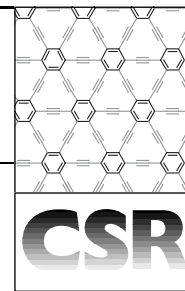


Polyethynylated cyclic π -systems: scaffoldings for novel two and three-dimensional carbon networks



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All-carbon materials with novel topologies are of interest in regard to their materials properties. These novel structures include graphite-like two-dimensional networks as well as fullerene-like three-dimensional cages. This article reviews recent developments in the synthesis of scaffolds for novel forms of carbon made of a core π -system carrying alkyne appendages, such as hexaethynylbenzene and its derivatives, pentaethynylcyclopentadienyl metal complexes, and tetraethynylcyclobutadiene metal complexes. Also included are the syntheses and properties of macrocyclic π -systems derived of these units which represent important substructures for the infinite lattices of novel carbon allotropes.

1 Introduction

The discovery of molecular allotropes of carbon, epitomized by buckminsterfullerene (C_{60}) and corresponding elongated structures called buckytubes, has precipitated research interests throughout the world on all-carbon materials with novel topologies that could show enhanced electronic and optical properties.^{1,2} Because of carbon's three hybridization states (sp^3 , sp^2 , and sp), there are numerous combinations by which atoms of this exceptional element can be bonded to each other. As a result, there are huge numbers of stereoregular networks that can be imagined. The simplest of these happen to be the two natural allotropes of carbon, namely diamond (sp^3 carbon atoms) and graphite (sp^2) (Fig. 1). The two types of bondings in

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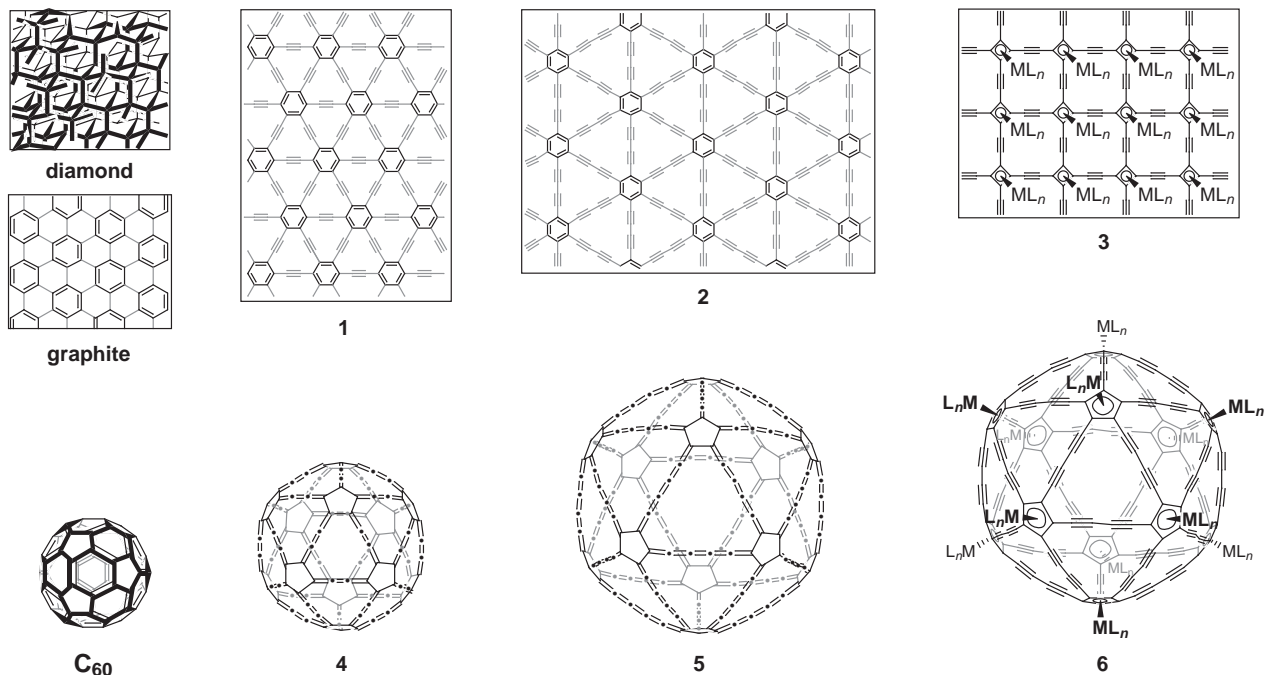
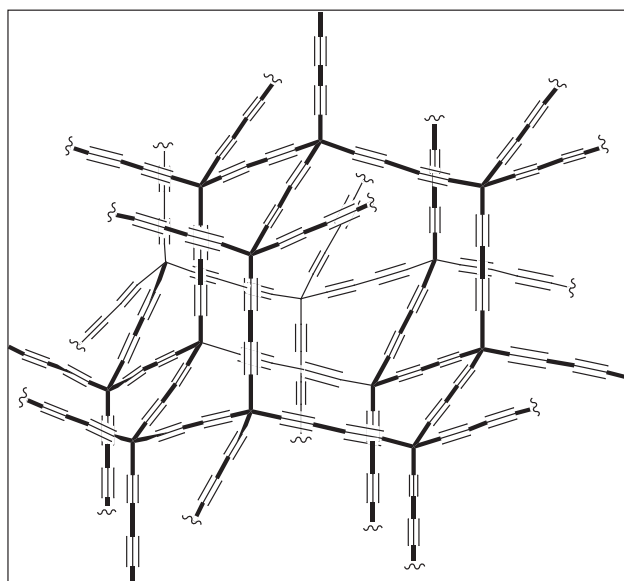


Fig. 1 Some networks and spherical carbon allotropes that can be built from sp^2 and sp -hybridized carbon atoms.

graphite and diamond give them very different bulk properties which are in most aspects exceptional. Diamond is the hardest, electrically most insulating, albeit most heat conductive substance known to man. Graphite has major technological applications as an electrode component and solid lubricant.

In the context of these important facts, carbon networks with delocalized π -systems are of particular relevance owing to the tunability of their properties with subtle changes in their electronic and geometric characteristics. Because the scope of this field is already beyond the space available for this review, only a few of the networks combining sp^2 and sp -hybridized carbons are treated (Fig. 1). Those combining sp^3 and sp^2 , or sp^3 and sp -hybridized carbons, such as the interesting diamondoid network below constituted of tetraethynylmethane units, are not included.



Infinite two-dimensional structures like **1**,³ termed *graphynes*, are derived from graphite by replacing single bonds with acetylenic linkages between every other hexagon (Fig. 1). The parent compound **1** was proposed to exhibit unusual nonlinear

optical and metallic properties when doped with an alkali metal.³ Graphyne has sizable pores within its dehydro[12]annulene units (Fig. 2) and can conceivably lead to transition metal complexes/intercalation compounds analogous to structures **45** and **46** described at the end of this review. A more extended version of this compound, *graphdiyne* (**2**),⁴ has the acetylene linkages of **1** replaced by buta-1,3-diyne units and has larger pores (2.5 Å diameter) within its dehydro[18]annulene perimeters (Fig. 2). Both graphyne **1** and graphdiyne **2** should lend themselves to intercalation with a number of metals, leading to conducting or perhaps even superconducting materials. The related structure **3**⁵ incorporating metal-complexed cyclobutadiene units should exhibit electronic and optical properties distinct from those of the benzene-derived networks **1** and **2** due to the antiaromatic character of the constituent sp^2 -hybridized system. In addition, the electronic nature of the coordinating metals should strongly influence the redox properties of **3**.

In addition to the formation of planar carbon networks, the linking of pentagonal scaffolds can give three-dimensional cages such as C_{120} (**4**)⁶ termed *fullereneyne* in analogy to the structure of fullerene C_{60} composed of 12 pentagons and 20 hexagons (Figs. 1,2). A more extended structure C_{180} (**5**),² which can be coined *fullerenediyne* in analogy to graphdiyne (**2**), is built from linear C_4 -units linking the pentagons. These carbon cages are derived from the insertion of cumulenic C_2 or C_4 units in between those bonds of fullerene C_{60} that have formal double bond character (bonds in between two six-membered rings). It is likely that both **4** and **5** will be very unstable because of the inherent reactivity associated with cumulenic centers. However, coordination to transition metals is a likely way to stabilize these structures by formation of complexes such as **6**,^{7,8} (for C_{180}), whereby tautomerization of the cumulenic bridges to alkynyl moieties is achieved. Fullereneyne **4** can also serve as a ligand for transition metals placing themselves within its [12]annulene pores in a manner similar to that of graphyne **1** (Fig. 2).⁸

In this spirit, a number of polyethynylated cyclic π -systems based on benzene, cyclobutadiene, and metal-complexed cyclopentadienyl have been synthesized as the scaffolds to construct the above mentioned carbon allotropes, or segments thereof, by forming either sp^2 - sp or sp - sp junctions.⁹ This article reviews recent developments in the synthesis of molecules with alkyne appendages based on transition metal-based synthetic methods.

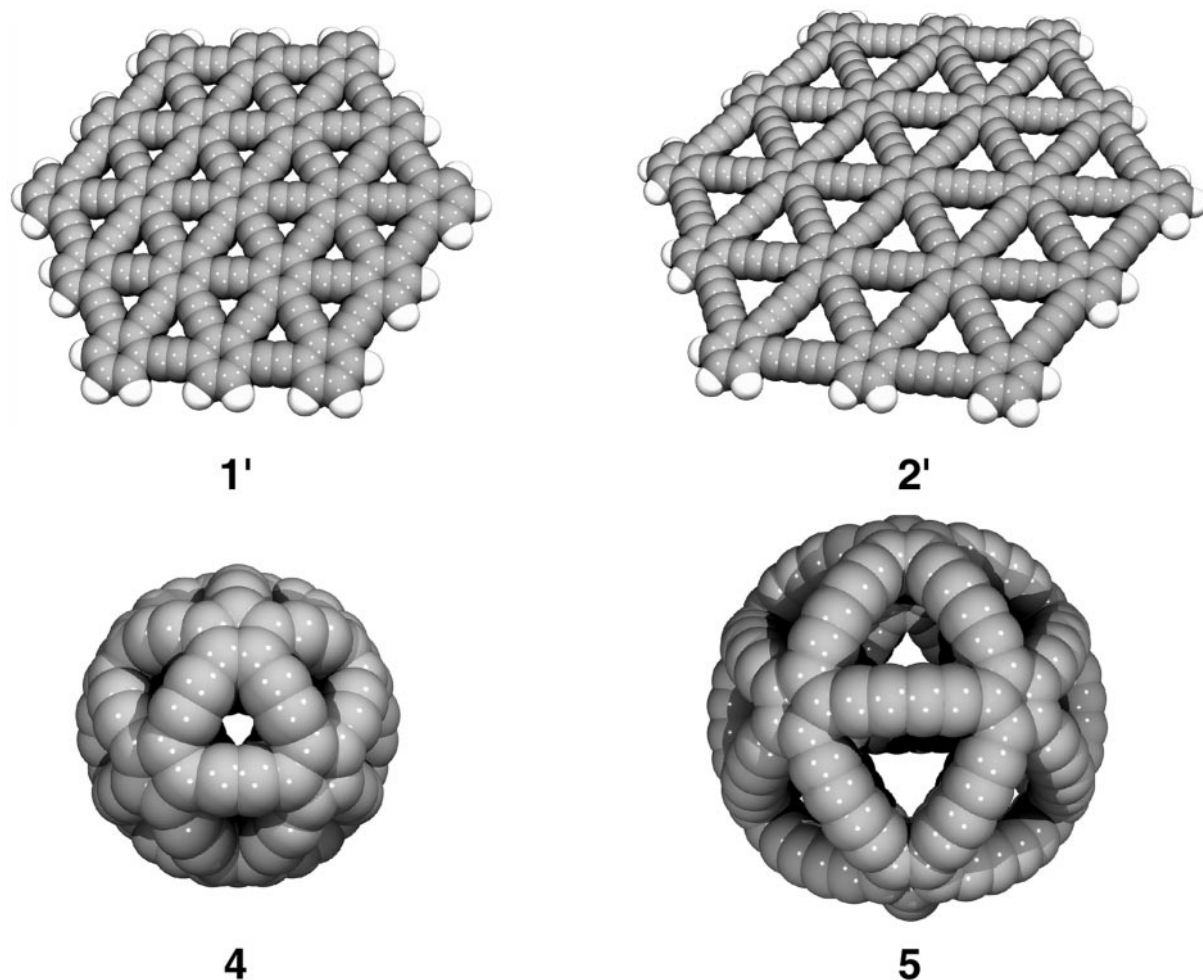


Fig. 2 Space-filling representations of snowflake-shaped fragments of the carbon networks (**1'** and **2'**), and of fullerene **4** and fullerenediene **5**.

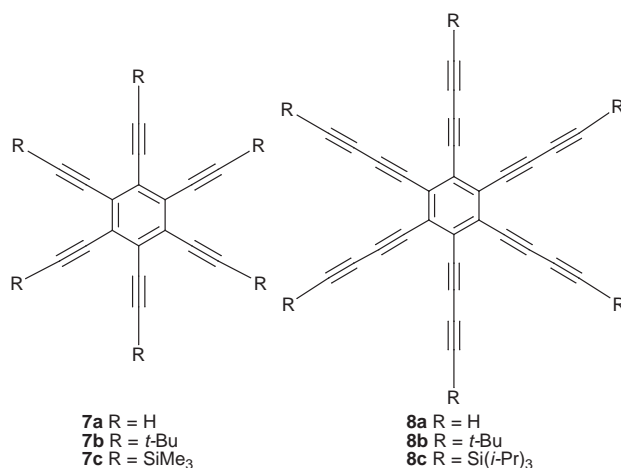
Some interesting properties and transformations of the unit molecules themselves will be discussed. Also described are small segments of the carbon networks **1–3** and **6** which were prepared as preliminary models to converge on the properties of the new forms of carbon.

2 Polyethynylated cyclic π -systems

2.1 Hexaethynylbenzenes

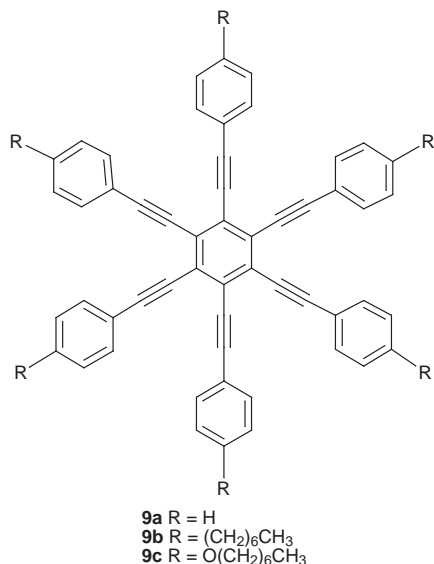
Hexaethynylbenzene (**7a**) represents a prototypical motif of the new carbon networks. Its derivatives **7b** and **7c** were first prepared by Vollhardt *et al.* from hexabromobenzene with the appropriately substituted acetylenes by application of the Sonogashira cross-coupling method involving palladium(0) and copper(I) as catalysts.¹⁰ The parent hydrocarbon **7a** can be obtained by deprotection of **7c** as an unstable solid. The same procedure was used to prepare the larger hexabutadiynylbenzenes **8b** and **8c**, while the parent compound **8a** was not obtained because of its extreme instability.¹¹ Attempts to form graphdiyne **2** by oxidative acetylene coupling of **7a** were unsuccessful. This is a general problem that can be readily understood in terms of the strong tendency these systems have to cross-link *via* irreversible formation of C–C bonds. Thus, stepwise formation of pieces of carbon networks is the only available alternative at this time.

Owing to the extended planar geometry of hexaethynylbenzene, its derivatives exhibit interesting properties due to the presence of weak intermolecular interactions between molecules. For example, hexakis(4-heptylphenylethynyl)ben-



zene (**9b**) and the heptoxy derivative **9c** undergo phase transitions to discotic nematic liquid crystals.¹² The parent compound **9a** was reported to have a large third-order nonlinear optical susceptibility.¹³

Similarly, differentially substituted hexaethynylbenzene derivatives are attractive targets due to their potential nonlinear optical properties when suitably substituted with both electron-donating and electron-accepting groups. They also serve as building blocks for the *stepwise* construction of graphyne (**1**), graphdiyne (**2**), and their substructures. In this respect, Anthony *et al.* have prepared 1,3,5/2,4,6-differentially functionalized hexaethynylbenzene derivatives such as **7d–h** having D_{3h} -symmetry. Their synthesis started from mesitylene as shown in



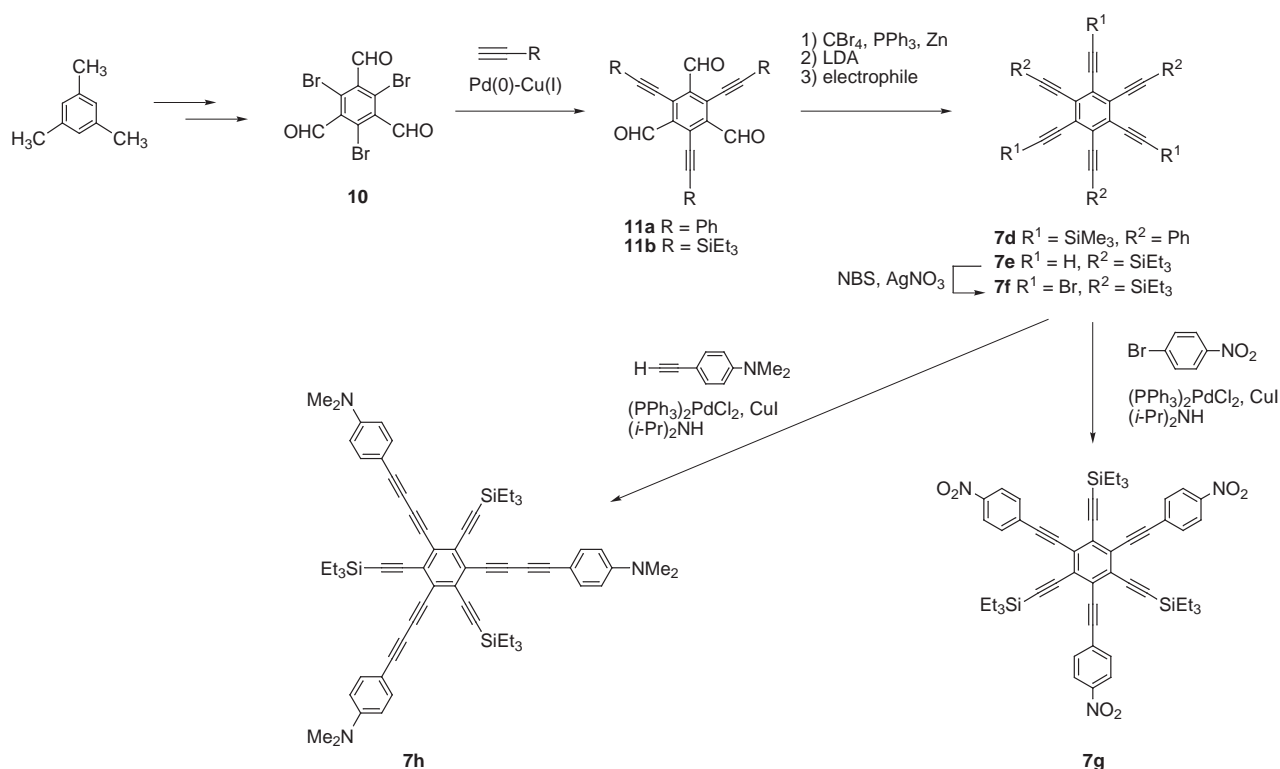
Scheme 1.¹⁴ Two bromination steps followed by hydrolysis and oxidation afforded tribromotrialdehyde **10** which coupled very efficiently with alkynes to give triynes **11a** and **11b**. Conversion of the formyl groups into the second set of ethynyl moieties by dibromomethylenation and subsequent dehydrobromination yielded the targets **7d** and **7e**. Pd(0)–Cu(I) catalyzed coupling of **7e** with *p*-bromonitrobenzene gave **7g** carrying electron-withdrawing groups, while coupling of the tris-bromoalkyne **7f** with *p*-ethynyl(dimethylamino)benzene gave nonayne **7h**. The electron donor-substituted system **7h** exhibits remarkable solvatochromism in its electronic absorption and fluorescence emission spectra due to an intramolecular charge transfer interaction existing between the electron-donating dimethylaminophenyl moieties and the electron-accepting hexaethynylbenzene core.

Synthesis of 1,2,3,4/5,6-differentially substituted derivatives such as **7i** and **7j** was achieved independently by the Rubin and

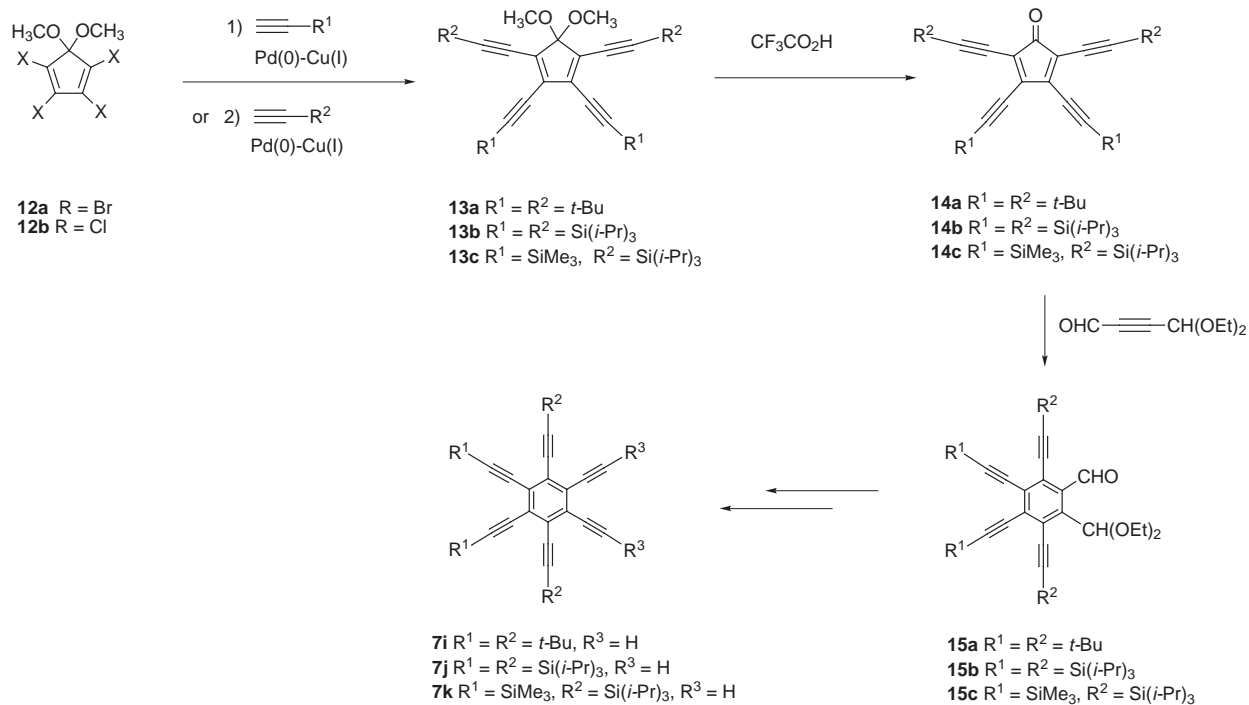
Tobe groups using similar methods (Scheme 2).^{15,16} The Pd(0)–Cu(I) catalyzed coupling of tetrabromocyclopentadienone acetal **12a** with the appropriate acetylene gave the tetraethynyl compounds **13a** and **13b**, respectively, and subsequent hydrolysis afforded the corresponding dienones **14a** and **14b**.¹⁷ The Diels–Alder reaction of **14a** and **14b** with diethoxybutynal with concomitant decarbonylation and subsequent hydrolysis gave the aldehyde acetals **15a** and **15b**. The formyl and ketal groups of **15a** and **15b** were sequentially transformed into the fifth and sixth ethynyl moieties to give **7i** and **7j**. Interestingly, the Pd(0)–Cu(I) catalyzed coupling of tetrachlorocyclopentadienone acetal **12b** can be carried out sequentially in a regioselective manner with two different acetylenes to give the 2,5/3,4-tetra-substituted dienone acetal **13c**, whereby substitution occurs first at the β-position and then at the α-position.¹⁵ Hydrolysis of **13c** gave the unstable dienone **14c** which was converted through **15c** to a 1,2/3,6/4,5-differentially functionalized hexaethynylbenzene (**7k**) with C_{2v}-symmetry.

Aside from the interest of hexaethynylbenzene (**7a**) as a motif for planar graphitic networks, this molecule can be used also as a bridgehead scaffold for polyyne bridged all-carbon cage molecules such as D_{6h}-C₆₀ (**16**), an isomer of I_h-buckminsterfullerene (C₆₀). This high-energy cage molecule has been proposed as a potential synthetic precursor to the fullerene C₆₀ and its endohedral metal complexes.^{8,18} A similar macrocycle (**20**) having better synthetic accessibility is based on the 1,3,5-triethynylbenzene scaffold. Synthetic predecessors of the cage compounds **16** and **20** more likely to be isolable are typified by cyclophane **17** with bis-skipped triyne linkages, and by the two macrocycles **18** and **19** bearing hexayne-diene units with alkyne-producing appendages to access macrocycle **20** (C₆₀H₆). These molecules were the subject of recent work in the Rubin and Tobe groups.^{19,20}

In laser desorption mass spectra of **18** and **19**, ions corresponding to C₆₀H₆[−] were observed, derived either by decarbonylation of **18** or elimination of indane fragments in a retro [2 + 2] mode from **19**.^{19,20} Significantly, base peaks for C₆₀[−] ions were observed with associated C₂-loss fragment ions (C₅₈[−], C₅₆[−]), indicating a likely fullerene structure for the ions

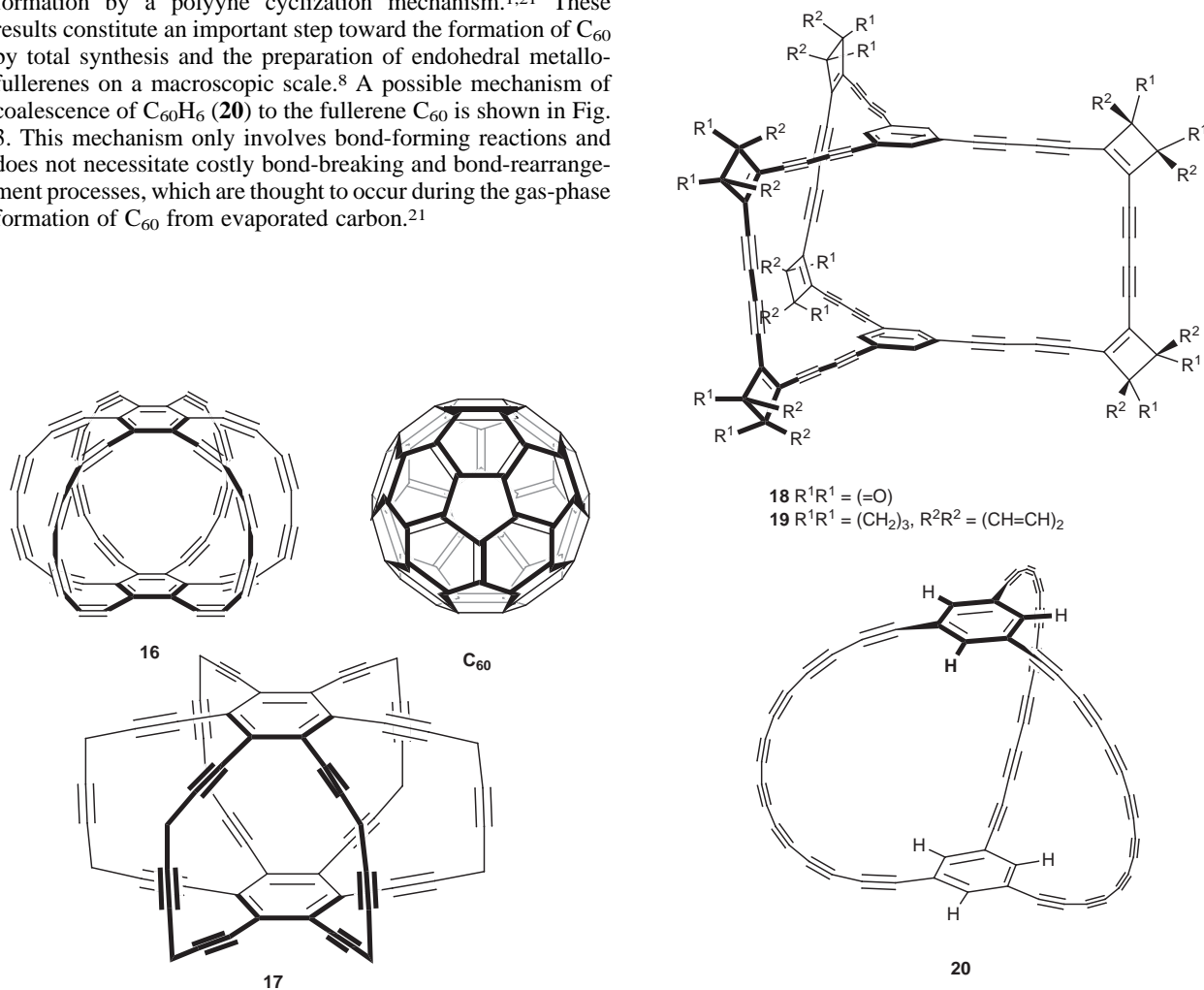


Scheme 1



Scheme 2

corresponding to C₆₀ and the involvement of **20** in their formation by a polyene cyclization mechanism.^{1,21} These results constitute an important step toward the formation of C₆₀ by total synthesis and the preparation of endohedral metallofullerenes on a macroscopic scale.⁸ A possible mechanism of coalescence of C₆₀H₆ (**20**) to the fullerene C₆₀ is shown in Fig. 3. This mechanism only involves bond-forming reactions and does not necessitate costly bond-breaking and bond-rearrangement processes, which are thought to occur during the gas-phase formation of C₆₀ from evaporated carbon.²¹



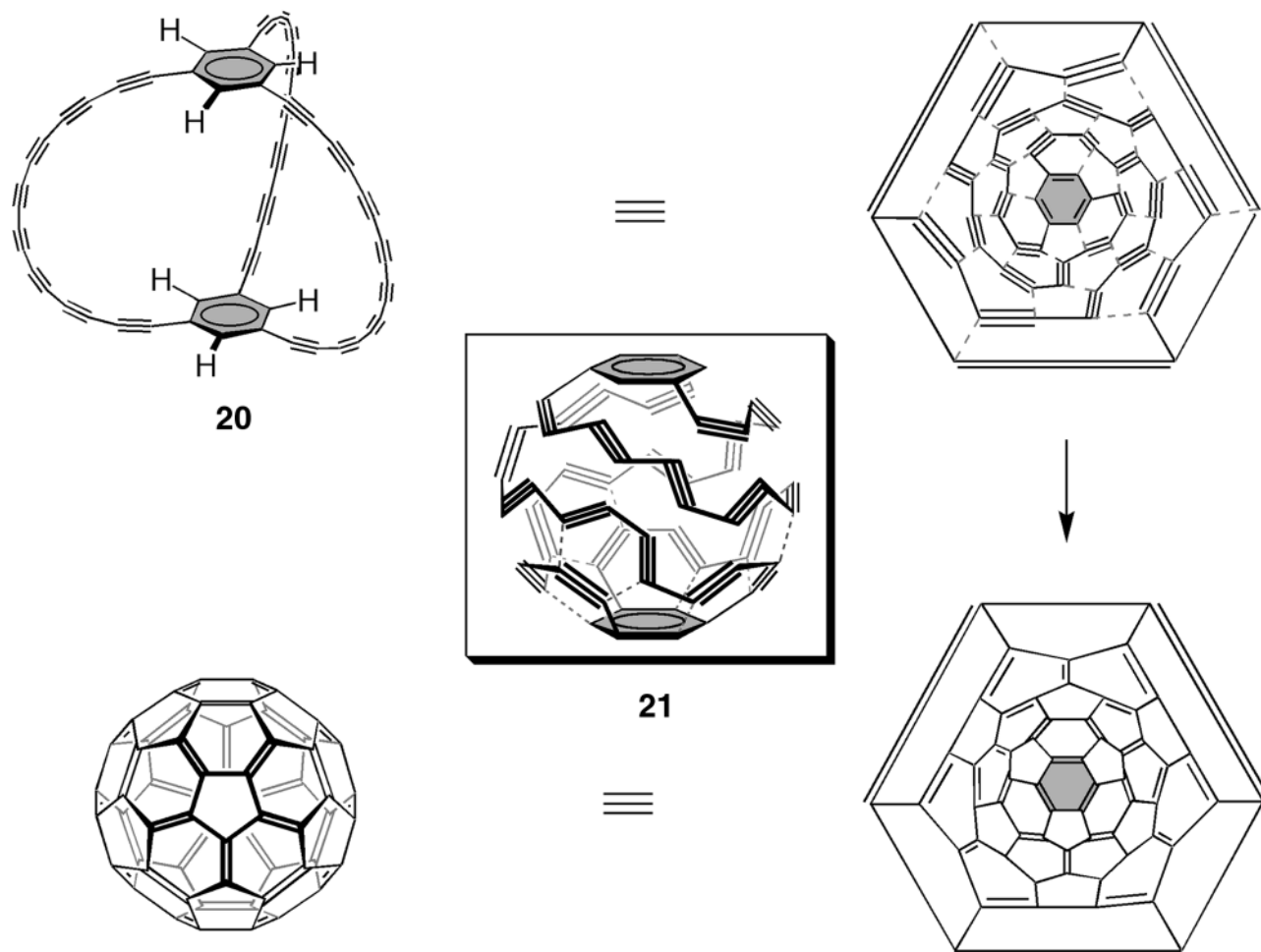


Fig. 3 Formal bond-rearrangement mechanism for $C_{60}H_6$ (**20**) to the fullerene C_{60} represented by Schlegel diagrams. The folded structure **21** is mapped to the C_{60} framework; the first (6π -electron cyclization) and second (diyne+alkyne [4+2] cycloaddition) likely cyclization pathways are indicated with dashed lines.

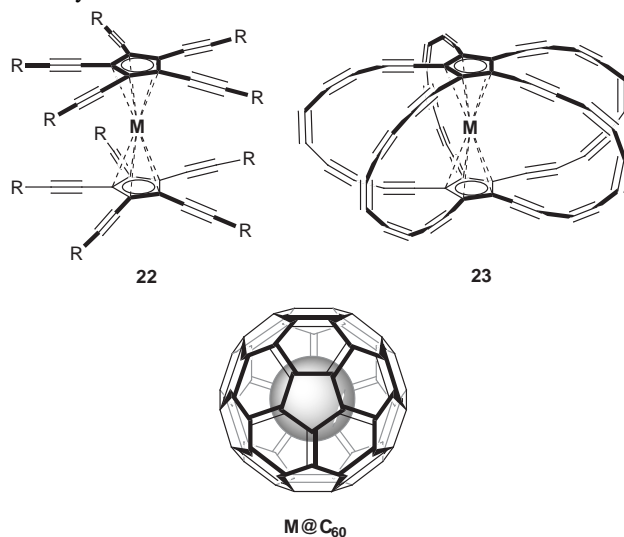
2.2 Pentaethynylcyclopentadienyl system

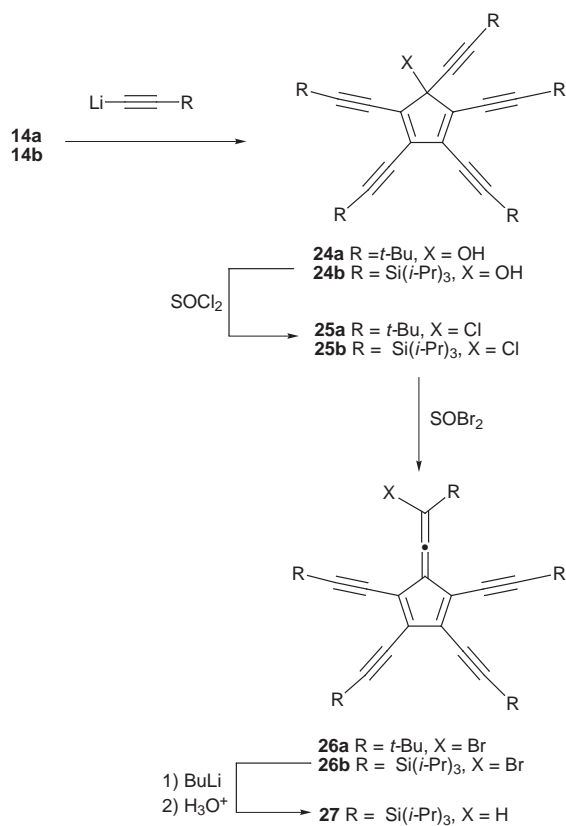
Decaethynylmetallocenes (**22**) are of interest as precursors of the D_{5h} -symmetric metallocene cyclophanes **23** (M = metal ion), which are also isomers of the endohedral metal fullerene complexes $M@C_{60}$. In order to synthesize decaethynylmetallocene derivatives, Jux *et al.* prepared tetraethynylcyclopentadienones such as **14a** and **14b** described in the previous section (Scheme 2).¹⁷

Treatment of **14a** and **14b** with appropriate alkynyllithium reagents gave the corresponding alcohols **24a** and **24b**, which were converted to chlorides **25a** and **25b** or their tautomeric bromides **26a** and **26b** by treatment with either $SOCl_2$ or $SOBr_2$ (Scheme 3). Attempts to convert bromide **26b** into a ferrocene derivative [**22**, M = Fe, R = tri(isopropyl)silyl] by reaction with BuLi followed by $FeCl_2$ have been so far unsuccessful. Instead, aqueous workup tends to afford the debromination product **27** and more complex byproducts. On the other hand, the unusually stable pentaethynylcyclopentadienyl radical **28a** was isolated by reduction of **26b** with $Fe(CO)_5$ or by oxidation of the dehalogenated compound **27** with tetrachloro-*p*-benzoquinone. Radical **28a** is unusual in that it is very easily oxidized ($E_{ox1/2} = 0.15$ V) compared to a peralkylated cyclopentadienyl radical (e.g. pentakis(isopropyl)cyclopentadienyl, $E_{ox1/2} = 0.58$ V), indicating that the formally antiaromatic cyclopentadienyl cation **28b** may be a stable entity at room temperature.

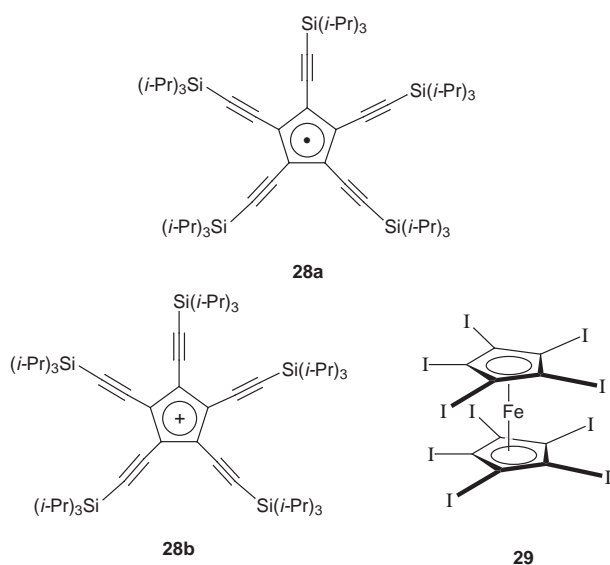
Substitution of the known decaiodoferrocene (**29**) with alkynyl groups as an alternate route to **22** was unsuccessful, perhaps due to the steric congestion in **29** or its palladium insertion intermediates.¹⁷ On the other hand, half-sandwich

complexes **31a** and **31b** were successfully synthesized by Bunz *et al.* using palladium-catalyzed coupling reactions (Scheme 4).²² Cyclopentadienylmanganese tricarbonyl ($CpMn(CO)_3$, **30a**), was converted to the penta-iodo derivative **30b**. Subsequent coupling of **30b** with the corresponding alkynylstannanes using Pd(0) catalysis afforded **31a** and **31b**. Terminal alkyne **31c** is so far unknown and **31d** could not be obtained by the above method. Access to the silyl-protected derivative **31e** was achieved by Rubin *et al.* through reaction of the cyclopentadienyl anion **28c** with bromomanganese penta-carbonyl.⁸



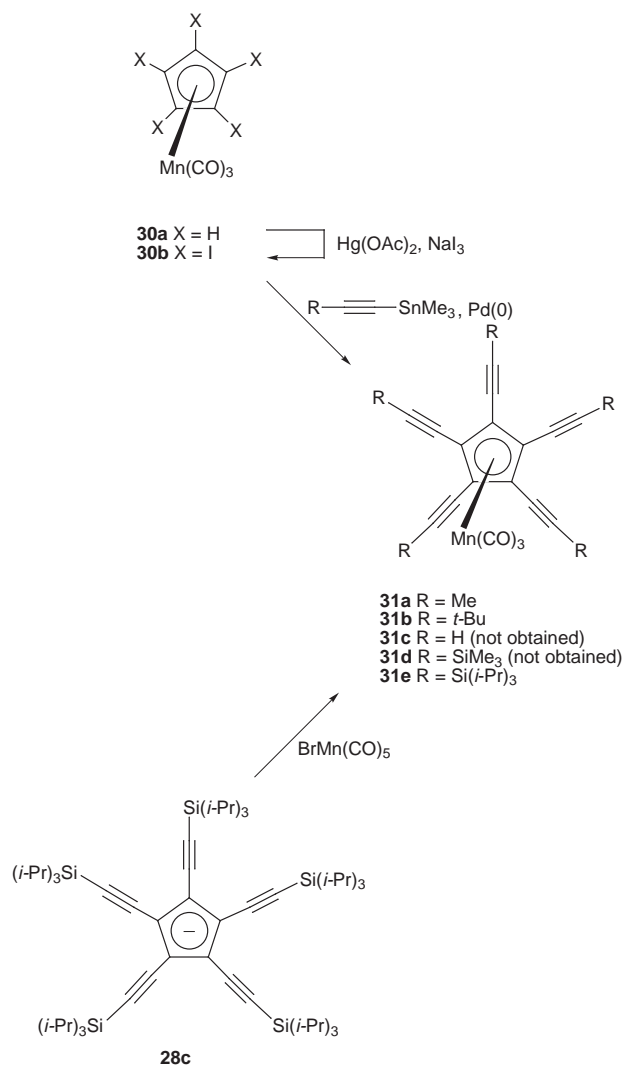


Scheme 3



2.3 Tetraethynylcyclobutadiene–metal complexes

Tetraethynylcyclobutadiene iron carbonyl complexes such as **33a** and **33b** have been prepared by Pd(0)–Cu(I) catalyzed coupling reactions of the known tetraiodide **32** with ethynylstannanes (Scheme 5).²³ The parent compound **33c**, obtained by deprotection of the trimethylsilyl groups of **33b**, decomposed readily upon isolation. In a similar fashion, a variety of tetraethynyl, tetrabutadienyl and tetrahexatrienyl derivatives like **33d–f** have been prepared.²⁴ It should be noted that the first generation dendritic complex **33d**, possessing five Fe(CO)₃



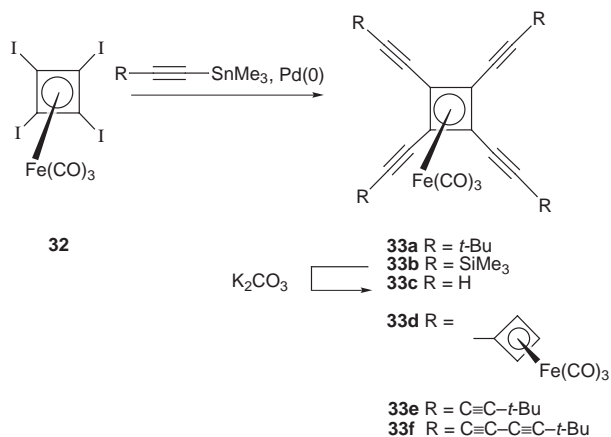
Scheme 4

units, represents a motif of infinite graphitic network **3**. Cyclobutadiene cobalt complex **35a** with a cyclopentadienyl ligand was obtained by a mechanistically interesting thermal isomerization first discovered by Vollhardt for the parent 1,2-diethynylcyclobutadiene cyclopentadienylcobalt system (Scheme 6).^{25,26} Flash vacuum pyrolysis of 1,2-butadienylcyclobutadiene complex **34** afforded cleanly the corresponding tetraethynylcyclobutadiene complex **35a** as a single product. This reaction proceeds presumably through a mechanism related to the Bergman rearrangement.²⁶ Deprotection of **35a** gave the terminal alkyne **35b** as a stable solid whose X-ray crystal structure was obtained. The remarkable stability of **35b** compared to the Fe(CO)₃ complex **33c** is ascribed to the steric protection of the π -system imparted by the bulky CpCo-group.

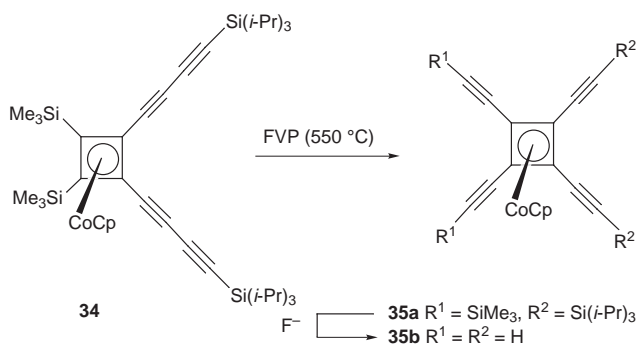
3 Segments of new forms of carbon allotropes

3.1 Hexadehydrotribenzo[12]annulene

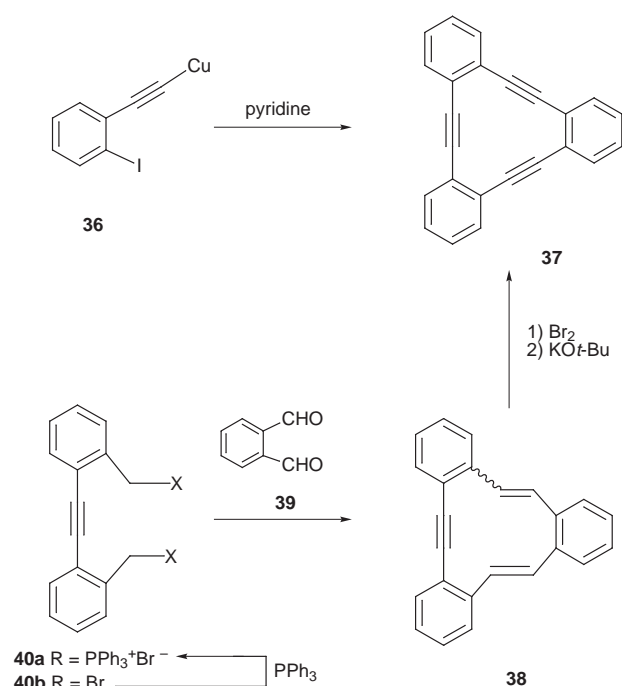
The study of small segments of infinite carbon networks should provide important information in regard to their electronic and optical properties. In addition, they are highly symmetrical synthetic targets of intrinsic beauty and have large delocalized π -systems of interest in the context of aromaticity. For these



Scheme 5



Scheme 6

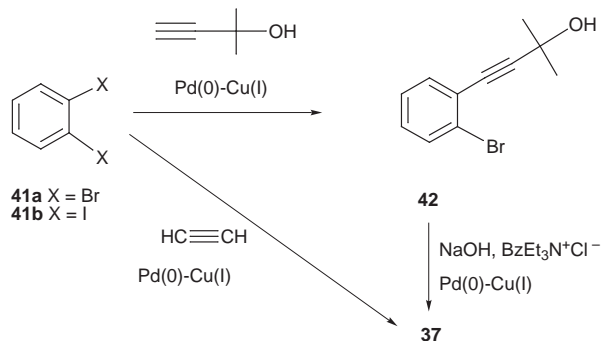


Scheme 7

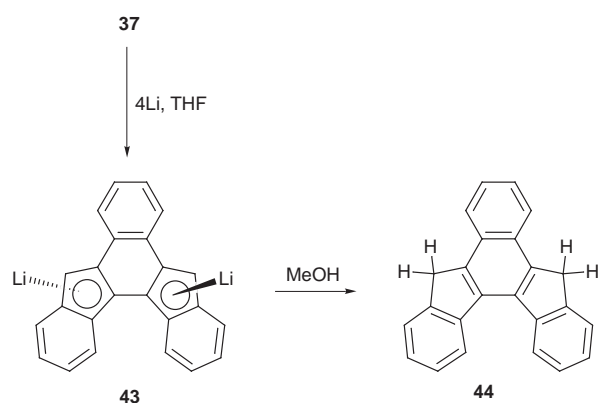
reasons, several alkyne-bridged *ortho*-cyclophane derivatives have been prepared.

Hexadehydrotribenzo[12]annulene (**37**), the smallest macrocyclic segment of graphyne (**1**), was first prepared more than thirty years ago from the view point of benzoannulene chemistry by Eglinton *et al.* using the Stephens–Castro coupling of copper(I) *o*-iodophenylacetylide (**36**).²⁷ Staab *et al.* followed on by using a bromination/dehydrobromination reaction on the corresponding triene **38** obtained by the Wittig reaction of phthalaldehyde (**39**) with phosphonium salt **40a** derived from *o,o'*-bis(bromomethyl)diphenylacetylene (**40b**) (Scheme 7).²⁸ Palladium(0)–copper(I) catalyzed coupling reactions between haloarenes and alkynes were also used to prepare the hydrocarbon **37** efficiently.²⁹ Thus, mono-coupling product **42** of *o*-dibromobenzene (**41a**) with 2-methylbut-3-yn-2-ol was subjected to phase transfer conditions under which *in situ* deprotection of the terminal alkyne moiety and arene–alkyne coupling took place to afford **37** (Scheme 8). Recently, a Pd(0)–Cu(I) catalyzed one-pot synthesis of **37**, using acetylene itself and *o*-diiodobenzene (**41b**), was reported by Iyoda *et al.*³⁰

In connection with the aromaticity of the dehydro[12]annulene system, detailed spectroscopic and structural studies of **37** as well as those of the radical anion species derived by one-electron reduction of **37** with sodium have been discussed.²⁸ Four-electron reduction of **37** with lithium in tetrahydrofuran was reported by Youngs *et al.* to give the biscyclopentadienyl dianion **43** whose structure was characterized as the *N,N,N',N'*-tetramethylethylenediamine complex with 1:2 stoichiometry (Scheme 9).³¹ Quenching of **43** with methanol gave hydrocarbon **44**.



Scheme 8

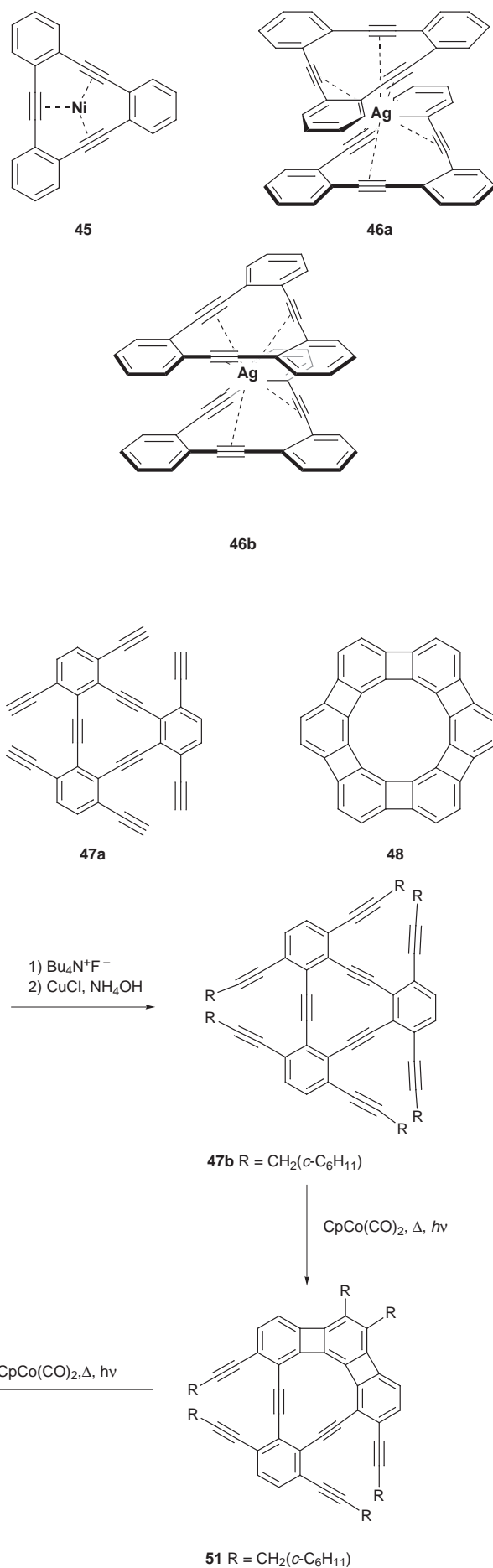


Scheme 9

Yongs investigated the syntheses, structures, and properties of metal complexes of the dehydro[12]annulene **37**. For example, reaction of **37** with bis(cycloocta-1,5-diene)nickel(0) (Ni(COD)₂), gave the planar Ni(0) complex **45** in which the nickel atom is coordinated equally by all three alkyne units.³² X-Ray structure analysis of **45** revealed that the C(sp)-Ni distance (1.958 Å) was longer than the typical length (1.88–1.90 Å) of other Ni(0)-alkyne complexes. The C≡C–C bond angle (173.8°) of the outwardly bent alkyne units in the Ni complex **45** is larger than that of free ligand **37** (178.4°), but the distortion from linearity is much smaller than those of known acyclic alkyne–nickel(0) complexes. These observations indicate that the coordination of the triple bonds of **45** to nickel is weaker than those of other alkyne–nickel(0) complexes. Reduction of **45** with potassium in the presence of [2.2.2]cryptand gave a dianion complex, (K[2.2.2]cryptand)₂·**45**, which shows low conductivity. Doping of insulating **45** with dianion (K[2.2.2]cryptand)₂·**45** yielded more conductive materials.

Combination of **37** with silver triflate gave the interesting 2:1 sandwich-type complex **46a/b**.³³ X-Ray crystallographic analysis of the complex revealed the presence of two conformers in the crystal, namely the staggered isomer **46a**, and the eclipsed isomer **46b**, for which the relative orientations of the ligands are rotated by 60°. The Ag–C bond distances of **46a** (2.67–2.81 Å) and **46b** (2.47–2.94 Å) are within normal values observed for related complexes (2.27–3.10 Å).

The hexaethynyl-substituted derivative of the [12]annulene system (**47a**) is of interest not only as an advanced intermediate in the construction of graphyne (**2**) but also as a precursor of the yet unknown circular oligophenylene called antikekulene (**48**). Antikekulene **48** is expected to exhibit 'super'-delocalization of its π-electrons due to the antiaromatic nature of the constituent biphenylenes. Recently Vollhardt *et al.* reported the synthesis of precursors of **48** starting from 1,2,3,4-tetrabromobenzene (**49**) (Scheme 10).³⁴ Sequential introduction of three ethynyl groups on **49** followed by bromine–iodine exchange and deprotection gave triyne **50**. After removal of the tri(isopropyl)silyl group,

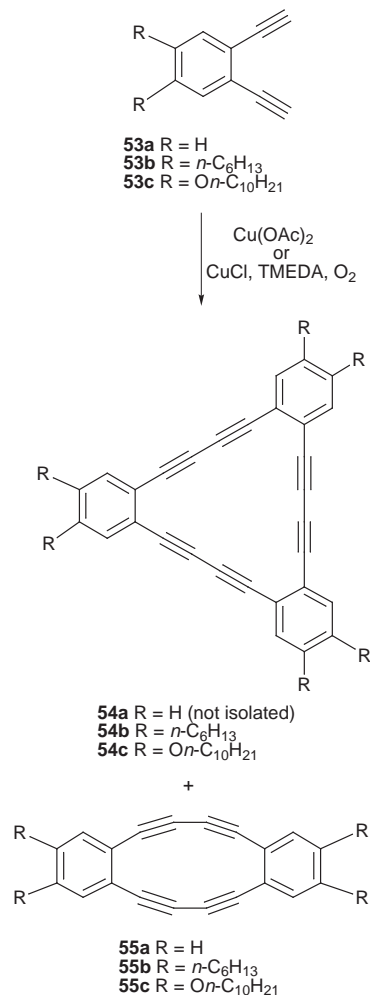


Scheme 10

the terminal acetylene unit was subjected to a Stephens–Castro coupling reaction to give the dehydro[12]annulene **47b**. Intramolecular CpCo(CO)₂-induced cyclotrimerization of **47b** afforded the cyclic angular triphenylene derivative **51**, and upon further cyclization, the pentaphenylene derivative **52**. Though final cyclization of **52** to the corresponding antikekulene structure has not been achieved yet, the inner 12π-electron systems of **51** and **52** already exhibit a large degree of delocalization as indicated by the upfield shifts of outer protons in the ¹H NMR spectra (antiaromaticity), and by the UV-vis spectra of **51** and **52**.

3.2 Dodecahydrotribenzo[18]annulene

It is rather surprising that the parent hydrocarbon of dodecahydrotribenzo[18]annulene (**54a**) and its derivatives were reported only recently. Dodecahydrotribenzo[18]annulene (**54a**) is the smallest substructure of graphdiyne (**2**). In attempted formation reactions from 1,2-diethynylbenzene (**53a**) using the usual copper(II)-mediated coupling conditions (Eglinton; Cu(OAc)₂, pyridine, or Hay; CuCl·TMEDA, O₂), the dimer **55a** was invariably the only isolated product (Scheme 11). On



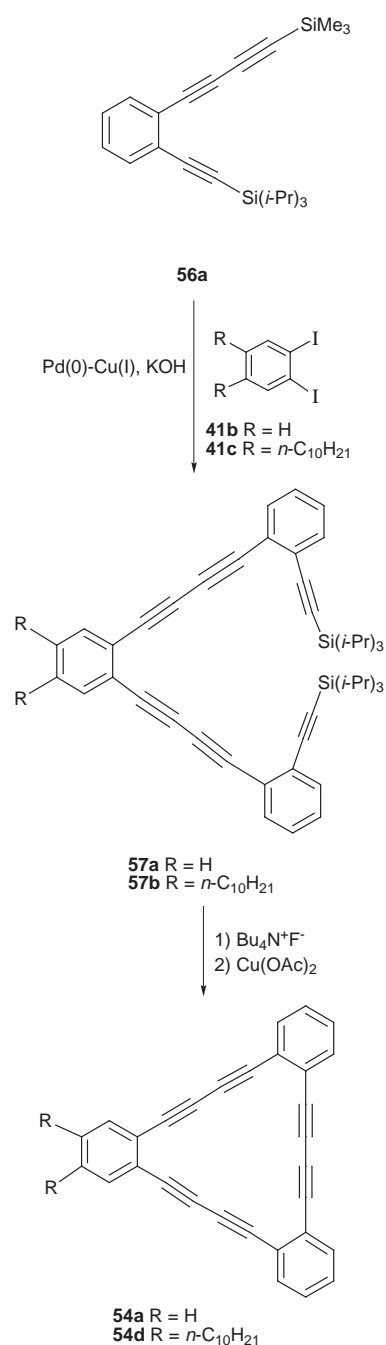
Scheme 11

the other hand, substituted *o*-diethynylbenzene derivatives **53b** and **53c** gave the trimers **54b** and **54c** together with the dimers **55b** and **55c**, respectively.³⁵

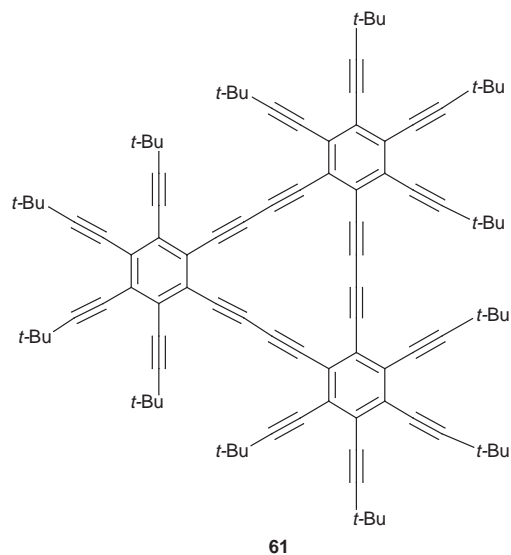
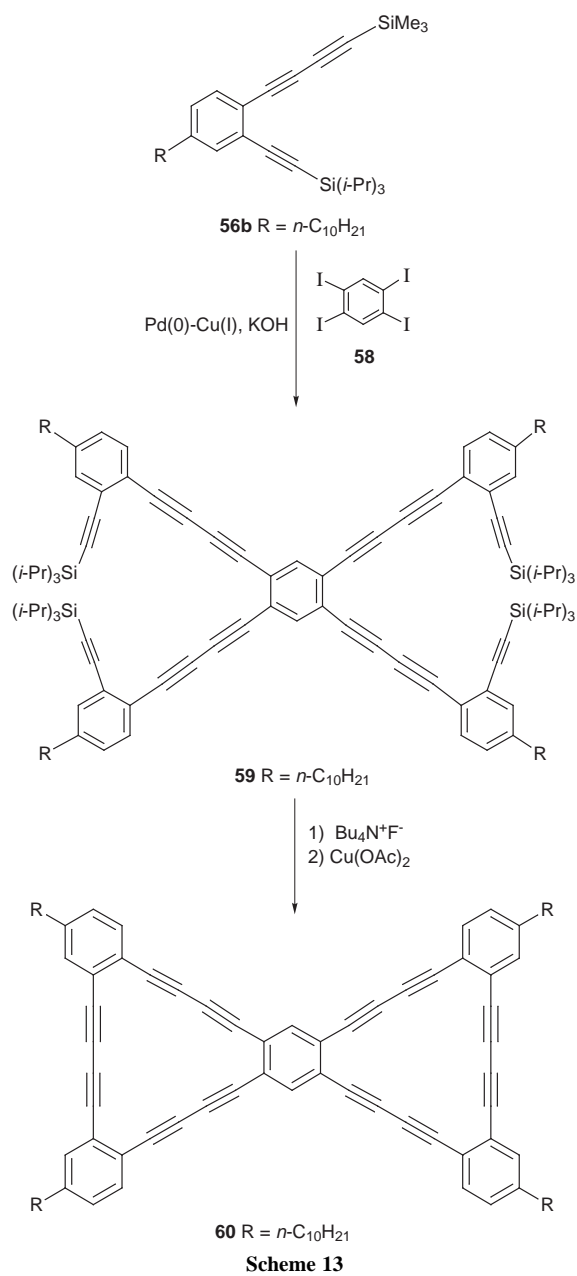
Haley *et al.* have developed a method for coupling reactive phenylbutadiyne derivatives with aryl halides using an *in situ* deprotection of the sensitive terminal alkynyl groups under Pd(0)–Cu(I)-catalyzed coupling conditions.³⁶ Accordingly, the parent dodecahydrotribenzo[18]annulene **54a** was prepared as shown in Scheme 12.⁴ TMS-protected *o*-ethynylphenylbuta-

diyne derivative **56a** was coupled with *o*-diiodobenzene (**41b**) with Pd(0)–Cu(I) catalyst in the presence of KOH to give the 2:1 coupling product **57a**. Removal of the protective group and subsequent intramolecular coupling afforded **54a** as a very poorly soluble substance, which is perhaps why it was not isolated in previous work. This solubility problem was circumvented by the use of 4,5-didecyl-1,2-diiodobenzene (**41c**) instead of **41b** to give **57b** which was cyclized to afford didecyldehydroannulene **54d** in fair yield. This technique was further applied to the preparation of advanced substructures of graphdiyne (**2**), for example the bis-dehydrobenzoannulene **60** (Scheme 13). Its synthesis was achieved starting from triyne **56b**, derived from *p*-decylaniline, which was coupled four times onto 1,2,4,5-tetraiodobenzene (**58**) to give the tetraalkynylated product **59**. Deprotection of **59** followed by Cu(II)-mediated intramolecular oxidative coupling yielded the bicyclic ‘butterfly’ structure **60** in very good yield (80%).

Finally, Rubin *et al.* prepared the dodecaethynyl derivative **61**, an advanced precursor of graphdiyne (**2**), by the Hay



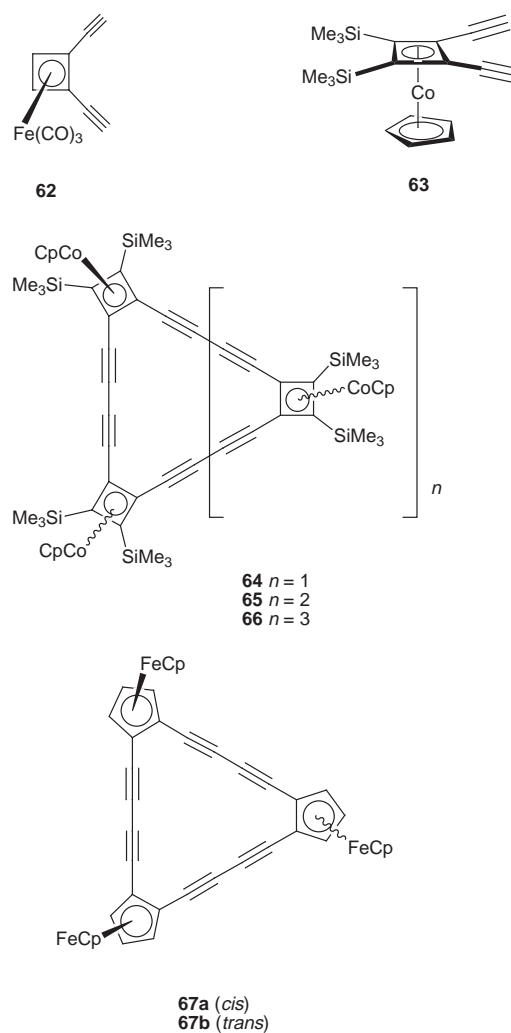
Scheme 12



coupling of hexaethynylbenzene derivative **7i** (see Scheme 2).¹⁶ Although at this moment **61** has only been obtained as an enriched mixture with the corresponding tetrameric homologue, the chemistry and physical properties of this relatively new class of dehydroannulenes appear to be interesting and are yet to be explored.

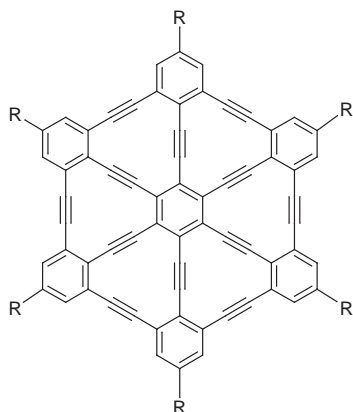
3.3 Segments of metal complexed carbon allotropes

Oxidative coupling of 1,2-diethynylcyclobutadieneiron tricarbonyl (**62**) did not give cyclic oligomers.³⁷ On the other hand, the modified Hay coupling of the cobalt complex **63**, having more bulky cyclopentadienyl and TMS groups to protect

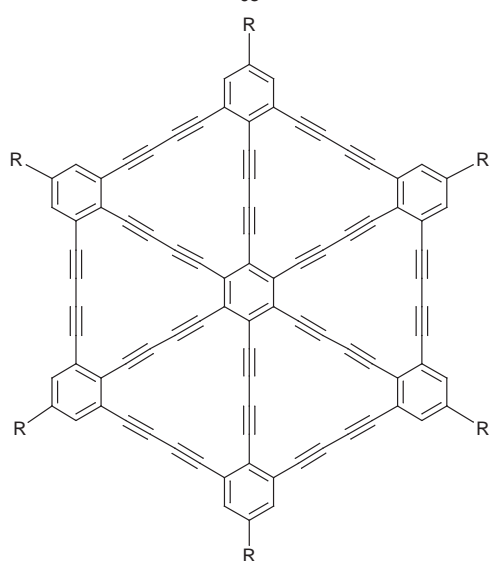


the alkyne moieties, afforded trimer **64** as two diastereomers, and tetramer **65** as four diastereomers together with pentamer **66** up to a total of 87% yield.³⁸ The tetramer **65** represents a substructure of diyne-bridged carbon network of cyclobutadiene-metal complex related to **3**.

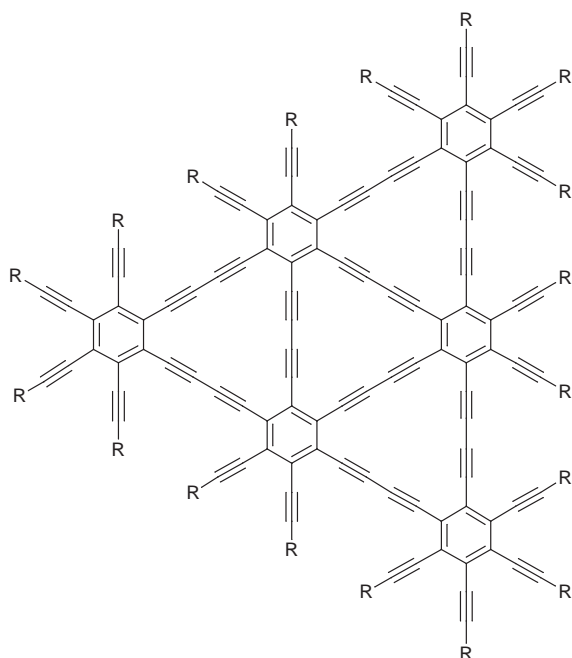
As to the cyclic oligomers of the cyclopentadienyl system which represent the substructure of carbon cage fullerene (4) and fullerenediyne (5), *cis* and *trans* isomers of trimers **67a** and **67b** were prepared from 1,2-diethynylferrocene by Bunz *et al.* using the Eglinton coupling.³⁸ The isomers **67a** and **67b** exhibit different oxidation potentials, suggesting the existence of through-space and through-bond interactions between the metal centers.



68



69



70

4 Conclusion

Stepwise synthesis of large fragments of new carbon networks such as **68**, **69**, and **70** will be achieved using the systematically alkynylated benzene derivatives described in this review. These

large substructures should not only exhibit electronic and optical properties unique to themselves owing to their π -conjugation extending to the nanometre scale, but also allow extrapolation of their properties to the ultimate infinite carbon allotropes. For the construction of the infinite carbon networks, it will be necessary to develop methods that link $sp-sp^2$ or $sp-sp$ carbon centers of appropriate precursors under reversible conditions (*i.e.* under thermodynamic control) so that the desired polymeric forms of carbon can be formed selectively. This may be achieved by preorganizing the substrates by weak noncovalent interactions such as hydrogen bonds and $\pi-\pi$ interactions or as a self-assembled single layer on a metal surface. In any event, developing such technology provides a true challenge in interdisciplinary areas of organic synthesis, organic materials, and nanoscale synthesis.

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