Chem. Rev. **2006,** *106,* 5317−5343 **5317**

From Macrocyclic Oligo-acetylenes to Aromatic Ring *Carbo*-mers

Valerie Maraval and Remi Chauvin*

Laboratoire de Chimie de Coordination du CNRS, UPR 8241, 205 Route de Narbonne 31 077, Toulouse Cedex 4, France

Received May 8, 2006

Contents

1. Introduction

The acetylene unit has long been regarded as just a useful functional tool in *synthetic* organic chemistry. Over the last 30 years however, it also gained the status of a peculiar structural element in *physical* organic chemistry, making polyacetylene chemistry a well identified field of research.[1] Rings inside molecules are "topological functions" and also essential features from both these points of view.[2] In synthetic organic chemistry, the selectivity of ring formation processes is indeed crucial and often limiting. In physical organic chemistry, rings impose rigidity and, if unsaturated, enhance or prevent electron π-conjugation, and allow for a specific orbital property of prevailing importance in the assessment of electronic properties, namely aromaticity.[3]

Cyclic oligo-acetylenes lie at the crossing of the above two concerns. These molecules are not only aesthetically attractive in Lewis' graphical language[4] but also chemically intriguing: the constrained vicinity of pseudocyclindrical clouds of high energy π electrons is indeed a priori expected to be rather instable. Even in biological conditions however, Nature succeeded to overcome borderline instability by fine-tuning the environment of the cyclo-enediyne anticancer pharmacophores.[5] In laboratory conditions and in the chemical literature, the proximity−stability tradeoff in cyclic oligo-acetylenes called upon the consideration of specific weaker orbital properties beyond aromaticity, namely transannular $\pi-\pi$ interactions and homoaromaticity.[6]

The combined cyclic acetylenic and oligo-acetylenic characters are however poorly restrictive for defining a reasonable nonredundant scope of review. Many recent reviews indeed dealt with macrocyclic acetylenic scaffolds with various nonacetylenic linking bricks, such as ethylene[1,7] and arylene units,[8] allowing for possible extended aromaticity.[9] As a third criterion, the scope might be restricted to *carbo*-meric molecules,[10] where all non-C_{sp} atoms are bound to C_{sp} atoms *only* and all C_{sp} atoms are bound to another one *at least*. To put it in a larger context however, a more general typology of cyclic oligo-acetylenes is first proposed. As a fourth scope limitation, this review will mainly—but not only—focus on experimental aspects: recent comprehensive reviews on theoretical aspects of oligo-acetylenes are indeed available.[11]

2. Typology of Cyclic Oligo-acetylenes

Owing to the rod divalent character of the acetylene C2 unit, any oligo-acetylene can be formally reduced to a smaller molecule by contraction of the $\text{A}\underline{:::}\text{CC}\underline{:::}\text{B}$ units to direct $\text{A}\underline{:::}\text{B}$ bonds. Apart from cyclo[*n*]carbons, any ring containing $C_{sp}-C_{sp}$ bonds can be associated to a parent ring defined by the extrusion of all the $C_{sp}-C_{sp}$ bonds. In most cases, the parent ring is unknown just because it has not be made (but it could be) or because it might be intrinsically instable. These two situations can be illustrated by cyclic even models of the long sought carbyne allotrope (infinite all-sp carbon chain), namely $\overline{\text{X}-(\text{C}\equiv\text{C})_n-\text{X}}$ molecules

---

* To whom correspondence should be addressed. Phone: 33 (0)5 61 33 31 13. Fax: 33 (0)5 61 55 30 03. E-mail: chauvin@lcc-toulouse.fr.

10.1021/cr050964e CCC: $59.00

Valerie Maraval graduated from the Univesrity Paul Sabatier (Toulouse, France) in 1997. She then prepared a thesis in the field of dendrimer chemistry under the supervision of Jean-Pierre Majoral, and she received her Ph.D. in 2000 (Toulouse). In 2001, she worked as a post-doctoral fellow with Bernard Meunier in collaboration with the Aventis company. She then came back to J.-P. Majoral's group as a CNRS Engineer for two years. In 2005, she joined the group of R. Chauvin as a research fellow, where she is developing the chemistry of *carbo*-meric molecules using novel approaches, in particular organometallic catalysis (alkyne metathesis). She is also involved in a project on natural products. Her expertise extends from phosphorus chemistry to dendrimer and polymer chemistry, sol-gel chemistry, homogeneous catalysis, and general organic and organometallic synthesis.

Remi Chauvin received his Ph.D. in 1988 under the supervision of Henri Kagan in Orsay (France). He pursued as a post-doctoral fellowship with K. B. Sharpless at MIT (MA, USA) and then with Andrea Vasella in Zürich (Switzerland). From 1990 to 1993, he worked at the Roussel Uclaf Company in Romainville (France). He finally came back to academic research at the CNRS by joining Jean-Jacques Brunet's group at the Laboratoire de Chimie de Coordination in Toulouse. In September 1998, he was appointed as a Professor at the Université Paul Sabatier and set up his own group. Today, his research activities focus on four aspects of molecular chemistry: (i) theoretical modeling (in collaboration with his colleague, Christine Lepetit)—analysis of electron delocalization (aromaticity, ELF, NLO properties, ...); (ii) organic synthesis—polyacetylenic chemistry (ring *carbo*-mers, OPEs, natural acetylenes, ...); (iii) organometallic chemistry and catalysis—functional alkyne ligands (Co, Ru), asymmetric synthesis of alkynyl carbinols (Zn), alkyne metathesis (Mo); and (iv) phosphorus chemistry for asymmetric catalysis—chiral phosphonium ylide ligand (Rh, Pd).

where the carbyne fragment is segregated from a bridging fatty chain by bulky organic or organometallic caps X.[12] Hirsh et al. recently described macrocyclic models **1a** (up to 62-membered, $n = 2-8$) where the caps are aromatic units derived from 4-*tert*-butylsalicylaldehyde.[13] Shortly before, Gladysz et al. described platina-bicycles **2a** where the sp-chain ($n = 3, 4$) is "insulated" inside a double helical arrangement of sufficiently long sp^3-chains ($\geq$C14).[14] While the parent biphenyls **1b** could surely be synthesized, the parent binuclear complexes **2b** might be more problematic to prepare (Figure 1).[15] These examples thus provide a basis for distinguishing two kinds of macrocyclic oligo-acetylenes: that is, the occurrence of a triple bond either stabilizes or destabilizes the topology of the parent acetylene-extruded molecule. Among conjugated macrocyclic oligo-acetylenes, the stabilizing effect can be illustrated by Diederich's radiaannulenes, namely hybrids between dehydroannulenes and expanded radialenes (see section 3.3.2).[16] Peralkynylated [4]radiaannulenes **3a** (Figure 2 were thus prepared by acetylenic scaffolding from TEE derivatives and were shown to possess a strong electron-accepting power. Their acetylene-extruded parents **3b** are derivatives of dimethylenecyclobutene, the second most stable monocyclic isomer of benzene (after fulvene).[17] This molecule (where the endocyclic bond angles at the C_{sp^2} corners are in the range $90 \pm 3° \ll 120°$) is however more strained than [4]radiaannulenes (where $C_{sp}-C_{sp^2}-C_{sp} \approx 111°$ and $C_{sp}-C_{sp^2}-C_{sp^2} \approx 120°$). Moreover, to the best of our knowledge, no peralkynyl derivatives of dimethylenecyclobutene are known. Bicyclic radiaannulenes **4a** were also described and can be associated with the parent tetramethylene–bicyclobutene core **4b**, which is poorly referenced.[18]

Beyond the above examples, systematic co-listing of cyclic oligo-acetylenes and their respective parent acetylene-extruded molecules, whenever they are known, would be a tedious task, devoted to a classification purpose only: the structural relationship between them is indeed finally quite poor.

A much stronger relationship exists between *carbo$_k$*-mers (where the parent molecule corersponds to $k = 0$): basic features recognized to control their physical properties are indeed preserved at a first level approximation (homogeneous connectivity, bonding shape, symmetry, π-resonance, configurations of chirality elements, ...). In the strict sense, a *carbo*-mer is obtained by the inserstion of C2 units into *all* the bonds of a given parent molecule.[10] Partial *carbo*-mers can however be defined, in which the C2 connectivity is selectively applied over a natural part of the Lewis architecture. The "terminal *carbo*-mer" is thus obtained by C2 insertion into all the terminal bonds, while a "ring *carbo*-mer" is obtained by C2 insertion into all the bonds of a ring (and all possible rings annelated to it).

Likewise, "peripheral *carbo*-mers" are obtained by C2 insertion into all (non-endocyclic) bonds attached to a ring (and all possible rings annelated to it). They can be first exemplified by the long known hexaethynylbenzene[19] and other hexaalkynyl benzenes **5**[20] or by the peralkynylcyclobutadiene and cyclopentadienyl ligands of complexes **6** and **7** (Figure 3).[21] Polycyclic peripheral *carbo*-mers are represented by tetraalkynylthiafulvalenes **8**,[22] hexaalkynylquinoxaline **9**, or octaalkynylphenazine **10**.[23] By extension, hexaalkynyl[3]radialene **11** is a peripheral *carbo*-mer of the [3]radialene core.[24]

As a very general definition, ring *carbo$_k$*-mers contain a ring of size $n(2k + 1)$ of the type $\overline{(C\therefore C)_k\therefore X^1\therefore(C\therefore C)_k\therefore X^2...(C\therefore C)_k\therefore X^n}$, where the X^i's are the vertex atoms of the sp^{m_i} hybridization state with $m_i - 1$ peripheral substituents or lone pairs. The typology of ring *carbo*-mers can be refined by including the first peripheral atoms bound to the vertex atoms (the X^i's are therefore one-atom centered

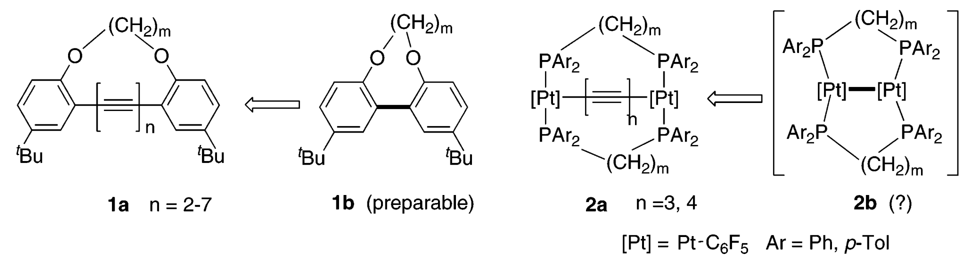


Figure 1. Two kinds of macrocyclic oligo-acetylenes serving as models of the carbyne allotrope: the acetylene-extruded parent molecules surely exist or are more questionable.

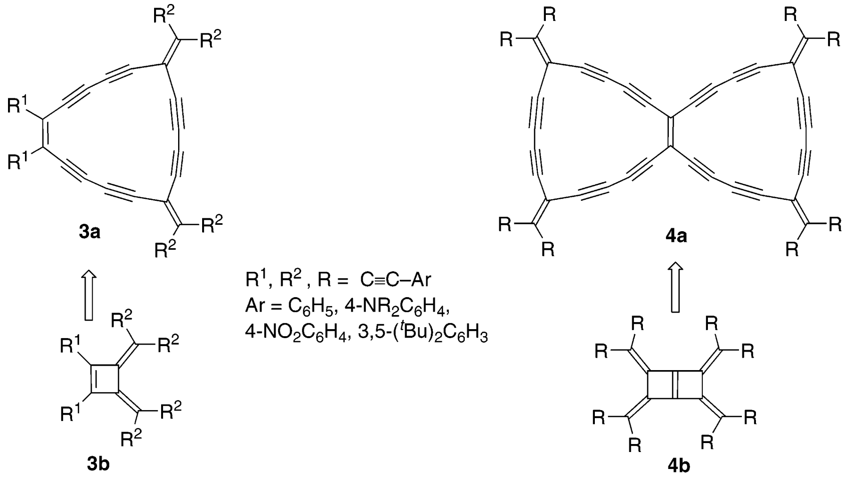


Figure 2.

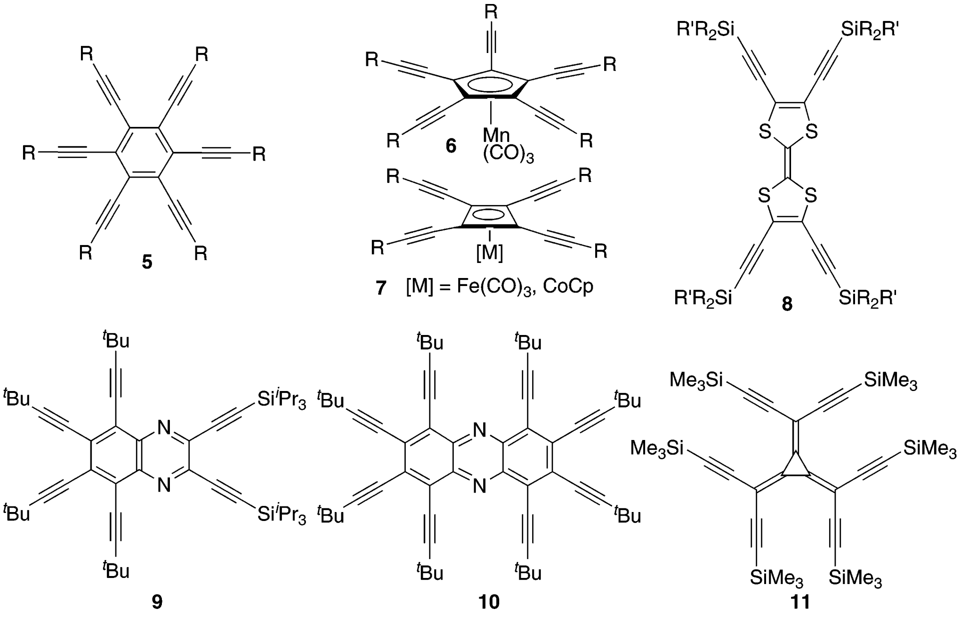


Figure 3. Peripheral *carbo*-mers of monocyclic and polycyclic molecules.

divalent groups such as :CR_2, :CH(OH), :C=CR_2, :C=O, :SiR_2, :P–R, :P(O)R, etc.).

This definition can be further extended by considering related "partial ring *carbo*-mers" with still a regular alternance of C_{2k} units but with a lower frequency: a ring "*p*-*carbo*$_k$-mer" might thus be defined by the existence of a parent ring $\overline{X^1-X^2-...-X^n}$ from which it can be deduced by systematic insertion of C_{2k} units into *one out of p* successive bonds.[25] In other words, in ring *p*-*carbo*-mers, successive C_{2k} units are separated by *p* atoms all around the ring. Obvious formal arithmetic properties follow from this definition,[26] and in particular, a cyclic molecule possesses at most *p* ring *p*-*carbo*$_k$-mers depending on the ring size and on the symmetry of substitution.

This formal definition drops the shape- and resonance-preserving properties of the full *carbo*-mers ($p = 1$)[10] and is surely a less informative typology. Nevertheless, it is actually a generalization of Dale's typology of cyclodiynes ($n = 2p$, $k = 1$) and cyclotetraynes ($n = 2p$, $k = 2$), which proved relevant in conformational analysis.[27] It also comes back to Sworski's proposition for the expansion of the benzene molecule.[28] Given a Kékulè form of benzene, insertion of

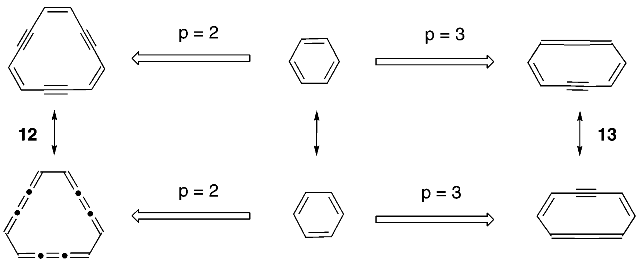


Figure 4. Sworski's expansions of benzene to 2-*carbo*-benzene (left) and 3-*carbo*-benzene (right).[28]

three C_2 units into the alternating double or triple bonds is compatible with VSEPR bond angles and results in two resonance forms of hexadehydro[12]annulene **12** (Figure 4).[29] Since these forms are nonequivalent,[30] resonance is thus *qualitatively* preserved, but not quantitatively, as is a priori possible upon complete ring *carbo*-merization (see section 3.5.1).[10] Upon similar insertion of only two C2 units into facing bonds, Sworski devised 1,2,6,7-tetradehydro[10]-annulene **13**, long before it was observed by Myers et al.[31] and proven to possess equivalent resonance forms.[32] According to the proposed definition, Sworski's dehydroannulenes **12** and **13** are therefore the 2-*carbo*-mer and 3-*carbo*-mer of benzene, respectively.[33]

Generalization of the Sworski-type insertions to any ring size is illustrated in Figure 5. The degenerate structures of the first line ($n/p = 1$) are represented by cyclomonoynes and cyclo-1,2,3-trienes, with the smallest stable representatives corresponding to $n = 8$ (ref 34) and $n = 9$,[35] respectively.

The *p-carbo*$_k$-mer relationship has been set out above from a synthetic standpoint. From the converse analytical standpoint, a given *N*-membered cyclyne is at least a first-line ring $[N - 2]$-*carbo*-mer (Figure 5). Beyond this trivial consideration, as soon as the cyclyne contains more than one $C_{sp}\underline{:::}C_{sp}$ bond, it should be referred to as a *p-carbo*$_k$-mer of the *smallest parent ring*, i.e., corresponding to the smallest possible *p* values and the largest possible *k* values.

All cycloacetylenics can thus be regarded as more or less degenerate ring *p-carbo*$_k$-mers. A restricted class corresponding to our original concern (first tackled by complete extrusion of the C_2 units: see above) is however marked off when the parent ring no longer contains any $C_{sp}\underline{:::}C_{sp}$ bond. Indeed, unsymmetrical cycloacetylenics may be devoid of any periodical occurrence of the $C_{sp}-C_{sp}$ bonds around the ring unless triple bonds are kept in the parent ring. This can be illustrated by a side result of Hirsch' synthesis of alternate expanded pericyclynes (see section 3.1.4).[36] Oxidative coupling of the bisterminal C_{12} pentayne **14** could produce two C24 cyclodecaynes of different optimal symmetry (Figure 6). The less symmetrical (ideally C_{2v}) isomer **15a** (which was assigned to the product on the basis of UV−vis spectroscopy) is a ring 4-*carbo*-mer of a C16 cyclohexayne **15b**. The most symmetrical (ideally D_{2h}) isomer **16a** is a ring 2-*carbo*$_2$-mer of the C_8 1,5-octadiyne **16b**.[37] Both the parent rings preserve at least the ideal symmetry (this is a general feature of the *p-carbo*$_k$-mer relationship) but are cyclynes still: cyclynes **15a** and **16b** cannot be reduced further by single *p-carbo*$_k$-merization. Another example will be later evoked (**83a**, in section 4.1.1), but this situation will otherwise not be considered in the following.

Even for a classification purpose, the *p-carbo*-mer relationship is more relevant at low *p* values. The next section (3) details the *carbo*-mer ideal case ($p = 1$). The last section (4) presents selected examples of *p-carbo*$_k$-mers of noncyclynic parent structures.

3. Ring *Carbo*-mers ($p = 1$)

3.1. Pericyclynes and Expanded Pericyclynes (*Carbo*$_k$-cycloalkanes, $k = 1, 2$)

Pericyclynes are ring *carbo*-mers of cycloalkanes,[10] but the term "pericyclyne" was previously coined by Scott et al. in 1983 as they reported the synthesis of the first known representative, decamethyl[5]pericyclyne.[38]

3.1.1. Pericyclyne Hydrocarbons

Pericyclynes of the first generation (i.e. full hydrocarbon derivatives) have been reviewed by de Meijere in 1999.[39]

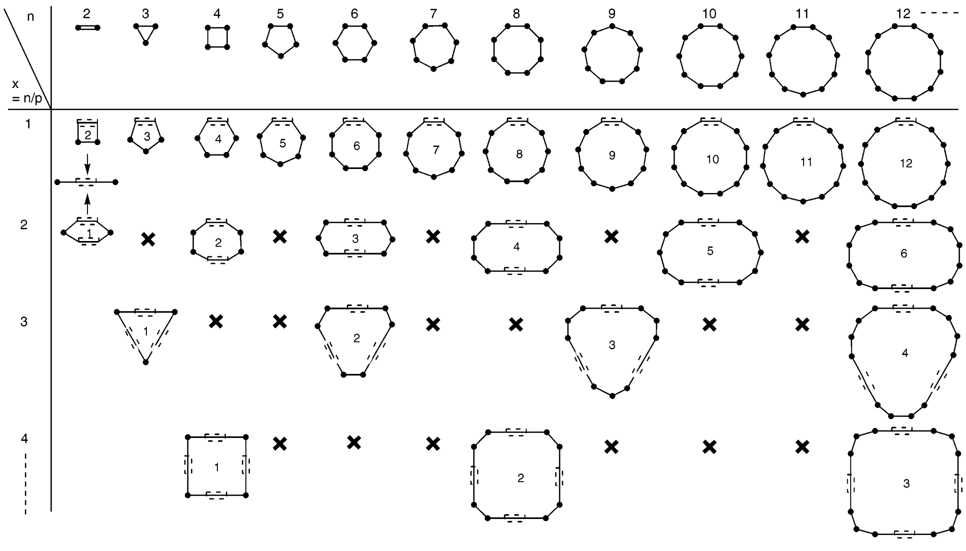


Figure 5. Schematic illustration of the first possible ring *p-carbo*-merizations ($k = 1$). Vertical entries correspond to a parent ring size of $n = 3-12$ (the case $n = 2$ is, of course, ambiguous). Horizontal entries correspond to a fixed number of inserted $C_{sp}\underline{:::}C_{sp}$ bonds ($x = 1-4$). The *p* value is indicated at the center of the rings. Each "broken" diagonal series corresponds to a fixed *p* value (the lowest diagonal $p = 1$ corresponds to the full *carbo*-mer or pericyclynic types).

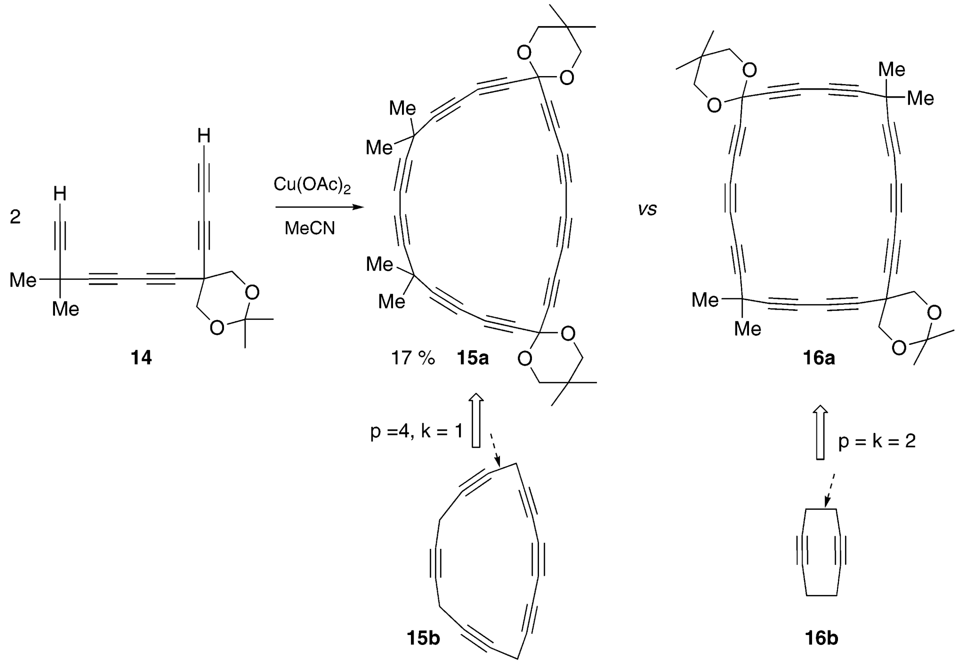


Figure 6. Illustration of the “weak” *p-carbo$_k$*-mer relationship for C24 macrocyclic oligo-acetylenes with a nonperiodical occurrence of the $C_{sp}-C_{sp}$ bonds: **15a** and **16a** are *not p-carbo$_k$*-mers of noncyclynic parent rings.[36] The dashed arrows indicate bonds where the first insertion has to be done.

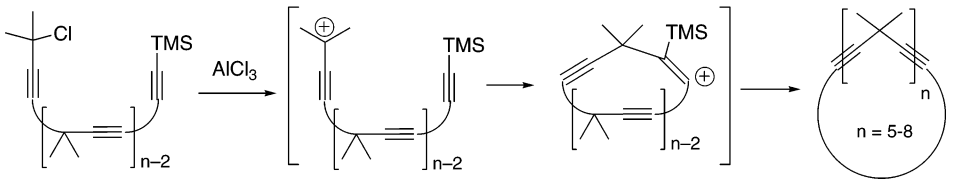


Figure 7. Scott’s ring-closing step to permethylated [*n*]pericyclynes.[44]

As a brief reminder, the first putative member, [2]pericyclyne (Figure 5, first column), has been evoked by Houk and Scott[40] and later studied at a moderate level of theory (SCF HF/6-21G, AM1, PM3).[41] The [3]pericyclyne ring remains unknown as well, but its stability (with respect to tricyclopropabenzene) has been adressed in more detail.[42] The [4]pericyclyne ring has been exemplified, but in functional derivatives only (pericyclynols and a pericyclynone: see section 3.1.2).[43] Finally, although the unsubstituted versions remain unknown, permethyl derivatives of [5]-, [6]-, [7]-, and [8]pericyclynes were synthesized by Scott et al. using sequential alkynyl−propargyl coupling reactions.[44] These compounds were obtained as white crystalline solids from an original cylization step (Figure 7) of acceptable selectivity (e.g. 22% yield for dodecamethyl[6]pericyclyne, mp = 249 °C).[44] Decamethyl[5]pericyclyne was characterized by X-ray crystallography.[40]

Despite their surprising stability, pericyclynes, and in particular [5]pericyclynes, were shown to be definitely *not* or *very poorly* homoaromatic:[45] all the triple bonds contribute in an additive manner to the structural, energetic, and magnetic (NMR, NICS, ...) properties of the molecules. This statement was recently confirmed and refined by electron localization function (ELF)-weighting of the cyclically delocalized σ/π resonance forms of [*n*]pericyclynes: homodelocalization was found to be definitely negligible in large rings (ca. 5% for $n \geq 4$), but it amounts to 8% in [3]pericyclyne.[46] In nonstrained acyclic models, recent calculations at the G3(MP2) level showed that triple bonds are *de*stabilized by local homoconjugation through a sp^3 carbon atom.[47] As a perspective, the lack of energetic evidence of possible homoaromaticity can be brought together with the fact that any topological cyclic effect should first overcome this destabilization.

To enhance homodelocalization and possible homoaromaticity, de Meijere, Scott, et al. focused on pericyclyne derivatives with “activated” quaternary vertexes of the spirocyclopropane type: a *trans*-vertex $C_{sp}-C_{sp}$ orbital interaction was expected to be relayed through the Walsh’s orbitals of the cyclopropane rings.[39,48] The synthesis of the corresponding simple pericyclynes however failed, but expanded versions were successfully obtained (see section 3.1.3).[39]

Peralkyl-pericyclynes are beautiful molecular objects, which were also investigated for their coordinating properties (toward Ag^+ cations or $Co_2(CO)_6$ units) and their covalent reactivity (complete hydrogenation to regularly substituted large cycloalkanes).[44] The latter is however intrinsically limited to the chemistry of localized triple bonds: the quaternary vertexes $Me_2C(C{\equiv}C)_2$ are indeed devoid of potential selective functionalization. Owing to the tautomeric instability of the $C{\equiv}C{-}CH_2{-}C{\equiv}C$ sequence however,[49] pericyclyne hydrocarbons with unsubstituted vertexes can be considered as pseudofunctional, and examples with one or two methylene vertexes have been known since 1990.[43] The compatibility of the pericyclynic ring with heteroatom substituents has been early adressed by Scott[50] and is updated in the following section.

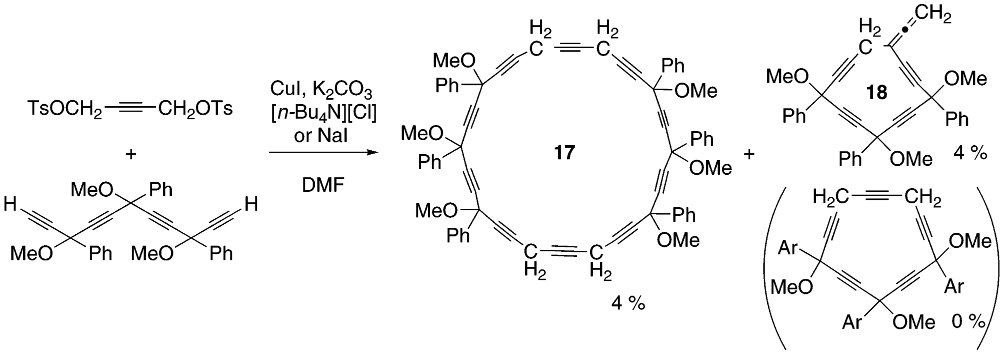


Figure 8. Cyclizing sequential propargylic substitution process leading to stereoisomeric mixtures of a highly functional [10]pericyclyne and an exoallenic isomer of the [5]pericyclyne.[51]

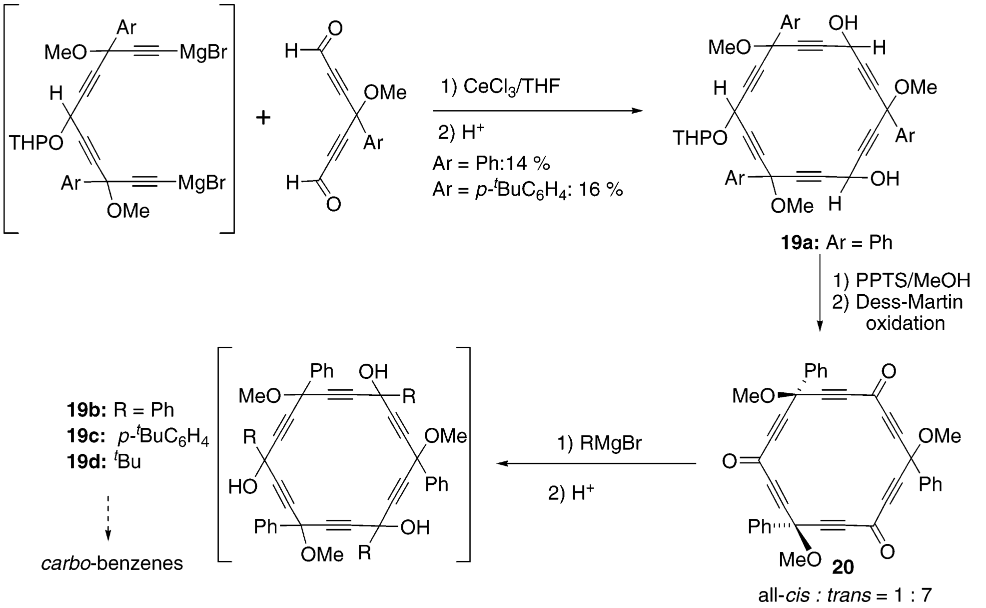


Figure 9. Ueda−Kuwatani's [11 + 7] route to *carbo*-[6]cyclitol derivatives.[54,55]

3.1.2. Functional Pericyclynes

Pericyclynols. The most widespread functional vertexes of pericyclynes are carbinols and carbinol ethers, which result from nucleophilic addition of terminal alkynes to carbonyl compounds. The first reported examples were [4]- and [5]pericyclynes with a single secondary carbinol vertex created by cyclization of bisterminal skipped oligoynes onto ethyl formiate.[43] Simultaneously, [8]- and [10]pericyclynes containing two secondary carbinol vertexes were isolated as mixtures of stereoisomers.[43] More generally, the carbinoxy vertexes become stereogenic as soon as several hetero-disubstituted vertexes are present, and most of corresponding pericyclynes were thus obtained as mixtures of stereoisomers.

The [10]pericyclyne **17** has thus been produced as a mixture of diastereoisomers (14 in theory) by quadruple propargylic substitution at 1,4-di(tosyloxy)but-2-yne with a bisterminal tetrayne (Figure 8).[51] Despite the presence of two pairs of adjacent CH_2 vertexes, the compound was found to be stable under standard conditions. Instead of the expected [5]pericyclyne cyclomonomer, a rather exotic exoallenic C_{13} cyclotetrayne **18** was obtained. DFT calculations on model compounds incidently showed that the exoallenic form is more stable than the [5]pericyclynic form.[51]

When all the vertexes are of the carbinol type, the pericyclynes can be regarded as ring *carbo*-mer derivatives of cyclitols (nonbranched cyclic isomers of carbohydrates)[52] and will termed here as "*carbo*-[*n*]cyclitols". These molecules were initially targeted as potential precursors of *carbo*-annulenic compounds, and their stereochemical resolution was rarely attempted: the stereochemical ambiguity is indeed destined to be wiped off in the final aromatization step (see section 3.5.2).

While Scott's syntheses of [*n*]pericyclynes hydrocarbons were based on a simple ring-closing process (the linear skipped oligoyne precursor already contains the right number ($3n$) of carbon atoms),[44] the syntheses of *carbo*-[*n*]cyclitol derivatives called for strategies of the $[m + (3n - m)]$ type: the ring formation process consists of the double nucleophilic attack of a ω-bisterminal *m*-carbon oligoyne to a ω-dioxo $(3n - m)$-carbon oligoyne.

Carbo-[6]cyclitols. In 1995, simultaneously to an attempt to prepare unsubstituted *carbo*-[6]cyclitol $(C_{18}(H_2O)_6)$,[53] Ueda, Kuwatani, et al. disclosed the first examples of substituted *carbo*-[6]cyclitol derivatives.[54] Their results were later detailed in 1998.[55] These *carbo*-[6]cyclitol ethers were prepared by [11 + 7] ring formation from the bis-Grignard reagent of a C_{11} tetrayne and a C_5 diyne dicarbaldehyde (Figure 9). The chimioselectivity was rather low (6%, and ca. 15% in the presence of cerium trichloride additive). Both the C_{11} dinucleophile and C_7 dielectrophiles were involved as mixtures of stereoisomers, and the overall stereoselectivity of the process (over 20 possible diastereoisomers) was not determined. Hydrolysis of the THP group of **19a** led to a

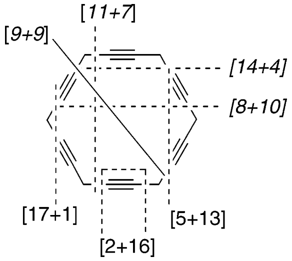


Figure 10. Possible [$m + (18 - m)$] strategies for ring formation of pericyclynes by double alkynyl−propargyl coupling reactions.[57]

[6]pericyclynetriol, which was then oxidized to pericyclynetrione **20**, possessing two diastereoisomers only: according to NMR analysis, their ratio is not statistical (*all-cis/trans* = 1:7 instead of 1:3) and suggests that some kind of stereoselection took place during either the preparation of the C_{11} precursor or the ring formation step itself. Remote 1,4-stereochemical control over triple bonds is apparently surprising but has been emphasized elsewhere.[56] Attack of **20** by 3 equiv of Grignard reagents was assumed to afford hexasubstituted *carbo*-[6]cyclitol triethers **19b**−**c**, which were not characterized: their structure was indirectly confirmed after conversion to *carbo*-benzenes (see section 3.5.2). Nonetheless, **19b** "was obtained as colorless *crystalline* materials" (in 93% crude yield) instead of an oil or a foam for other stereoisomeric mixtures of *carbo*-[6]cyclitol ethers (see below): this suggests that one diastereoisomer might have been preferentially formed.

Other *carbo*-[6]cyclitol derivatives were targeted by alternative [$m + (18 - m)$] strategies. The most symmetrical [9 + 9] scheme, corresponding to cyclodimerization of a C_9 ω-ynal, was attempted in 1995, without success.[53] Other "triplex" schemes ([15 + 3], [12 + 6]) involve different ambivalent nucleophilic/electrophilic reagents and are destined to be nonselective. Among the five remaining possibilites, $m = 2, 5, 8, 14$, and 17 ($m = 11$ corresponds to the Kuwatani's strategy), the most equilibrated schemes, $m = 8$ and $m = 14$, were envisioned (Figure 10).[57]

The [14 + 4] strategy was first applied to dibenzoylacetylene as the C_4 dielectrophile and various C_{14} pentadiynes (Figure 11). Two hexaphenyl *carbo*-[6]cyclitol derivatives **21a**, **21b** with either two or four free OH groups were obtained in good yield (ca. 40%). NMR spectroscopy clearly indicated that the compounds were obtained as mixtures of stereoisomers.[58]

The same route led to another hexaaryl *carbo*-[6]cyclitol diether **21c**, with 4-anisyl and 4-pyridyl substituents.[59] The ring formation followed by double desilylation proceeded in acceptable yield (14%) and afforded **21c** as a mixture of stereoisomers, all devoid of any symmetry.

Finally, the [14 + 4] strategy was applied from a C_{14} heptayne to give a stereoisomeric mixture of dialkynyl *carbo*-[6]cyclitol tetraether **21d** in good yield (43%).[59]

To introduce adjacent secondary carbinol vertexes, the [14 + 4] strategy was also applied to a C_4 dialdehyde (Figure 12).[57,58] Butyndial itself is instable, but it can be stabilized by complexation to a $Co_2(CO)_6$ unit,[60] and the electrophilic reactivity of the aldehyde functions of the complex was previously demonstrated.[61] This reactivity was thus exemplified in a cyclizing version which resulted in the formation of the pericyclyne complex **22a** in 18% yield. Simultaneous decomplexation and desilylation afforded pericyclynediol **22b** as a stable mixture of stereoisomers.

All these results indicate that [14 + 4] ring formation processes (14−43%) are more efficient than [11 + 7] processes (14−16%).[55]

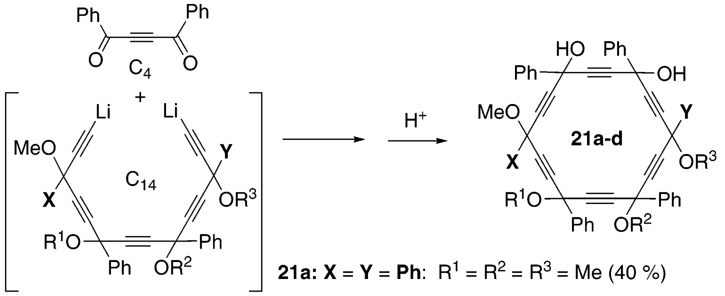
The [8 + 10] route was first investigated in view of preparing an isomeric derivative of **22b** with nonadjacent CH(OH) vertexes. The dilithium salt of a C_8 triyne (Figure 13) was reacted with a C_{10} dialdehyde,[62] to give the *carbo*-[6]cyclitol tetraether **23** in 12% yield as a mixture of diastereoisomers (14 in theory).[57,63] Oxidation of both the carbinol vertexes afforded pericyclynedione **24**, the five steroisomers of which were identified by NMR spectroscopy.

The [8 + 10] route was recently adapted for the preparation of hexaethynyl *carbo*-[6]cyclitol ether **25** from a C_8 pentayne and a C_{10} heptaynedione (Figure 14).[64] X-ray diffraction analysis of a crystalline isomer **25a** showed that the C_{18} rings adopt a chair conformation and perfectly stack up into channels of regular hexagonal sections. This arrangement suggested the theoretical design of *carbo*-meric zigzag (3,0) carbon nanotubes.[65]

The latter [18 + 10] ring formation step proceeded in 34% yield (Figure 14). As a general trend, it may finally be concluded that the efficiencies of the ring formation schemes rank in the following order: [11 + 7] < [8 + 10] < [14 + 4].

Carbo-[5]cyclitols. The formation of the C_{15} ring of *carbo*-[5]cyclitols resorted to two kinds of strategies: [11 + 4] and [5 + 10].[62]

The [11 + 4] route consisted in the reaction of dilithium salts of C_{11} tetraynes with two C_4 synthons (Figure 15).



21a: X = Y = Ph: $R^1 = R^2 = R^3 = Me$ (40 %)

21b: X = Y = Ph: $R^1 = R^2 = H$, $R^3 = Me$ (39 %)

21c: X =4-MeO-C$_6$H$_4$, Y = 4-C$_5$H$_4$N: $R^1 = Me$, $[R^2 = R^3 = TMS]$ $\longrightarrow$ $R^2 = R^3 = H$ (14 %)

21d: X = Y = C≡C–TMS: $R^1 = R^2 = R^3 = Me$ (43 %)

Figure 11. [14 + 4] strategy for the synthesis of *carbo*-[6]cyclitol ethers.[57,58,59]

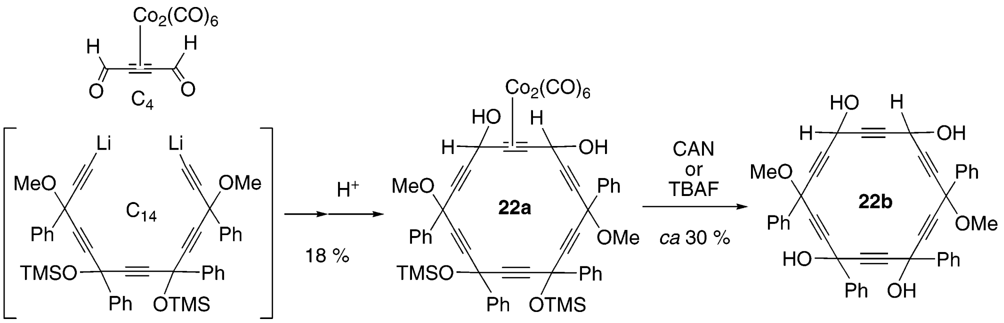


Figure 12. [14 + 4] strategy applied to the C_4 butyndial cobalt complex for the preparation of a [6]pericyclynediol with two adjacent CH(OH) vertexes.[57,58]

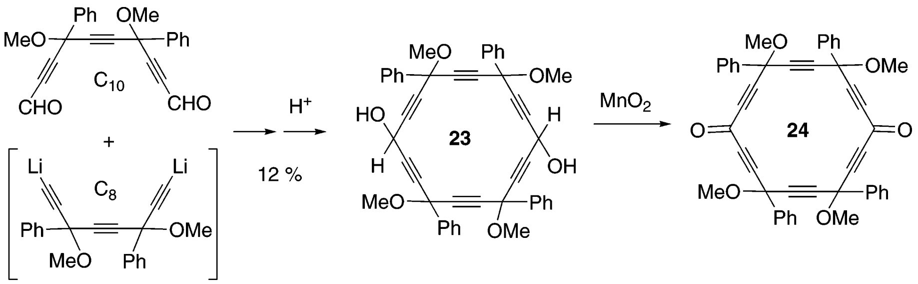


Figure 13. [8 + 10] route for the preparation of a [6]pericyclynediol with two nonadjacent CH(OH) vertexes and the corresponding pericyclynedione.[57,63]

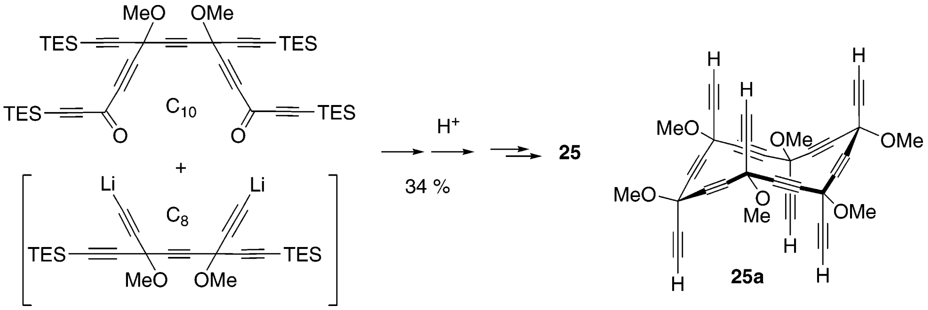


Figure 14. Synthesis of a stereoisomeric mixture of hexaethynyl-*carbo*-[6]cyclitol hexamethyl ether **25**, and selective crystallization of the fully alternate isomer **25a**.[64]

Dibenzoylacetylene and the butyndial cobalt complex gave the [5]pericyclynediols **26a**, **26b** and the [5]pericyclynediol complexes **27a**, **27b** in 37−31% and 5−6% yield, respectively. Oxidative decomplexation of the latter afforded the free *carbo*-[5]cyclitol triethers **28a**, **28b** as stable compounds. These results were established from statistical mixtures of the three diastereoisomers of the C_{11} tetraynes (as determined by HPLC analyses): all 10 diastereoisomers of the [5]pericyclynediols could therefore occur in the product mixture.

Symmetrization of **26a** was achieved by methylation of the remaining OH groups, which afforded all four possible diastereoisomers of **29a**. The reaction sequence was then repeated from a pure chiral diastereoisomer of the C_{11} tetrayne (i.e. the major (R^*,R^*) isomer, obtained by preparative HPLC): the three expected diastereoisomers of **29a** were formed in a statistical ratio, and two of them could be purified as crystalline solids by semipreparative HPLC (Figure 16).[62]

The [5 + 10] route was first envisioned for preparing the regioisomer of pericyclynediols **28a**, **28b** (Figure 15) with nonadjacent CH(OH) vertexes. It was finally tested from three C_5 diynes and two C_{10} triyne dicarbaldehydes (Figure 17): the *carbo*-[5]cylitol products were obtained with a similar yield (15−19%) to that for mixtures of diastereoisomers (at most 10 for **30a**, **30b** and 6 for **30c**).[62] Ketal **30c** was regarded as a protected version of the corresponding [5]pericyclynone, itself a functional version of Scott's octamethyl[5]pericyclynone.[43] In agreement with previous literature data, however, the 5,5-dimethyldioxolane group resisted selective cleavage (see section 3.1.4).[62] Nevertheless, treatment of **30c** with $SnCl_2$/HCl, followed by DCI/NH_3 MS analysis, allowed detection of a peak whose mass corresponds to the NH_3 adduct of a protonated cyclopentadienone **30d**: this can be considered as a sign of the existence of the ring *carbo*-mer of the cyclopentadienyl cation, which was predicted to indeed exist and be aromatic by DFT calculations.[11]

3.1.3. Expanded Pericyclyne Hydrocarbons

Expanded pericyclynes are obtained by insertion of 1,4-butyndiyl C_4 units into each edge of the parent rings. The chemistry of expanded pericyclynes is falicitated by the wealth of efficient methods for oxidative (Glaser,[66] Eglinton,[67] Hay,[68]...) or isohypsic (Cadiot−Chodkiewicz[69]) C_{sp}−C_{sp} coupling reactions,[70] in particular under Breslow cyclization conditions.[71] Indeed, the key process in the synthesis of simple pericyclynes (see section 3.1.2) is propargylic C_{sp^3}−C_{sp} cross-coupling, which has been recently reviewed[72] but is generally less effective.

Expanded [*n*]pericyclyne hydrocarbons have been reviewed by de Meijere in 1999:[39] study of them was initiated by Scott for dimethyl substituents (n = 3−6)[73] and then

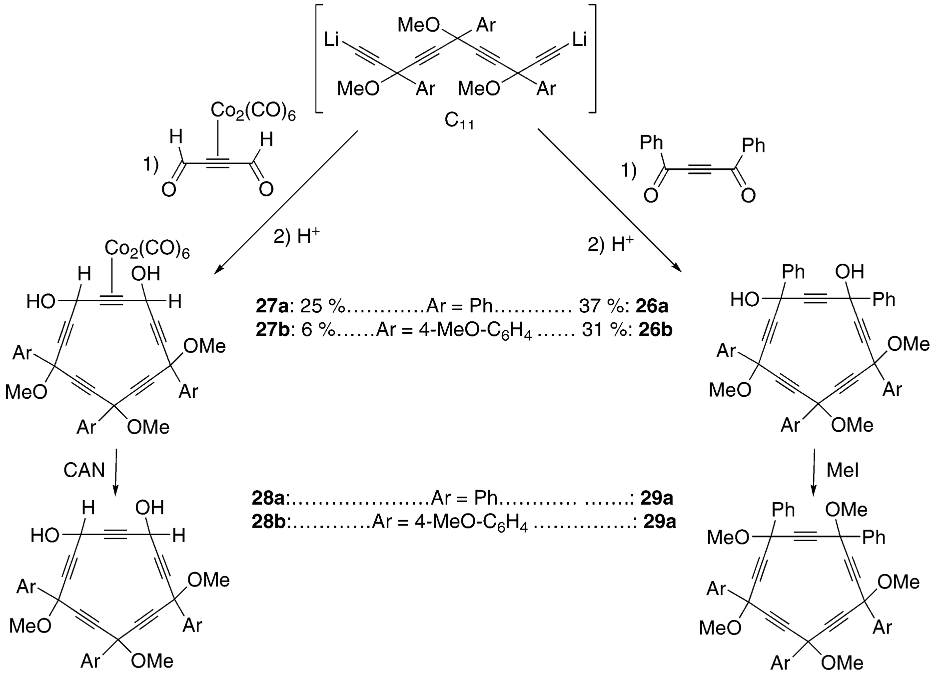


Figure 15. Synthesis of pentaaryl- and triaryl-*carbo*-[5]cyclitols ethers by a [11 + 4] route.[62]

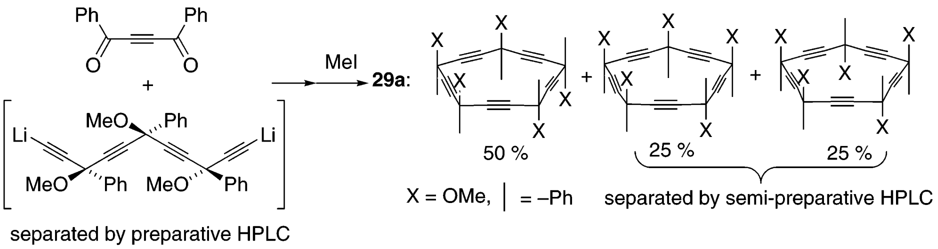


Figure 16. Statistical stereoisomeric ratio of the *carbo*-cyclitol pentamethyl ether **29a** obtained by a [11 + 4] route from a single stereoisomer of the C_{11} tetrayne.[62]

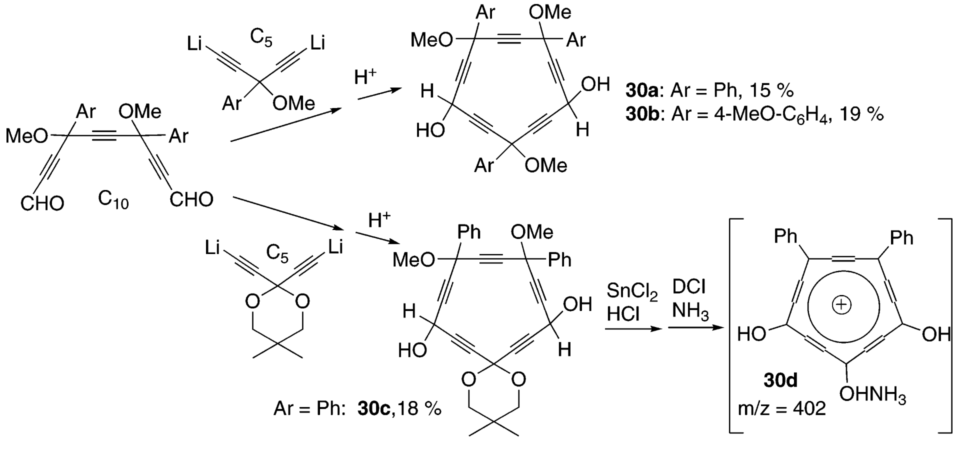
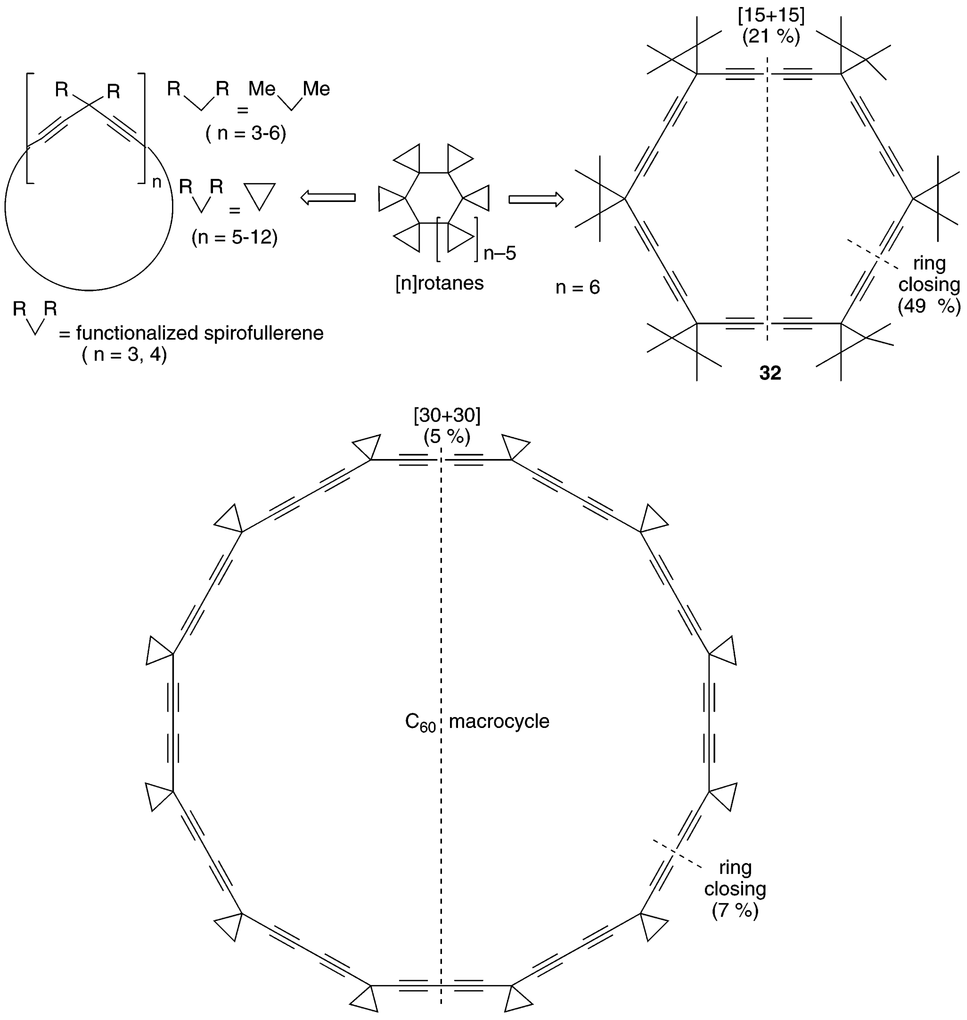


Figure 17. [5 + 10] route to [5]pericyclynediols and a ketal-protected keto-*carbo*-[5]cyclitol ether with two nonadjacent CH(OH) vertexes. After treatment of **30d** with $SnCl_2$, a MS peak was assigned to an aromatic *carbo*-cyclopentadienone adduct.[62]

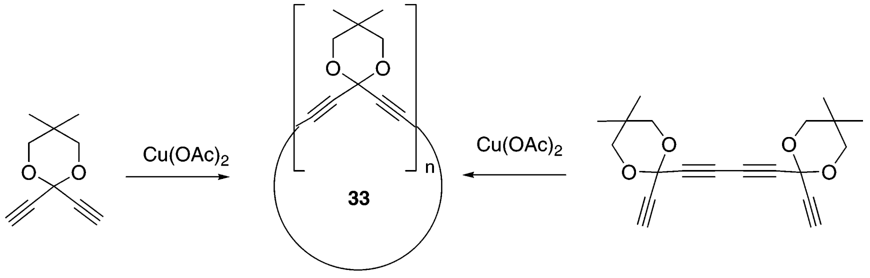
developed by Scott and de Meijere for spirocyclopropane substituents ($n = 5-12$)[74] and by Diederich for spirofullerene substituents ($n = 3, 4$) (Figure 18).[75]

The spirocyclopropanated pericyclynes are ring *carbo*$_2$-mers of [*n*]rotanes.[76] With respect to acyclic dehydrooligomers of diethynylcyclopropane, the observed UV bathochromic shift was ascribed to an enhanced interaction between homoconjugated triple bonds transmitted by the Walsh orbitals of the cyclopropane vertexes.[48] A salient explosive shock sensitivity was emphasized as a common feature of these strained π-electron-rich macrocyles.[74] Since then, novel representatives were described, in particular the spirocyclopropanated [12]pericyclyne **31** containing a C_{60} macrocyclic core (Figure 18).[77] Permethylated spirocyclopropanated [6]pericyclyne **32** was prepared by dehydrodimerization and dehydrocyclization of corresponding precursors with either terminal ($\equiv C-H$) or silylated ends ($\equiv C-SiMe_3$). Rapid scan FT-IR spectroscopy monitoring of the thermal decomposition of this compound showed that the only gaseous product evolved is tetramethylethylene: assuming that the resulting



31

Figure 18. "Exploding" permethylcycloalkanes and [*n*]rotanes.[39,74,77]



6 %	n = 4	9 %
13 %	n = 5	
9 %	n = 6	33 %
3 %	n = 7	
-	n = 8	18 %

Figure 19. Bunz's syntheses of ketal-protected versions of the challenging *carbo*$_2$-[*n*]oxocarbons (see section 3.4).[78]

carbene might undergo further similar fragmentation, the molecule was proposed as a potential source of cyclo[30]-carbon.[77]

Let us finally remark that expanded pericyclyne hydrocarbons also appear as faces of cage compounds such as expanded cubane and other tetrahedranes which were studied at the theoretical level as models of functional derivatives (see below).[83]

3.1.4. Functional Expanded Pericyclynes

In 1996, Bunz et al. reported the synthesis of non-stereogenic expanded [*n*]pericyclynes **33** ($n = 4-8$) with a cyclic ketal function at each vertex (Figure 19).[78] The first method consisted in the oxidative coupling of *n* 1,4-diyne units. Even-membered representatives were obtained in better yields from 1,4,6,9-tetrayne units, with a high selectivity in the expanded [6]pericyclyne (33%). These molecules were targeted as protected versions of cyclic oligo-carbonyl-butadiynylenes ("OCEs"), namely the second *carbo*-mers of neutral oxocarbons (see section 3.4). As later observed for ketal **30c** (Figure 17),[62] no cleavage of the ketal vertexes was however reported.

More recently, Hirsch et al. reported the synthesis of hybrid expanded pericyclyne with alternating dimethylmethylene

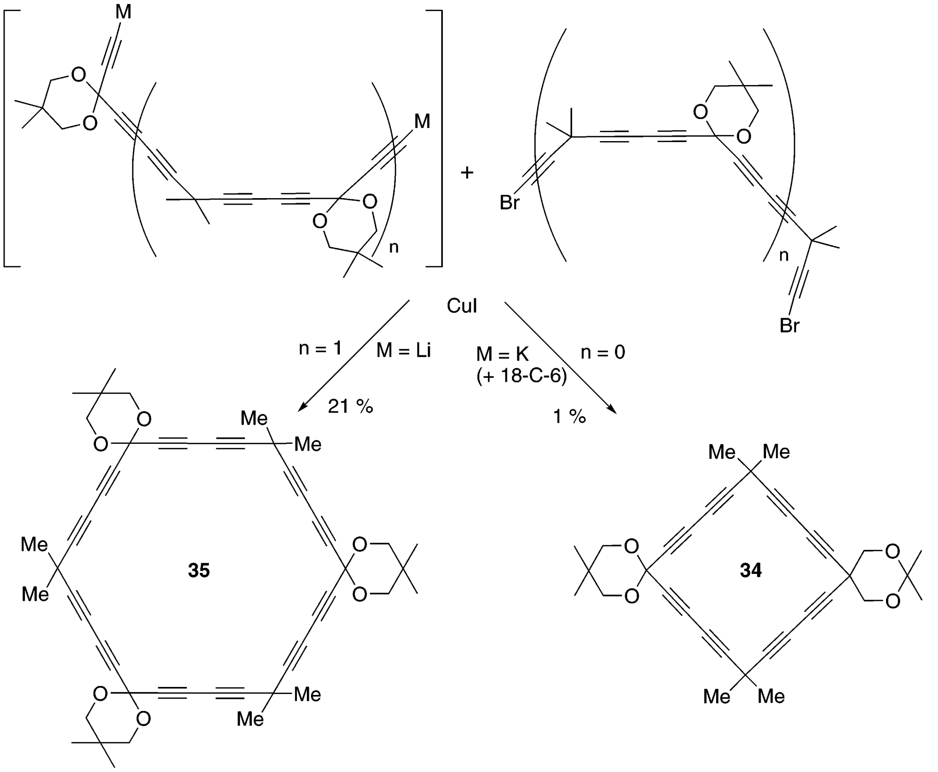


Figure 20. Hirsch's synthesis of alternate functional expanded pericyclynes.[36]

and dioxolane vertexes.[36] Since the Glaser-type oxidative coupling would not be selective, they resorted to Cadiot–Chodkiewicz dehydrobromination between the 2-ethynyl-1,3-dioxolane termini of one reactant and the 2-bromoethynyl propane termini of the other (Figure 20). Random coupling of single vertex units ($n = 0$) afforded a minute quantity of the four-membered ring **34** only. Step by step construction of two C_{15} units followed by their mutual cyclo-dehydrobromination gave the C_{30} six-membered ring **35** as a sensitive white crystalline solid.

On the route to expanded cubanes (see below), Diederich et al. later reported the synthesis of *per*-alkynyl perhydroxylated expanded pericyclynes.[79] The ring formation step was based on oxidative coupling of a *meso/dl* mixture of an alkynyl-substituted bisterminal deca-1,4,6,9-tetrayne (Figure 21): the reaction proceeded with remarkable selectivity, giving the tetraalkynyl expanded [4]pericyclyne **35** in 72% yield The four stereoisomers could be separated, and one of them was characterized by X-ray crystallography.

On the route to hexaphenyl *carbo*$_2$-benzene (see section 3.5.3), similar oxidative coupling of a *meso*/*dl* mixture of a phenyl-substituted bisterminal deca-1,4,6,9-tetrayne under slightly more concentrated conditions afforded the tetraphenyl expanded [4]pericyclyne **36** as the major product (49%) along with the homologous expanded [6]pericyclyne **37** (15%) and [8]pericyclyne **38** (4%).[80] The reaction was also conducted from the analogous 4-anisyl substrate.[81]

The expanded [4]pericyclyne ring is also found on the six faces of a C_{56} expanded cubane **39** obtained by 4-fold oxidative coupling of the deprotected *all-cis* isomer of the expanded tetraalkynyltetramethoxy[4]pericyclyne (Figure 22).[79] Under MALDI MS conditions, **39** undergoes loss of methoxy groups and subsequent C_2 fragmentations and rearrangement to fullerene ions (negative mode detection). For comparison, the parent octamethoxy cubane is not known, but octa-heteroatom-substituted cubanes are attracting interest as promising propellant materials (especially octanitrocubane).[82]

These results prompted theoretical chemists to study hydrocarbon models of *carbo*$_k$-meric cubanes ($k = 1, 2$) and other polyhedranes ($k = 2$) at various levels of calculation.[83]

3.2. Hetero-pericyclynes and Extended Hetero-pericyclynes

Heteroatoms of the third or fourth periods placed at one or more vertexes of a pericyclyne ring allow minimization of the ring strain: with respect to carbon, their greater covalent radius indeed allows for smaller bond angles at low energetic cost. Moreover, their higher softness (reduced HOMO–LUMO gap) is expected to facilitate homoconjugation to the adjacent triple bonds and, thus, possible homoaromaticity (Figure 23).[6] This perspective also applies to expanded radialenes (section 3.3).

3.2.1. Mixed H/C-Pericyclynes: H = Vertex Heteroatom

Mixed hetero-pericyclynes with various combinations of heteroatomic (SiRR′, PR, S) and dimethylmethylene (CMe_2) vertexes have been reviewed by Scott et al. (Figure 24a).[43]

Very recently, monophospha- and monosila[5]pericyclynes have been envisaged in the functional series (Figure 24b). A stereoisomeric mixture of a *carbo*-phospholane oxide **40a** has been obtained in very good yield (86%) by a [14 + 1] ring formation route.[58] The analogous route did not work in the silicon series, but analogous silolanes **41a** were obtained by a [5 + 10] route (20%).[59] The occurrence of only four potentially stereogenic vertexes allowed for the chromatographic resolution of two pure diastereoisomers. These compounds were regarded as possible precursors of phosphole oxide and silole ring *carbo*-mers (**40b**, **41b**) whose aromatic character was investigated at the theoretical level.[84,85]

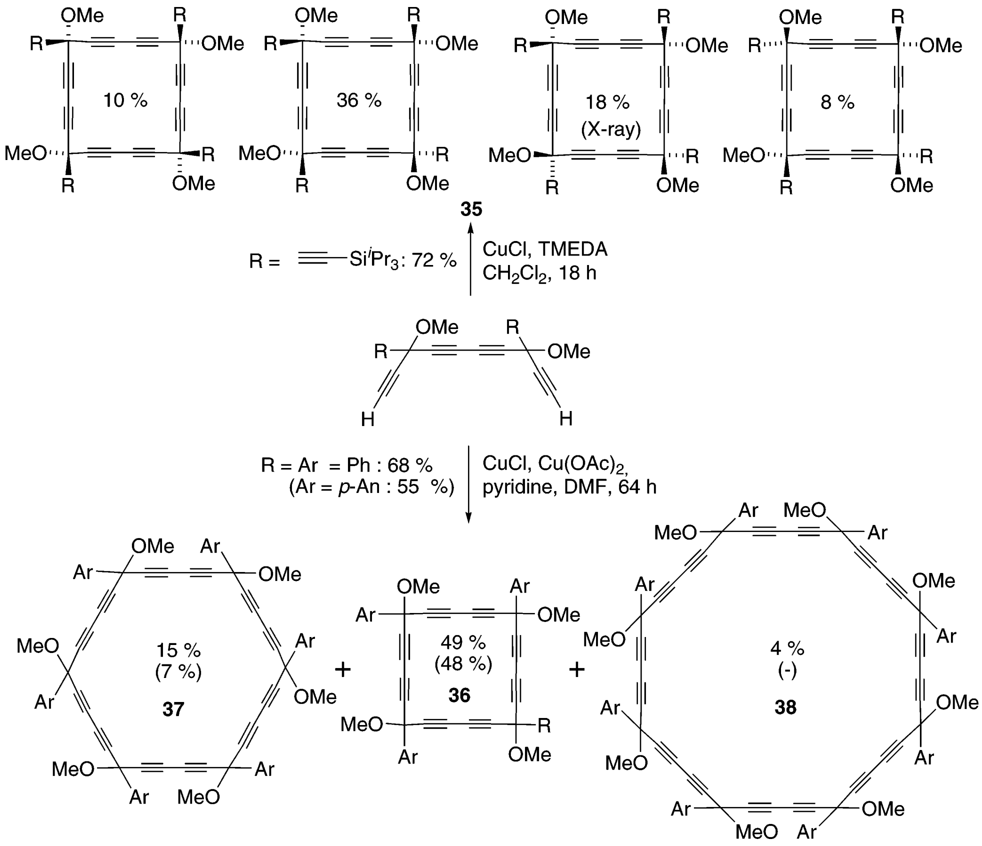


Figure 21. Synthesis of expanded permethoxy[*n*]pericyclynes with alkynyl or aromatic substituents by oxidative coupling of bisterminal deca-1,4,6,9-tetrayne precursors.[79,80]

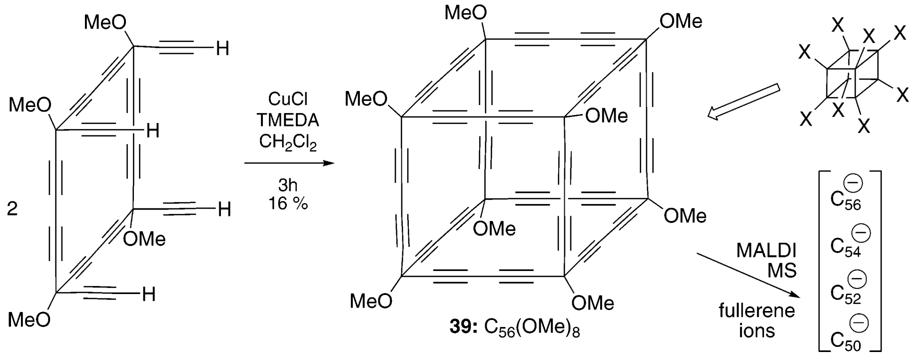


Figure 22. Diederich's synthesis of octamethoxy expanded cubane.[79]

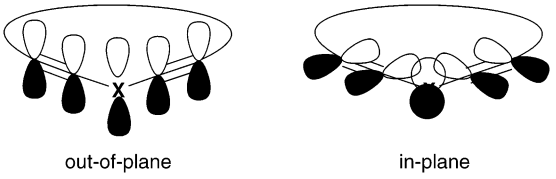


Figure 23. In cyclynes with vertex atoms of sp^{x}d^y hybridization state ($x + y \geq 2$), limiting orientations of accessible frontier orbitals (n, σ, π, δ, ...) of heteroatomic vertexes X (S, PR, SiR$_2$, ...).

3.2.2. Pure Hetero-pericyclynes

Cyclosilanes (SiR$_2$)$_n$ (R = ^{t}Bu, Me, ...; $n \geq 3$) have long been known.[86] While the [3]pericyclyne ring has so far escaped isolation,[44] hexamethyltrisila[3]pericyclyne **42** (Figure 25) was obtained by extrusion of dimethylsilylene from the hexasila precursor (the ring 2-*carbo*-mer of cyclohexasilane: see section 4.1.1),[87] and the role of the silicon vertexes on homoconjugation was analyzed on the basis of photoelectron spectra.[88] Tetrasila[4]pericyclynes **43** are also known,[89] and beyond $n \geq 5$, a complete series of persila-[*n*]pericyclynes such as **44** and **45** has been described.[90] More recently, persila[*n*]pericyclynes with methyl and isopropyl substituents ($n = 6, 8, 10$) have been characterized by X-ray crystallography.[91] Whereas dodecamethylhexasila[6]pericyclyne **45a** exhibits a classical chair conformation,[92] the near planar structure of the dodecaisopropyl version **45b** was ascribed to the steric demand of the substituents.[91]

Very recently, sila- and germana[*n*]pericyclynes (n = 3−12) with various substituents (H, aryls, C$_1$−C$_{15}$ alkyls) have been claimed in a patent (Figure 26).[93] In particular, germana[4]- and -[6]pericyclynes **46** and **47** were prepared by random lithium-mediated dehydrochlorination between diethynylgermanes and the corresponding dichlorogermanes. Dodecaphenylgermana[6]pericyclyne is mentioned to form inclusion compounds with AgBF$_4$ and to give ceramic powders by heating.

Triphospha[3]- and tetraphospha[4]pericyclynes **48** and **49** (Figure 25) have also been described, and UV spectroscopy

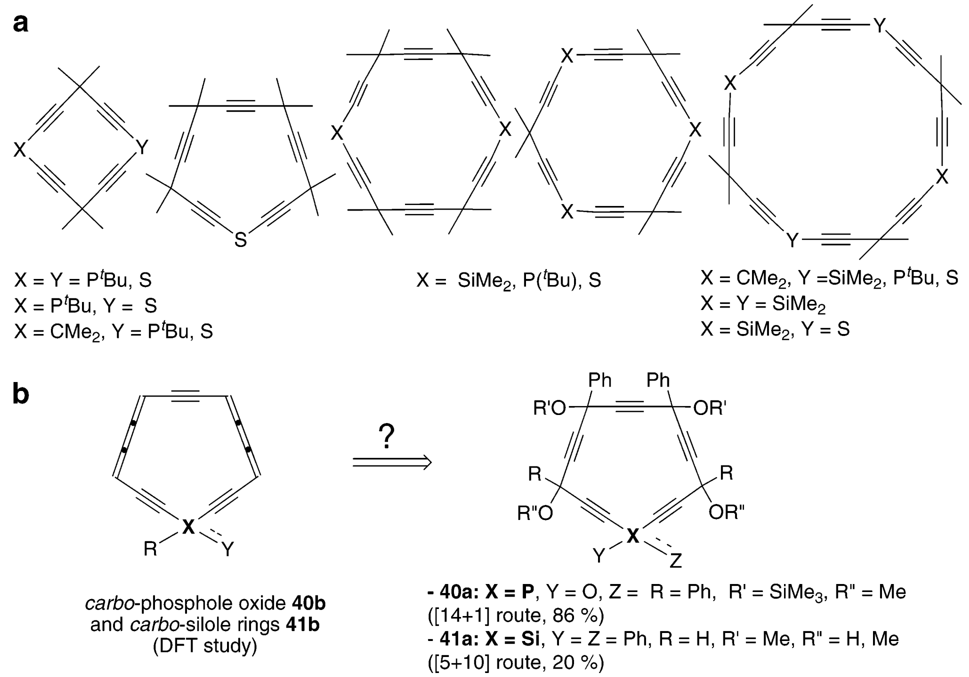


Figure 24. (a) Representative mixed H/C-pericyclynes with one, two, or three heteroatom vertexes.[43] (b) Oxy-derivatives of a *carbo*-phospholane oxide **40a** and a *carbo*-silolane **41a**, as possible precursors of phosphole oxide and silole ring *carbo*-mers **40b** and **41b**, respectively. The latter rings were predicted to be weakly aromatic by DFT calculations.[58,59,84]

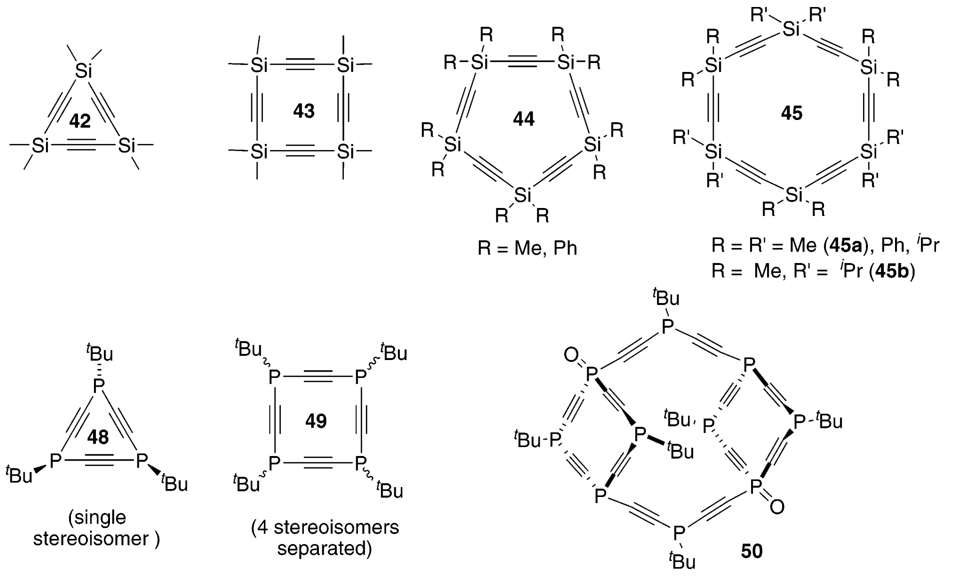


Figure 25. Persila- and perphospha[*n*]pericyclynes.[87−92]

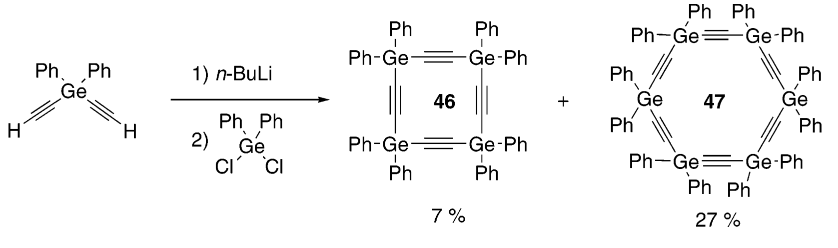
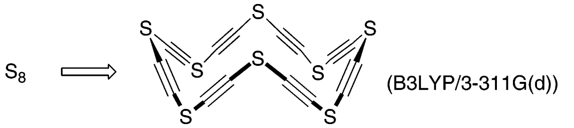


Figure 26. Direct random synthesis of germanapericyclynes from vertex-half edge units.[93]

gave evidence of strong cyclic electronic interactions.[94] Despite the inherent stereogenicity of the vertexes, one stereoisomer of each compound could be characterized by X-ray crystallography.[43] Partly oxidized tetraphospha[4]- and octaphospha[8]pericyclyne rings were also exemplified in a bridged compound **50**.[44]

Perchalcogena[*n*]pericyclynes $C_{2n}X_n$ (X = O, S, Se, Te) are unknown, even octathia[8]pericyclyne **51**, the *carbo*-mer



51

Figure 27. DFT calculation of the *carbo*-mer of the S8 molecular allotrope.[95]

of the S_8 allotrope of sulfur (Figure 27). Recently however, theoretical (DFT) investigations showed that perchalcogena[*n*]pericyclynes ($n = 3-6, 8$) are viable molecules with high (uncorrected) heats of formation (1506 kJ·mol^{-1} with zero strain energy for $C_{16}S_8$).[95]

3.2.3. Expanded Hetero-pericyclynes

In 2001, Matsumoto et al. reported the preparation of expanded silapericyclynes **52**−**55** by reaction of dilithiobutadiyne with dichlorodiisopropylsilane (Figure 28).[96] This random method afforded a mixture of cyclic compounds with four to seven silicon vertexes, while the oxidative coupling strategy from diethynylsilane derivatives failed. The better yield (8%) was obtained for the sila[4]pericyclyne **52**, for which X-ray crystallography indicated a column-like molecular packing. The UV spectra of the four compounds showed no significant dependence of the electronic transition energies versus ring strain.

Expanded pure hetero[*n*]pericyclynes **56** have also been exemplified (for $n = 3-8$) in the phosphorus series (Figure 29).[97] Four different substrates containing $m = 1, 2, 3, 4$, or 8 potential vertexes were used: the ring closing processes $m = 3 \rightarrow n = 3$ and $m = 4 \rightarrow n = 4$ were found to be the most selective (65−70%). All the compounds exhibited temperature dependent ^{31}P and ^{1}H NMR spectra, from which a dramatic lowering of the inversion barriers at the phosphorus atoms could be determined. In particular, the strain-free expanded [8]pericyclyne already displays a single broad ^{31}P NMR signal at 20 °C. On the basis of DFT calculations on acyclic models, this observation was ascribed to extended $\pi_{C\equiv C}/n_P$ orbital interactions in the nearly planar transition states of a more or less synchronous process.[97]

The vertexes of expanded pericyclinic rings can also be occupied by a transition metal, namely platinum(II). After a pioneering synthesis of expanded platina[4]- and -[8]pericyclynes by CuI-mediated coupling of $P_2Pt(C\equiv C-C\equiv C-H)_2$ complexes with P_2PtCl_2 (P_2 = dcpe, $[P(Bu_3]_2)$),[98] other expanded platina[4]pericyclynes **57** have been obtained by direct condensation of similar bisbutadiynyl complexes with platinum triflates in the presence of a weak base (Figure

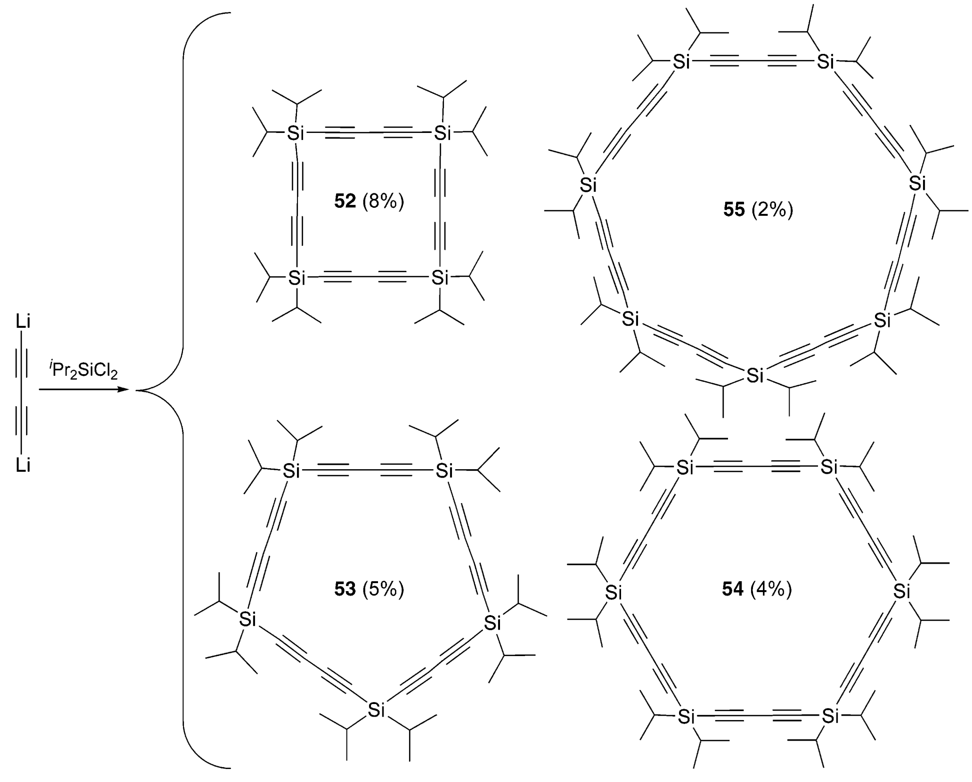


Figure 28. Radom synthesis of expanded persila[n]pericyclynes from independent edge and vertex units.[96]

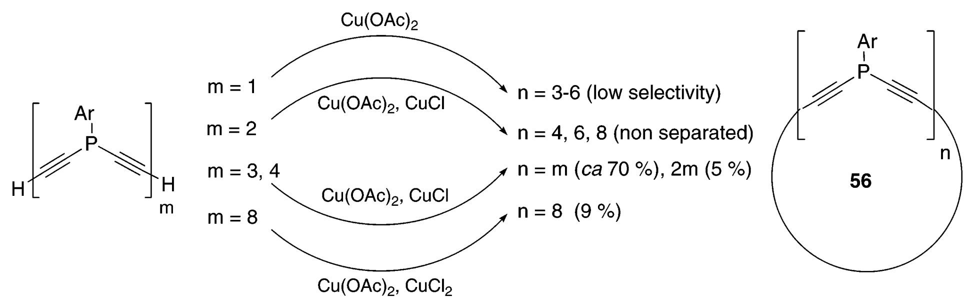


Figure 29. Alternative ring formation routes to expanded perphospha[*n*]pericyclynes.[97]

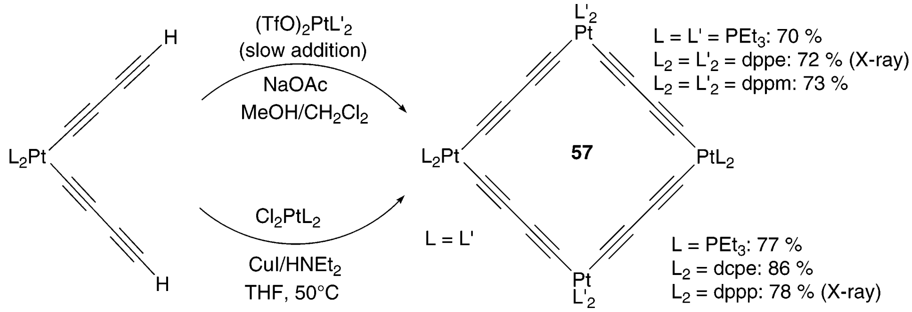
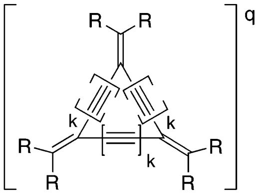


Figure 30. Synthesis of expanded tetraplatina[4]pericyclynes.[98−100]



R = H, C≡CH, k = 0, 1, 2; q = 0, −1, −2

Figure 31. Family of *carbo*$_k$-[3]radialenes and anions thereof studied at the theoretical level.[104]

30).[99] One of them was characterized by X-ray diffraction, and DFT studies emphasized a significant delocalization between the carbon edges through the metal vertexes. More recently, the CuI-mediated method was resumed, allowing for a further X-ray diffraction analysis (Figure 30).[100] All these complexes were found to form adducts with polar solvent molecules (DMSO, acetonitrile, ethanol, water) and various cations (ammoniums, Cu^+, Ag^+, Cs^+, K^+, ...).

3.3. Expanded Radialenes (*Carbo*$_k$-radialenes, $k = 1, 2$)

Radialenes are cross-conjugated all-C_{sp}^2 rings displaying poor aromatic character,[101] in particular [3]radialene (a cyclic isomer of benzene) and [6]radialenes (with the same cyclic core of sp^2 carbon atoms as benzene).[102] This fact continues to stimulate fundamantal interest, as illustrated by recent reports on radialenes and their acetylene-expanded versions at either semiempirical[103] or DFT levels of theory (Figure 31).[104] In particular, systematic theoretical studies of *carbo*$_k$-[3]radialene prototypes and their anions showed that the electron affinity of peralkynyl *carbo*$_k$-radialenes ($k = 0$, 1, 2) relies on the enhancement of cyclic and peripheral electron delocalization over the *carbo*$_k$-radialenic core and the ethynyl arms.[104]

3.3.1 *Carbo*$_1$-radialenes

Experimental reports on *carbo*-radialenes (with a single inserted triple bond per edge) have been so far limited to the C_{18} *carbo*-[6]radialene ring.[105] The representative **58** was thus obtained via a [17 + 1] ring formation step from a diethynyl[3]dendralene and a dibromoolefin, along with a C_{17} cyclohexayne **59** (Figure 32). Very recently however, a breakthrough has been mentioned by Tykwinski et al.[106]

3.3.2. *Carbo*$_2$-radialenes

The development of several synthetic strategies for the preparation of differently silyl-protected TEEs provided suitable building blocks for the construction of perethynylated expanded [*n*]radialenes. The first representatives ($n = 4$−6, with triisopropylsilyl termini) were reported in 1994.[107] Since then,[108] three novel series of perethynylated expanded [*n*]radialenes ($n = 3$−6) were prepared using an acetylenic coupling reaction (Figure 33): the selected aryl donor substituents were 3,5-di(*tert*-butyl)phenyl (**60a**−**60c**) and long chain 4-anisyl (**61a**−**61d**) and 4-anilinyl derivatives (**62a**−**62c**).[109] All these compounds were found to be stable and present a good solubility in organic chlorinated solvents. Only small shifts were observed for the $^{13}C_{sp}$ resonances of these new expanded radialenes compared to the case of dimeric TEEs, thus indicating a weak strain of the macrocyclic perimeters. The X-ray crystal structure of the di(*tert*-butyl)-substituted expanded [6]radialene **60b** showed a high distortion of the cyclic framework which adopts a chairlike conformation, with almost planar TEE units. Bond lengths were found to be very similar to those occurring in acyclic TEE dimers. The macrocyclic π-conjugation effect is revealed by a large UV−vis bathochromic shift of the longest wavelength absorption maxima, which increases with the strength of the peripheral donors. The redox properties showed an increased capacity of these cyclic π-conjugated systems to stabilize radical anions formed upon electron uptake: this finding could be later explained by the enhanced aromaticity of the anions.[104]

Tobe designed a labile type of capping for expanded radialenes, namely methylenebicyclo[4.3.1]deca-1,3,5-triene units.[110] Indeed, photolytic [2 + 1] cheletropic fragmentation of isolated dialkynylmethylenebicyclo[4.3.1]deca-1,3,5-trienes proved to afford indane and the extruded *linear* 1,3,5-triyne derivatives. Copper(II)-mediated oxidative coupling

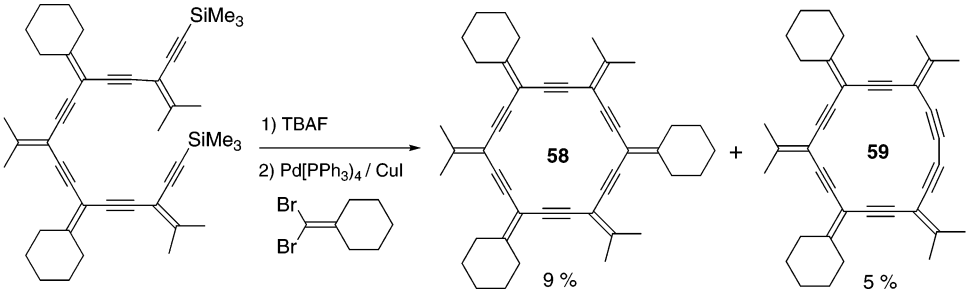


Figure 32. [17 + 1] route to the *carbo*-[6]radialene ring.[105]

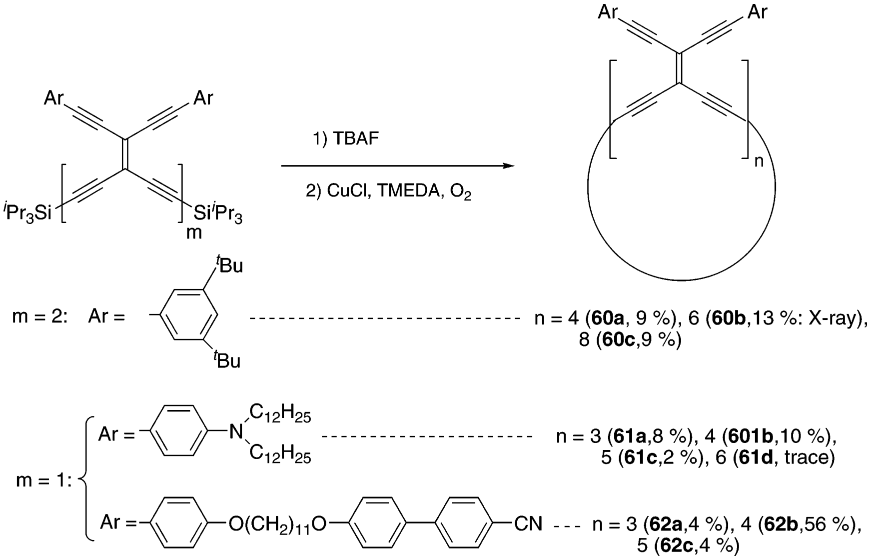


Figure 33. Diederich's synthesis of alkynyl-substituted expanded radialenes.[109]

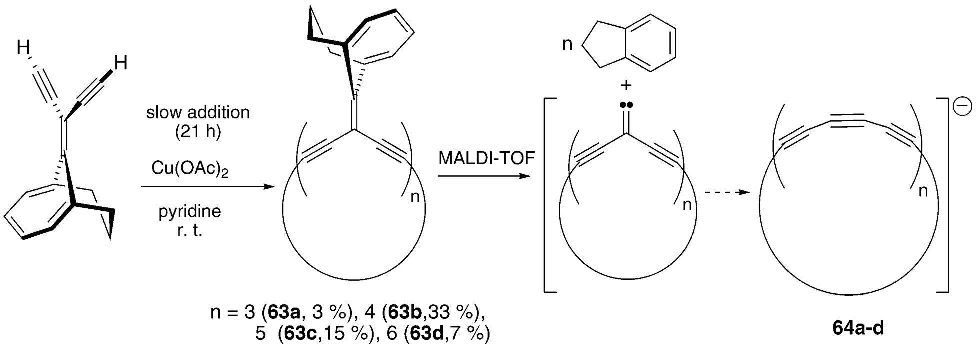


Figure 34. Synthesis of expanded [*n*]radialenes with [4.3.1]deca-1,3,5-triene vertexes and laser-desorption induced fragmentation to cyclo-[6*n*]carbons (MALDI-TOF spectra).[110]

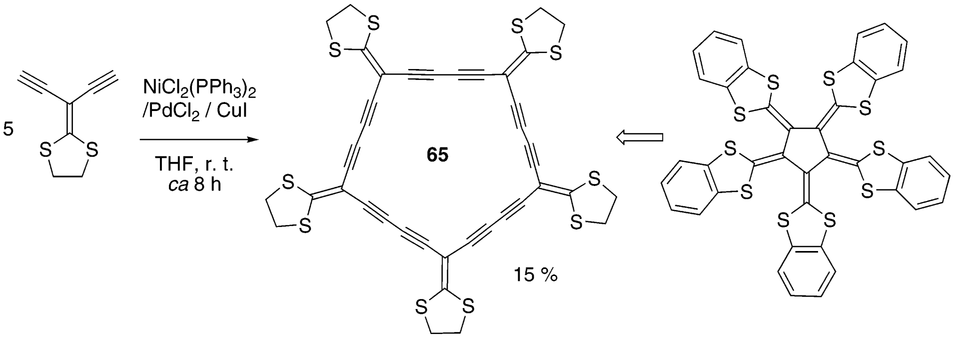


Figure 35. Liu−Zhang's synthesis of expanded pentadithiolane[5]radialene.[111a]

of bisterminal diethynylmethylenebicyclo[4.3.1]deca-1,3,5-triene allowed isolation of four types of expanded [*n*]radialenes: **63a** (*n* = 3), **63b** (*n* = 4), **63c** (*n* = 5), and **63d** (*n* = 6) (Figure 34). Owing to the dissymmetry of the [4.3.1]deca-1,3,5-triene units, and as indicated by ^{13}C NMR analyses, the compounds were obtained as mixtures of diastereoisomers differing by the relative orientations of the *n* peripheral caps. The lability of the caps was revealed by MALDI-TOF mass spectroscopy in the negative mode: the peaks of the corresponding cyclo[6*n*]carbon anions **64a**−**d** were indeed detected.

Liu, Zhang, et al. reported on the use of a ternary metallic system (Ni−Pd−Cu) for achieving the sequential coupling of five α-diethynylmethylidene dithiolane units into the expanded [5]radialene **65**,[111a] a pentadithiolane[5]radialene parent of which had been previously reported (Figure 35).[111b] Electron richness and extended cross-conjugation in **65** is revealed by a strong bathochromic shift of UV−vis absorptions.

3.4. *Carbo*-oxocarbons

Replacement of the methylene ends of [*n*]radialenes with oxygen defines [*n*]oxocarbons, which are known in their doubly reduced state $[(CO)_n]^{2-}$ only:[112] despite its unsaturated valence shell, neutral :C=O is indeed not prone to (cyclo)polymerize. Ring *carbo*-mers of neutral oxocarbons, $[C{\equiv}C{-}C(O)]_n$, would be cyclooligomers of C_3O (the *carbo*-mer of CO), a known but highly instable species.[113] Acyclic oligocarbonylethynylene models $R{-}[C{\equiv}C{-}C(O)]_nC{\equiv}C{-}R$ (OCEs, $n = 1{-}4$) are also known,[114] and investigations

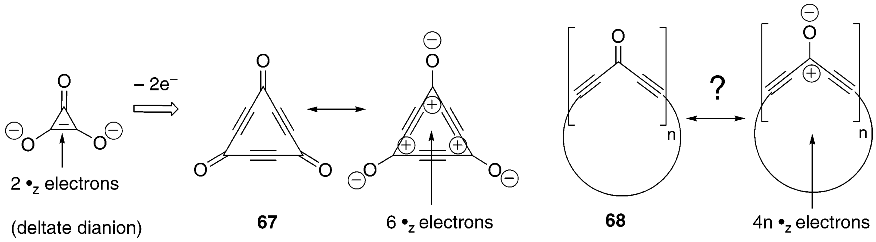


Figure 36. Putative ring *carbo*$_k$-mers of neutral oxocarbons ($k = 1, 2$).[115,78]

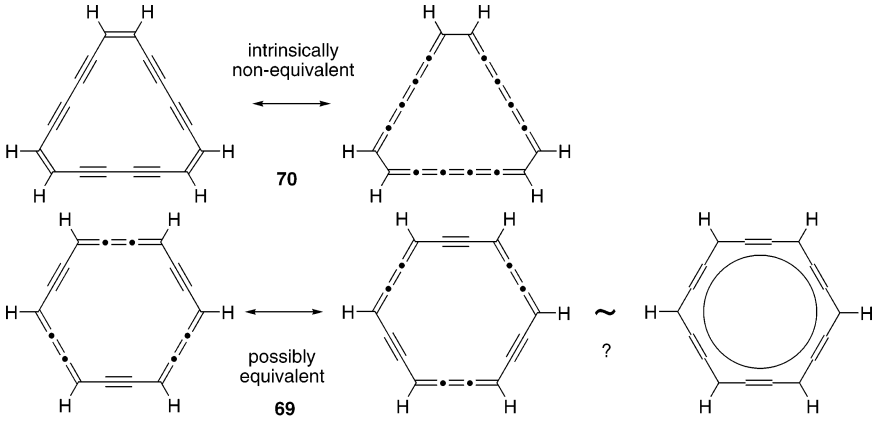


Figure 37. Sondheimer's D_{3h} $C_{18}H_6$ dehydroannulene (the 2-*carbo*$_2$-mer of benzene),[117] and the possibly more symmetric (D_{6h}) *carbo*-benzene isomer.[10,11,53]

at the DFT level and higher levels of theory showed that *carbo*-[*n*]oxocarbons ($n = 3, 5$) could be viable species. In particular, the *carbo*-[3]oxocarbon structure **67** corresponds to a minimum on the potential energy surface and is more stable in the singlet spin state than in higher spin states (Figure 36). It is also more stable than simple valence isomeric structures or is separated from them by high energy barriers. Finally, it displays evidence of weak aromatic character, likely favored by the polarity of the C═O bonds and the dilution of the formal positive charges over the C9 ring.[115] *Carbo*$_2$-oxocarbons **68** have been targeted by Bunz et al., who described ketal-protected versions thereof (see section 3.1.4).[78] Although related macrocyclic cycloacetylenes C_xO_y have been described,[116] these molecules are still awaiting detailed theoretical and experimental studies. The same basic argument as above (based on the strong $C^+{-}O^-$ polarity) suggests however that *carbo*$_2$-[*n*]oxocarbons might be rather antiaromatic with 4*n* formal electron counts in the central C_{5n} rings.

3.5. *Carbo*-Benzenes

3.5.1. Theoretical Studies of the $C_{18}H_6$ Carbo-benzene Molecule: The Aromaticity Challenge

For the sake of brevity, the unsubstituted ring *carbo*-mer of benzene **69** ($C_{18}H_6$) is termed as "*carbo*-benzene" (Figure 37).[11] It is a an isomer of Sondheimer's dehydroannulene **70** (i.e. 2-*carbo*$_2$-benzene),[117] and the challenge of its synthesis was highlighted in 1995.[10,53,118] Substituted derivatives are known (see section 3.5.2), but **69** itself (without possible external conjugation) remains a synthetic challenge. While semiempirical SCF calculations (AM1, HF) predicted a reduced D_{3h} symmetry,[119] DFT calculations showed that the ring is aromatic in the structural (D_{6h} symmetry), energetic, and magnetic sense.[120] The calculation levels (B3PW91/6-31G** and B3LYP/6-31+G*) were validated by comparison of the optimized geometry and calculated (^1H, ^{13}C) NMR chemical chemical shifts of substituted derivatives with available experimental data (see below).[11]

Regarding structural aspects, the D_{6h} symmetry entails that the Kékulè forms are equivalent (Figure 37). It thus indicates a perfect delocalization over the six edges, but the exact geometry also reveals an extended delocalization over individual bonds: $d(C_{sp}\doteq C_{sp}) = 1.239$ Å, $d(C_{sp}\underline{\cdots}C_{sp^2}) = 1.369$ Å.[121] The latter values indeed have to be compared with the optimized bonds delocalized according to the Harmonic oscillator model:[122] $R_{opt}(C_{sp}\doteq C_{sp}) = 1.24$ Å and $R_{opt}(C_{sp}\underline{\cdots}C_{sp^2}) = 1.35$ Å.[123] By comparison, the corresponding values for the benzene molecule are $d(C_{sp^2}\underline{\cdots}C_{sp^2}) = 1.394$ Å and $R_{opt}(C_{sp^2}\underline{\cdots}C_{sp^2}) = 1.39$ Å, and benzene is indeed perfectly aromatic in the structural sense. As measured by the local difference $d(C_{sp}\underline{\cdots}C_{sp^2}) - R_{opt}(C_{sp}\underline{\cdots}C_{sp^2}) = 0.02$ Å, *carbo*-benzene **69** is therefore slightly less structurally aromatic than benzene. Molecular structure is ultimately controlled by the electron density, and the electron localization function (ELF) is an analytical tool of choice for aromaticity.[124] It allows for giving a ground to the equivalent Kékulè resonance forms of Figure 37.[46] Recently, a derived index of π-aromaticity (ELF$_\pi$, a critical value of the bifurcation tree of localization domains)[125] proved to be discriminative.[126] This index was calculated at the B3PW91/6-31G** level for *carbo*-benzene (ELF$_\pi = 0.86$) and benzene (ELF$_\pi = 0.91$), showing that the former is indeed slightly less "electronically" aromatic than the latter.[80]

Regarding energetic aspects, excellent correlations of the HF π MO levels with their Hückel expression allowed for the extraction of a mean "spectroscopic" resonance integral ($\beta = -156$ kcal·mol^{-1}).[121] The Breslow resonance energy was then calculated for the out-of-plane MO's (BRE$_{\pi z} = -128$ kcal·mol$^{-1}\pi_z$) and for in-plane MO's (BRE$_{\pi xy} \approx 0$): the results definitely show that *carbo*-benzene is aromatic and is not homoaromatic. It is however slightly less energetically π-aromatic than benzene ($\beta = -131$ kcal mol^{-1}, BRE$_\pi = -132$ kcal·mol^{-1}).[121] This statement has been extended

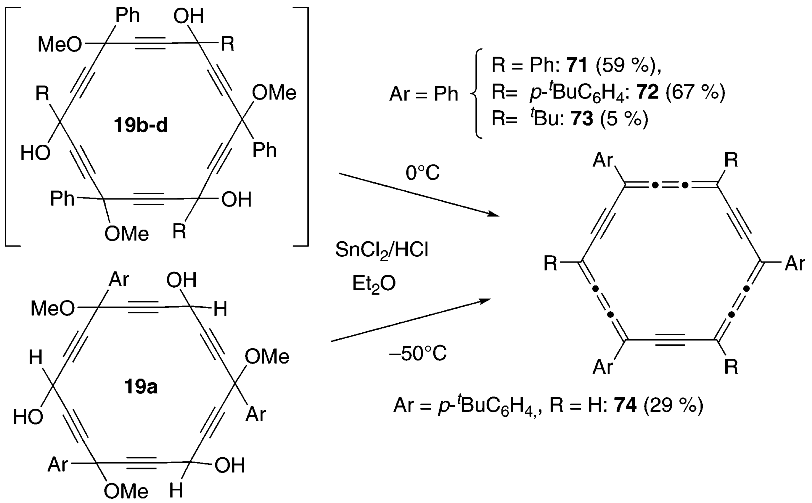


Figure 38. Ueda–Kuwatani's synthesis of hexaaryl- and triaryl-*carbo*-benzene derivatives.[55]

to the overall ($\sigma + \pi$) aromaticity through alternative resonance energies and aromatic stabilization energies based on various thermochemical schemes.[11,80]

Magnetic aromaticity has been long recognized as fundamentally independent from "classical aromaticity" revealed by both structural and energetic criteria.[127] A global measure of magnetic aromaticity is the Schleyer's NICS calculated for a ghost atom at the center of the ring:[128] the NICS value was found to be much more negative in *carbo*-benzene (−17.9 ppm) than in benzene (−8 ppm) at the same level of calculation (B3LYP/6-31+G*).[120] The NICS is actually a local effect of the ring current induced by an external magnetic field perpendicular to the ring: complete ring current maps of *carbo*-benzene have also been established, showing a strong diamagnetic circulation around the C_{18} ring.[129] Finally, the calculated ^{1}H NMR chemical shift of $C_{18}H_6$ is strongly deshielded at +11.4 ppm (in qualitative accordance with experimental data on partially substituted derivatives). All these results show that *carbo*-benzene is more aromatic than benzene in the magnetic sense. Since the converse holds in the structural and energetic senses, the *carbo*-meric couple provides an example of orthogonality of magnetic and classical aromaticity.[80]

Substituted derivatives of *carbo*-benzene were also studied, allowing for comparison with experimental data (see below). Theoretical studies of *carbo*-benzene derivatives also focused on physicochemical properties ultimately governed by aromaticity, in particular in nonlinear optics (quadratic hyperpolarizability).[123,130] The *carbo*-benzene ring also occurs in theoretical carbon allotropes, such as α-graphyne (the *carbo*-mer of graphene),[131] the corresponding α-graphyne nanotubes,[132] and related *carbo*-meric carbon nanotubes.[65] Theoretical investigations were extended to related aromatic structures (other *carbo*-annulenic species,[120,121] *carbo*-cyclopentadienone,[123] *carbo*-pyridine, *carbo*-phosphole oxide,[84] *carbo*-siloles,[85]...). Finally, the total *carbo*-mer of benzene (where C2-insertion also applies to the C–H bonds)[65] and the expanded *carbo*-benzene (*carbo*$_2$-benzene), which are both $C_{30}H_6$ isomers, were studied at the DFT level (see below).[11,80]

3.5.2. Synthesis of Carbo-benzene Derivatives

Although eliminative aromatization was attempted for the preparation of nonsusbtituted *carbo*-benzene,[53] aryl derivatives were obtained by reductive aromatization of *carbo*-[6]cyclitol ether precursors **19a**–**d** (see section 3.1.2). Ueda, Kuwatani, et al. thus prepared hexasubstituted *carbo*-benzenes **71**–**73** by treatment of crude triethers **19b**–**d** with $SnCl_2$ in etheral hydrochloric solution at 0 °C (Figure 38).[55] The hexaaryl derivatives **72** and **73** were produced in much better yield (59–67%) than was a triaryl–trialkyl derivative **73** (5%). The same procedure also afforded the trisubstituted (triaryl) *carbo*-benzene **74** (29%) from **19a** but required a much lower temperature (−50 °C).

These *carbo*-benzenes were obtained as purple crystals for **71**, **72**, and **74** and as orange-red crystals for **73**. The melting point of **73** was measured at 235 °C, while **71**, **72**, and **74** decompose at 175, 250, and 220 °C, respectively. X-ray diffraction analysis of the hexaphenyl-*carbo*-benzene **71** confirmed that the ring is planar, with a quasi D_{6h} symmetry and bond distances in accordance with DFT-calculated values for the nonsubstituted ring **69** (see section 3.5.1). In the ^{1}H NMR spectra, the *ortho* protons of the aromatic substituents resonate at low field (ca. 9 ppm), and the protons directly attached to the macrocycle of **74** are even more deshielded (9.87 ppm), showing the existence of a strong diatropic ring current. This effect does not depend on the temperature, thus evidencing the conformational stability of these molecules. All the analytical data are thus consistent with a significant energetic and structural aromaticity and with a strong magnetic aromaticity, as previously suggested by model DFT calculations (see section 3.5.1).

Several *carbo*-benzene derivatives have been prepared through a similar reductive aromatization method (Figure 39).[133] Hexaphenyl *carbo*-benzene **71** was first re-prepared from periclynediol **21a** and pericyclinetetraol **21b** in 12% and 22% yield, respectively.[58] Despite the lower yield of the final step, the synthesis based on a [14 + 4] ring formation route is more straightforward (9 steps) than the Ueda–Kuwatani synthesis based on a [11 + 7] route (16 steps).[55]

Another hexaaryl-*carbo*-benzene **75**, with 4-anisyl and 4-pyridyl substituents in *para* (1,10) position, was obtained as dark violet crystals by reductive aromatization of pericyclynetetraol **21c** at room temperature (5%).[59] Despite its poor solubility, the structure of this weak donor–acceptor chromophore was ultimately confirmed by MALDI-TOF mass spectrometry and UV–vis spectroscopy.[59] The quadratic hyperpolarizability of **77** was estimated by EFISH measurements at 1.907 μm ($\beta_{1.907} \approx 66 \times 10^{-30}$ cm^5

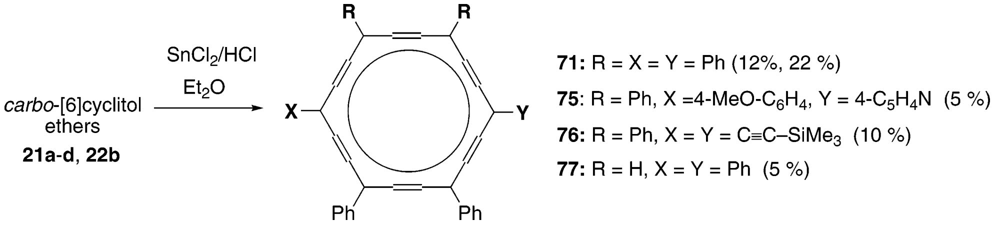


Figure 39. Reductive aromatization of *carbo*-[6]cyclitol ethers to diphenyl-*carbo*-benzene derivatives with various kinds of substituents.[58,59,133]

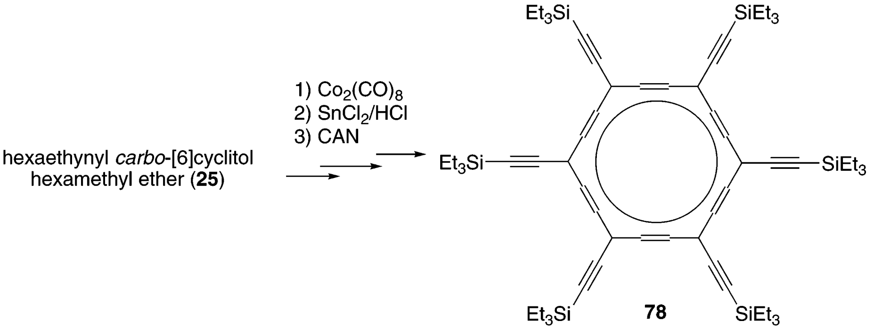


Figure 40. Synthesis of a protected version of the total *carbo*-mer of benzene.[64,80]

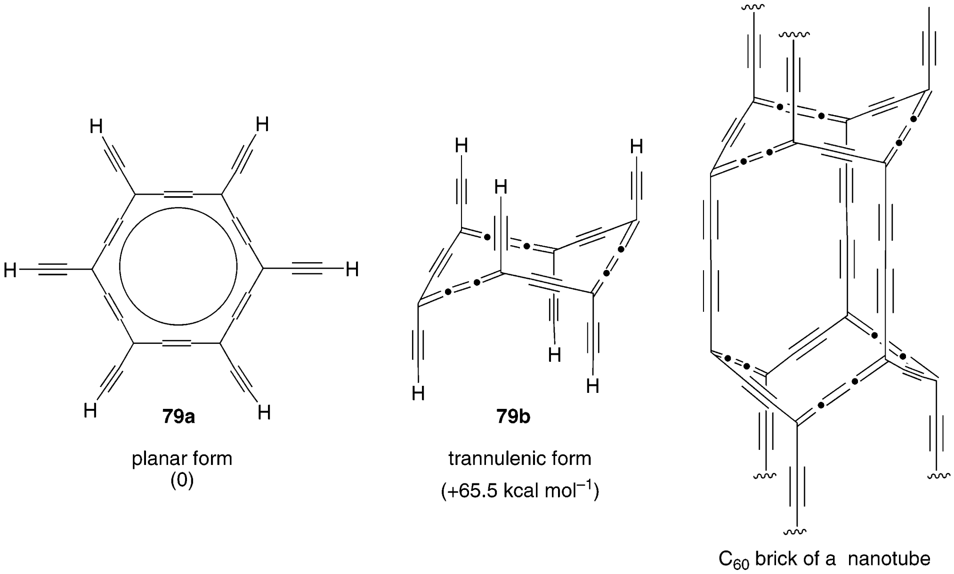


Figure 41. Theoretical constructs from the total *carbo*-mer of benzene (B3PW91/6-31G**).[65]

esu^{-1}),[134] in qualitative accordance with the ZINDO-calculated value.[123]

The dialkynyl *carbo*-benzene **76** was obtained from **21d** (10% yield, mp = 224 °C).[59] The higher solubility brought by the terminal trimethylsilyl groups allowed for complete spectroscopical characterization, including ^{13}C NMR. The exact structure was established by X-ray diffraction analysis.[59,133]

Tetraphenyl-*carbo*-benzene **77**, with adjacent (*ortho*) unsusbtituted CH vertexes, was obtained by careful treatment of pericyclynediol **22b** with etheral $SnCl_2$/HCl at −50 °C, followed by direct chromatography of the reaction medium over a TLC plate (ca. 5% yield).[58] In the ^{1}H NMR spectrum, the equivalent *ortho* protons directly attached to the macrocycle resonate at 9.70 ppm (9.87 ppm for **74**),[55] confirming a strong magnetic aromaticity of the macrocycle.

The X-ray crystal structure of **77** was compared with the DFT-calculated exact structure: the excellent agreement found demonstrates the adequacy of the calculation level (B3PW91/6-31G**) for exploratory studies of *carbo*-benzene derivatives.[11] Despite the dissymmetic substitution pattern, the C_{18} ring is nearly locally D_{6h} symmetric, with quasi identical C−C bond lengths of a given type.[58] Here, and in all X-ray crystal structures, the phenyl-substituted C_{18} ring exhibits characteristics of strong structural aromaticity. The phenyl substituents remain, however, moderately twisted from the macrocyclic plane (below 30°), thus allowing for residual C_{18}−Ph conjugation. The fact that the bond lengths remain close to the values calculated for the unsubstituted ring **69** (1.369 and 1.239 Å for the $C_{sp}-C_{sp^2}$ and $C_{sp}-C_{sp}$ bonds, respectively: see section 3.5.1) shows that the *carbo*-benzene ring is and remains structurally aromatic upon substitution.[133]

It is finally noteworthy that X-ray crystallography reveals a columnar packing of the C_{18} rings which are only slightly tilted from the channel axis (the hexagonal section is quasi regular).[58,133] The channels also contain chloroform molecules interacting with and through the *carbo*-cycles, thus suggesting that the crystals might exhibit conducting properties.[135]

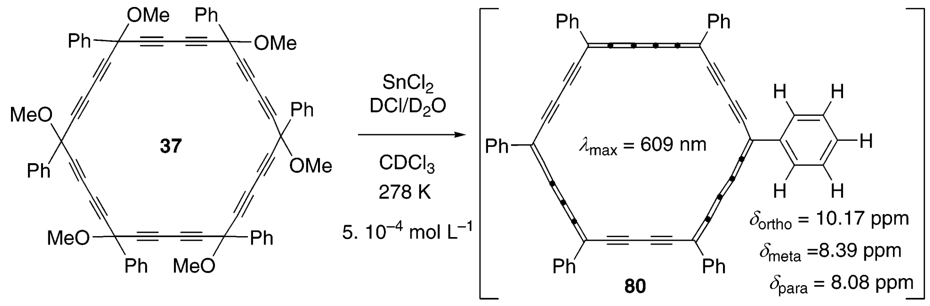


Figure 42. NMR and UV−vis chracaterization of hexaphenyl-*carbo*$_2$-benzene.[80]

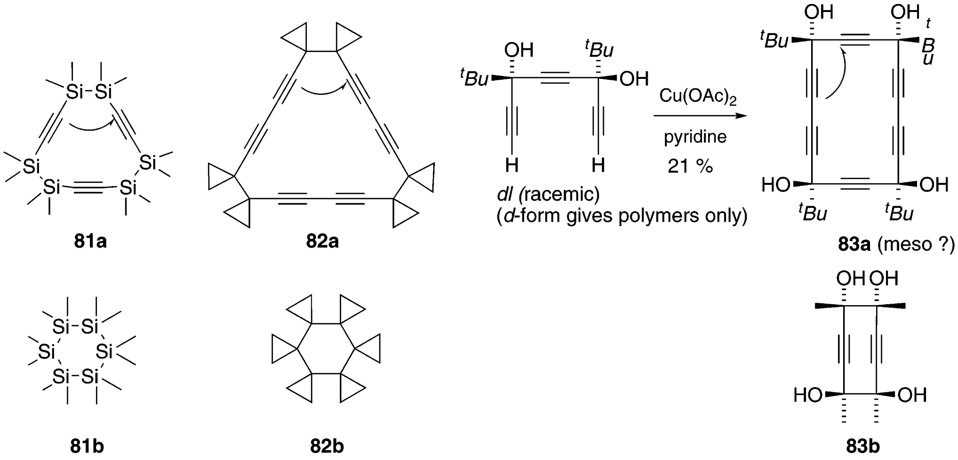


Figure 43. Examples of nonconjugated 2-*carbo*$_k$-meric rings. The two-atom links between successive inserted $(C_{sp})_2$ units may exert electronic communication or simple steric separation.

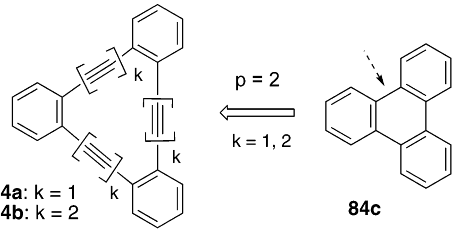


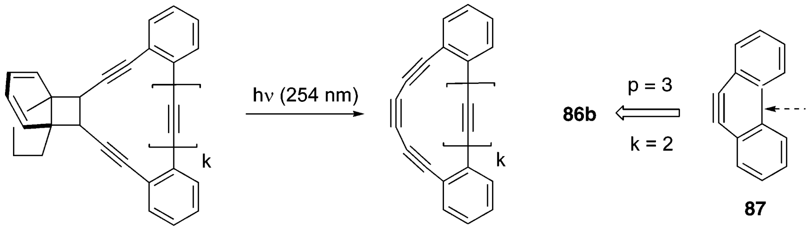
Figure 44. Dehydrobenzoannulenes **84a**−**b** are ring 2-*carbo*-mers of triphenylene **84c**.

Hexaethynyl *carbo*-benzene is the total *carbo*-mer of benzene (C_2 units are inserted into all C−C and C−H bonds) and has been challenged in 1995.[10] Synthesis of the silylated version **78** has been recently achieved through a modified reductive aromatization method (Figure 40).[64,80] Indeed, in the absence of phenyl substituents, the initial trialkynyl carbocation is not stabilized enough, unless a few triple bonds are transiently η^2-complexed to $Co_2(CO)_6$ units. The silylated compound was thus obtained from hexaethynyl hexamethoxy[6]pericyclyne **25** in 12% yield over three steps. The high solubility brought by the $SiEt_3$ protections allowed for exhaustive spectroscopic characterization supporting the aromatic character of the molecule.

Deprotection of the peripheral acetylene units would afford a versatile *carbo*-benzenic substrate for further electrophilic or oxidative functionalization.[80] DFT studies showed that the total *carbo*-mer of benzene **79a** is slightly less aromatic than the unsubstituted ring **69**, in the structural and magnetic sense (Figure 41).[65] The trannulenic form **79b** was also calculated at the B3PW91/6-31G** level: despite its relatively high energy (+66 kcal·mol^{-1}), a D_{3d} minimum was obtained. The C_{60} dimer of its carbon core was used to construct and study novel theoretical *carbo*-meric zigzag carbon nanotubes.[65]

3.5.3. Hexaphenyl Carbo$_2$-benzene

DFT calculations showed that *carbo*$_2$-benzene ($C_{30}H_6$) has a D_{6h} structure and is as aromatic as *carbo*-benzene; their central NICS values, for example, are almost identical (ca. −18.9 ppm).[11] Preparation of the hexaphenyl derivative **80** was attempted from the hexaphenylhexamethoxy expanded [6]pericyclyne **37**, but the use of the $SnCl_2$/HCl system in various preparative conditions did not allow isolation of or even detection of the expected product (Figure 42).[80] Under diluted conditions, however (ca. 5×10^{-4} mol·L^{-1}), ^{1}H NMR monitoring of the reaction in a $SnCl_2/DCl/D_2O/CD_3Cl_3$ mixture allowed the corresponding full characterization: the resonances of the *ortho*, *meta*, and *para* protons of the equivalent phenyl substituents were assigned at 10.17, 8.39, and 8.08 ppm, respectively. The corresponding protons in hexaphenyl *carbo*-benzene **71** resonate at 9.45, 8.38, and 7.72 ppm, respectively:[55,133] the ring current effect is thus ca. +0.5 ppm stronger in the *carbo*$_2$ series than in the *carbo*$_{(1)}$ series. Likewise the UV−vis spectrum of the blue solution containing **80** displays an intense absorption band at $\lambda_{max} = 609$ nm, while diluted orange solutions of **71** absorb at lower wavelength ($\lambda_{max} = 472$ nm). Assignment of the NMR and UV−vis data was supported by a good agreement with B3LYP/6-31+G** and ZINDO calculated values, respectively.[80] The fully optimized structures (B3PW91/6-31G**) showed that while the phenyl rings of hexaphenyl-c*arbo*-benzene **71** are tilted from the C_{18} macrocycle (in accordance with experimatal data), hexaphenyl-c*arbo*$_2$-benzene **80** is perfectly planar (D_{6h}): it is therefore not clear whether the corresponding bathochromic shit ($\Delta\lambda_{max} = 137$ nm) is mainly due to the extended macrocyclic delocalization or to the allowed peripheral delocalization.

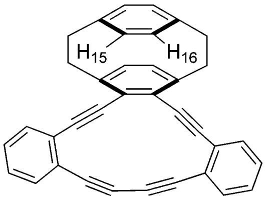


85a: k =1
85b: k =2

86a: k =1
86b: k =2

87

Figure 45. Tobe's preparation of highly strained dibenzodehydroannulenes.[139]



88

Figure 46. Haley's NMR probe for the detection of ring current in a tribenzo[14]annulene core.[141]

4. Ring *p-Carbo*-mers, *p* > 1

Highly symmetric *p-carbo*$_k$-mers of non-acetylenic rings (see section 2) are exemplified below for $p = 2$ and $p \geq 3$, in both nonconjugated and conjugated series. This section just intends to illustrate the *p-carbo*$_k$-meric classification, and it does not pretend to be exhaustive.

4.1. Ring 2-*Carbo*-mers

4.1.1. Nonconjugated Ring 2-Carbo-mers

The question whether electronic interaction between endocyclic (but "isolated") sp carbon atoms could be transmitted through a link of two σ-bonded atoms has been adressed for "optimal" candidates such as a disilylene (Si_{sp^3}—Si_{sp^3}), a dicyclopropylene ($C_{sp^{3/2}}$—$C_{sp^{3/2}}$), or a methylene—methylidyne (C_{sp^3}—C_{sp}).

The 12-membered hexasilacyclotriyne **81a** is the ring 2-*carbo*-mer of cyclohexasilane **81b** (Figure 43). **81a** is the precursor of trisila[3]pericylyne **42** (see section 3.2.2),[87] and a strong interaction of the triples bonds with the Si—Si bonds has been established by photoelectron spectroscopy.[88]

The 18-membered spirocyclopropacyclohexayne **82a** is the 2-*carbo*$_2$-mer of [6]rotane **82b** (see section 3.1.3).[39] Analysis of the X-ray crystal structure and UV—vis spectra showed that the bicyclopropyl "vertex" completely blocks the electronic transmission from one diyne unit to the next.[136]

The 16-membered hydroxylated cyclohexayne **83a** is a ring 2-*carbo*-mer of **83b**, i.e. 2-*carbo*-[4]cyclitol (see sections 3.2 and 3.1.4).[137] The parent molecule, however, still contains triple bonds: this is a second example of the "weak" *p-carbo*-mer relationship, previouly illustrated by Hirsch's molecules **15a** and **15b** (see section 2).[36]

4.1.2. Conjugated Ring 2-Carbo-mers

The paradigm of the conjugated ring 2-*carbo*-mer is Sworski—Myers' hexadehydro[12]annulene **12** (see section 2).[28,29] This nonsubstituted 2-*carbo*-benzene possesses 12 π_z electrons and is therefore antiaromatic.[30] The macrocylic antiaromaticity can however be balanced by annelation to aromatic rings: this occurs in dehydrobenzoannulenes **84a**, the allowed central ring 2-*carbo*-mers of triphenylene **84c** (Figure 44). By contrast, Sondheimer's dodecadehydro[18]annulene **70** (see section 3.5.1) possesses 18 π_z electrons, and benzannelation to **84b** introduces competing aromaticity.[30]

More generally, the balancing/competing aromatic/antiaromatic properties of dehydrobenzo[*n*]annulenes (DBAs) have motivated extensive experimental and theoretical studies in the 1960s and 1970s. More recently, the DBAs attracted renewed attention as precursors of carbon-rich or all-carbon materials and for their potential properties (NLO, optoelectronic, ...). Several recent comprehensive reviews on this topic are available.[8d,138] Owing to the importance of the field

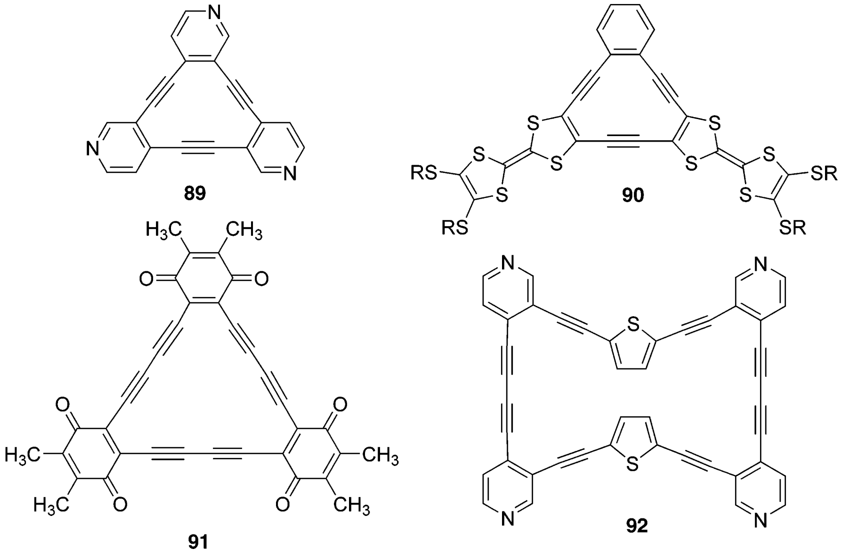


Figure 47. Selected recent examples of DBA derivatives annelated with pyridine, thiophene, or quinone rings.

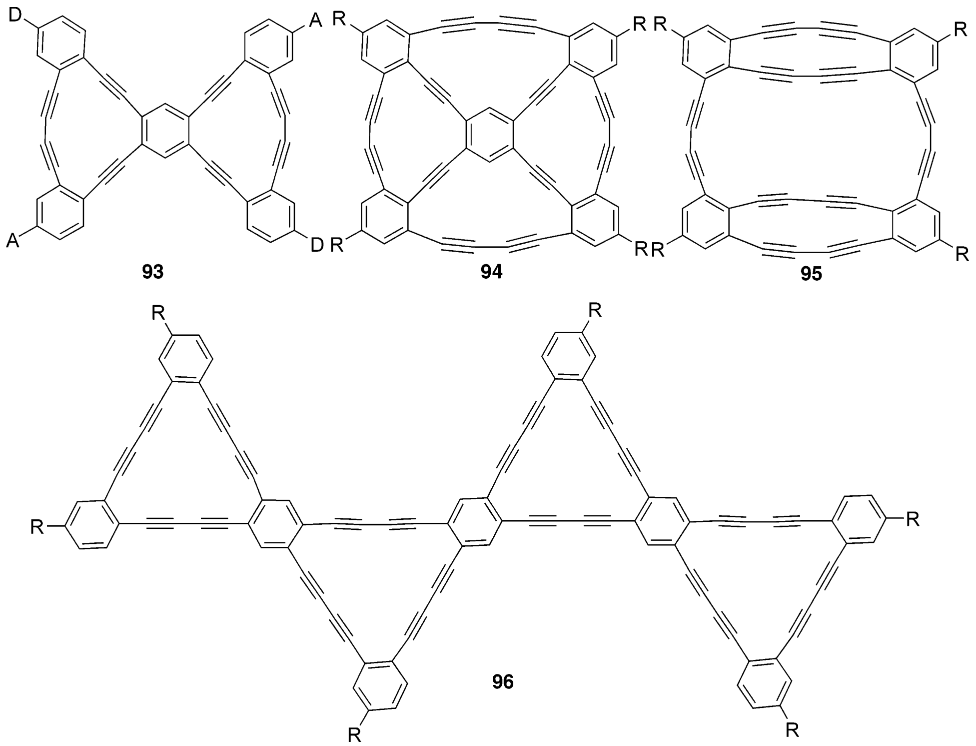


Figure 48. Recently described sophisticated multimacrocyclic DBA derivatives.[147−149]

however, most recent advances in the chemistry of these 2-*carbo*$_k$-meric structures are briefly evoked below.

The synthesis of DBAs possessing a highly strained triyne unit and the correlated effect on aromaticity have been recently studied by Tobe.[139] Photochemical [2 + 2] cycloreversion of [4.3.2]propellatriene-annelated DBAs **85a** and **85b** led to dibenzopentakisdehydro[14]annulenes **86a** and **86b**, respectively (Figure 45). It may be incidentally noticed that **86b** is a central ring 3-*carbo*$_2$-mer of phenanthyne **87**.[140]

The above transformation (Figure 45) was reported to induce a substantial change in the chemical shifts of aromatic protons, which was attributed to the decrease of tropicity of the 14-membered ring of **86b** and to the change of local anisotropy. In a related concern, Haley proposed an alternative method for detecting an induced ring current in less strained DBAs, by introducing a spectroscopic probe in the shielding cone of the DBA core.[141] Thus, a dehydro[14]annulene which is *ortho*-fused to one of the benzene decks of [2.2]paracyclophane, **88**, was prepared (Figure 46). As compared to the acyclic precursor, the upfield shift of the cyclophane protons H15 and H16 of **88** confirmed the existence of diatropic ring current in the [14]annulene ring.

Related to DBAs are dehydroannulenes annelated by conjugated unsaturated heterocycles. Annelation of hexadehydro[12]annulene by several pyridine moieties was thus envisioned ("dehydropyridoannulenes"), and representatives such as **89** were reported to be fluorescent chromophores (Figure 47).[142] They were also found to be precursors for the construction of coordination polymers by autoassembly with Ag(I) cations. DBA analogues annelated with one or two TTF units **90** have also been synthesized and their solvatochromic properties studied.[143] Finally, annelation by *p*-benzoquinone rings was envisoned in dehydro[18]annulenes (such as **91**) which display a weak intramolecular charge transfer due to the delocalization of both the HOMO and LUMO over the whole π-framework.[144]

Thiophene annelation of Sonheimer dehydro[18]annulene **70** is known,[145] and recently a hybrid dehydrobenzannulene **92** containing both C2 and C4 edges and both thiophene and pyridyne annelated rings has been reported by Baxter.[146] This molecule was found to function as a fluorescence sensor for Ag(I) and to exhibit a reversible proton-triggered fluorescence quenching behavior.

Advances in the field of Pd-mediated cross-coupling reactions allow for the construction of increasingly large and more complex DBA systems. Haley et al. recently reported sophisticated multimacrocyclic derivatives using either Pd-catalyzed or Cu-mediated oxidative homocoupling in the ring-closure steps. To freeze the rotation about phenyl−ethynyl bonds, rigid molecules such as **93** have thus been prepared (Figure 48) and studied by absorption and emission spectroscopy.[147] More complex architectures (**94**, **95**) were also designed.[148] Finally, the synthesis of multinanometer-sized fused DBAs (graphdiyne oligomers **96**) with high molar electronic absorption values is to be mentioned.[149]

4.2. Ring *p-Carbo*-mers, $p \geq 3$

4.2.1. Nonconjugated Ring p-Carbo-mers, $p \geq 3$

Symmetrical cyclodiynes have been extensively exemplified in both the carbocyclic and heterocyclic series.[150] These compounds were long obtained by classical acetylenic chemistry, namely based on the nucleophilicity of terminal alkynes and alkadiynes. In the general case of *p-carbo*-meric cyclo-oligoynes $[-C{\equiv}C(CH_2)_p-]_n$ however, a direct synthesis by sequential metathesis of 1,*p*-dipropynyl precursors is an attracting idea, which has been attempted in the most challenging case, namely with $p = 1$ for the synthesis of [*n*]pericyclynes.[151] Although sequential metathesis of a dipropynylsilane was found possible, no cyclic product was detected.[151a] A recent report by Gleiter et al. showed that slightly longer 1,*p*-dipropynyl precursors ($p = 4, 5$) do not proceed, while the monoacetylenic ring-closing product was

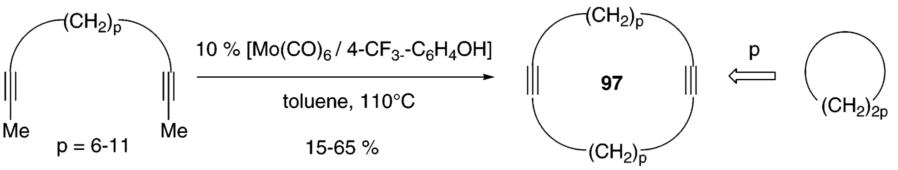


Figure 49. Gleiter's synthesis of *p*-*carbo*-meric cycloalkadiynes by cyclizing double metathesis.[152]

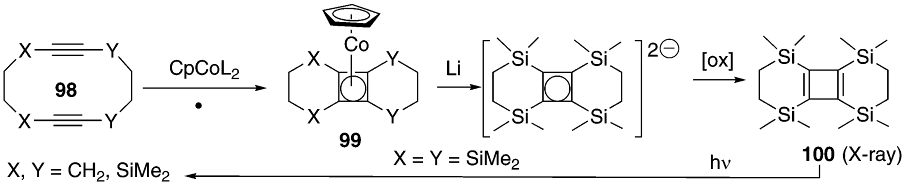


Figure 50. Intramolecular [2 + 2] cycloaddition of 4-*carbo*-meric cyclodiynes with carbon and/or silicon propargylic vertexes, and application to the generation of stable annelated cyclobutadienes.[155−158]

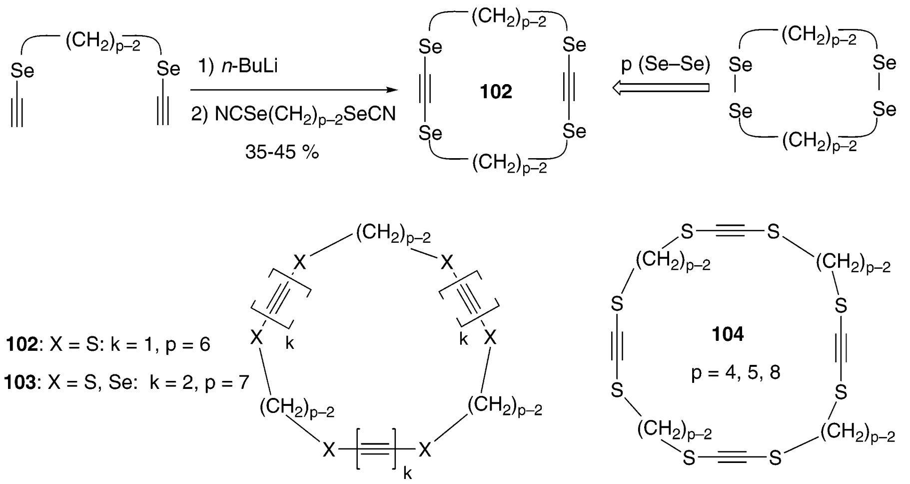


Figure 51. Synthesis of *p*-*carbo*-meric cyclodiynes with chalcogen atoms (S, Se) at all the propargylic positions ($p = 4-8$),[159,160] and related cyclotriynes and cyclotetraynes.[161]

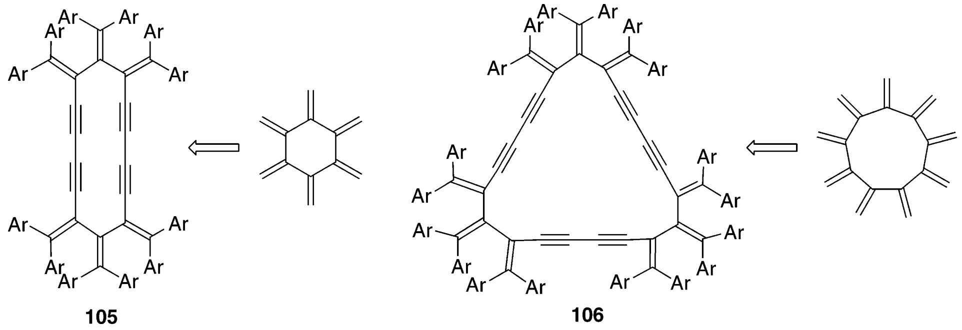


Figure 52. Synthesized ring 3-*carbo*$_2$-mers of [6]- and [9]radialenes.[164]

obtained for $p = 12$ only (Figure 49).[152] For intermediate sizes however ($p = 6-11$), double metathesis afforded the *p*-*carbo*-meric cyclodiynes **97** in 15−72% yield. X-ray diffraction analysis of the largest cyclodiynes indicated that the facing triple bonds adopt either parallel ($p = 11$) or twisted ($p = 10$) mutual orientations, as generally observed for odd or even *p* values, respectively.[153]

A chief chemical property of sufficiently large and flexible cyclodiynes is their ability to undergo transannular ring closure.[154] The C_{12} 4-*carbo*-meric cyclodiyne **98** (X = Y = CH_2) thus reacts with $CpCoL_2$ complexes through an intramolecular [2 + 2] process to give the corresponding bisannelated cyclobutadiene complex **99** (Figure 50).[155] As in the case of the more strained C_{10} 3-*carbo*-meric cyclodiynes,[156] intramolecular selectivity is enhanced or preserved by replacement of carbon vertexes for silicon vertexes, in particular when the silicon vertexes occupy two propargylic positions,[157] or the four propargylic positions as in **98** (X = Y = $SiMe_3$). In the latter case, reductive decomplexation followed by two-electron oxidation afforded a stable bisannelated tetrasilylcyclobutadiene **100**, which reverted to the starting cyclodiyne **98** upon photolysis (Figure 50).[158]

Examples of symmetric cyclodiynes with all-heteroatomic propargylic positions have also been provided in the chalcogen series. Thus, *p*-*carbo*-meric tetrathiacyclodiynes ($p = 4-8$)[159] and analogous tetraselenacyclodiynes **101** ($p = 4-7$) were prepared by double alkynyl-chalcogenapropargyl coupling (Figure 51).[160] X-ray crystallography of selanacyclodiynes **101** indicated that the triple bonds are quasi linear and adopt either parallel or twisted ($p = 10$) mutual

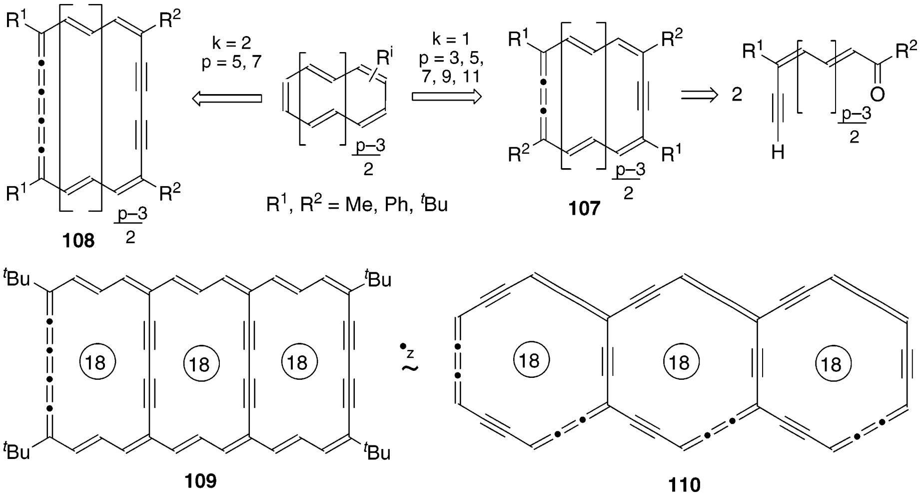


Figure 53. Nakagawa's 4k-dehydro[2p + 4k]annulenes and condensed analogues. The relationship with the total ring *carbo*-mer (p = 1) of anthracene is outlined.

orientations and that the shortest $C_{sp}\cdots C_{sp}$ transannular distance increases with p (4.71−8.27 ppm). The overall structure is governed by the C−SeC$_2$Se−C dihedral angles, which tend to lie between 60 and 90°. For p = 5, 7, the molecules adopt a columnar packing with close contacts (ca. 3.7 Å) between Se atoms of neighboring rings. Similar chalcogen−chalcogen interactions are responsible for tight stacking of larger 6-*carbo*-meric or 7-*carbo*$_2$-meric thia- (**102**) and selenacyclotriynes (**103**);[161] the largest nanotubes were found to act as hosts for solvent molecules.[162] A similar method allowed synthesis of ring *p-carbo*-meric cyclotetraynes **104** with sulfur atoms at the eight propargylic positions.[163]

4.2.2. Conjugated Ring p-Carbo-mers, p ≥ 3

A recent illustration has been provided by Iyoda et al. in the radialenic series.[164] While [6]radialene and ring *carbo*$_k$-mers thereof (k = 1, 2) have been experimentally studied (see section 3.3), the [9]radialene core has been theoretically considered but remains unknown,[165] just as do its ring *carbo*$_k$-mers. Recently however, ring 3-*carbo*$_2$-mers of [6]- and [9]radialene (**105**, **106**) have been described (Figure 52).[164] Their synthesis was performed by Eglinton−Glaser coupling of a diethynyl[3]dendralene precursor (**105** was however obtained in trace quantity). Due to steric repulsions between the aryl groups, the dendralenes exist in a twisted chiral conformation, and in the cyclic trimer, the three units adopt the same sense of chirality, inducing an overall D_3 symmetry. AM1 calculations suggest that the C_{21} ring of **106** has a inner cavity of ca. 2.6 Å, which indeed proved to form silver complexes from Ag(O$_2$CCF$_3$) or AgClO$_4$. The UV−vis spectrum of this expanded [9]radialene exhibits longer wavelength absorptions than the [3]dendralene precursor, thus reflecting an extension of π-conjugation and an increase of planarity.

To finish, let us come back to the 1970s and then to the title of this review. According to the Hückel rule, the aromaticity or antiaromaticity of [2p]annulenes is preserved by *p-carbo$_k$*-merization. For p > 3 and k = 1, tetrasubstituted isomers **107** with *all-trans* −HC⋯CH− ethylene units have been synthesized by Nakagawa et al. via a [p + p] cyclodimerization route.[166] In the series k = 2, a few representatives, **108**, were also prepared (Figure 53).[167] For p = 3, the series k = 1 is completed by Sworski−Myer's tetradehydro[10]annulene **13** (see section 2, Figure 4),[28,31] while, to the best of our knowledge, the series k = 2 still awaits completion. It is noteworthy that, for 2p + 4k = 18 (k = 1, p = 7 or k = 2, p = 5), the π_z electron system is identical to that of the full ring *carbo*-mer of benzene **69** (see section 3.5.1). Annelation of three 5-*carbo*$_2$-meric rings was also achieved in the tricyclic molecule **109**: the topology of the fascinating π_z electron system of **109** should also occur in the ring *carbo*-mer of anthracene **110**, a putative molecule so far.[168]

5. Acronyms

CAN	ceric ammonium nitrate
DBA	dehydrobenzoannulene
DCID	desorprtion chemical ionization
dcpe	dicylohexylphosphinoethane
DFT	density functional theory
DMF	dimethylformamide
dppe	diphenylphosphinoethane
dppm	diphenylphosphinomethane
dppp	diphenylphosphinopropane
EFISH	electric field inducing second harmonic
ELF	electron localization function
esu	electrostatic unit
MALDI-TOF	matrix assisted laser desorption ionization−time-of-flight
NMR	nuclear magnetic resonance
PPTS	pyridinium *para*-toluenesulfonate
SCF	self-consistent field
TBAF	tetrabutylammonium fluoride
TEE	tetraethynylethene
THP	tetrahydropyran
TLC	thin-layer chromatography
TMEDA	tetramethylethylenediamine
TTF	tetrathiafulvalene
UV−vis	ultraviolet−visible
VSEPR	valence shell electron pair repulsion

6. Acknowledgments

The authors wish to thank the French Ministère de l'Education Nationale de la Recherche et de la Technologie and the Centre National de la Recherche Scientifique for financial support. They are also indebted to all talented students, post-docs, and investigators who contributed to

recent advances in the chemistry of *carbo*-meric structures, and especially those whose work is cited in this review and not published yet.

7. References and Notes

(1) (a) Stang, P. J., Diederich, F., Eds.; *Modern Acetylene Chemistry*; Wiley-VCH: Weinheim, 1995. (b) de Meijere, A., Ed. *Top. Curr. Chem.* **1998**, 196. (c) de Meijere, A., Ed. *Top. Curr. Chem.* **1999**, 201. (d) Hopf, H. *Classics in Hydrocarbon Chemistry*; Wiley-VCH: Weinheim, 2000; Chapter 8, p 151. (e) Diederich, F., Stang, J. P., Tykwinski, R. R., Eds. *Acetylene Chemistry. Chemistry, Biology and Material Sciences*; Wiley-VCH: Weinheim, 2005. (f) Haley, M. M., Tykwinsky, R. R., Eds. *Carbon-Rich Compounds*; Wiley-VCH: Weinheim, 2006. (g) Viehe, H. G., Ed. *Chemistry of Acetylenes*; Marcel Dekker: New York, 1969.

(2) For an appending review on the "*carbo*-mers of classical organic functions", see: Maraval, V.; Chauvin, R. To be submitted.

(3) (a) Full issue: *Chem. Rev.* **2001**, *101* (5). (b) Full issue: *Chem. Rev.* **2005**, *105* (10).

(4) An emotive "soft point for alkynes" can be claimed: Bunz, U. H. F. *Synlett* **1997**, 1117.

(5) Galm, U.; Hager, M. H.; Lanen, v. S. G.; Ju, J.; Thorson, J. S.; Shen, B. *Chem. Rev.* **2005**, *105* 739.

(6) Williams, R. V. *Chem. Rev.* **2001**, *101*, 1185.

(7) (a) Diederich, F. *Pure Appl. Chem.* **1999**, *71*, 265. (b) Bunz, U. H. F.; Rubin, Y.; Tobe, Y. *Chem. Soc. Rev.* **1999**, *28*, 107. (c) Nielsen, M. B.; Diederich, F. *Chem. Rec.* **2002**, *2*, 189.

(8) (a) Youngs, W. J.; Tessier, C. A.; Bradshaw, J. D. *Chem. Rev.* **1911**, *11*, 3153. (b) Grave, C.; Schlüter, D. *Eur. J. Org. Chem.* **2002**, 3075. (c) Yamaguchi, Y.; Yoshida, Z.-i. *Chem.—Eur. J.* **2003** *9*, 5430. (d) Jones, C. S.; O' Connor, M. J.; Haley, M. M. In *Acetylene Chemistry. Chemistry Biology and Material Sciences*; Diederich, F., Stang, P. J., Tykwinski, R. R., Eds.; Wiley: Weinheim, 2005; Chapter 8, p 303.

(9) Toyota, S.; Iyoda, M.; Toda, F. *Annu. Rep. Prog. Chem., Sect. B* **2002**, *98*, 359.

(10) Chauvin, R. *Tetrahedron Lett.* **1995**, *36*, 397.

(11) Chauvin, R.; Lepetit, C. In *Acetylene Chemistry. Chemistry, Biology and Material Sciences*; Diederich, F., Stang, P. J., Tykwinski, R. R., Eds.; Wiley: Weinheim, 2005; Chapter 1, p 1.

(12) (a) Mohr, W.; Stahl, J.; Hampel, F.; Gladysz, J. A. *Chem.—Eur. J.* **2003**, *9*, 3324. (b) Szafert, S.; Gladysz, J. A. *Chem. Rev.* **2003**, *103*, 4175.

(13) Klinger, C.; Vostrowsky, O.; Hirsch, A. *Eur. J. Org. Chem.* **2006**, 1508.

(14) (a) Stahl, J.; Bohling, J. C.; Bauer, E. B.; Peters, T. B.; Mohr, W.; Martin-Alvarez, J. M.; Hampel, F.; Gladysz, J. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1871. (b) Owen, G. R.; Stahl, J.; Hampel, F.; Gladysz, J. A. *Organometallics* **2004**, *23*, 5889.

(15) Many dinuclear phosphine−platinum complexes with Pt−Pt bonds are however known, in particular with a bicyclic core or $Pt-C_6F_5$ bonds. See for example: (a) Rashidi, M.; Jennings, M. C.; Puddephatt, R. J. *Organometallics* **2003**, *22*, 2612. (b) Alonso, E.; Fornies, J.; Fortuno, C.; Martin A.; Orpen, A. G. *Organometallics* **2003**, *22*, 2723.

(16) (a) Mitzel, F.; Boudon, C.; Gisselbrecht, J.-P.; Seiler, P.; Gross, M.; Diederich, F. *Chem. Commun.* **2003**, 1634. (b) Mitzel, F.; Boudon, C.; Gisselbrecht, J.-P.; Seiler, P.; Gross, M.; Diederich, F. *Helv. Chim. Acta* **2004**, *87*, 1130.

(17) Dinadayalane, T. C.; Priyakumar, U. D.; Sastry, G. N. *J. Phys. Chem. A* **2004**, *108*, 11433 and references therein.

(18) To the best of our knowledge, the only experimental report on this kind of structure can be found in: Ziegler, E.; Brandmueller, J. *Z. Anal. Chem.* **1965**, *210*, 193.

(19) Diercks, R.; Armstrong, J. C.; Boese, R.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1986**, *26*, 268.

(20) (a) Sonoda, M.; Inaba, A.; Itahashi, K.; Tobe, Y. *Org. Lett.* **2001**, *3*, 2419. (b) Ito, S.; Inabe, H.; Morita, N.; Ohta, K.; Kitamura, I.; Imafuku, K. *J. Am. Chem. Soc.* **2003**, *125*, 1669.

(21) For a review, see: Bunz, U. H. F. *J. Organomet. Chem.* **2003**, *683*, 269.

(22) Solooki, D.; Parker, T. C.; Kahn, S. I.; Rubin, Y. *Tetrahedron Lett.* **1998**, *39*, 1327.

(23) (a) Miao, S.; Bangcuyo, C. G.; Smith, M. D.; Uwe, H. F.; Bunz, U. H. F. *Angew. Chem., Int. Ed.* **2006**, *45*, 661. (b) Miao, S.; Smith, M. D.; Bunz, U. H. F. *Org. Lett.* **2006**, *8*, 756.

(24) Lange, T.; Gramlich, V.; Amrein, W.; Diederich, F.; Gross, M.; Boudon, C.; Gisselbrecht, J.-P. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 805.

(25) The insertion can be *freely* applied to monocyclic (nonannelated) rings only.

(26) The following properties can be readily checked: (i) the number of atoms in a p-$carbo_k$-meric ring must be a multiple of p; (ii) if n is a prime number (namely a common odd ring size: 3, 5, 7, ...), the sole ring p-$carbo_k$-mers of an n-membered ring are degenerate ($p = n$: only one C_{2k} unit can be inserted); (iii) a p-$carbo_k$-mer of a n-membered ring is a $(n/p)(2k + p)$-membered ring.

(27) Dale, J. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 1000.

(28) Sworski, T. J. *J. Chem. Phys.* **1948**, *16*, 550.

(29) Untch, K. G.; Wysoki, D. C. *J. Am. Chem. Soc.* **1966**, *88*, 2608.

(30) (a) Martin, R. E.; Gubler, U.; Cornil, J.; Balakina, M.; Boudon, C.; Bosshard, C.; Gisselbrecht, J. P.; Diederich, F.; Günter, P.; Gross, M.; Brédas, J.-L. *Chem.—Eur. J.* **2000**, *6*, 3623. (b) Jusélius, J.; Sundholm, D. *Phys. Chem. Chem. Phys.* **2001**, *3*, 2433. (c) Alkorta, I.; Rozas, I.; Elguero, J. *Tetrahedron* **2001**, *57*, 6043.

(31) Myers, A. G.; Finney, N. S. *J. Am. Chem. Soc.* **1992**, *114*, 10986.

(32) Schleyer, P. v. R.; Jiao, H.; Sulzbach, H. M.; Schaeffer, H. F., III. *J. Am. Chem. Soc.* **1996**, *118*, 2093.

(33) It must be emphasized that *p-carbo*-merization of substituted benzene derivatives ($p = 2$ or 3) is not univocal: the *p-carbo*-meric structure depends on the selected starting vertex and on the sense of application of the C2 insertion around the ring.

(34) (a) Moore, W. R.; Ozretich, T. M. *Tetrahedron Lett.* **1967**, 3205. (b) For a recent review on cyclooctynes, see: Heber, D.; Rösner, P.; Tochtermann, W. *Eur. J. Org. Chem.* **2005**, 4231.

(35) (a) Angus, R. O., Jr.; Johnson, R. P. *J. Org. Chem.* **1984**, *49*, 2880. (b) For a general discussion, see: Hopf, H. *Classics in Hydrocarbon Chemistry*; Wiley-VCH: Weinheim, 2000, Chapter 9, p 171.

(36) Leibrock, B.; Vostrowsky, O.; Hirsch, A. *Eur. J. Org. Chem.* **2001**, 4401.

(37) Kloster-Jensen, E.; Wirz, J. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 671. This molecule is also a ring 2-*carbo*-mer of the corresponding less "primitive" [4]pericyclyne.

(38) Scott, L. T.; DeCicco, G. J.; Hyun, J. L.; Reinhardt, G. *J. Am. Chem. Soc.* **1983**, *105*, 7760.

(39) de Meijere, A.; Kozhushkov, S. I. *Top. Curr. Chem.* **1999**, *201*, 1.

(40) Houk, K. N.; Scott, L. T.; Rondan, N. G.; Spellmeyer, D. C.; Reinhardt, G.; Hyun, J. L.; DeCicco, G. J.; Weiss, R.; Chen, M. H. M.; Bass, L. S.; Clardy, J.; Jorgensen, F. S.; Eaton, T. A.; Sarkozi, V.; Petit, C. M.; Ng, L.; Jordan, K. D. *J. Am. Chem. Soc.* **1985**, *107*, 6556.

(41) Zahradnik, R.; Hobza, P.; Burcl, R.; Hess, B. A., Jr.; Radziszewski, J. G. *THEOCHEM* **1994**, *313*, 335.

(42) Dewar, M. J. S.; Holloway, M. K. *J. Chem. Soc., Chem. Commun.* **1984**, *17*, 1188.

(43) (a) Scott, L. T.; Cooney, M. J. Macrocyclic homoconjugated polyacetylenes. In *Modern Acetylene Chemistry*; Stang, P. J., Diederich, F., Eds.; Wiley: Weinhem, 1995; p 321. (b) Cooney M. J. Ph.D. dissertation, University of Nevada, Reno, 1993.

(44) Scott, L. T.; DeCicco, G. J.; Hyun, J. L.; Reinhardt, G. *J. Am. Chem. Soc.* **1985**, *107*, 6546.

(45) (a) Scott, L. T.; Cooney, M. J.; Rogers, D. W.; Dejroongruang, K. *J. Am. Chem. Soc.* **1988**, *110*, 7244. (b) Schaad, L. J.; Hess, B. A., Jr.; Scott, L. T. *J. Phys. Org. Chem.* **1993**, *6*, 316. (c) Jiao H.; Hommes, N. J. R. v. E.; Schleyer, P. v. R.; de Meijere, A. *J. Org. Chem.* **1996**, *61*, 2826.

(46) Lepetit, C.; Silvi, B.; Chauvin, R. *J. Phys. Chem. A* **2003**, *107*, 464.

(47) Rogers, D. W.; Matsunaga, N.; McLafferty, F. J.; Zavitsas, A. A.; Liebman, J. F. *J. Org. Chem.* **2004**, *69*, 7143.

(48) Scott, L. T.; Cooney, M. J.; Otte, C.; Puls, C.; Haumann, T.; Boese, R.; Carroll, P. J.; Smith, A. B., III; de Meijere, A. *J. Am. Chem. Soc.* **1994**, *116*, 10275.

(49) (a) Musso, H.; Wagner, A. *Chem. Ber.* **1988**, *121*, 2239. (b) Gensler, W. J.; Casella, J., Jr. *J. Am. Chem. Soc.* **1958**, *80*, 1376.

(50) Cooney, M. J.; Scott, L. T. *Abstr. Pap. Am. Chem. Soc.* 199: 205-ORGN Part 2, Apr. 22, 1990.

(51) Maurette, L.; Godard, C.; Frau, S.; Lepetit, C.; Soleihavoup, M.; Chauvin, R. *Chem.—Eur. J.* **2001**, *7*, 1165.

(52) IUPAC nomenclaure of cyclitols: *Biochem. J.* **1976**, *153*, 23.

(53) Chauvin, R. *Tetrahedron Lett.* **1995**, *36*, 401.

(54) Kuwatani, Y.; Watanabe, N.; Ueda, I. *Tetrahedron Lett.* **1995**, *36*, 119.

(55) Suzuki, R.; Tsukuda, H.; Watanabe, N.; Kuwatani, Y.; Ueda, I. *Tetrahedron* **1998**, *54*, 2477.

(56) (a) Holmes, A. B.; Jennings-White, C. L. D.; Schulthess, A. H.; Akinde, B.; Walton, D. R. M. *J. Chem. Soc., Chem. Commun.* **1979**, 840. (b) Abele, E.; Rubina, K.; Popelis, J.; Mazeika, I.; Lukevics, E. *J. Organomet. Chem.* **1999**, *586*, 184. (c) Sui-Seng, C.; Soleilhavoup, M.; Maurette, L.; Tedeschi, C.; Donnadieu, B.; Chauvin, R. *Eur. J. Org. Chem.* **2003**, *9*, 1641.

(57) Saccavini, C.; Tedeschi, C.; Maurette, L.; Sui-Seng, C.; Zou, C.-H.; Soleilhavoup, M.; Vendier, L.; Chauvin, R. Accepted for publication in *Chem.—Eur. J.*

(58) Maurette, L. Ph.D. Dissertation, Université Paul Sabatier, Toulouse, Sept. 21, 2001.

(59) Saccavini, C. Ph.D. Dissertation, Université Paul Sabatier, Toulouse, Oct. 24, 2004.

(60) Meyer, A.; Gorgues, A.; Le Floc'h, Y.; Pineau, Y.; Guilleviv, J.; Le Marouille, J. Y. *Tetrahedron Lett.* **1981**, *22*, 5181.

(61) (a) Sui-Seng, C.; Soleilhavoup, M.; Maurette, L.; Tedeschi, C.; Donnadieu, B.; Chauvin, R. *Eur. J. Org. Chem.* **2003**, *9*, 1641. (b) Soleilhavoup, M.; Maurette, L.; Lamirand, C.; Donnadieu, B.; McGlinchey, M. J.; Chauvin, R. *Eur. J. Org. Chem.* **2003**, *9*, 1652.

(62) Maurette, L.; Tedeschi, C.; Sermot, E.; Soleilhavoup, M.; Hussain, F.; Donnadieu, B.; Chauvin, R. *Tetrahedron* **2004**, *60*, 10077.

(63) Tedeschi, C.; Soula, S.; Zou, C.-H.; Chauvin, R. Unpublished results.

(64) Zou, C.-H.; Duhayon, C.; Maraval, V.; Chauvin, R. Unpublished results.

(65) Lepetit, C.; Zou, C.-H.; Chauvin, R. *J. Org. Chem.* **2006**, *71*, 6317.

(66) Glaser, C. *Chem. Ber.* **1869**, *2*, 422.

(67) Behr, O. M.; Eglinton, G.; Galbraith, A. R.; Raphael, R. A. *J. Chem. Soc.* **1960**, 3614.

(68) Hay, A. S. *J. Org. Chem.* **1962**, *27*, 3320.

(69) Cadiot, P.; Chodkiewicz, W. Couplings of acetylenes. In *Chemistry of acetylenes*; Viehe, H. G., Ed.; Dekker: New York, 1969; Vol. 9, p 630.

(70) (a) Siemsen, P.; Livingston, R. C.; Diederich, F. *Angew. Chem., Int. Ed.* **2000**, *39*, 2632. (b) Batsanov, A. S.; Collings, J. C.; Fairlamb, I. J. S.; Holland, J. P.; Howard, J. A. K.; Lin, Z.; Marder, T. B.; Parsons, A. C.; Ward, R. M.; Zhu, J. *J. Org. Chem.* **2005**, *70*, 703.

(71) O'Krongly, D.; Denmeade, S. R.; Chiang, M. Y.; Breslow, R. *J. Am. Chem. Soc.* **1985**, *107*, 5544.

(72) Tedeschi, C.; Saccavini, C.; Maurette, L.; Soleilhavoup, M.; Chauvin, R. *J. Organomet. Chem.* **2003**, *670*, 151.

(73) Scott, L. T.; Cooney, M. J.; Johnels, D. *J. Am. Chem. Soc.* **1990**, *112*, 4054.

(74) (a) de Meijere, A.; Kozhushkov, S. I.; Puls, C.; Haumann, T.; Boese, R.; Cooney, M. J.; Scott, L.T. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 869. (b) de Meijere, A.; Kozhushkov, S. I.; Haumann, T.; Boese, R.; Puls, C.; Cooney, M. J.; Scott, L. T. *Chem.—Eur. J.* **1995**, *1*, 124.

(75) Isaacs, L.; Seiler, P.; Diederich, F. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1466. (b) Isaacs, L.; Diederich, F.; Haldimann, R. F. *Helv. Chim. Acta* **1997**, *80*, 317.

(76) Prange, T.; Pascard, C.; de Meijere, A.; Behrens, U.; Barnier, J. P.; Conia, J. M. *Nouv. J. Chim.* **1980**, *4*, 321.

(77) de Meijere, A.; Kozhushkov, S. I. *Chem.—Eur. J.* **2002**, *8*, 3195.

(78) Brake, M.; Enkelmann, V.; Bunz, U. H. F. *J. Org. Chem.* **1996**, *61*, 1190.

(79) Manini, P.; Amrein, W.; Gramlich, V.; Diederich, F. *Angew. Chem., Int. Ed.* **2002**, *41*, 4339.

(80) Zou, C.; Lepetit, C.; Coppel, Y.; Chauvin, R. *Pure Appl. Chem.* **2006**, *78*, 791.

(81) Zou, C.-H.; Maraval, V.; Chauvin, R. Unpublished results.

(82) See for example: Hrovat, D. A.; Borden, W. T.; Eaton, P. E.; Bart, K. *J. Am. Chem. Soc.* **2001**, *123*, 1289.

(83) (a) Bachrach, S. M. *J. Phys. Chem. A* **2003**, *107*, 4957. (b) Jarowski, P. D.; Diederich, F.; Houk, K. N. *J. Org. Chem.* **2005**, *70*, 1671.

(84) Lepetit, C.; Peyrou, V.; Chauvin, R. *Phys. Chem. Chem. Phys.* **2004**, *6*, 303.

(85) Saccavini, C.; Yahi, L.; Tedeschi, C.; Lepetit, C.; Chauvin, R. Manuscript in preparation.

(86) (a) Schuster, H. G.; Hengge, E. *Monatsh. Chem.* **1983**, *114*, 1305. (b) Weidenbruch, M.; Brndt-Roth, B.; Siegfried, P.; Saak, W. *J. Organomet. Chem.* **1989**, *379*, 217. (c) Weidenbruch, M.; Lesch, M.; Peters, K.; Schnering, v. H. G. *J. Organomet. Chem.* **1992**, *423*, 329. (d) Chernyavskii, A. I.; Larkin, D. Y.; Chernavskaya, N. A. *J. Organomet. Chem.* **2003**, *679*, 13.

(87) Sakurai, H.; Eriyama, Y.; Hosomi, A.; Nakadaira, Y.; Kabuto, C. *Chem. Lett.* **1984**, 595.

(88) Gleiter, R.; Schäfer, W.; Sakurai, H. *J. Am. Chem. Soc.* **1985**, *107*, 3046.

(89) (a) Voronkov, M. G.; Pavlov, S. F. *J. Gen. Chem. USSR* **1973**, *43*, 1397. (b) Hengge, E.; Baumegger, A. *J. Organomet. Chem.* **1989**, *369*, C39. (c) Baumegger, A.; Hengge, E.; Gamper, S.; Hardtweck, E.; Janoschek, R. *Monatsh. Chem.* **1991**, *122*, 661. (d) Voronkov, M.; Yarosh, O.; Zhilitskaya, L. *Phosphorus, Sulfur Silicon Relat. Elem.* **1992**, *65*, 33.

(90) Bortolin, R.; Parbhoo, B.; Brown, S. S. D. *J. Chem. Soc., Chem. Commun.* **1988**, 1079.

(91) Unno, M.; Saito, T.; Matsumoto, H. *Bull. Chem. Soc. Jpn.* **2001**, *74*, 2407.

(92) Bortolin, R.; Brown, S. S. D.; Parbhoo, B. *Inorg. Chim. Acta* **1989**, *158*, 137.

(93) Kakiuchi, K.; Tsutsumi, T.; Suzuka, T.; Arai, Y.; Iseta, F. Jpn. Kokai Tokkyo Koho 2006, JP 2006076959 A2 20060323. Application: JP 2004-264399 20040910.

(94) Scott, L. T.; Unno, M. *J. Am. Chem. Soc.* **1990**, *112*, 7823.

(95) Werz, D. B.; Gleiter, R. *Org. Lett.* **2004**, *6*, 589.

(96) Unno, M.; Negishi, K.; Matsumoto, H. *Chem. Lett.* **2001**, 340.

(97) Markl, G.; Zollitsch, T.; Kreitmeier, P.; Prinzhorn, M.; Reithinger, S.; Eibler, E. *Chem.—Eur. J.* **2000**, *6*, 3806.

(98) ALQuaisi, S. M.; Galat, K. J.; Chai, M.; Ray, D. G., III; Rinaldi, P. L.; Tessier, C. A.; Youngs, W. J. *J. Am. Chem. Soc.* **1998**, *120*, 12149.

(99) Bruce, M. I.; Costuas, K.; Haley, J.-F.; Hall, B. C.; Low, P. J.; Nicholson, B. K.; Skelton, B. W.; White, A. H. *Dalton Trans.* **2002**, 383.

(100) Janka, M.; Anderson, G. K.; Rath, N. P. *Organometallics* **2004**, *23*, 4382.

(101) Hopf, H.; Maas, G. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 931.

(102) Höpfner, T.; Jones, P. G.; Ahren, B.; Dix, I.; Ernst, L.; Hopf, H. *Eur. J. Org. Chem.* **2003**, 2596.

(103) Konstantinova, E.; Galvao, D. S.; Barone, P. M. V. B.; Dantas, S. O. *THEOCHEM* **2005**, *729*, 203.

(104) Lepetit, C.; Nielsen, M. B.; Diederich, F.; Chauvin, R. *Chem.—Eur. J.* **2003**, *9*, 5056.

(105) Eisler, S.; Tykwinski, R. R. *Angew. Chem., Int. Ed.* **1999**, *38*, 1940.

(106) Gholami, M.; Tykwinski, R. R. *11th International Symposium on Novel Aromatic Compounds*; Abstract 288 2005.

(107) (a) Boldi, A. M.; Diederich, F. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 468. (b) Anthony, J.; Boldi, A. M.; Boudon, C.; Gisselbrecht, J.-P.; Gross, M.; Seiler, P.; Knobler, C. B.; Diederich, F. *Helv. Chim. Acta* **1995**, *78*, 797.

(108) Schreiber, M.; Tykwinski, R. R.; Diederich, F.; Spreiter, R.; Gubler, U.; Bosshard, C.; Poberaj, I.; Günter, P.; Boudon, C.; Gisselbrecht, J.-P.; Gross, M.; Jonas, U.; Ringsdorf, H. *Adv. Mater.* **1997**, *9*, 339.

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

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

(111) (a) Zhao, Y.-L.; Liu, Q.; Zhang, J.-P.; Liu, Z. Q. *J. Org. Chem.* **2005**, *70*, 6913. (b) Kano, K.; Sugimoto, T.; Misaki, Y.; Enoki, T.; Hatakeyama, H.; Oka, H.; Hosotani, Y.; Yoshida, Z. *J. Phys. Chem.* **1994**, *98*, 252. Kano, K.; Sugimoto, T.; Misaki, Y.; Enoki, T.; Hatakeyama, H.; Oka, H.; Hosotani, Y.; Yoshida, Z. *J. Phys. Chem.* **1994**, *98*, 252.

(112) For recent references, see for example: (a) Quiñonero, D.; Garau, C.; Frontera, A.; Ballester, P.; Costa, A.; Deyà, P. M. *Chem.—Eur. J.* **2002**, *8*, 433. (b) Städeli, W.; Hollenstein, R.; von Philipsborn, W. *Helv. Chim. Acta* **2004**, *60*, 948.

(113) Ortman, B. J.; Hauge, R. H.; Margrave, J. L.; Kafafi, Z. H. *J. Phys. Chem.* **1990**, *94*, 7973.

(114) (a) Li, M.; Zou, C.; Duhayon, C.; Chauvin, R. *Tetrahedron Lett.* **2006**, *47*, 1047. (b) Zou, C.-H.; Chauvin, R. Unpublished results.

(115) (a) Gicquel, M.; Lepetit, C.; Heully, J.-L.; Chauvin, R. *Chimia* **2005**, *59*, 448, P206. (b) Gicquel, M.; Lepetit, C.; Heully, J.-L.; Chauvin, R. Full paper in preparation. (c) Chermette, H.; Lepetit, C.; Heully, J.-L.; Gicquel, M.; Chauvin, R. *J. Phys. Chem. A*, Accepted under revision.

(116) These molecules are 2-*carbo*$_2$-mers of dioxocyclopropa[n]annulenes (n = 6, 8, 10): Rubin, Y.; Kahr, M.; Knobler, C. B.; Wilkins, L. *J. Am. Chem. Soc.* **1991**, *113*, 495.

(117) Okamura, W. H.; Sondheimer, F. *J. Am. Chem. Soc.* **1967**, *89*, 5991.

(118) Albrecht, K.; Belzner, J. *Nachr. Chem., Tech. Lab.* **1996**, *44*, 147.

(119) Yvari, I.; Jabbari, A.; Samadizadeh, M. *J. Chem. Res., Synop.* **1999**, 152.

(120) Godard, C.; Lepetit, C.; Chauvin, R. *Chem. Commun.* **2000**, 1833.

(121) Lepetit, C.; Godard, C.; Chauvin, R. *New J. Chem.* **2001**, *25*, 572.

(122) (a) Kruszewski, J. *Tetrahedron Lett.* **1972**, 3839. (b) Krygowski, T. M.; Cyrañski, M. K. *Chem. Rev.* **2001**, *101*, 1385.

(123) Lepetit, C.; Lacroix, P.; Peyrou, V.; Saccavini, C.; Chauvin, R. *J. Comput. Methods Sci. Eng.* **2004**, *4*, 569.

(124) Poater, J.; Duran, M.; Solà, M.; Silvi, B. *Chem. Rev.* **2005**, *105*, 391.

(125) Fuster, F.; Sevin, A.; Silvi, B. *J. Phys. Chem.* **2000**, *104*, 852.

(126) Santos, J. C.; Tiznado, W.; Contreras, R.; Fuentealba, P. *J. Chem. Phys.* **2004**, *120*, 1670.

(127) Katritsky, A. R.; Barczynski, P.; Musumarra, G.; Pisano, D.; Szafran, M. *J. Am. Chem. Soc.* **1989**, *111*, 7.

(128) (a) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes, N. J. R. v. E. *J. Am. Chem. Soc.* **1996**, *118*, 6317. (b) Fallah-Bagher-Shaidaei, H.; Wannere, C. S.; Corminboeuf, C.; Puchta, R.; Schleyer, P. v. R. *Org. Lett.* **2006**, *8*, 863.

(129) Soncini, A.; Fowler, P. W.; Cernusak, I.; Steiner, E. *Phys. Chem. Chem. Phys.* **2001**, *3*, 3920.

(130) Ducere, J.-M.; Lepetit, C.; Lacroix, P. G.; Heully, J.-L.; Chauvin, R. *Chem. Mater.* **2002**, *14*, 3332.

(131) Baughman, R. H.; Eckhardt, H. *J. Chem. Phys.* **1987**, *87*, 6687.

(132) Coluci, V. R.; Braga, S. F.; Legoas, S. B.; Galvao, D. S.; Baughman, R. H. *Nanotechnology* **2004**, *15*, S142.

(133) Saccavini, C.; Sui-Seng, C.; Maurette, L.; Lepetit, C.; Soula, S.; Zou, C.-H.; Donnadieu, B.; Chauvin, R. Accepted for publication in *Chem.—Eur. J.*

(134) Nakatani, K.; Lacroix, P. G.; Saccavini, C.; Chauvin, R. Unpublished results.

(135) Schön, J. H.; Kloc, C.; Batlogg, B. *Science* **2001**, *293*, 2432.

(136) de Meijere, A.; Jackel, F.; Simon, A.; Borrmann, H.; Köhler, J.; Johnels, D.; Scott, L. T. *J. Am. Chem. Soc.* **1991**, *113*, 3935.

(137) Toda, F.; Okada, J.; Mori, K. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 859.

(138) Hisaki, I.; Sonoda, M.; Tobe, Y. *Eur. J. Org. Chem.* **2006**, 833.

(139) Hisaki, I.; Eda, T.; Sonoda, M.; Niino, H.; Sato, T.; Wakabayashi, T.; Tobe, Y. *J. Org. Chem.* **2005**, *70*, 1853.

(140) Tomioka, H.; Okuno, A.; Sugiyama, T.; Murata, S. *J. Org. Chem.* **1995**, *60*, 2344.

(141) Hinrichs, H.; Fischer, A. K.; Jones, P. T.; Hopf, H.; Haley, M. M. *Org. Lett.* **2005**, *7*, 3793.

(142) Baxter, P. N. W.; Dali-Youcef, R. *J. Org. Chem.* **2005**, *70*, 4935.

(143) Hara, K.; Hasegawa, M.; Kuwatani, Y.; Enozawa, H.; Iyoda, M. *Chem. Commun.* **2004**, 2042.

(144) Nishinaga, T.; Miyata, Y.; Nodera, N.; Komatsu, K. *Tetrahedron* **2004**, *60*, 3375.

(145) Sarkar, A.; Haley, M. M. *Chem. Commun.* **2000**, 1733.

(146) Baxter, P. N. W. *J. Org. Chem.* **2004**, *69*, 1813.

(147) Marsden, J. A.; Miller, J. J.; Shirtcliff, L. D.; Haley, M. M. *J. Am. Chem. Soc.* **2005**, *127*, 2464.

(148) Marsden, A. M.; O'Connor, M. J.; Haley, M. M. *Org. Lett.* **2004**, *6*, 2385.

(149) Marsden, J. A.; Haley, M. M. *J. Org. Chem.* **2005**, *70*, 10213.

(150) Gleiter, R.; Meger, R. Cyclic alkynes: Preparation and Properties. In *Modern Acetylene Chemistry*; Stang, P. J., Diederich, F., Eds.; Wiley-VCH: Weinheim, 1995; p 285.

(151) (a) Huc, V.; Weihofen, R.; Martin-Jimenez, I.; Oulié, P.; Lepetit, C.; Lavigne, G.; Chauvin, R. *New J. Chem.* **2003**, *27*, 1412. (b) Maraval, V.; Lepetit, C.; Caminade, A.-M.; Majoral, J.-P.; Chauvin, R. *Tetrahedron Lett.* **2006**, *47*, 2155.

(152) Hellbach, B.; Gleiter, R.; Rominger, F. *Synthesis* **2003**, 2535.

(153) Gleiter, R.; Pflästerer, G.; Nuber, B. *J. Chem. Soc., Chem. Commun.* **1993**, 454.

(154) Habberhauer, G.; Gleiter, R. *J. Am. Chem. Soc.* **1999**, *121*, 4664.

(155) King, R. B.; Efraty, A. *J. Am. Chem. Soc.* **1972**, *94*, 3021.

(156) (a) Haberhauer, G.; Gleiter, R.; Irngartinger, H.; Oeser, T.; Rominger, F. *J. Chem. Soc., Perkin Trans. 2* **1999**, 2093. (b) Gleiter, R.; Haberhauer, G.; Irngartinger, H.; Oeser, T.; Rominger, F. *Organometallics* **1999**, *18*, 3615.

(157) Gleiter, R.; Stahr, H.; Nuber, B. *Organometallics* **1997**, *16*, 646.

(158) Sekiguchi, A.; Tanaka, M.; Matsuo, T.; Watanabe, H. *Angew. Chem., Int. Ed.* **2001**, *40*, 1675.

(159) Benisch, C.; Bethke, S.; Gleiter, R.; Oeser, T.; Pritzkow, H.; Rominger, F. *Eur. J. Org. Chem.* **2000**, 2479.

(160) Werz, D. B.; Gleiter, R.; Rominger, F. *J. Org. Chem.* **2002**, *67*, 4290.

(161) Gleiter, R.; Werz, D. B.; Rausch, B. J. *Chem.—Eur. J.* **2003**, *9*, 2676.

(162) Werz, D. B.; Gleiter, R.; Rominger, F. *J. Am. Chem. Soc.* **2002**, *124*, 10638.

(163) Rausch, B. J.; Werz, D. B.; Tittinger, S.; Gliter, R.; Oeser, T.; Rominger, F. *J. Chem. Soc., Perkin Trans. 2* **2002**, 72.

(164) Iyoda, M.; Kuwatani, Y.; Yamagata, S.; Nakamura, N.; Todaka, M.; Yamamoto, G. *Org. Lett.* **2004**, *6*, 4667.

(165) Aihara, J. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1751.

(166) (a) Kukui, K.; Nomoto, T.; Nakatsuji, S.; Nakagawa, M. *Tetrahedron Lett.* **1972**, *31*, 3157. (b) Nakagawa, M. *Pure Appl. Chem.* **1975**, *44*, 885.

(167) (a) Ojima, J.; Katakami, T.; Nakaminami, G.; Nakagawa, M. *Bull. Chem. Soc. Jpn.* **1976**, *49* 292. (b) Nomoto, T.; Kukui, K.; Nakagawa, M. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 305. (c) Iyoda, M.; Miyazaki, H.; Nakagawa, M. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 2306. (d) Akiyama, S.; Iyoda, M.; Yoshitsugu, K.; Kukuoka, M.; Nakagawa, M. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 3351.

(168) Iyioda, M.; Ogura, F.; Akiyama, S.; Nakagawa, M. *Chem. Lett.* **1983**, 1883.

CR050964E