b** by treatment with tetrabutylammonium fluoride and subsequent filtration through silica gel (Et_2O).



Scheme 2. Synthesis of the protected macrocycle **9b**. a) TIPSC≡CLi, THF, −78 °C; b) TMSCl, −78 to 25 °C; c) $TMSOCH_2CH_2OTMS$ or TMSOMe, cat. TMSOTf, THF, 55 or 25 °C; d) TMSC≡CLi, Et_2O, −78 to −45 °C; e) concd H_2SO_4, 25 °C, or 3 M HCl, −45 to 25 °C; f) K_2CO_3, MeOH; g) LiHMDS, THF, then CuBr; h) 1,3,5-tris(bromoethynyl)benzene, pyridine or THF, 25 °C; i) TBAF, THF; *j*) CuCl · TMEDA (3 equiv), ODCB, 25 °C; k) CF_3COOH, 25 °C, 4–6 h. All OCH_2CH_2O-bridged acetals are spiroannulated. TMS = $SiMe_3$; TIPS = Si*i*Pr_3; Tf = CF_3SO_2; LiHMDS = lithium hexamethyldisilazide; TBAF = tetra-*n*-butylammonium fluoride; TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenedimamine; ODCB = *o*-dichlorobenzene.

Table 1. Selected spectroscopic data for **4b**, **5b**, **7b**, **9b**, and **3**.

4b: ^1H NMR (400 MHz, $CDCl_3$): $\delta = 0.23$ (s, 9H), 1.06 (m, 21H), 3.92 (s, 3H), 4.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 1.18$, 11.12, 18.48, 58.40, 59.57, 79.56, 91.23, 102.37, 135.07, 165.46, 180.09; IR (neat): $\tilde{\nu} = 2945$, 2156, 1784, 1650 cm^{-1}; EI-HR-MS: calcd for $C_{20}H_{36}O_4Si_2$: 396.2152, found: 396.2147

5b: ^1H NMR (200 MHz, $CDCl_3$): $\delta = 1.08$ (m, 21H), 3.52 (s, 6H), 4.38 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 11.07$, 18.42, 53.15, 61.01, 91.86, 94.69, 99.39, 112.24, 184.07, 186.15; IR (neat): $\tilde{\nu} = 2945$, 2148, 1790, 1614 cm^{-1}; EI-HR-MS: calcd for $C_{18}H_{30}O_4Si$: 338.1913, found: 338.1915

7b: ^1H NMR (400 MHz, $CDCl_3$): $\delta = 1.09$ (m, 63H), 3.52 (s, 18H) 3.53 (s, 18H), 7.59 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 11.10$, 18.50, 52.00, 52.05, 73.45, 75.41, 83.68, 85.52, 97.86, 108.15, 108.44, 109.96, 122.77, 133.42, 136.50, 138.88; IR (KBr): $\tilde{\nu} = 2943$, 2207, 2130, 1600, 1576, 1463 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 235 (79200), 269 (74400), 291 (71200), 308 (70300), 318 sh (74800), 326 sh (85200), 341 (107000), 368 nm^{-1} (96400); FAB-HR-MS: calcd for $C_{75}H_{102}O_{12}Si_3$ (M^+): 1278.6679, found: 1278.6646; elemental analysis calcd for $C_{75}H_{102}O_{12}Si_3$: C 70.38, H 8.03; found: C 70.41, H 8.03

9b: ^1H NMR (400 MHz, $CDCl_3$): $\delta = 3.48$ (s, 36H), 3.50 (s, 36H), 7.55 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 52.08$, 52.09, 73.12, 75.08, 78.19, 85.22, 87.07, 87.97, 108.52, 108.54, 122.43, 136.26, 136.61, 138.00; IR (KBr): $\tilde{\nu} = 2942$, 2206, 1576, 1463, 1085 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 280 (197000), 300 sh (112000), 322 (80900), 341 (84700), 382 (70500), 414 nm^{-1} (48400); FAB-HR-MS: calcd for $C_{96}H_{78}O_{24}Na$ ($M + Na^+$): 1637.4781, found: 1637.4724

3: ^1H NMR (400 MHz, CD_2Cl_2): $\delta = 7.70$ (s); ^{13}C NMR (100 MHz, [D_8]THF): $\delta = 79.1$, 79.4, 80.7, 97.1, 102.8, 108.1, 122.8, 137.8, 175.3, 178.4, 192.0, 192.5; IR (KBr): $\tilde{\nu} = 1784$, 2136, 2198 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (rel. intensity) = 245 (100), 282 (98), 316 sh (63), 347 (59), 407 sh (56), 442 nm^{-1} sh (37)

Deprotection of the methoxyacetal moieties of macrocycle **9b** necessitated some fine-tuning. Surprisingly, we found that the cyclobutenedione macrocycle **3** was considerably less stable than the carbon oxide precursors of C_{18}, C_{24}, and

C_{30};[2a, 7] it could be characterized only with difficulty. Macrocycle **3** was prepared by dissolution of **9b** in trifluoroacetic acid. After three to six hours an orange-yellow precipitate had formed, which was redissolved in CH_2Cl_2 after evaporation of the acid. In CH_2Cl_2 **3** decomposed to a brown precipitate within one to two hours. In $[D_8]$THF a ^{13}C NMR spectrum could be obtained; it shows 12 lines in the expected range (Table 1).

We were very pleased to find that macrocycle **3**, despite its instability, undergoes clean loss of its carbonyl groups in FT-ICR LD-MS experiments (Figure 1). Fragment ions are observed with both CO_2 (10.6 μm) and N_2 lasers (337 nm), but much more intense ion signals are obtained with the former. In the negative-ion mode, prominent ions corresponding to $C_{60}H_6^{\cdot-}$ and $C_{60}^{\cdot-}$ appear at $m/z = 726$ and 720 together with their isotopic clusters, whose intensities match superbly with the theoretical ratios (Figure 1, inset). The resolution of the ICR-LD mass spectrum is excellent and reaches values of up to 7500. With authentic C_{60}/C_{70} as external standards (for calibration after LD-MS measurements of **3**), the observed masses for $^{12}C_{60}$ (719.9951), $^{12}C_{60}H_6^{\cdot-}$ (726.0380), $^{12}C_{59}{}^{13}CH_6^{\cdot-}$ (727.0416), and $^{12}C_{58}{}^{13}C_2H_6^{\cdot-}$ (728.0599) are within 8, 13, 13, and 8 ppm of their theoretical values (720.0006, 726.0475, 727.0509, and 728.0542). In the positive-ion mode (spectrum not shown), no fragment ion corresponding to $C_{60}H_6^{\cdot+}$ is observed; only the peak for $C_{60}^{\cdot+}$ and less intense peaks for the higher fullerenes $C_{62}-C_{70}$ appear. In one instance C_{2n} clusters centered around multiples of C_{60} (C_{120}, C_{180}) were also observed; they are attributed to oligomerization of the unstable precursor during laser desorption or to coalescence of $C_{60}^{\cdot+}$ or radical cationic intermediates with neutral species in the gas phase.[10] In the negative-ion spectrum, fragment ions for $C_{62}-C_{70}$ are also found, but with lower intensities (Figure 1).

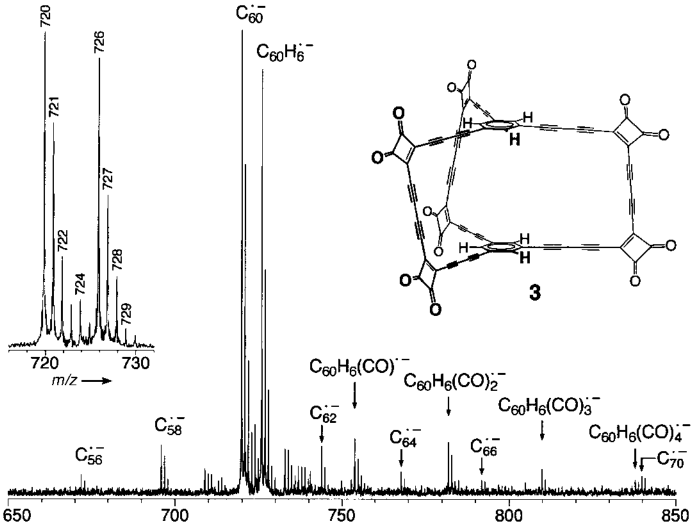


Figure 1. Negative-ion ICR-LD mass spectrum of macrocycle **3** after desorption at 10.6 μm.

The parent ion of **3** is not observed in either the positive- or negative-ion mass spectra, but its involvement is clearly implied by its fragmentation to $C_{60}H_6(CO)_4$, $C_{60}H_6(CO)_3$, $C_{60}H_6(CO)_2$, and $C_{60}H_6(CO)$ in the negative-ion spectrum (calcd: 838.0272, 810.0322, 782.0373, 754.0424; found: m/z (deviation) = 838.0096 (21 ppm), 810.0231 (11 ppm), 782.0327 (6 ppm), 754.0460 (5 ppm)). The fullerenic nature of the C_{60} ions can be unambiguously inferred from the characteristic loss of C_2 units to give peaks at $m/z = 696$ (C_{58}) and 672 (C_{56}).[11] At higher laser powers in both negative and positive modes, the degree of C_2 loss increases greatly. On the other hand, fragmentation with C_2 loss is not observed from $C_{60}H_6^{\cdot-}$, indicating that its structure is most likely non-fullerenic in nature and possibly that of **1**.

The formation of fullerene ions (e.g. C_{60}, C_{70}) from the precursors of the carbocycles C_{18}, C_{24}, and C_{30} was an important observation.[2a,b] Interestingly, this conversion was only found in the positive-ion mode. Cations of carbon clusters are generally highly excited thermally in LD-MS experiments, which tends to induce intermolecular coalescence and fragmentation reactions.[10, 11] In this study, we find concurrently that positive ions give rise to increased fragmentation and coalescence. In contrast, this is the first time that rearrangement of a precursor such as **1** to C_{60} is found to occur in the negative-ion mode under seemingly milder conditions. It is likely that the three-dimensional framework of cyclophane **1** lends itself ideally to fullerene isomerization. On the other hand, the negative ions of the carbocycles C_{18}, C_{24}, and C_{30} do not react with neutral species because of their excess charge.[2a,b, 12] In addition, the three-dimensional shape of precursors such as **1** may display better suitability for metal complexation in the potential formation of endohedral metallofullerenes.

Preliminary attemps at preparative isolations showed that the precipitates obtained from the solutions of **3** in trifluoroacetic acid or from pulsed femtosecond laser irradiation at 400 nm of a dilute solution of **3** in THF did not contain buckminsterfullerene or other apolar material. Further experiments aimed at the incorporation of metals into C_{60} and preparative-scale isolations (e.g. by flash vacuum pyrolysis) are in progress.

Experimental Section

4b: To $iPr_3SiC{\equiv}CH$ (4.53 g, 24.8 mmol) in THF (25 mL) was added 2.5 M *n*BuLi (9.90 mL, 24.8 mmol) dropwise at 0 °C. The solution was stirred for 30 min and then added to dimethyl squarate (3.35 g, 23.6 mmol) in THF (100 mL) at −78 °C dropwise with a syringe. After 1 h at −78 °C TMSCl (3.26 g, 30.0 mmol) was added dropwise, and the reaction was allowed to warm to 25 °C. Aqueous workup ($NaHCO_3$) and removal of the solvent in vacuo gave **4b** (9.36 g, 99 %) as a pale yellow oil.

5b: To **4b** (9.36 g, 23.6 mmol) in THF (10 mL) was added MeOTMS (2.60 g, 24.8 mmol) followed by TMSOTf (0.30 mL, 1.5 mmol). The reaction was initially exothermic, and the mixture was stirred for 30 min at 25 °C. Aqueous workup ($NaHCO_3$) and removal of solvent in vacuo gave a brown oil, which was purified by filtration on silica gel (Et_2O/hexanes 1/2) to give **5b** (7.99 g, 99 %) as a yellow oil.

6b: 1) To $Me_3SiC{\equiv}CH$ (0.66 mL, 0.46 g, 4.7 mmol) in Et_2O (10 mL) at 0 °C was added dropwise 2.5 M *n*BuLi (1.9 mL, 4.7 mmol). After the reaction mixture had been stirred for 30 min the temperature was lowered to −78 °C. Compound **5b** (1.50 g, 4.43 mmol) in Et_2O (20 mL) was added dropwise. The reaction mixture was stirred for 1 h at −45 °C. To the resulting red solution was added 3 M HCl (20 mL), and the reaction mixture was stirred at 25 °C for 1 h. Aqueous workup ($NaHCO_3$) and removal of the solvent in vacuo gave the desired enediyne (1.67 g, 93 %) as a brown oil, which was used directly in the next step. 2) To the enediyne (1.67 g, 4.13 mmol) in MeOTMS (2.0 mL, 1.5 g, 15 mmol) was added TMSOTf (0.10 mL, 0.12 g, 0.52 mmol). After the reaction mixture had been stirred for 48 h at 25 °C, aqueous workup ($NaHCO_3$), removal of the solvent in vacuo, and filtration through silica gel (Et_2O/hexanes 1/1) gave the desired bis(acetal) (1.38 g, 74 %) as a yellow oil. 3) To the bis(acetal) (7.34 g, 16.3 mmol) in MeOH (50 mL) was added K_2CO_3 ($\approx$100 mg). After the reaction mixture had been stirred for 15 min at 25 °C, aqueous workup, removal of the solvent in vacuo, and filtration through silica gel (Et_2O/hexanes 1/1) gave **6b** (5.80 g, 94 %) as a yellow oil. It was diluted with THF (100 mL) and used directly in the next step.

7b: To **6b** (6.28 g, 16.6 mmol) in THF (100 mL) at −78 °C was added LiHMDS, which was prepared from $(Me_3Si)_2NH$ (3.50 mL, 2.68 g, 16.6 mmol) and 2.5 M *n*BuLi (6.60 mL, 16.6 mmol) in THF (15 mL). After 30 min CuBr (2.38 g, 16.6 mmol) was added, and the mixture warmed to 0 °C. To this solution was added 1,3,5-tris(bromoethynyl)benzene[1a] (2.03 g, 5.25 mmol). After the reaction mixture had been stirred for 12 h at 25 °C, aqueous workup ($NaHCO_3$) and removal of the solvent in vacuo gave a brown oil, which was purified by chromatography on silica gel (hexanes to hexanes/Et_2O 3/1) to afford **7b** (3.25 g, 48 %) as a colorless foam.

8b: To **7b** (500 mg, 0.391 mmol) in THF (10 mL) was added five drops of H_2O followed by 1.0 M TBAF (2.0 mL, 2.0 mmol). The reaction mixture was stirred for 2 h, diluted with hexanes (50 mL), and filtered through silica gel (Et_2O). The resulting yellow fractions were concentrated to 5 mL and diluted with ODCB (400 mL) for the immediately following cyclization.

9b: To the solution of **8b** obtained above was added CuCl (119 mg, 1.20 mmol) followed by TMEDA (1.0 mL, 0.77 g, 6.6 mmol). After the reaction mixture had been stirred for 1 h under air, the solution was poured on top of a pad of silica gel and eluted with $CHCl_3$ to remove most of the ODCB. Elution with $Et_2O/CHCl_3$ (1/2) provided a yellow fraction with the desired product. The solvent was removed, and the brown oil purified by chromatography on silica gel ($Et_2O/CHCl_3$ 5/95). Removal of the solvent in vacuo gave cyclophane **9b** (150 mg, 48 %) as a yellow foam.

3: Aliquots of **9b** (5 - 30 mg) were dissolved in trifluoroacetic acid (1–3 mL). Over 3–6 h a precipitate began to form (the reaction could be monitored by ^1H NMR spectroscopy in CF_3CO_2D). After 6–12 h the trifluoroacetic acid was removed in vacuo at 25 °C in the absence of light. $[D_8]THF$ ($\approx$0.5 mL) was immediately added to the remaining orange-red solid under argon. This solution was used for ^{13}C NMR spectroscopy. For the LD-MS experiments, anhydrous CH_2Cl_2 or THF were added to dissolve the precipitate, and the solution was used immediately.

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[12] A possible mechanism for the rearrangement of $C_{60}H_6$ (**1**) to C_{60} is available from the authors upon request.

A Dendritic Macrocyclic Organic Polyradical with a Very High Spin of $S = 10$**

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Organic molecules with a very high spin possess a large number of ferromagnetically coupled unpaired electrons.[1] The design and synthesis of such molecules must overcome the challenging problem of maintaining strong through-bond interactions between multiple sites within the molecule.[1d, 2] Highly efficient generation of unpaired electrons and/or multiple pathways for ferromagnetic coupling provided organic molecules with S greater than 5.[3–6] The highest spin for an organic molecule to date, a nonacarbene with $S = 9$, was reported by Iwamura and co-workers in 1993.[3]

Polyradical **1** was designed as an "organic spin cluster".[6, 7] Because ferromagnetic coupling through 1,3-phenylene is significantly stronger than that through a 3,4′-biphenylene unit, unpaired electrons in the four dendritic branches and the macrocyclic core can effectively be lumped into component spins (S').[6] Such a ferromagnetically coupled spin pentamer with $S' = 5/2, 5/2, 5/2, 5/2, 2$ should have a ground state with $S = 12$ (Scheme 1). We describe here the synthesis and magnetic studies of polyradical **1**.

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