

News about acepentalene, cyclopentadienyl cations and other elusive aromatic and antiaromatic compounds*

Armin de Meijeret, Rainer Haag, Franz-Manfred Schüngel,
Sergei I. Kozhushkov and Ingo Emme

*Institut für Organische Chemie der Georg-August-Universität Göttingen,
Tammannstrasse 2, D-37077 Göttingen, Germany*

Abstract: Dipotassium acepentalenediide **7-K₂** is easily available in quantitative yield from triquinacene **3**, it can be trapped with a variety of electrophiles to give 4,7-dihydroacepentalene derivatives **15-R₂**. The unsubstituted **15-H₂** obtained by hydrolysis of **7-K₂** rapidly dimerizes and also undergoes other [4+2] cycloadditions with added dienes. The crystalline dilithium acepentalenediide **7-Li₂** has been obtained by metal-metal exchange on **15**-(SnMe₃)₂, characterized by a crystal structure analysis and used to prepare the novel metal complexes **19–22**. The bis(trimethylstannyl) derivative **15**-(SnMe₃)₂ also led to the first unequivocal detection of neutral acepentalene **5**. Computational results indicate that the antiaromatic cyclopentadienyl cation is significantly stabilized in its singlet state by two or more cyclopropyl groups. The readily accessible (tetracyclopropylcyclopentadienone)tricarbonyliron **32** can be alkylated and protonated to yield complexes **40-R** and **41-X** with a formal tetracyclopropylcyclopentadienyl cation ligand. Tetracyclopropylcyclopentadiene **43**, easily prepared in one step from dicyclopropylacetylene, can be deprotonated, and the resulting anion **46** chlorinated to **45** and transformed to metallocenes **44** and **47**. Butadiyne-expanded [*n*]rotanes **49** and permethylated analogues **50** are considered as potential precursors to C_{*n*} carbon clusters. Differential scanning calorimetry with evolved gas analysis has revealed that compounds **49** (*n* = 5, 6, 8) cleave off ethylene, while the permethylated analogue **50** (*n* = 6) cleaves off tetramethylethylene. If fragmentation would occur 12 times from exp[12]rotane **49** (*n* = 12), a C₆₀ carbon cluster would be left over.

THE TALE OF ACEPENTALENE AND ACEPENTALENEDIIDE

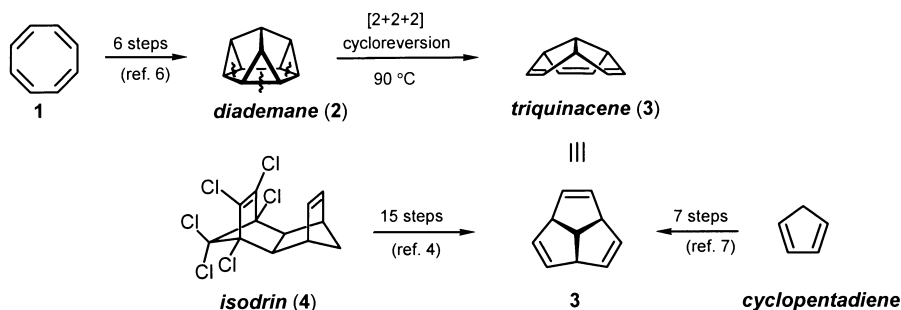
Acepentalene, the fully unsaturated periannulated triquinane hydrocarbon, has long intrigued theoreticians as well as experimentalists. With the eyes of a current day chemist, acepentalene can be considered as the smallest bowl-shaped segment of C₂₀-fullerene, as much as corannulene is the smallest bowl-shaped segment of C₆₀-fullerene [1].

According to Hückel MO theory, acepentalene (**5**) would have a triplet ground state, its central carbon atom would be highly pyramidalized ($\Sigma\text{CCC} = 332.4^\circ$) [2]. More recent density functional theory (B3LYP/6-31G*) calculations placed the singlet state of acepentalene (**5**) with C_s symmetry 2.5 kcal/mol lower than the triplet state (pyramidalization at the central carbon $\Sigma\text{CCC} = 340.5^\circ$). According to calculated nucleus independent chemical shifts (NICS) and magnetic susceptibility exaltations, acepentalene is antiaromatic, whereas the closed shell acepentalenediide (**7**) with a C_{3v}-symmetric structure (pyramidalization at the central carbon $\Sigma\text{CCC} = 350^\circ$) is aromatic by these criteria [3]. The calculated inversion barriers for the hydrocarbon **5** and its dianion **7** are 7.1 and 5.4 kcal/mol, respectively.

*Lecture presented at the 9th International Symposium on Novel Aromatic Compounds (ISNA-9), Hong Kong, China, 2–7 August 1998, pp. 209–302.

†Corresponding author: E-mail: ameijer1@uni-goettingen.de

Triquinacene (**3**) had long been suggested to be the most suitable precursor to the highly strained acepentalene (**5**) [4] and, most probably, numerous futile attempts to approach acepentalene (**5**) have remained unpublished, after triquinacene (**3**) had first been reported in 1964 by Woodward *et al.* [4]. Several other syntheses have been developed in the meantime (Scheme 1) [5–8], the most productive one being the seven-step sequence developed by Deslongchamps *et al.* [7].



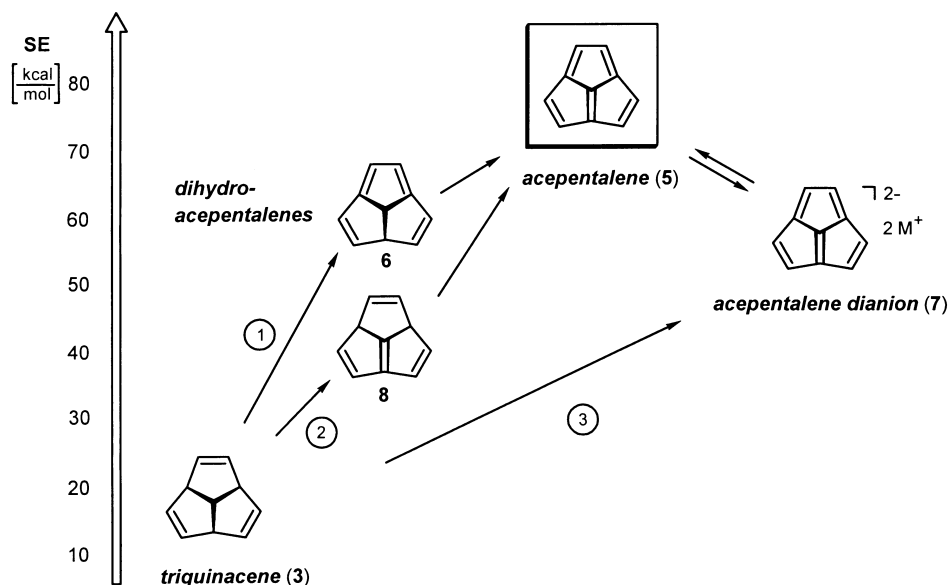
Scheme 1 Synthesis of triquinacene: an historic [4], an interesting [6], and the most productive one [7].

Triquinacene (**3**), which can be considered as a triply bridged 1,4,7-cyclononatriene, is an interesting hydrocarbon in itself. Derived from measurements of heats of hydrogenation, it had been concluded that the ground state of triquinacene (**3**) is stabilized by 4.5 kcal/mol, and had thus been termed trishomoaromatic [9]. However, theoreticians have cast some doubt on this experimental result [10,11], and a more recent accurate determination of the heat of combustion led to a heat of formation of triquinacene (**3**) which rules out any ground state stabilization [12]. Thus, triquinacene is not homoaromatic in line with earlier and recent computational results [10–12]. Despite of this, neutral trishomoaromatic systems can, in principle, exist, they require, however, a much closer proximity of the interacting centers. According to the criteria of nuclear independent chemical shifts (NICS) and magnetic susceptibility exaltations, the transition state for the rearrangement of diademane to triquinacene would be trishomoaromatic according to calculations at the B3LYP/6-311+G** level of theory [12,13]. To arrive at acepentalene (**5**) starting from triquinacene (**3**), two additional double bonds have to be introduced. Most probably, this cannot be achieved in a single step, and therefore a route via the less highly strained dihydroacepentalene (**8**) should be more favourable than the alternative one via the more highly strained isomer **6** (Scheme 2). However, the extremely strained acepentalene (**5**) [3] must be expected to be so reactive that it will probably not be isolable at room temperature, and thus success along a route to the dianion **7** via the free hydrocarbon **5** will be less probable than a direct access to **7** (Scheme 2).

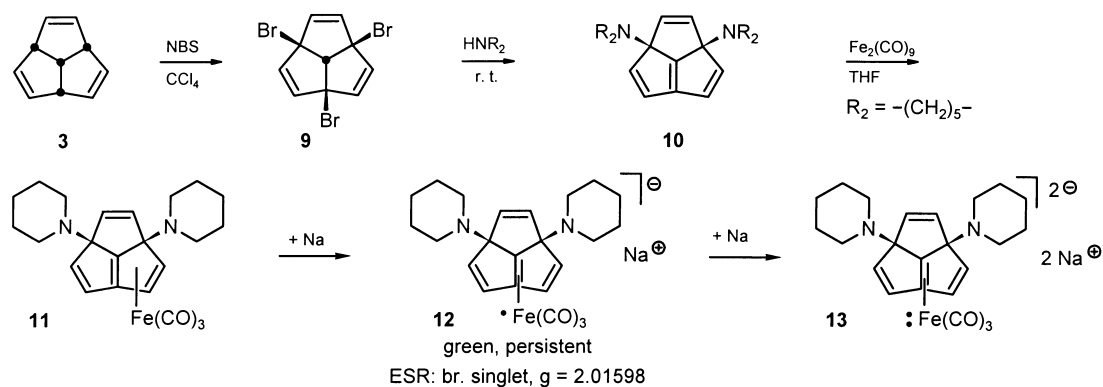
In fact, bisdialkylamino derivatives **10** of dihydroacepentalene **8** are easily accessible by treatment of tribromotriquinacene (**9**) [14], which is obtained by bromination of triquinacene (**3**) with *N*-bromosuccinimide, with secondary amines (Scheme 3) [15]. Unfortunately, however, direct reduction of these tetraenes **10** with alkali metal did not produce the acepentalenediide **7** [15], nor did an attempted Hofmann elimination succeed to give signs of an intermediate formation of acepentalene (**5**) [16]. Tricarbonyliron complexes **11** of tetraenes **10** could readily be prepared [17,18], and their reduction with sodium metal led to an interesting persistent radical anion **12** and further to an η^2 -dihydroacepentalene-tricarbonyl ferrate **13**, but not to the expected acepentalenetricarbonyliron complex [17].

The breakthrough came when triquinacene (**3**) was treated with the strongly basic system butyllithium-potassium *tert*-butoxide in the presence of TMEDA in hexane solution [19] (the so-called Lochmann–Schlosser base) which gave a virtually quantitative yield of the insoluble dipotassium acepentalenediide (Scheme 4) [20,21].

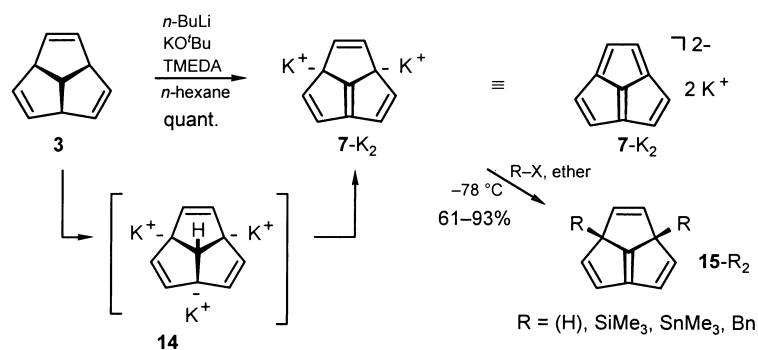
By model studies it has been shown that triquinacene (**3**) is first deprotonated at all three allylic positions to yield the trianion **14** which cleaves off the central hydrogen as a hydride ion. The dipotassium acepentalenediide (**7-K**₂) can be trapped with a number of electrophiles to yield the correspondingly 4,7-disubstituted dihydroacepentalene derivatives **15-R**₂ (Scheme 4) [20,21]. These are bowl-shaped molecules, in which the bridgehead-bridgehead double bond experiences a severe out-of-plane deformation with the two angles $\Phi_1 = 43.5^\circ$ and $\Phi_2 = 34.6^\circ$, the sum of which falls just 7.7° short of



Scheme 2 Acepentalene (5) from triquinacene (3): a case of dramatic increase in strain energy.

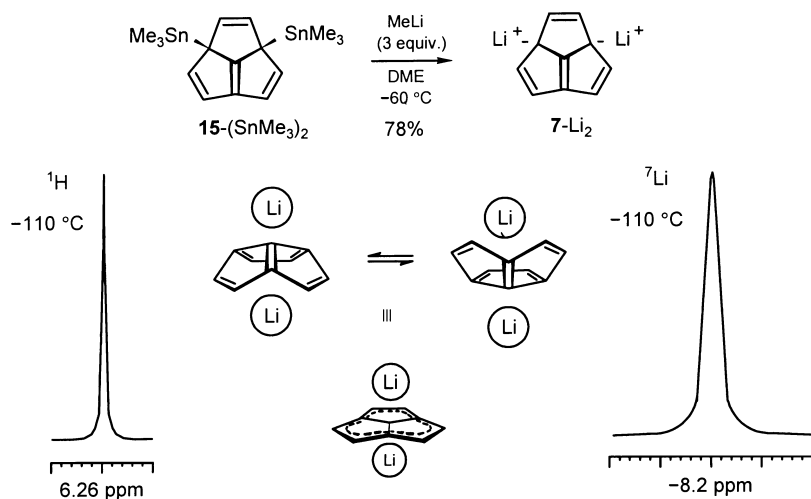


Scheme 3 Facile preparation of 4,7-bis(dialkylamino)-1(10)-bisdehydrotriquinacenes **10** and their tricarbonyliron complexes [14–18].



Scheme 4 The breakthrough: direct deprotonation and dehydrogenation of triquinacene (3) to acepentalenediide (7) [20,21].

the corresponding out-of-plane deformations in dodecahedrene [22]. Due to this severe strain, the 4,7-bis(trimethylsilyl) derivative **15**-(SiMe₃)₂ adds carboxylic acids and, under HCl catalysis, alcohols and water across its deformed bridgehead-bridgehead double bond. While the dipotassium acepentalenediide (**7**-K₂) could not be purified due to its insolubility, pure dilithium acepentalenediide (**7**-Li₂) could be obtained from the 4,7-bis(trimethylstannyl)dihydroacepentalene [**15**-(SnMe₃)₂] by metal–metal exchange with saltfree methyllithium in dimethoxyethane (DME) [23]. The ¹H- and ⁷Li-NMR spectra of the dilithium derivative **7**-Li₂ are characterized by single lines at 6.26 and –8.2 p.p.m., respectively (Scheme 5).



Scheme 5 Pure dilithium acepentalenediide **7**-Li₂ [23].

Good crystals of **7**-Li₂ could be obtained from a DME solution, and an X-ray crystal structure analysis could be performed. This disclosed a dimer in which the two bowl-shaped acepentalene dianion fragments are held together by two DME-solvated lithium cations between the convex surfaces (Fig. 1), while two lithium cations, each one solvated with a DME molecule, are placed on the outer concave surfaces [23]. This dimeric structure is different from the one proposed for the corannulene tetraanion dimer, for which a convex-concave stacking of the two bowl-shaped surfaces has been proposed with a rapid bowl to bowl inversion [24] (Fig. 1). The solid state ⁷Li-NMR spectrum of these crystals of **7**-Li₂ shows two lithium signals corresponding to the inner and outer cations. However, in solution, a single line (see Scheme 5) persists even at –110 °C. Eventually, the bis(trimethylstannyl)dihydroacepentalene **15**-(SnMe₃)₂ also led to the first unequivocal detection of neutral acepentalene (**5**) in the gas phase by an ionization-neutralization-reionization experiment in a tandem mass spectrometer [25]. From the bis(trimethylstannyl) compound **15**-(SnMe₃)₂ by chemical ionization with N₂O as the reagent gas, the radical anion of acepentalene **5**^{•–} was generated, mass selected, neutralized by collision with oxygen and reionized by a second collision with oxygen leading to the radical cation **5**^{•+} which formed the base peak in the mass spectrum. In this experiment, **5**^{•+} could only be formed from the neutral acepentalene (**5**)

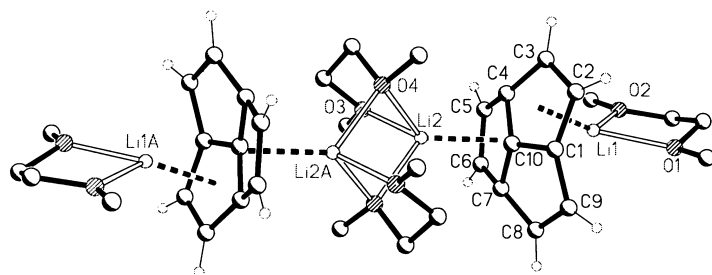
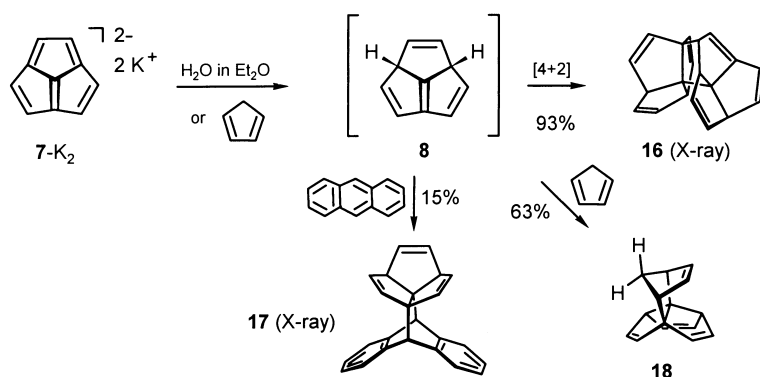


Fig. 1 Structure of dilithium acepentalenediide in the crystal [23].

which must have survived as an intermediate during the flight along the field free zone of 10 and even an extended one of 80 cm, which corresponds to a minimum lifetime of the neutral molecules **5** of 8 μ s.

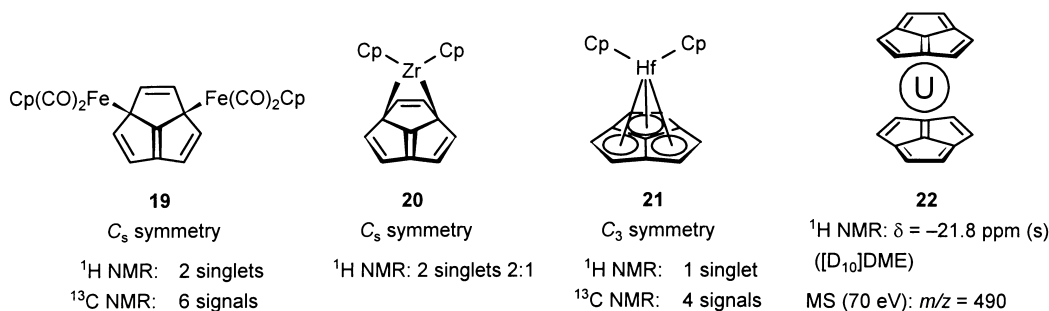
When dipotassium acepentalenediide **7-K₂** is hydrolyzed with water, dihydroacepentalene (**8**) is formed, but **8** cannot be isolated due to its rapid dimerization in a [4+2]-cycloaddition mode. The structure of the dimer **16** was finally proved by an X-ray crystal structure analysis [21]. The dipotassium salt **7-K₂** can also be protonated with cyclopentadiene which, at the same time, serves as a trapping agent to give the [4+2]-cycloadduct **18** of dihydroacepentalene (**8**) (Scheme 6).



Scheme 6 Trapping of 4,7-dihydroacepentalene (**8**) [21].

Dihydroacepentalene (**8**) can also be trapped with anthracene to give the Diels–Alder adduct **17**, the structure of which was also proved by an X-ray crystal structure analysis as well (Scheme 6) [21]. Purified dilithium acepentalenediide **7-Li₂** also served as a precursor to a number of transition metal complexes. Reaction with $\text{CpFe}(\text{CO})_2\text{I}$ in tetrahydrofuran (THF) solution gave the C_s -symmetric dinuclear complex **19**, treatment with Cp_2ZrCl_2 led to a C_s -symmetric η^2 -complex **20**, while Cp_2HfCl_2 gave a C_3 -symmetric complex **21** [26].

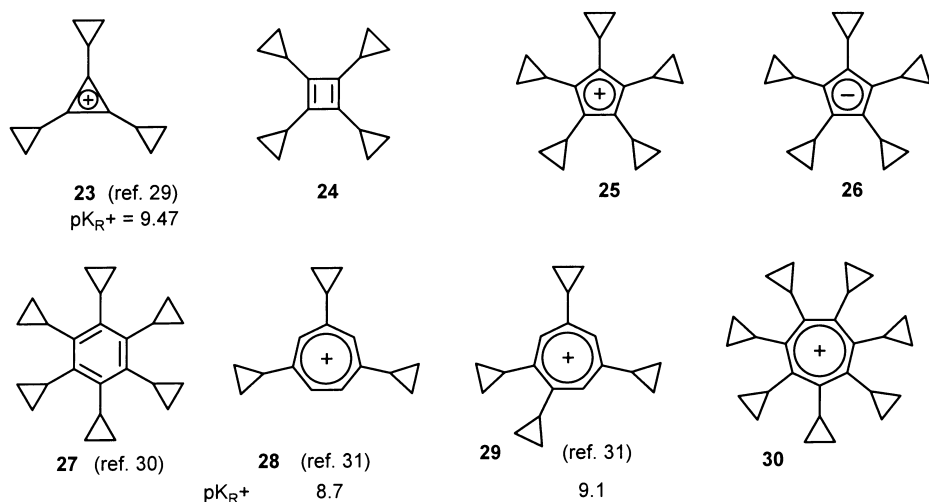
The structures of all of these complexes (Scheme 7) so far have only been derived from their ^1H - and ^{13}C -NMR spectra. Probably the most interesting observation was made upon treatment of dilithium acepentalenediide (**7-Li₂**) with uranium tetrachloride. According to its mass spectrum, the resulting complex had a molecular ion peak at $m/z = 490$ and in the ^1H -NMR spectrum a single peak at $\delta = -21.8$ p.p.m. ($[\text{D}_{10}]\text{DME}$). This is consistent with the structure **22** resembling that of the cyclooctatetraenediide-derived uranocene with a lowfield singlet at $\delta = -36.7$ ($[\text{D}_8]\text{THF}$) [27]. Attempts to crystallize the interesting acepentalenediide analogue **22** of uranocene [27] to rigorously prove its structure, have not yet been successful due to the low solubility of this complex.



Scheme 7 Isolable transition-metal complexes of acepentalenediide [26].

HOW DO CYCLOPROPYL GROUPS AFFECT AROMATIC AND ANTIAROMATIC SYSTEMS

Cyclopropyl groups are known to be particularly good donors and thus electronic stabilizers of electron deficient species [28]. Thus, tricyclopropylcyclopropenylum cation with $\text{pK}_{\text{R}^+} = 9.47$ is the most stable nonheteroatom-substituted cyclopropenylum cation known so far [29] (Scheme 8).



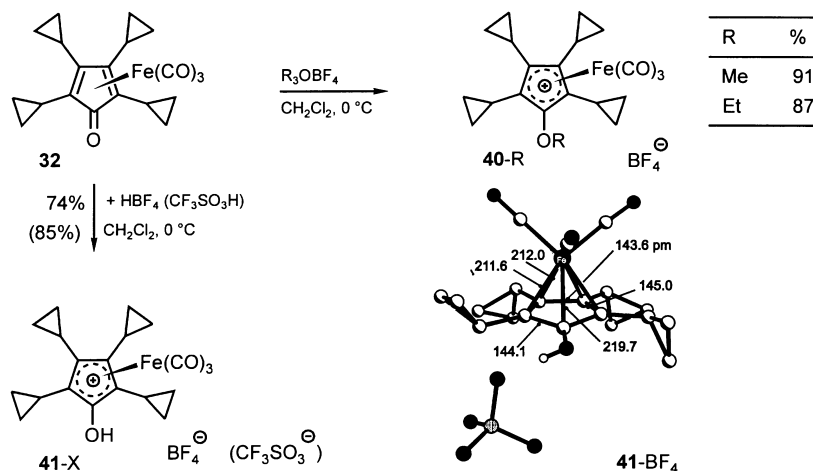
Scheme 8 Cyclopropyl-substituted aromatic and antiaromatic systems [29–31].

Up to four cyclopropyl groups have been attached to the cycloheptatrienylium cation [31] and found to stabilize it significantly with respect to the unsubstituted tropylium cation [31]. It is particularly striking that even the fourth cyclopropyl group can contribute an extra stabilization compared to the tricyclopropyl-substituted system **28** [31], since two adjacent cyclopropyl groups can no longer adopt the necessary bisected conformation, and thus it is questionable whether seven cyclopropyl groups around the cycloheptatrienyl cation as in **30** would have an additional beneficial effect. It is known that cyclopropyl groups do not stabilize neutral systems, thus hexacyclopropylbenzene (**27**) [30] is just an interesting hydrocarbon, and the yet elusive tetracyclopropylcyclobutadiene (**24**) would not be expected to be electronically stabilized with respect to the unsubstituted parent system. However, pentacyclopropylcyclopentadienyl cation (**25**) appears to be a reasonable target for synthesis, since the five cyclopropyl substituents can very well be expected to overcome the electronic destabilization of the antiaromatic cyclopentadienyl cation. With an appropriate precursor to **25** available, one would also be able to test the features of pentacyclopropylcyclopentadienide (**26**), although it would not be expected to be any more unusual than other cyclopentadienides with five substituents of comparable steric bulk [32]. The effect of five cyclopropyl substituents on the cyclopentadienyl cation as in **25** was probed by density functional theory calculations at the BLYP/3-21G level of theory [33]. The singlet is found to be stabilized over the triplet by 7.8 kcal/mol although only two cyclopropyl groups—the ones in 1,3-relationship—are found to be in a bisected orientation to contribute electron density to the central ring [33]. For pentaethylcyclopentadienyl cation, the triplet is more stable than the singlet by 5.6 kcal/mol. NICS values calculated for the centers of the five-membered rings (at HF/3-21G) also indicate that singlet pentacyclopropylcyclopentadienyl cation (**25**) is far less antiaromatic than the pentaethyl analogue (+14.8 vs. +44.3), whereas the two triplets are very similar (−3.7 vs. −3.2).

(Tetracyclopropylcyclopentadienone)tricarbonyliron (**32**) can easily be prepared by heating dicyclopropylacetylene (**31**) [34] with $Fe_3(CO)_{12}$ in a sealed tube at 180–190 °C, **32** is isolated in 23% yield along with hexacyclopropylbenzene (**27**, 18%) [30], tetracyclopropyl-*p*-benzoquinone (**34**, 3%) [33] and (tetracyclopropylcyclobutadiene)tricarbonyliron (**35**, 1%) [33] (Scheme 9).

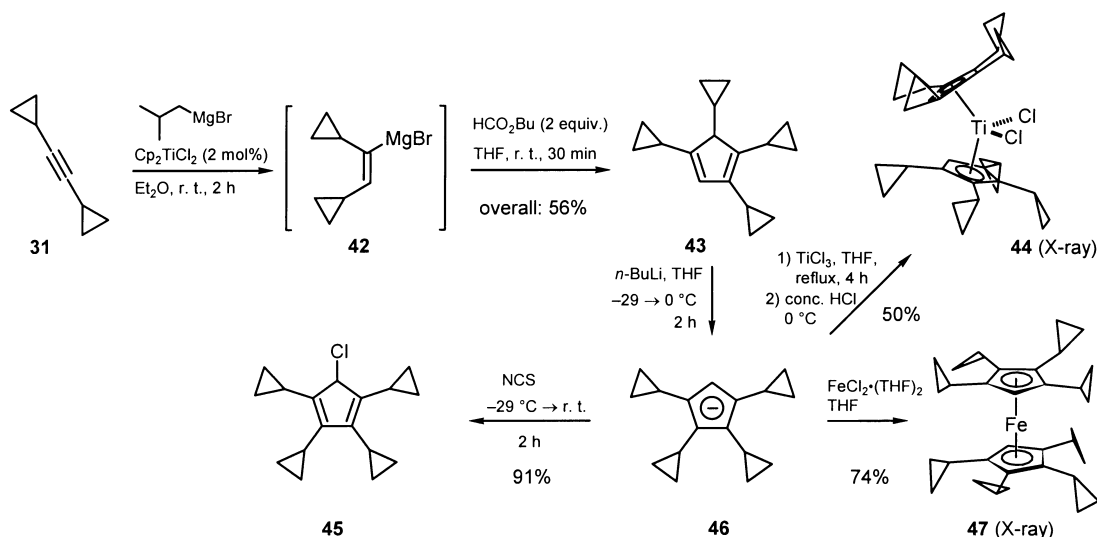
An attempted decomplexation of **32** by oxidation with Me_3NO , however, only led to the dimer **36**, the structure of which was proved by X-ray crystal structure analysis [33]. Apparently, the four cyclopropyl groups do not provide sufficient steric bulk to prevent the cyclopentadienone **33** from undergoing Diels–Alder dimerization (Scheme 9). More efficient steric protection was expected from four 1-methylcyclopropyl groups on the cyclopentadienone ring, however, the reaction of bis(1'-methylcyclopropyl)acetylene with $Fe_3(CO)_{12}$ failed to give any of the corresponding (cyclopentadienone)tricarbonyliron complex. Albeit in low yield (3%), however, the interesting [tetrakis(1'-methylcyclopropyl)cyclobutadiene]tricarbonyliron (**37**), as corroborated by an X-ray crystal structure analysis (Fig. 2) was isolated [35].

complex **32** is 19.7° [33], i.e. the carbonyl group in the unprotonated species **32** is more significantly bent away from the tricarbonyliron unit (Scheme 11).



Scheme 11 Alkylation and protonation of (tetracyclopropylcyclopentadienone)tricarbonyliron (**32**) and structure of the protonated complex **41-BF₄** in the crystal [33].

As it turned out, tetracyclopropylcyclopentadiene **43** is even more easily accessible than the cyclopentadienone complex **32**. Treatment of dicyclopropylacetylene (**31**) with isobutylmagnesium bromide in the presence of Cp_2TiCl_2 yielded a Grignard reagent **42** which reacted with butyl formate to give tetracyclopropylcyclopentadiene **43** right away in 56% overall yield (Scheme 12). In contrast to the corresponding transformation of 2-butyne [36], the tetrasubstituted open-chain penta-1,4-diene-3-ol and its allyl isomer were obtained only as by-products [35].



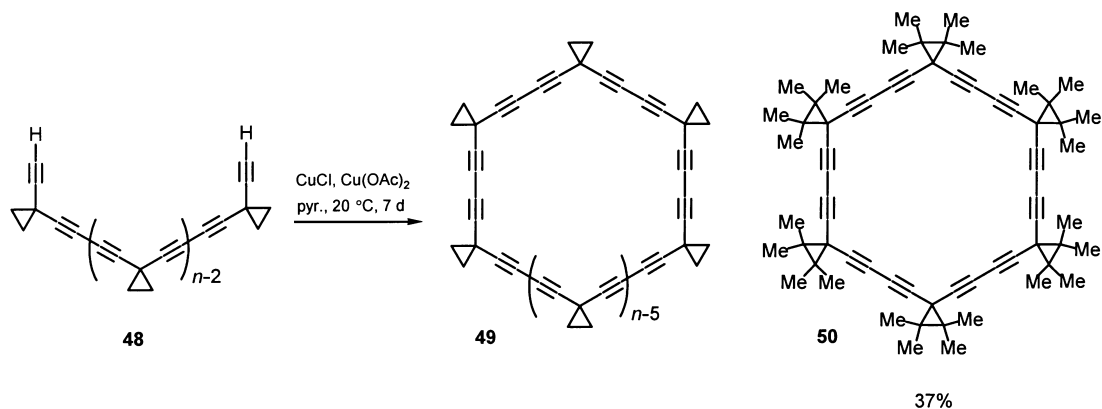
Scheme 12 Facile preparation of tetracyclopropylcyclopentadiene **43** and its metallocene complexes [35].

The cyclopentadiene **43** was deprotonated by treatment with *n*-butyllithium, and the anion **46** could be chlorinated with *N*-chlorosuccinimide to give the chlorocyclopentadiene **45** (and its 1,5-hydrogen shift isomer, ratio 7:1), a potential precursor to a tetracyclopropylcyclopentadienyl cation, in high yield (91%). The anion **46** reacted with $FeCl_2 \cdot (THF)_2$ and $TiCl_3$ to yield the octacyclopropyl-substituted ferrocene and titanocenedichloride, respectively (Scheme 12) [35]. Treatment of the chloride **45** with $AgBF_4$ in methylene chloride in the presence of methanol [37] gave two trapping products of an intermediate cation, both derived by attack of methanol on one of the cyclopropyl groups accompanied by its ring

opening. On the other hand, treatment of **45** with HBF_4 in CD_2Cl_2 led to a mixture of a C_s -symmetric *cis*- and a C_2 -symmetric *trans*-1,3,4,5-tetracyclopropylcyclopent-2-enyl cation, as corroborated by its ^1H - and ^{13}C -NMR spectra.

BUTADIYNE-EXPANDED [M]ROTANES AS POTENTIAL PRECURSORS TO C_N CARBON CLUSTERS

As has previously been demonstrated [38], completely spirocyclopropanated macrocyclic oligodiacyetylenes, so-called ‘exploding $[n]$ rotanes’, can be prepared by oxidative coupling of acyclic dehydrooligomers **48** of 1,1-diethynylcyclopropane. Depending on the acyclic precursor all ring sizes from the cyclic dehydropentamer to the cyclic dehydrotodecamer except for the cyclic dehydroundecamer have been obtained (Scheme 13 and Table 1).



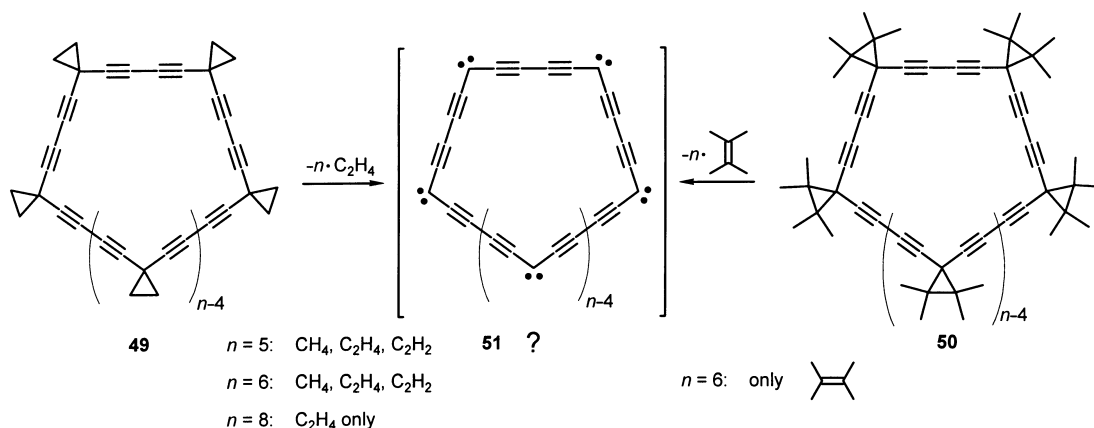
Scheme 13 Completely spirocyclopropanated macrocyclic oligodiacyetylenes (‘exploding $[n]$ rotanes’) [38,39]. For details see Table 1.

Table 1 Ring sizes of completely spirocyclopropanated macrocyclic oligodiacyetylenes **49** (‘exploding’ $[n]$ rotanes, see Scheme 13) [38]

Acyclic precursor $[n]$	Exploding $[n]$ Rotane $[n]$				
[2] + [3]	[5]: 35%	[6]: 20%	[7]: 13%	[8]: 3%	[9]: trace
[3]	[6]: 39%	[9]: 8%			
[3] + [4]	[6]: 28%	[7]: 44%	[8]: 14%	[9]: trace	
[4]	[8]: 46%	[12]: 1%			
[5]	[5]: 70%	[10]: 0.2%			

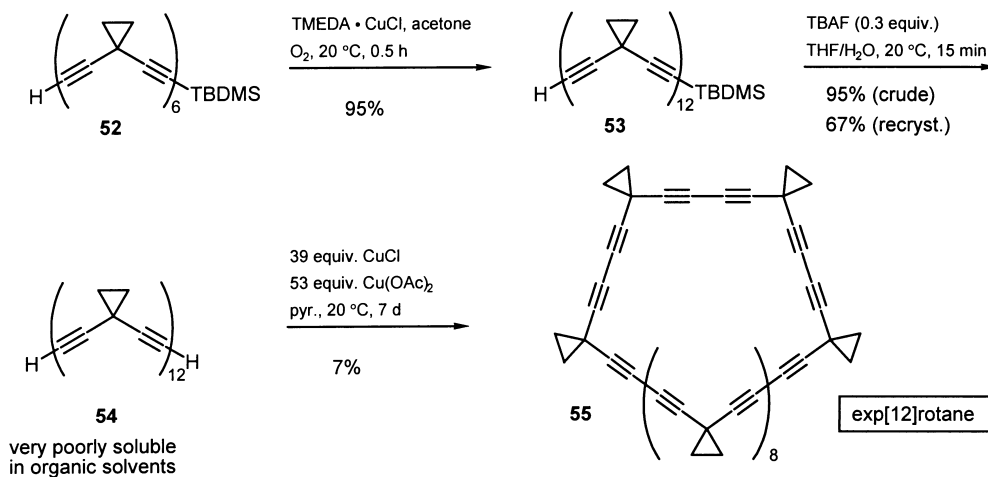
These macrocyclic oligodiacyetylenes **49** turned out to be rather fragile: When heated to above 150°C or when hit in a mortar with pestle, these compounds go up in flames and leave just a cloud of black soot. This ignition does not require any oxygen, but can be carried out under an argon atmosphere as well. The cyclic dehydrohexamer **50**, permethylated at all the spirocyclopropane units, could be prepared from the corresponding acyclic dehydrotrimer in 37% yield, and turned out to be slightly more stable than the parent compound, but does not melt without decomposition either [39] (Scheme 14).

These butadiyne-expanded $[n]$ rotanes are among the most energy-rich molecules known [40]. Their decompositions were studied by differential scanning calorimetry including analysis of evolved gases by mass spectrometry and online rapid-scan FT-IR spectroscopy. The heats of reaction are higher than that of trinitrotoluene, and the evolved gases are only methane, ethylene and acetylene from the expanded [5]- and [6]rotane. Only ethylene was evolved from the exp[8]rotane. From the permethylated exp[6]rotane, only tetramethylethylene was evolved [39]. It is uncertain, whether n -fold extrusion of ethylene from the exp $[n]$ - or tetramethylethylene from the permethylated exp $[n]$ rotanes does actually yield monocyclic



Scheme 14 Thermogravimetry on 'exploding' $[n]$ rotanes **49** and **50** with evolved gas analysis [38,39].

carbon clusters **51** with multiples of five carbon atoms. In order to have a precursor for a monocyclic C_{60} carbon cluster, the preparation of permethylated exp[12]rotane was attempted by oxidative cyclodimerization of the permethylated acyclic dehydrohexamer of 1,1-diethynylcyclopropane. However, due to the very poor solubility of this acyclic precursor in organic solvents, the oxidative cyclodimerization did not proceed at all, and only the cyclic dehydrohexamer was obtained. The solubility problems were not quite as severe with the acyclic oligomers of the parent 1,1-diethynylcyclopropane, thus the acyclic dehydrododecamer **54** could be prepared and oxidatively cyclized to the exp[12]rotane **55** [39]. It remains to be seen, whether extrusion of 12 ethylene units will be observed in a mass spectrometric experiment, and whether the possibly resulting C_{60} monocyclic carbon cluster will collapse to C_{60} fullerene (Scheme 15).



Scheme 15 Expanded [12]rotane, a precursor to a C_{60} monocycle [39]?

ACKNOWLEDGEMENT

The work presented here was supported by the Alexander von Humboldt-Stiftung, Deutsche Forschungsgemeinschaft, Fonds der Chemischen Industrie, Volkswagen-Stiftung and the companies BASF AG, Bayer AG, Chemetall GmbH, Degussa AG, Hoechst AG, and Hüls AG, through generous gifts of chemicals. The previously unpublished results presented in this context were obtained by the coauthors. Authors of previously published results are mentioned in the references. Fruitful collaborations with Prof. Larry T. Scott, Boston College (expanded $[n]$ rotanes), Prof. Christoph

Rüchardt, Universität Freiburg (heats of combustion) and Prof. Roland Boese, Universität-GH Essen (X-ray crystal structure analyses) are gratefully acknowledged. The authors are indebted to Dr B. Knieriem, Göttingen, for his careful reading of the final manuscript.

REFERENCES

- 1 R. Haag, A. de Meijere. *Topics Curr. Chem.* **196**, 135–163 (1998), and refs cited therein.
- 2 A. Streitwieser Jr. *Molecular Orbital Theory for Organic Chemists*. Wiley, New York (1961), and refs cited therein.
- 3 T. K. Zywiets, H. Jiao, P. v. R. Schleyer, A. de Meijere. *J. Org. Chem.* **63**, 3417–3422 (1998).
- 4 R. B. Woodward, T. Fukunaga, R. C. Kelly. *J. Am. Chem. Soc.* **86**, 3162–3165 (1964).
- 5 T. Jacobsen. *Acta Chem. Scand.* **21**, 2235–2246 (1967); *Chem. Sr* **2**, 121–125 (1972).
- 6 A. de Meijere, D. Kaufmann, O. Schallner. *Angew. Chem.* **83**, 404–405 (1971); *Angew. Chem. Int. Eds. Engl.* **10**, 417–418 (1971); D. Kaufmann, H.-H. Fick, O. Schallner, W. Spielmann, L.-U. Meyer, P. Gölitz, A. de Meijere. *Chem. Ber.* **116**, 587–609 (1983).
- 7 C. Mercier, P. Soucy, W. Rosen, P. Deslongchamps. *Synth. Commun.* **3**, 161–164 (1973); P. Deslongchamps, U. O. Cheriyan, Y. Lambert, J. C. Mercier, L. Ruest, R. Russo, P. Soncy. *Can. J. Chem.* **56**, 1687–1704 (1978); see also: A. K. Gupta, G. S. Lannoye, G. Kubiak, J. Schkeryantz, S. Wehrli, J. M. Cook. *J. Am. Chem. Soc.* **111**, 2169–2179 (1989).
- 8 M. J. Wyvratt, L. A. Paquette. *Tetrahedron Lett.* 2433–2436 (1974).
- 9 J. F. Liebman, L. A. Paquette, J. R. Peterson, D. W. Rogers. *J. Am. Chem. Soc.* **108**, 8267–8268 (1986).
- 10 A. Holder. *J. Comp. Chem.* **14**, 251 (1993), and refs cited therein.
- 11 M. A. Miller, J. M. Schulman, R. L. Disch. *J. Am. Chem. Soc.* **110**, 7681–7684 (1988).
- 12 S. P. Verevkin, H.-P. Beckhaus, C. Rüchardt, R. Haag, S. I. Kozhuskov, T. Zywiets, A. de Meijere, H. Jiao, P. v. R. Schleyer. *J. Am. Chem. Soc.* **120**, 11130–11135 (1998).
- 13 H. Jiao, P. v. R. Schleyer. *J. Phys. Org. Chem.* 622–655 (1998).
- 14 H. Butenschön, A. de Meijere. *Chem. Ber.* **118**, 2757–2776 (1985).
- 15 H. Butenschön, A. de Meijere. *Tetrahedron Lett.* **25**, 1693–1696 (1984); H. Butenschön, A. de Meijere. *Helv. Chim. Acta* **68**, 1658–1669 (1985).
- 16 H. Butenschön, A. de Meijere, unpublished results.
- 17 H. Butenschön, A. de Meijere. *Angew. Chem.* **96**, 722–723 (1984); *Angew. Chem. Int. Eds. Engl.* **23**, 707–708 (1984); H. Butenschön, A. de Meijere. *Tetrahedron* **42**, 1721–1729 (1986).
- 18 (η^5 -Cyclopentadienyl)(η^4 -4,7-dihydroacepentalene)cobalt (i) complexes have also been prepared. cf. G. Schröder, H. Butenschön, R. Boese, T. Lendvai, A. de Meijere. *Chem. Ber.* **124**, 2423–2427 (1991).
- 19 L. Lochmann, J. Pospisil, D. Lim. *Tetrahedron Lett.* 257–260 (1966); M. Schlosser, S. Strunk. *Tetrahedron Lett.* **25**, 741–744 (1984).
- 20 T. Lendvai, T. Friedl, H. Butenschön, T. Clark, A. de Meijere. *Angew. Chem.* **98**, 734–735 (1986); *Angew. Chem. Int. Eds. Engl.* **25**, 719–720 (1986).
- 21 R. Haag, F.-M. Schüngel, B. Ohlhorst, T. Lendvai, H. Butenschön, T. Clark, M. Noltemeyer, T. Haumann, R. Boese, A. de Meijere. *Chem. Eur. J.* **4**, 1192–1200 (1998).
- 22 J.-P. Melder, R. Pinkos, H. Fritz, H. Prinzbach. *Angew. Chem.* **101**, 319–322 (1989); *Angew. Chem. Int. Eds. Engl.* **28**, 310–313 (1989).
- 23 R. Haag, R. Fleischer, D. Stalke, A. de Meijere. *Angew. Chem.* **107**, 1642–1644 (1995); *Angew. Chem. Int. Eds. Engl.* **34**, 1492–1495 (1995).
- 24 A. Ayalon, A. Sygula, P.-C. Cheng, M. Rabinovitz, P. W. Rabideau, L. T. Scott. *Science* **265**, 1065–1067 (1994).
- 25 R. Haag, D. Schröder, T. Zywiets, H. Jiao, H. Schwarz, P. v. R. Schleyer, A. de Meijere. *Angew. Chem.* **108**, 1413–1415 (1996); *Angew. Chem. Int. Eds. Engl.* **35**, 1317–1319 (1996).
- 26 R. Haag, F.-M. Schüngel, P. Poremba, F. T. Edelmann, A. de Meijere, unpublished results.
- 27 A. Streitwieser Jr, S. A. Kinsley. In *Fundamental and Technological Aspects of Organo-F-Element Chemistry* (T. J. Marks, I. L. Fragala, eds), Vol. 155, pp. 77–114. D. Reidel Publishing Company, Dordrecht; NATO ASI Series C (1985).

- 28 Reviews see: A. de Meijere. *Angew. Chem.* **91**, 867–884 (1979); *Angew. Chem. Int. Eds. Engl.* **18**, 809–826 (1979); K. B. Wiberg. In *Houben-Weyl, Methods of Organic Chemistry* (A. de Meijere, ed.), Vol. E 17a, pp. 1–27. Thieme, Stuttgart (1997).
- 29 K. Komatsu, I. Tomioka, K. Okamoto. *Tetrahedron Lett.* **21**, 947–950 (1980); R. A. Moss, R. C. Munjal. *Tetrahedron Lett.* **21**, 1221–1224 (1980).
- 30 V. Usieli, R. Victor, S. Sarel. *Tetrahedron Lett.* **17**, 2705–2706 (1976); X-ray crystal structure of **27**: I. Bar, J. Bernstein, A. Christensen. *Tetrahedron* **33**, 3177–3180 (1977).
- 31 K. Komatsu, K. Takeuchi, M. Arima, Y. Waki, S. Shirai, K. Okamoto. *Bull. Chem. Soc. Jpn.* **55**, 3257–3261 (1982).
- 32 For recent reviews on sterically congested cyclopentadienyl ligands and their complexes see: J. Okuda. *Top. Curr. Chem.* **160**, 97 (1992); C. Janiak, H. Schumann. *Adv. Organomet. Chem.* **33**, 291 (1991).
- 33 I. Emme, T. Labahn, G. M. Sheldrick, P. R. Schreiner, A. de Meijere, unpublished results.
- 34 H.-C. Militzer, S. Schömenauer, C. Otte, C. Puls, J. Hain, S. Bräse, A. de Meijere. *Synthesis* 998–1012 (1993).
- 35 I. Emme, T. Labahn, G. M. Sheldrick, A. de Meijere, unpublished results.
- 36 C. M. Garner, M. E. Prince. *Tetrahedron Lett.* **35**, 2463–2464 (1994).
- 37 In analogy to a trapping experiment with methanol of the pentamethylcyclopentadienyl cation generated from the corresponding bromide and silver tetrafluoroborate. cf. P. Jutzi, A. Mix. *Chem. Ber.* **125**, 951–954 (1992).
- 38 A. de Meijere, S. I. Kozhushkov, T. Haumann, R. Boese, C. Puls, M. J. Cooney, L. T. Scott. *Chem. Eur. J.* **1**, 124–131 (1995).
- 39 A. de Meijere, S. I. Kozhushkov, S. Löbbecke, A. Pfeil, L. T. Scott, unpublished results.
- 40 S. Löbbecke, A. Pfeil. *Thermochim. Acta* **323**, 83–91 (1998).