Chem. Rev. **1999,** 99, 1863–1933

Molecular Rods. 1. Simple Axial Rods

Peter F. H. Schwab,[†] Michael D. Levin,[‡] and Josef Michl*,[†]

Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309-0215, and Department of Chemistry, University of Utah, Salt Lake City, Utah 84112-0850

Received February 9, 1999 (Revised Manuscript Received April 23, 1999)

Contents

I. Introduction 1863
II. General Considerations 1865
  A. Why Molecular Rods? 1865
    1. The Promise 1865
    2. The Difficulties 1869
  B. Modules and Rods 1871
    1. Modules for Singly Linked Axial Rods 1871
    2. Modules for Doubly Linked Axial Rods 1872
    3. Module Properties 1872
  C. Overview of Synthetic Methods 1873
III. Singly Linked Axial Rods 1876
  A. Oligoynes 1876
    1. Organic Terminal Substitution 1876
    2. Metal Terminal Substitution 1878
  B. Oligomers of Cage Modules 1880
    1. Staffanes 1880
    2. Bicyclo[2.2.2]octane 1881
    3. Cubane 1882
    4. Carboranes 1882
  C. Oligomers of Planar Modules 1884
    1. Benzene 1884
    2. Other Arenes 1886
    3. Pyridine 1888
    4. Porphyrin 1890
  D. Co-Oligomers 1892
    1. Ethyne/Cage 1892
    2. Ethyne/Planar Module 1893
    3. Bicyclo[1.1.1]pentane/Other Cages 1908
    4. Benzene/Cage 1910
    5. Benzene/Other Planar Module 1911
    6. Cage/Other/Other 1919
IV. Doubly Linked Axial Rods 1921
  A. Cumulenes 1921
    1. Organic Terminal Substitution 1921
    2. Metal Terminal Substitution 1922
  B. Carbocyclic Spiro Rods 1923
  C. Heterocyclic Spiro Rods 1924
  D. Co-Oligomers 1924
    1. Ethene//Cycloalkane 1924
    2. Ethene//Cyclohexadiene 1925
    3. Ethene//Stellane 1925
    4. Ethene//Adamantane 1925
    5. Ethene//Diazafluorene 1925
    6. Tetrathiafulvalenes 1926
    7. Ethene//Adamantane//Other 1927
    8. Ethene//Cyclohexadiene//Other 1927
V. Concluding Remarks 1927
VI. Acknowledgments 1928
VII. References 1928

I. Introduction

Widespread interest in rigid-rod molecules is largely a phenomenon of the past decade as is easily verified by a glance at the reference list in this article. It has been primarily driven by interest in two areas: (i) long-distance interaction phenomena such as electron and energy transfer, magnetic coupling of transition-metal atoms, etc., and (ii) use of molecular rods and connectors for the construction of supramolecular assemblies and giant molecules.[1−5] Tables 1 and 2 and Chart 1 list the formulas **1**−**24** of the structural elements that will be dealt with in this review.

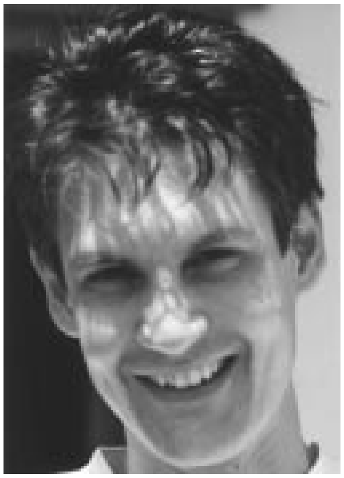
Although polymer chemists had been interested in rigid-rod polymers for a long time, if we limit our horizon to well-characterized and pure individual molecular structures, as we do in the present review, very few rigid-rod molecules were available when our group's interest in the subject was triggered at the end of 1986 by an accidental observation of oligomers of [1.1.1]propellane (**2**), since named [*n*]staffanes (**[*n*]2**) (section III.B.1).[6] True, oligoynes (**[*n*]1**) (section III.A), cumulenes (**[*n*]15**) (section IV.A), and oligophenylenes (**[*n*]7**) (section III. C.1) had been around for a long time, but few such molecules were available with axial functionalization at the termini, required for use in a molecular construction kit, and structures such as 4,4′-bipyridyl were the lone exceptions. Zimmerman's clear formulation of the concept, his rod based on bicyclo[2.2.2]octane[7] (**[1]3**), and Zakharkin's carborane dimers (**[2]5**, **[2]6**[8,9]) were harbingers of developments to come.

Since that time, entirely new types of rod structures have been developed and old structures have been greatly extended and elaborated. Yet we are not aware of prior reviews devoted specifically to molecular rods. A review of molecular wires[10] and recent books on oligomers[11] and modular chemistry[3] probably come the closest. Our initial enthusiasm for

---

[†] University of Colorado.
[‡] University of Utah.

10.1021/cr970070x CCC: $35.00



Peter Schwab was born in 1971 in Offenbach, Germany. He received his "Vordiplom" in Chemistry in 1992 from the Technische Hochschule, now Technische Universität, in Darmstadt, Germany. In 1994, he began graduate school at the University of Colorado at Boulder where he is currently pursuing his Ph.D. in the research group of Professor Josef Michl. His research interests include organic and organometallic synthesis for the development of a molecular-size construction kit, in particular the synthesis of a two-dimensional hexagonal grid polymer and of molecular dipolar rotors.

Michael Levin was born in 1965 in Moscow, Russia. He graduated with honors from the Moscow Institute of Fine Chemical Technology in 1990 and spent one year as a junior research associate at the Nesmeyanov Institute of Organometallic Compounds in Moscow before attending graduate school at the University of Colorado at Boulder. He obtained his Ph.D. in 1997 under the supervision of Professor Josef Michl and spent two years as a postdoctoral scholar, first with Professor Seth R. Marder (Caltech) and then with Professor Peter J. Stang (University of Utah). He is interested in physical organic chemistry and organic synthesis as it applies to creation of materials with useful properties.

Josef Michl was born in 1939 in Prague, Czechoslovakia. He received his M.S. in Chemistry in 1961 under V. Horák and P. Zuman at Charles University, Prague, and his Ph.D. in 1965 under R. Zahradník at the Czechoslovak Academy of Sciences, also in Prague. He left Czechoslovakia in 1968. He did postdoctoral work with R. S. Becker at the University of Houston, with M. J. S. Dewar at the University of Texas at Austin, with J. Linderberg at Aarhus University, Denmark, and with F. E. Harris at the University of Utah, where he stayed and became a full professor in 1975 and served as chairman in 1979–1984. In 1986–1990 he held the M. K. Collie-Welch Regents Chair in Chemistry at the University of Texas at Austin and subsequently moved to the University of Colorado at Boulder. He is a member of the National Academy of Sciences, the American Academy of Arts and Sciences, and of the International Academy of Quantum Molecular Science. Dr. Michl's current research interests are the development of a molecular-size "Tinkertoy" construction set for the assembly of giant molecules and new solids, photochemistry, chemistry of silicon and boron, preparation and study of reactive organic and main-group organometallic molecules, and use of quantum chemical and experimental methods for better understanding of electronic structure. He has been the editor of *Chemical Reviews* since 1984.

writing a review on all known well-defined rigid-rod molecular structures for the thematic issue on nanotechnology, including synthesis, properties, and applications, gradually dwindled as we dug through more than 1000 relevant articles and faced a definite deadline.

In the end, the resulting set of two reviews concentrates on synthesis and deals with most classes of linear or nearly linear structures that have been used or are likely to be used as relatively rigid and robust molecular rods of well-defined length in "molecular construction kit" work on giant molecules or supramolecular structures. It does not treat floppy linear structures such as *n*-alkanes or oligosilanes, and it does not deal with chemically ill-defined mixtures of rigid rods of similar constitution but different lengths, and thus, it is a review of individual well-defined rodlike oligomers as opposed to traditional rigid-rod polymers or carbon nanotubes. Covalently linked structures that owe their rigid linearity to secondary interactions such as hydrogen bonds, e.g., α-helical[12] and β-sheet[13] polypeptides, or peptide-like synthetic oligomers, e.g., oligo(isocyanides),[14] somewhat rod-shaped natural products such as brevetoxin S,[15] or monomeric, dimeric, and oligomeric steroids,[16] and supramolecular structures such as DNA (reviewed elsewhere in this issue[17]) or helicates[18] are also excluded. Many of the excluded types of rod structures are important and interesting, and we realize that the definition of the scope of this review is arbitrary.

We define sturdy covalent rods as "simple rods" and call linear structures held together by the weaker metal−ligand or metal−metal interactions "linked rods". In Part 1, we review simple axial rods, i.e., those covalent structures that are built from axial modules linked by single bonds or by sharing terminal atoms. An axial module has two collinear but opposed terminal bonds (or vectorial sums of terminal bonds if there is more than one on one side). In Part 2,[19] which is comparable in size, we survey simple rods of zigzag shape and ladder rods, whose modules are linked by more than one single bond or share more than a single atom. With our definition of a simple rod, we treat any functional group or metal atoms located at rod termini as belonging to connectors or potential connectors, i.e., as substituents and not as a part of the rod. The only time this leads to a serious ambiguity is in the case of a metal connector that binds two rods at a 180° angle, thus producing a longer linear rod. Such a connector is referred to as a linker. Linearly linked rods are not "simple" in our definition and are treated separately in Part 2,[19] whether they are axial or not. Rods connected in a more complicated fashion are not covered.

We have attempted to present a comprehensive description of modern synthetic approaches to each class of rods, and the two reviews are primarily reviews of rod synthesis. A few of the rod structures, such as biphenyl, *p*-terphenyl, 1,1′-binaphthyl, 9,9′-bianthryl, 4,4′-bipyridyl, tolan, and a few others, go so far back in time that the literature on them is vast and they are not covered comprehensively. In these cases, we have merely attempted to draw attention to recent important advances regarding terminally functionalized structures.

For added interest, we provide selected representative information on rod structure and properties, particularly the terminal functionalization, solubility, vibrational and electronic spectra, and transmission of electronic effects. Even less comprehensively, we add a few illustrations of the uses that have been made of the rods for the construction of more complex molecular and supramolecular structures. Such "modular chemistry" is not the subject of this review.

Our ultimate interest is in the use of molecular rods as modules in the controlled construction of molecular networks and scaffolds. Typically, however, the rod itself consists of a small number of rigidly connected axially aligned smaller structural units ("modules") at a lower level in a hierarchy of structures, and this is the usage of the word "module" that we shall employ. Individual smaller modules can be connected by bonds (e.g., the benzene units in oligophenylenes **[*n*]7**, section III.C.1) or by sharing their terminal atoms (e.g., double bonds in cumulenes **[*n*]-15**, section IV.A).

The organization of the present set of reviews is based on the constituent modules and links between them. The modules are listed in Tables 1 and 2 and Chart 1. Their formula numbers, **1**−**24**, refer to a parent module with no terminal substituents and a dangling bond on each end (unless the two terminal valences mutually saturate, as in the propellanes). The related hydrocarbons, with hydrogen atoms as the terminal substituents, are given formula numbers **[1]1**−**[1]20**. The higher homo-oligomers are given formula numbers **[*n*]1**−**[*n*]20**, where *n* is the count of elementary modules in the oligomer. Co-oligomers are treated separately and given ordinary formula numbers. In our notation, constituent modules in co-oligomers are separated by a slash when they are attached to each other by bonds, as in ethyne/benzene, or by a double slash when they share an atom, as in ethene//adamantane. In section headlines, we use the names of oligomers when they are short, e.g., oligoynes, cumulenes, and staffanes, and give the name of the constituent module or modules otherwise, e.g., bicyclo[2.2.2]octane.

II. General Considerations

A. Why Molecular Rods?

As is often the case, the current surge of interest in the synthesis of molecular rods and the study of their properties results from a combination of opportunity and desire. Difficulties that seemed insurmountable just a few short years ago, such as the selective synthesis, dissolution, separation, and characterization of individual chemically unique and well-defined species of high molecular weight, can now be faced with somewhat less trepidation due to advances in several fields of chemistry. Molecular rods have always held a certain fascination for chemists, and in areas such as liquid-crystal chemistry, their synthesis has long been essential. More recently, additional desire to prepare such structures arose from the realization that giant molecules and supramolecular structures might be able to perform functions that small molecules do not, primarily in biochemical and material science applications. The process has derived much momentum from biomimetic considerations. As the chemical structure and functioning of the very complex superstructures in a living cell gradually become somewhat less of a mystery, chemists naturally attempt to mimic some of these structures and functions, e.g., photosynthesis, with the ultimate hope of improving upon it. The construction of complex structures is often easiest with straight beams, hence the need for molecular rods. Nature rarely builds with straight beams, and man does not need to either, as many half-timbered buildings in Northern Europe amply demonstrate, but for beginners, this is not a bad way to start. Besides, imitating nature, although often useful, is not always optimal since the goals of the chemist's construction effort and the conditions under which such construction is performed can be vastly different from those that applied in the process of natural selection.

1. The Promise

A long separate review could be written on the many uses and potential uses of molecular rods. Here, we exemplify their utility by considering them as spacers and construction elements in giant molecules and supramolecular assemblies. The discussion is coached in general terms; specific examples with references will be provided in the discussion of the individual types of rods.

a. Spacers and Wires. Molecular rods offer the opportunity to position two active centers at a known distance apart and connect them by a medium whose properties can be controlled at least to some degree. The degree of interaction between the centers can be studied by a variety of tools and provides information about the electronic structure of the rod and about the coupling of the centers to the rod, ultimately contributing to the theory of chemical bonding. It often falls off exponentially with the rod length. Simple examples are the investigation of NMR coupling constants between nuclei located in the two centers and EPR coupling constants between one center and an unpaired electron located at the other center. These are usually detectable only in relatively

Table 1. Modules for Singly Linked Axial Molecular Rods

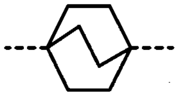
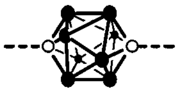
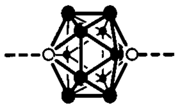
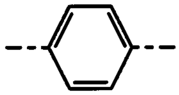
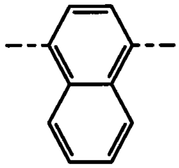
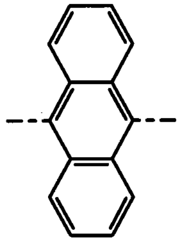
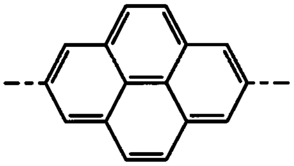
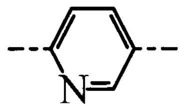
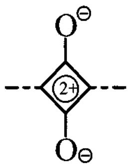
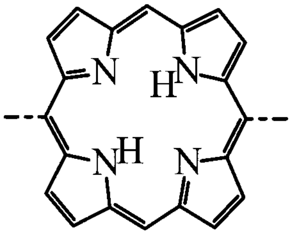
Module	Incremental Length /Å[a]	Module Width /Å[b]	Corresponding Hydrocarbon	IP[c] /eV	EA[d] /eV	E_{exc}[e] /10^{3}cm^{-1}	Section
 **1**	2.66	3.4	ethyne **[1]1**	11.41[f]	-2.6[g]	~45[h]	III.A
 **2**	3.35	5.5	bicyclo[1.1.1]pentane **[1]2**	9.65[i]	-5.35[j]	> 50	III.B.1
 **3**	4.18	6.8	bicyclo[2.2.2]octane **[1]3**	9.9[k]	< 0	> 50	III.B.2
 **4**	4.19	7.8	cubane **[1]4**	8.56[l]	< 0	> 50	III.B.3
 **5**[m]	4.85	7.1	1,10-dicarba-*closo*-decaborane **[1]5**	10.5[n]	< 0	> 50	III.B.4
 **6**[m]	4.63	7.9	1,12-dicarba-*closo*-dodecaborane **[1]6**	10.32[o]	< 0	> 50	III.B.4
 **7**	4.31	6.7 3.4	benzene **[1]7**	9.2438[p]	-0.7[q] -1.15[g]	~39[h]	III.C.1
 **8**	4.32	9.1 3.4	naphthalene **[1]8**	8.1442[r]	-0.191[s] 0.140[t,u]	~33[h]	III.C.2.a
 **9**	4.33	11.5 3.4	anthracene **[1]9**	7.4392[v]	0.66[w]	~27[h]	III.C.2.b
 **10**	8.51	9.1 3.4	pyrene **[1]10**	7.4256[v]	0.500[x]	~29[h]	III.C.2.c

Table 1 (Continued)

 **11**	4.22	6.7 3.4	pyridine **[1]11**	9.34[y]	-0.62[z]	~39[h,aa]	III.C.3
 **12**	~ 3.4	~ 7.3	squaraine **[1]12**			~ 39[bb]	III.D.5.a
 **13**	3.53	6.6 >8[cc]	cyclobutadiene metal complex **[1]13**	7.65[dd,ee]		[cc]	III.D.2.e
 **14**	8.35	11.4 3.4	porphyrin **[1]14**	6.6[ff]		~16[h]	III.C.4

[a] Contribution to rod length: one module plus one single CC bond, averaged from crystallographic data (Cambridge Database). [b] van der Waals module width including contributions from the hydrogen atoms, in two perpendicular directions, averaged from crystallographic data (Cambridge Database). [c] First ionization potential. [d] Electron affinity. [e] The lowest singlet excitation energy. [f] Plessis, P.; Marmet, P. *Int. J. Mass Spectrom. Ion Processes* **1986**, *70*, 23. [g] Jordan, K. D.; Burrow, P. D. *Acc. Chem. Res.* **1978**, *11*, 341. [h] Perkampus, H.-H. *UV-Vis Atlas of Organic Compounds*; VCH: New York, 1992. [i] Wiberg, K. B.; Connor, D. S. *J. Am. Chem. Soc.* **1966**, *88*, 4437. [j] Schafer, O.; Allan, M.; Szeimies, G.; Sanktjohanser, M. *Chem. Phys. Lett.* **1992**, *195*, 293. [k] Bieri, G.; Burger, F.; Heilbronner, E.; Maier, J. P. *Helv. Chim. Acta* **1977**, *60*, 2213. [l] Lifshitz, C.; Eaton, P. E. *Int. J. Mass Spectrom. Ion Phys.* **1983**, *49*, 337. [m] Black dots represent BH groups, white dots represent C atoms. [n] Fehlner, T. P.; Wu, M.; Meneghelli, B. J.; Rudolph, R. W. *Inorg. Chem.* **1980**, *19*, 49. [o] Orlov, V. M.; Pustobaev, V. N.; Olshevskaya, V. A.; Zakharkin, L. I.; Galchenko, G. L. *Dokl. Phys. Chem.* **1988**, *300*, 518. [p] Nemeth, G. I.; Selzle, H. L.; Schlag, E. W. *Chem. Phys. Lett.* **1993**, *215*, 151. [q] Ruoff, R. S.; Kadish, K. M.; Boulas, P.; Chen, E. C. M. *J. Phys. Chem.* **1995**, *99*, 8843. [r] Cockett, M. C. R.; Ozeki, H.; Okuyama, K.; Kimura, K. *J. Chem. Phys.* **1993**, *98*, 7763. [s] Burrow, P. D.; Michejda, J. A.; Jordan, K. D. *J. Chem. Phys.* **1987**, *86*, 9. [t] Zlatkis, A.; Lee, C. K.; Wentworth, W. E.; Chen, E. C. M. *Anal. Chem.* **1983**, *55*, 1596. [u] Heinis, T.; Chowdhury, S.; Kebarle, P. *Org. Mass Spectrom.* **1993**, *28*, 358. [v] Hager, J. W.; Wallace, S. C. *Anal. Chem.* **1988**, *60*, 5. [w] Ruoff, R. S.; Kadish, K. M.; Boulas, P.; Chen, E. C. M. *J. Chem. Phys.* **1995**, *99*, 8843. [x] Lyons, L. E.; Morris, G. C.; Warren, L. J. *J. Phys. Chem.* **1966**, *72*, 3677. [y] Arimura, M.; Yoshikawa, Y. *Mass. Spectrosc. (Tokyo)* **1994**, *32*, 375. [z] Nenner, I.; Schulz, G. J. *J. Chem. Phys.* **1975**, *62*, 1747. [aa] Lowest $\pi-\pi^*$ transition. [bb] Value for the squarate anion $C_4O_4^{2-}$. [cc] Depends on metal ligand. [dd] Hall, M. B.; Hillier, I. H.; Connor, J.; Guest, M. F.; Lloyd, D. R. *Mol. Phys.* **1975**, *30*, 839. [ee] Value for the iron tricarbonyl cyclobutadiene complex, $ML_n = Fe(CO)_3$. [ff] Dupuis, P.; Roberge, R.; Sandorfy, C. *Chem. Phys. Lett.* **1980**, *75*, 434.

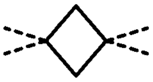
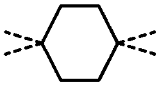
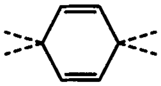
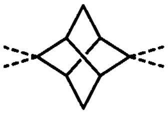
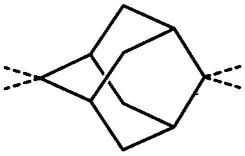
---

short rods. A somewhat more complex case is the examination of the propagation of substituent effects through a conjugated or saturated molecular framework, which is complicated by the need to separate the part of the effect that propagates through surrounding space.

Electronic interaction between the active centers through the molecular rod can be probed by photoelectron spectroscopy and electron transmission spectroscopy, whose simplified interpretation in terms of Koopmans' theorem provides information about orbital energy splittings that result from the interaction through the rod. Weaker interactions can be probed by examination of energy or electron transfer between the centers. This transcends the use of the rods as mere spacers and brings us to consider them as photonic, electronic, protonic, or ionic wires which mediate the directional motion of electronic excitation energy, an electron, a proton, or another ion from one active center to the other.

Although little work has been directed toward protonic and ionic wires, much more remains to be done; so far most of the attention has been focused on the use of molecular rods as photon and electron wires. Despite all this work, very little has been sufficiently systematic to permit quantitative statements about the relative ease with which excitation or charge move along one or another kind of wire, the wire length at which the mechanism changes from coherent transfer to incoherent hopping when the latter is possible, the relative role of σ and π symmetry orbitals when both are present, the im-

Table 2. Modules for Doubly Linked Axial Molecular Rods

Module	Incremental Length /Å[a]	Module Width /Å[b]	Corresponding Hydrocarbon	IP[c] /eV	EA[d] /eV	E_{exc}[e] /10^3 cm^{-1}	Section
 **15**	1.30 - 1.34[f]	3.4	ethene **[1]15**	10.5138[g]	-1.78[h]	~ 62[i]	IV.A
 **16**	2.10	6.4	cyclobutane **[1]16**	9.82[j]	< 0	> 50	IV.B
 **17**	2.86	6.6	cyclohexane **[1]17**	9.80[j]	< 0	> 50	IV.D.1
 **18**	2.84	6.7 3.4	1,4-cyclohexadiene **[1]18**	8.82[k]	- 1.75[h]	~40[i]	IV.D.2
 **19**	3.17	7.7	stellane **[1]19**		< 0	> 50	IV.D.3
 **20**	3.51	8.1	adamantane **[1]20**	9.25[l]	< 0	> 50	IV.D.4

[a] Module length averaged from crystallographic data (Cambridge Database). [b] van der Waals module width including contributions from the hydrogen atoms, in two perpendicular directions, averaged from crystallographic data (Cambridge Database). [c] First ionization potential. [d] Electron affinity. [e] Lowest singlet excitation energy. [f] Depends on rod length. [g] Williams, B. A.; Cool, T. A. *J. Am. Chem. Soc.* **1995**, *99*, 14247. [h] Jordan, K. D.; Burrow, P. D. *Acc. Chem. Res.* **1978**, *11*, 341. [i] Perkampus, H.-H. *UV-Vis Atlas of Organic Compounds;* VCH: New York, 1992. [j] Holmes, J. L.; Lossing, F. P. *Org. Mass Spectrom.* **1991**, *26*, 537. [k] Kimura, K.; Katsumata, S.; Achiba, Y.; Yamazaki, T.; Kwata, S. In *Handbook of HeI Photoelectron Spectra of Fundamental Organic Compounds*; Japan Scientific Society Press: Tokyo, 1981. [l] Bewick, A.; Edwards, C. J.; Jones, S. R.; Mellor, J. M. *Tetrahedron Lett.* **1976**, 631.

portance of the relative disposition of the energies of the electron at the two centers and on the rod (where its presence may but need not be merely virtual), or the effects of lateral substituents. As a result, it is not yet possible to predict the transfer rates or to design rods in which they have been tuned to desired values, let alone rationally design rods in which the transfer rate can be tuned by the change of state of a lateral substituent.

Little is known about the redox potentials of the conjugated wires, although these are essential if the wires are to be ever used for actual transfer of charge to molecules that are to be reduced or oxidized or if they are to be used in molecular diodes. Many of the conjugated wires probably have a sufficiently low electron affinity that their reduced form would be oxidized by molecular oxygen, making them of little use in the open atmosphere. The role of solution counterions in codetermining charge-transfer rates has been little explored. Here, it would most likely be interesting to attach ions permanently along the rod, as occurs naturally in DNA, but this does not appear to have been examined.

b. Construction Elements. The use of molecular rods as construction elements depends critically on our ability to adjust the length of the rod to a desired value, to attach the desired terminal or possibly lateral connectors, and to secure sufficient rigidity. The control of rod length is facile, down to perhaps ±1 Å if the electronic structure does not matter, as might often be the case in construction applications, since a variety of modules are available and can be combined in a large number of ways. This is not to say that all such combinations will be synthetically easy, as noted below. A fair number of terminal groups are available for connector attachment.

However, in contrast to freshman students' expectations, molecular "rigid" rods are not rigid at all but are highly flexible, even though their equilibrium structure may be linear. At room temperature, even quite short rods bend and flex vigorously and should be thought of as rubber sticks rather than steel rods. With the possible exception of nanotubes, truly long rods many nanometers in length should be thought of as boiled rather than raw spaghetti. To increase the rigidity, it may be possible to bundle the rods, and the first reports of efforts directed to this goal have appeared. The rigidity issue is likely to complicate the construction of structures that use rods longer than 2−3 nm.

The structures assembled so far have been mostly free-floating in solution. This would be acceptable in some applications, such as rod-based racks used to force a particular conformation on a flexible chain attached to rack ends or artificial enzymes[20,21] in which functional groups have been adjusted into controlled locations by attachment to a scaffold, and not in others, such as sieves in which a molecule shaped like a tennis net would be used for size-selective separation of solutes, but would have to be mounted rigidly, i.e., over a metal mesh with large openings. Also, various proposed molecular machines, switches, and other devices will frequently need to be anchored. Only a limited amount of work has been performed on anchoring giant molecules on surfaces in a controlled fashion.

If there is a need to communicate with a molecular machine or other device from the outside world, the situation complicates further. Electrical communication requires attachment to electrodes, and although wholesale coating of electrodes with molecules is performed commonly, controlled attachment of a single albeit giant molecule to an electrode, not to mention attachment to two electrodes, is another matter. Even attempts to bridge a small gap between electrodes with a single molecular rod-based wire and measure current through it have met with limited success so far. Much more effort is required in this area. Photonic communication with a single molecule by scanning near-field optical microscopy (SNOM) is easy in comparison as long as the molecules are relatively far apart. However, when they are not, selective addressing has not been accomplished. It is possible that altogether different modes of communication will be more useful, based on biomimetic analogies such as chemical reaction with a species generated in the vicinity and brought close along a specific diffusion path, etc.

2. The Difficulties

The three primary difficulties encountered in the synthesis of molecular rods are poor solubility, difficult separations and purification, and demanding characterization.

Solubility. Of the three primary obstacles, low solubility is probably the worst. If a mixture of high molecular weight materials cannot be brought into a solution (or perhaps at least a melt), there is very little hope of separating the components and even a full characterization of the mixture will be very hard.

The chief tool that has been used over the years to increase the solubility of molecular rods is the attachment of a sufficient number of flexible side chains. Most often, each module of which the rod is composed has to carry at least one such side chain. It would be very useful to know more about solubility as a function of the structure of the rod itself and of the nature and number of the attached chains, but sufficiently systematic studies have not been performed, and quantitative information about solubilities is almost entirely missing in the synthetic literature.

For some intended uses, such as purely structural purposes, the presence of flexible chains presents no interference and they may be considered innocent. For others, such as charge or energy transfer, it may be useful or detrimental and needs to be carefully considered. Even alkyl chains, and more so, alkoxy chains, modify the electronic structure and properties of the fundamental modules, such as redox potentials and electronic excitation energies.

A less well-recognized tool is the use of co-oligomers instead of homo-oligomers, which appears to enhance solubility as well, although here, still less is known even in a semiquantitative sense.

Finally, an obvious tool that has seen virtually no use is the attachment of charged moieties to the rod or placement of charges directly into the rod. Very few highly charged molecular rods other than oligonucleotides have been synthesized, and the likely solubilizing properties of the charges remain almost entirely unexplored. One could imagine that either temporary or permanent attachment of charged groups to otherwise poorly soluble molecular rods might offer considerable advantages.

Separation and Purification. The development of high-performance liquid chromatography and gel-permeation chromatography permitted a revolutionary improvement in the separability of complex mixtures of materials of high molecular weight, both on an analytical and a preparative scale.

If and when work with charged molecular rods becomes more popular, it is likely that electrophoresis will turn out to be another tool worth borrowing from the biochemists. Even for nominally neutral rods, the presence of dissociable groups or their temporary introduction would be worth considering.

Characterization. The relentless push of NMR spectroscopy to higher magnetic fields permits the separate observation of protons and other nuclei that would have been unthinkable not long ago. Perhaps even more important, the development of soft ionization methods such as matrix-assisted laser desorption ionization (MALDI) and electrospray ionization (ESI), suitable for very high molecular weight species, combined with the high resolving power of modern mass spectrometers provide an indispensable characterization tool.

Unfortunately, ion fragmentation often intervenes even with these methods and more so with the less gentle secondary-ion mass spectrometry (SIMS), fast-ion bombardment mass spectrometry (FABMS), and plasma desorption mass spectrometry (PDMS), and there are many giant molecules that have been synthesized but remain incompletely characterized. Additional developments in this area will be of crucial importance.

Chart 1

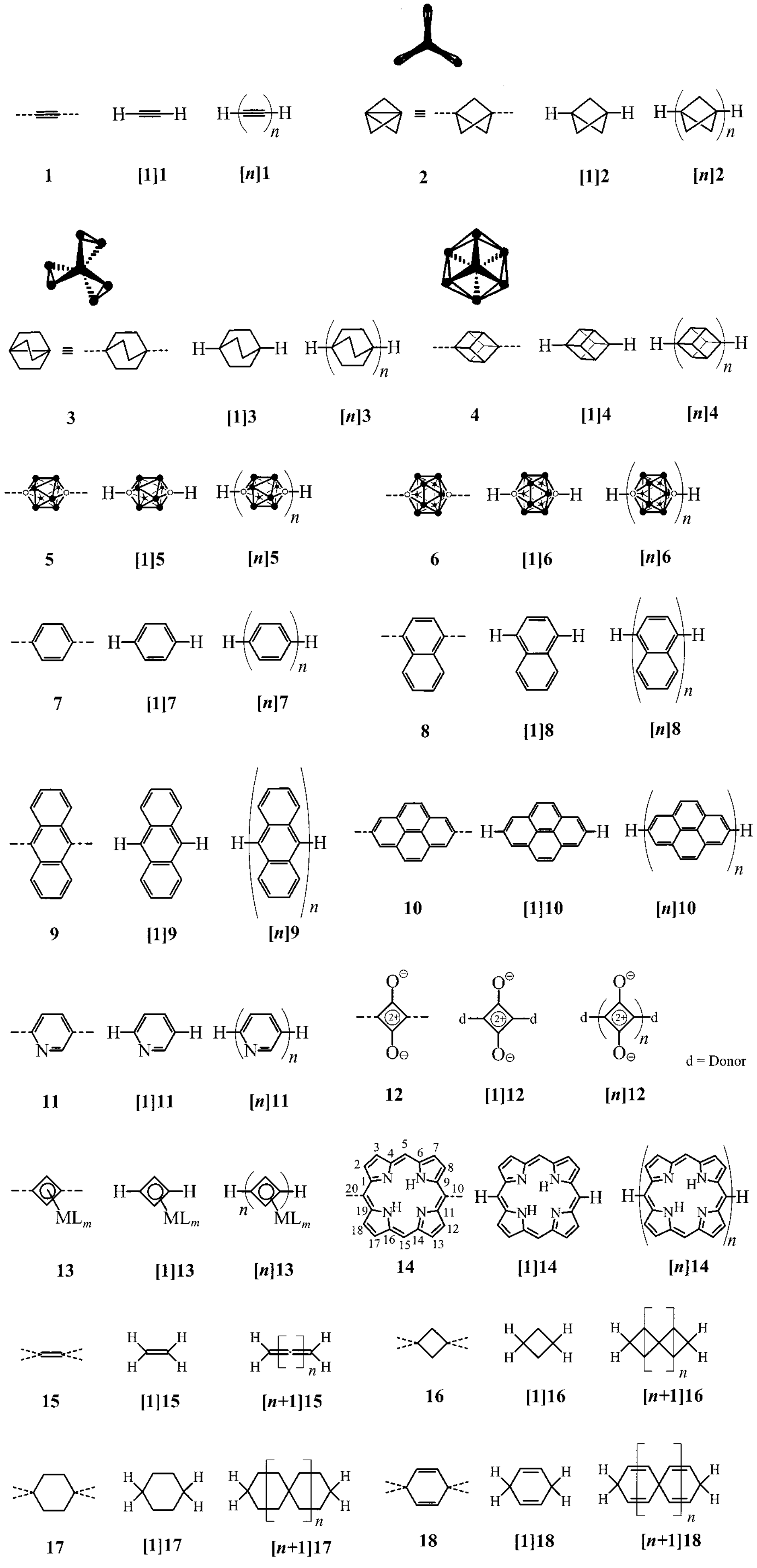
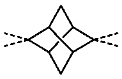
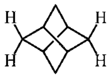

1
[1]1
[n]1
2
[1]2
[n]2
3
[1]3
[n]3
4
[1]4
[n]4
5
[1]5
[n]5
6
[1]6
[n]6
7
[1]7
[n]7
8
[1]8
[n]8
9
[1]9
[n]9
10
[1]10
[n]10
11
[1]11
[n]11
12
[1]12
[n]12
d = Donor
13
[1]13
[n]13
ML_m
14
[1]14
[n]14
15
[1]15
[n+1]15
16
[1]16
[n+1]16
17
[1]17
[n+1]17
18
[1]18
[n+1]18

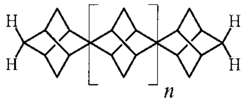
Chart I (Continued)



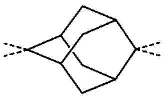
19



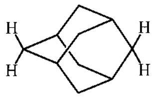
[1]19



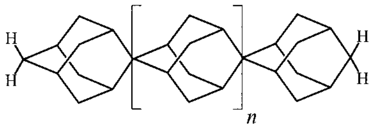
[*n*+2]19



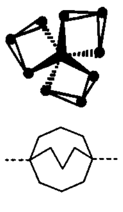
20



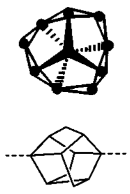
[1]20



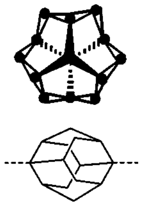
[*n*+2]20



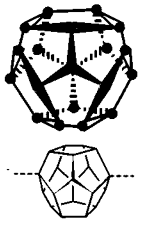
21



22



23

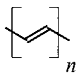


24

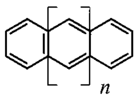
As molecular rod size increases and scanning probe microscopy techniques improve, it is likely that scanning tunneling microscopy (STM), atomic force microscopy (AFM), and related techniques will contribute to the characterization of well-defined and separated molecular rods.

B. Modules and Rods

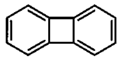
Axiality and integrity of a simple molecular rod are determined by the geometry of the constituent modules and the bonds that link them together. *Axial rods*, treated in this review (Part 1), are of two types. In singly linked axial rods, each link connects a pair of atoms on adjacent modules by a single bond along the rod axis, permitting a more or less free rotation, as exemplified by oligophenyls (**[*n*]7**) (section III.C.1). In doubly linked axial rods, neighboring modules share a terminal atom, either doubly bonded as in cumulenes (**[*n*]15**) (section IV.A) or spiro bonded as in oligo(spirocyclohexadiene)s (**[*n*]18**). *Zigzag rods* (e.g., oligoenes **[*n*]25**), treated in Part 2,[19] are similar to axial rods but maintain only a long-range axiality.



[*n*]25



[*n*]26



27

In a *ladder rod* such as [*n*]acene (**[*n*]26**), also treated in Part 2,[19] the link is either represented by two bonds between two pairs of atoms located on adjacent modules or by an edge shared by adjacent modules.

Table 1 lists the modules commonly used in singly linked axial rods, and Table 2 lists those commonly used in doubly linked axial rods.

1. Modules for Singly Linked Axial Rods

These are required to hold two opposed and collinear C−H groups rigidly at a fixed distance in space. On paper, when the modules are used to build rods, the terminal hydrogens are removed and the dangling terminal bonds are used to form single links between modules. The requirement of axiality and the tetravalency of carbon in its stable compounds place considerable restrictions on module structure.

a. Cylindrical Modules. When the three remaining bonds on each CH terminus are connected directly, the highly symmetric ($D_{\infty h}$) ethyne module (**1**) results. When they are connected through bridging groups, cage structures result. The preservation of axial symmetry requires 3-fold symmetry (at least C_3). The simplest bridging group is CH_2, and its use leads to the bicyclo[1.1.1]pentane module (**2**). The next is CH_2CH_2, which produces the bicyclo[2.2.2]-octane module (**3**). The tendency of its CH bonds to avoid eclipsing endows it with a partially twisted structure, but flipping between the structures twisted in opposite directions is facile. When the twist is increased to 60° and each of the bridge carbons on the left in bicyclo[2.2.2]octane (**3**) is connected to the closest bridge carbon on the right, the highly symmetric rigid cubane module (**4**) results.

Further increase of the length of the three bridges to $CH_2CH_2CH_2$ leads to bicyclo[3.3.3]undecane (**21**), a structure that is too floppy to be useful as a rigid module and is not listed in Table 1. Of the various ways in which it could be made more rigid, the trishomocubane module[22] (**22**) is the most obvious, but to our knowledge, this has not yet been used in rod construction and is, therefore, not listed in Table 1 either. The hexahomocubane (**23**) and dodecahedrane[23] (**24**) structures are additional examples of cage modules that might become interesting in the future.

Additional possibilities are offered by the symmetric replacement of CH_2 groups with heteroatoms such as O or NH groups and by the replacement of the terminal CH groups by groups such as SiH and NH^+. To our knowledge, these have not yet been used in the synthesis of molecular rods.

Special opportunities open when the bridges are built from boron atoms. Because of their propensity toward three-center bonding, they can produce stable deltahedral cage structures in which the terminal CH groups have three ($C_2B_3H_5$), four ($C_2B_4H_6$ and $C_2B_8H_{10}$), or five ($C_2B_{10}H_{12}$) boron neighbors. Two of these carborane structures, **5** and **6**, have been used in rod construction and are listed in Table 1.

b. Planar Modules. A less symmetrical way of holding two opposed collinear CH groups rigidly in space is offered by planar unsaturated cyclic modules with an even number of atoms in the perimeter.

In *aromatic modules*, the perimeter has ($4N + 2$) electrons and planarity is provided by the aromatic stabilization. The benzene ring has seen the most use by far, while the larger rings are distorted and/or insufficiently rigid. These shortcomings can be overcome by cross-linking or bridging of the aromatic perimeter, which lead to a variety of polycyclic structures. The most important of these modules benzene (**7**) (section III.C.1), naphthalene (**8**) (section III.C.2.a), anthracene (**9**) (section III.C.2.b), pyrene (**10**) (section III.C.2.c), and pyridine (**11**) (section III.C.3) are listed in Table 1. The modules are very stable and have been used for the synthesis of molecular rods in their parent or variously substituted forms. Some of the ($4N + 2$)-electron perimeters are formally charged, and their charges can be compensated by introduction of heteroatoms such as O or NH. The porphyrin ring system (**14**) (section III.C.4) provides a prime example.

In *antiaromatic modules*, such as cyclobutadiene, the perimeter has $4N$ electrons. At the regular polygon geometry, the molecule then is a perfect biradical. Pseudo Jahn–Teller distortion reduces the symmetry (e.g., rectangular cyclobutadiene[24]), converts the species into a homosymmetric[25] biradicaloid, and stabilizes it somewhat, but this is insufficient. Even though cyclooctatetraene and highly substituted cyclobutadienes can be isolated, their antiaromatic nature makes them unstable and disfavors planarity, making them less suitable for the construction of molecular rods. This remains true even if cross-linking enforces planarity, as in pentalene.

There are several ways in which sufficient stability can be achieved. Much stronger homosymmetric perturbation,[26] sufficient to remove biradicaloid character, such as benzo annelation to produce biphenylene (**27**) (Part 2[19]), is one possibility. Another is strong heterosymmetric[25] perturbation, which produces stable structures such as 1,3-diboradiazetes. However, the two strategies that have been employed the most are transition metal π complexation (cyclobutadiene metal complex, **13**, section III.D.2.e) and push–pull substitution (squaraine, **12**, section III.D.5.a). Both of these possibilities have been utilized in the co-oligomeric synthesis of molecular rods and are listed in Table 1.

2. Modules for Doubly Linked Axial Rods

These have to hold two opposed CH_2 groups rigidly at a fixed separation, with the bisectors of the HCH angles coincident. When used for rod construction, neighboring modules share one terminal atom. One therefore needs to remove both hydrogens at a terminus and use the two dangling valences either to make a double bond (doubly linked axial rods) or a spiro bond (spiro linked rods) within another module.

The simplest among these modules is ethene (**15**), in which the two remaining free valences of the CH_2 groups are connected directly. This is the parent of the long-known cumulene rods. The remaining two valences of each CH_2 terminus can also be connected through bridging groups, leading to cyclobutane (**16**), cyclohexane (**17**), and similar modules, but these are increasingly flexible and on the borderline of what could still be considered a rigid module (the axes of the terminal CH_2 group are not coincident, and some of those rods could be considered zigzag rods and moved to Part 2[19]). Connection through vinylene bridges, as in 1,4-cyclohexadiene (**18**), enhances the rigidity somewhat. However, truly rigid modules are obtained only when the bridge carbons are cross-connected into a cage: two cross-links convert the floppy cyclooctane into the rigid stellane (**19**), and adamantane (**20**) can be viewed as bishomostellane.

3. Module Properties

Tables 1 and 2 provide information on some of the basic module features. Module thickness was roughly estimated from crystal packing in experimental structures by assuming standard C–H bond lengths and a hydrogen van der Waals radius of 1.2 Å. For rods that are not axially symmetrical, two thickness values are given (in-plane and out-of-plane). Typical thickness is 6–8 Å, and only the ethyne (**1**) and ethene (**15**) modules are significantly thinner. These are the minimum module widths, and the use of lateral substituents in place of hydrogens can increase them considerably.

Module length is characterized by a rod length increment that results when a rod is extended by a single module. In singly linked rods, this is equal to the distance between the terminal carbon atoms of the modules plus the average of the lengths of the C–C bonds that emanate from the termini. Most of these modules have a length of a little over 4 Å, and only the shortest one, ethyne (**1**), and those based on four-membered rings (bicyclo[1.1.1]pentane **2**, squaraine **12**, cyclobutadiene **13**, and cyclobutane **16**) provide smaller increments. The increment length in doubly linked rods is given by the terminus-to-terminus (C–C) separation in the module (in zigzag rods this needs to be projected into the direction of the rod axis) and is therefore generally smaller, permitting a finer tuning of the rod lengths. The values listed in the tables were obtained by averaging experimental structural information obtained on modules or rods with various terminal (and lateral) substituents and are necessarily approximate. We have used our best judgment in estimating the contributions provided by the terminal bonds in those cases for which a single-crystal structure of an actual rod was not available. In addition to the experimental values of the rod length increment, we list in Table 3 terminal carbon–terminal carbon distances obtained by geometry optimization at the HF/6-31G* level of theory, performed on a module terminally substituted with hydrogen atoms. In addition to equilibrium geometrical characteristics, the resistance of the modules to applied stress is of great importance for the mechanical behavior of the rods built from them. We attempted to provide some feeling for the relative values for the ease of bending of the various single molecules in Table 3. We also listed results for the ease of longitudinal compression of the modules.

The numerical values listed were obtained by repeating the HF/6-31G* calculation for a module whose symmetry was preserved except that one of the terminal C−H bonds (or bisector of the terminal HCH angle) was bent 20° away from its equilibrium position and whose geometry was otherwise optimized. Since this can often be accomplished independently in two orthogonal directions (in-plane and out-of-plane bend), one or two values for the increase in energy $\Delta E_\perp$ are listed. The $\Delta E_\perp$ values thus provide a rough indication of the relative rigidity of the modules with respect to a bending distortion. Analogous values $\Delta E_\parallel$ for the relative resistance to longitudinal compression were obtained by repeating the calculations for a module whose terminal carbon atoms were fixed at a distance 5% shorter and whose symmetry was preserved but whose geometry was otherwise optimized.

The values of module distortion energies $\Delta E_\perp$ and $\Delta E_\parallel$ given in Table 3 have relative rather than absolute significance, but it is worth noting for comparison that the value of thermal energy kT is ~0.6 kcal/mol at room temperature. The bending motion is particularly easy for the ethyne and ethene modules. Given their short length, this suggests that a rather small radius of curvature will be easily achieved in oligoyne and cumulene rods. Similar ease of bending is calculated for the out-of-plane distortion of aromatic modules, whose larger length, however, suggests that small radii of curvature will not be so easily achieved. The bending of the cage modules and the in-plane bending of aromatic modules are significantly more difficult.

Longitudinal compression of the modules is generally harder to achieve than bending, and unconstrained optimization at a geometry in which the terminal atoms have been brought 5% closer together relative to the optimized geometry leads to module flexing rather than its longitudinal compression. When the latter is enforced by a symmetry constraint to obtain the $\Delta E_\parallel$ values, we note considerable stiffness in polycyclic aromatics but not in the porphyrin macrocycle. Among the other modules, ethyne and 10-vertex carborane stand out as longitudinally stiffer than most.

Rod structure, width, length, and resistance to longitudinal and transverse distortion follow qualitatively from the properties of the constituent modules and their numbers. The ease of bending increases dramatically as the rod length increases. The corresponding transverse vibrations are of low frequency and difficult to observe experimentally, and an appraisal of rigidity often rests on calculations[27] or indirect information, such as the relative stability of different conformers and the strain energy of compounds containing a bent rod.

In addition to increasing the dimensionality of rod construction, e.g., converting an axial rod into a ladder rod,[28−30] the rigidity of a molecular rod can be increased by the introduction of bulky substituents at the backbone,[31] which restricts bending motions, or by threading the backbone through rigid macrocycles.[32−34] Then, even very flexible oligomers, such as oligo(ethylene glycol)s, can be converted into more rigid rods.

Saturated and conjugated rods neatly fall into two separate classes with regard to their excitation energies, ionization potentials, and electron affinities. The *closo* carboranes, although sometimes referred to as “aromatic” because of their delocalized bonding, behave as if they were saturated. When modules are combined into rods, their electronic characteristics asymptotically approach a limiting value as the rod length increases. For practical purposes, the limit is usually reached already at a fairly short rod length, referred to as the conjugation length. This is an approximate concept and a function of the particular property measured. In a better approximation, one can speak about the length of an exciton for electronic excitation (at ground state geometry for the absorption spectrum and at singlet or triplet excited state geometry for the fluorescence or phosphorescence spectrum), and the length of a positive polaron for ionization and a negative polaron for electron attachment. In solution, these lengths may also depend on the nature of the solvent, particularly for the polarons. In oligomers that are differentially terminally substituted and in co-oligomers, the dependence of electronic properties on chain length can be more complicated and need not even be monotonic.

C. Overview of Synthetic Methods

The preparation of rods of a predetermined length represents a considerable synthetic challenge.[10] Two approaches exist:[35] targeted and random synthesis.

Targeted synthesis usually involves a long series of controlled steps in which modules are transformed or combined such that only one oligomer is involved in each reaction and the target product, a rod of particular length, is virtually the only product. The advantage of the targeted method is in the relatively easy purification of the resulting oligomers. However, the reaction sequence is usually long, and several distinct sequences may be required to obtain all the oligomers desired. In the divergent approach, one module is added at a time, and in the convergent approach, large pieces of the rod are coupled. A combination of the divergent and convergent approaches leads to “iterative” synthesis,[36−38] which permits exponential growth of the oligomeric chain with high overall yields of individual oligomers, and was used to synthesize some of the longest well-defined molecular rods known. An efficient general algorithm for such exponential synthesis is shown in Scheme 1, where a prime indicates a protected (unreactive) form of a functional group, and selective deprotection must be possible.

Random synthesis converts a module or a shorter rod into a mixture of oligomers whose length distribution may be controlled to some extent by the choice

Table 3. Calculated Mechanical Properties of Axial Modules

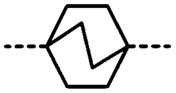
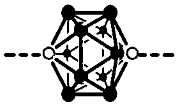
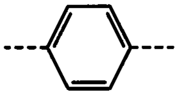
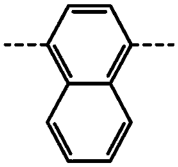
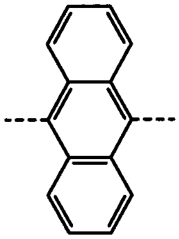
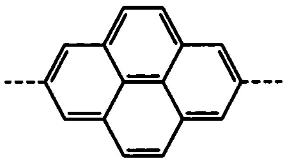
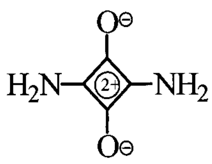
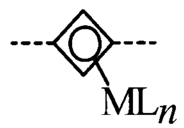
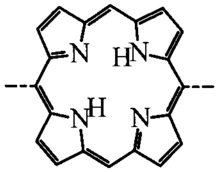
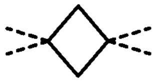
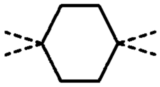
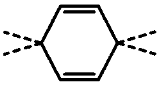
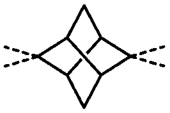
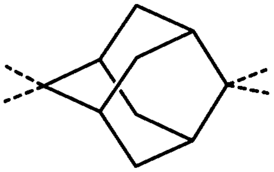
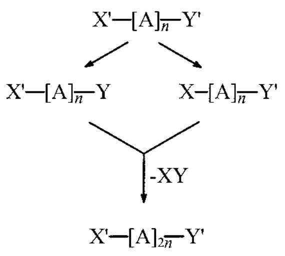
Module	Name[a]	CC distance /Å[b]	$E_{\parallel}$ /kcal mol^{-1}[c]	$E_{\perp}$ /kcal mol^{-1}[d]
	ethyne **[1]1**	1.18	5.8	3.1
	bicyclo[1.1.1]pentane **[1]2**	1.87	3.3	7.5
	bicyclo[2.2.2]octane **[1]3**	2.59	3.0	8.0
	cubane **[1]4**	70	3.4	6.9
	1,10-dicarba-*closo*-decaborane **[1]5**[e]	3.33	6.7	7.3
	1,12-dicarba-*closo*-dodecaborane **[1]6**[e]	3.04	4.2	7.1
	benzene **[1]7**	2.77	3.4	5.1[f] 9.5[g]
	naphthalene **[1]8**	2.79	3.5	4.3[f] 9.6[g]
	anthracene **[1]9**	2.78	3.5	4.2[f] 9.8[g]
	pyrene **[1]10**	7.00	15.4	3.1[f] 9.6[g]

Table 3 (Continued)

	squaraine[h] **[1]12**	1.99	4.0	3.7[f,i] 8.4[g,i]
	cyclobutadiene metal complex[j] **[1]13**	2.04	3.8	1.3[f,k] 3.5[f,l] 7.2[g]
	porphyrin **[1]14**	6.84	3.3	2.6[f] 8.2[g]
	ethene **[1]15**	1.32	4.0	3.0[f] 10.8[g]
	cyclobutane **[1]16**	2.16	2.4	4.3[m] 6.4[n]
	cyclohexane **[1]17**	2.96	2.1	8.2[o] 7.1[m] 6.7[n]
	1,4-cyclohexadiene **[1]18**	2.99	3.3	6.8[f] 6.5[g]
	stellane **[1]19**	3.26	4.4	8.8[p] 5.0[q]
	adamantane **[1]20**	3.55	3.1	6.3[r] 6.2[s]

[a] Name of the hydrocarbon obtained by attaching hydrogens to the dangling bonds of the modules. [b] The distance between the terminal carbon atoms of the hydrocarbon at optimized (HF/6-31G*) geometry. [c] Increase in energy (HF/6-31G*) upon compression of the CC distance by 5% from the optimized values with geometry reoptimization subject to this constraint and preservation of symmetry. [d] Increase in energy (HF/6-31G*) upon 20° deflection of one C(terminal)–H vector or a H–C(terminal)–H bisector off its optimized orientation (connecting the two terminal C atoms) and geometry reoptimization subject to this constraint. [e] Empty circles, C; full circles, BH. [f] Out-of-plane deflection. [g] In-plane deflection. [h] NH_2 groups were attached to the dangling bonds. [i] The CN bond was deflected. [j] ML_n = CoCp. [k] Deflection away from the Co atom. [l] Deflection toward the Co atom. [m] HCH bisector deflected in the HCH plane away from axial H on adjacent CH_2 groups. [n] HCH bisector deflected out of the HCH plane by rotation about an axis perpendicular to the C(terminal)–C(terminal) line. [o] HCH bisector deflected in the HCH plane toward axial H on adjacent CH_2 groups. [p] HCH bisector deflected in the plane of the four bridge carbons. [q] HCH bisector deflected out of the plane of the four bridge carbons. [r] HCH bisector deflected in the HCH plane. [s] HCH bisector deflected out of the HCH plane.

Scheme 1



of the mechanism of oligomerization and the reaction conditions. This is followed by separation of oligomers if individual compounds need to be prepared (sometimes libraries of homologous oligomers need to be obtained, but this is not our concern here). The advantage of the random method is the minimal number of synthetic steps needed, frequently only one. The disadvantages are the often laborious oligomer separation and low yields of the individual oligomers.

Methods for the preparation of the axial (Part 1) and zigzag (Part 2[19]) rods are dominated by metal-catalyzed coupling reactions[39,40] forming single or multiple covalent bonds. The choice of the catalyst is dictated by the propensities of the precursors to add oxidatively to the active site of the catalyst and by the product rod to eliminate reductively. Those metal complexes which add rod precursors but do not eliminate them can serve as connectors for attaching the rods to other rods or to other modules (see Part 2[19]). Given the immense variety of available metal-containing catalysts, the coupling reactions usually can be tuned to give good yield and selectivity. An alternative to these methods are classical condensations, radical coupling and telomerization, and rearrangements of suitable precursors. These methods are somewhat less versatile, but in many cases they are the only available synthetic route when the reactive intermediates involved do not survive a proximity of electropositive metals (cf. section III.D.1.a). At present, the metal-catalyzed coupling reactions are well worked out for the coupling of aryl, vinyl, ethynyl, and carboranyl groups to each other and less so to other cage modules. General and selective bridgehead-to-bridgehead cross-coupling of other cage modules with each other is an unresolved synthetic problem, and even bridgehead-to-bridgehead dimerization is difficult in several instances.

Carbon-based spiro rods (Part 1) are hard to make and are the least well studied. Ladder-type rods (Part 2[19]) are usually prepared by Diels–Alder reactions. However, such approaches as zipper-type rearrangements and condensations are also useful in certain cases.

An important consideration in the synthesis of terminally functionalized molecular rods from modules is the timing of the terminal substitution. Most modules, such as cubane (**[1]4**) or bicyclo[2.2.2]octane (**[1]3**), cannot be selectively functionalized at the terminal CH group and need to carry a substituent from the outset of the synthesis, whether it is needed for the construction of the rod itself or for the attachment to connectors when the rod is used for its ultimate purpose. Notable exceptions are the ethyne and carborane modules, whose acidic terminal CH groups permit facile selective activation with common strong bases, some of the arenes that undergo selective electrophilic substitution at the terminal carbon, and those heterocycles that carry a terminal aza nitrogen, susceptible to selective electrophilic attack on the nitrogen lone pair.

Finally, for many intended uses, lateral substitution of the rods will be of critical importance as well. This has received little attention so far, with the exception of long-chain attachment for solubilization purposes. Selective lateral funtionalization of long molecular rods remains a synthetic problem to be tackled.

III. Singly Linked Axial Rods

The ethyne (**1**) and ethene (**15**) modules are the simplest considered in this article, and oligoynes (**[*n*]1**, section III.A)[41] along with cumulenes (**[*n*]15**, section IV.A) represent the simplest molecular rods. Oligoyne rods terminate in one single bond on each side and have strongly alternating bond lengths, while cumulene rods terminate with two single bonds or a double bond on each side and have almost equal bond lengths. In longer oligoynes (**[*n*]1**), the alternation is small close to the center of the chain but near the ends it is still substantial.[42] There is an interesting oxidation–reduction relation between the oligoynes and cumulenes, most clearly brought out when the terminal substituents are metals.

A. Oligoynes

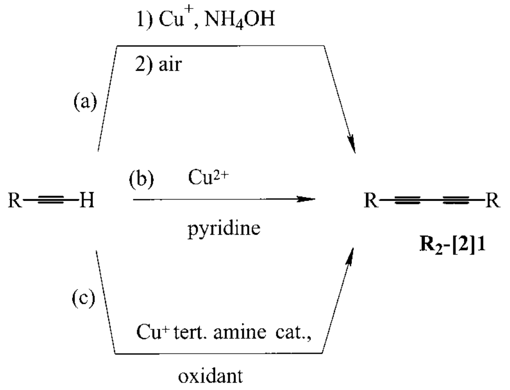
The formal monomer, carrying no terminal substituents, is C_2. Although known in the gas phase, it is too reactive to be used as a bulk reagent. However, the dianionic form, C_2^{2-} (as well as C_4^{2-}) is readily available and represents an important starting material.

Because of the ease with which metal atoms are attached to ethyne termini and because of the large number of metalated rods known, we are treating them separately from oligoyne rods carrying purely organic substituents.

1. Organic Terminal Substitution

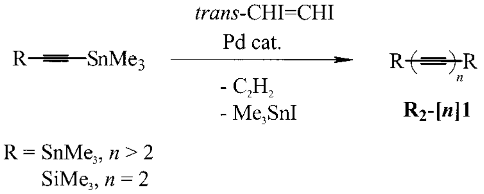
Synthesis. Symmetric coupling of free acetylenes under mild conditions was discovered over a century ago by Glaser (Scheme 2a),[43,44] and his procedure has

Scheme 2

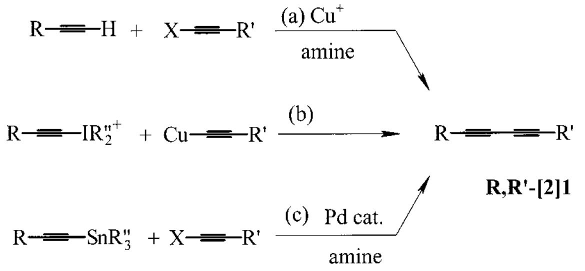


been significantly improved since by Eglinton and co-workers[45,46] and Hay (Schemes 2b and 2c).[47] Stannylated alkynes can also be symmetrically coupled (Scheme 3).[48] Unsymmetric coupling of terminal free acetylenes developed by Cadiot and Chodkiewicz (Scheme 4a)[49] can be accomplished under a variety of conditions.[50−56] In most of these reactions copper acetylides seem to be the key intermediates. Coupling of alkynyliodonium salts with copper(I) acetylenides gives diynes in good yields (Scheme 4b),[57] and Stille coupling (Scheme 4c) of stannylated alkynes provides a copper-free coupling method.[58] A novel approach to medium-length oligoynes ($n = 3-7$) via solution spray flash vacuum pyrolysis of cyclobutenedione precursors **28** developed in Diederich's group does not involve coupling in the last step (Scheme 5).[59]

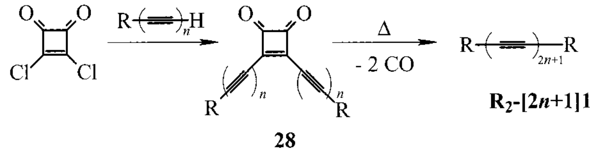
Scheme 3



Scheme 4



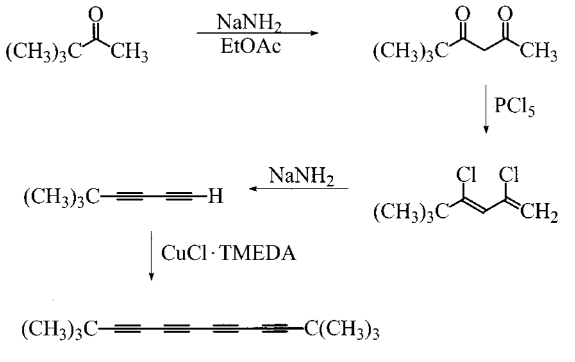
Scheme 5



The longest individual isolated oligoyne with 16 triple bonds and an estimated length of ∼42 Å was prepared by the Cadiot−Chodkiewicz coupling and the divergent−convergent approach using singly triethylsilylated acetylenes.[60] Lagow et al.[61] reported the synthesis of a C_8 chain **29** with *tert*-butyl end groups (Scheme 6) in four steps from methyl-*tert*-butyl ketone and characterized it by single-crystal X-ray diffraction. By the condensation of lithium compound $Li-C\equiv C-Br$ in liquid NH_3, a mixture of phenyl-capped ethyne chains with up to 28 carbon atoms was prepared but not separated. Laser-based gas-phase synthesis in the presence of end-capping groups yielded mixtures of chains with up to 300 carbon atoms.[62]

Properties and Uses. The major advantages of oligoynes (**[*n*]1**) as rods are minimal steric demand, synthetic accessibility from cheap precursors, adequate thermal and photochemical stability of the shorter ones, and above all the availability of numerous effective procedures for the selective protection or activation of a terminal CH group toward axial coupling to other modules. At ambient conditions, oligoynes are compatible with most functional groups on other construction modules. They are stable toward strong bases and moderately strong acids. However, carbocations and radicals add readily to $C\equiv C$ bonds, and reactions involving these and similar reactive intermediates need to be avoided on rods containing the oligoyne linker, if the structure is to be preserved. Another shortcoming is the absence of positions suitable for lateral substitution.

Scheme 6



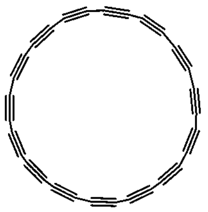
29

The triple bond can be cleanly reduced to a *cis*-olefin with diimide[63] or by hydrogenation on the Lindlar catalyst.[64−66] Selective transformation to a *trans*-olefin may be achieved by Birch reduction.[64] Butadiynes react with hydrogen sulfide to yield thiophenes.[67] Dicobaltoctacarbonyl reversibly forms complexes with acetylenes and butadiynes[68,69] and reduces the C−C−C angle from 180° to around 138°.[70] These transformations can be used to bend an oligoyne rod.[71] Butadiynes add benzylmercaptane and after one additional step yield 1,2-dithia-3,6-phenylenes.[72] This reaction sequence will shorten the rod without substantial loss of axiality.

Oligoynes (**[*n*]1**) are stable toward visible light, but 254 nm light excites butadiynes to a chemically reactive state.[73] In crystals or ordered films, a string of butadiyne moieties on neighboring molecular rods can be oligomerized or polymerized into the corresponding *trans*-[74−76] or *cis*-[77] polybutadiyne derivatives.[78−80] The occurrence of the polymerization and its course are determined by the mutual orientation of the butadiyne groups.[76] End groups bulkier than hydrogen, such as *tert*-butyl, triethylsilyl, and phenyl, have an important stabilizing effect. Thus, the tetrayne **29** melts at 99 °C and is stable to at least 130 °C and 60 kbar.[62]

Oligoynes are very flexible linkers (Table 3), and bent butadiyne units are found in dehydrobenzoannulenes[81−83] and dehydroannulenes.[84] According to pioneering extended Hückel[85] and more recent DFT[86,87] calculations, large carbon clusters C_m, $m \geq 10$, actually prefer the cyclic geometry to linear geometry since it allows them to avoid dangling bonds at the termini. Bent oligoynes were proposed as intermediates in the formation of C_{60} in carbon arc;[88] cycloalkynes, such as cyclo-C_{30} **30** and cyclo-

C_{60}, were prepared by Diederich, and their cations undergo an efficient ion−molecule coalescence to give fullerene ions.[89−91] Excessive flexibility and reduced stability of the longer oligoynes are some of the reasons why only short oligoyne linkers (ethyne and butadiyne) are frequently used in molecular assembly and why they are most often used as co-oligomers.



30

Oligoynes (**[*n*]1**) are worse conductors of charge and spin than oligoenes,[42] presumably because of the large bond-length alternation between the single and the triple bonds.

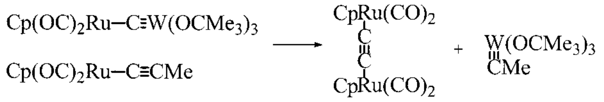
Some oligoyne derivatives show potent antimicrobial activity.[92]

2. Metal Terminal Substitution

Terminal metal atoms on an oligoyne rod usually carry other ligands, frequently including a cyclopentadienyl ring.[93,94] These bimetallic complexes have been investigated as model systems for surface carbides in heterogeneous catalysis, substrates for spectroscopic investigations of electronic communication across oligoyne rods, building blocks for organometallic polymers, and intermediates in the quest for carbyne, a carbon allotrope built from one-dimensional molecules.

Synthesis. Bimetallic complexes of acetylene itself are by far the most extensively investigated group. The two terminal organometallic substituents are frequently identical. Such complexes are usually obtained by metal−halogen exchange or metal−metal exchange from dilithiated, dihalogenated, or otherwise activated acetylene.[95] The metathesis reaction between −W≡C− and −C≡CMe has also been exploited in this context (Scheme 7).[96,97] Examples with W,[98] Fe,[99] Sc,[100] Cr,[101] Ti,[102] Au,[103] Re,[104] Ru (**31**),[96] and Mn[105] are known, and recently, the first example of an early transition metal (Hf)[106] has been added. Woodworth et al.[107] reported the unusual structure M≡C−C≡C−C≡M (**32**) where two robust carbyne moieties are brigded by an acetylene unit (Scheme 8).

Scheme 7

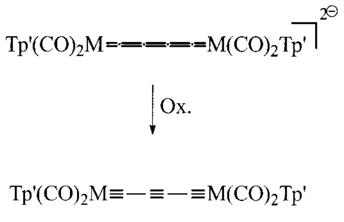


$Cp(OC)_2Ru{-}C{\equiv}W(OCMe_3)_3 + Cp(OC)_2Ru{-}C{\equiv}CMe \longrightarrow CpRu(CO)_2{-}C{\equiv}C{-}CpRu(CO)_2 + W(OCMe_3)_3{\equiv}CMe$

31

The synthesis of compounds with two different metals is reported less frequently and requires the isolation of a monoacetylide complex which can react further at the remaining acetylene terminal. An example (**33**) is shown in Scheme 9.[108] The reaction mechanisms are discussed in a review article by Beck et al.[95]

Scheme 8

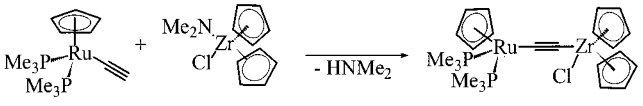


32

M = W, Mo

Tp' = hydridotris(3,5-dimethylpyrazolyl)borate

Scheme 9

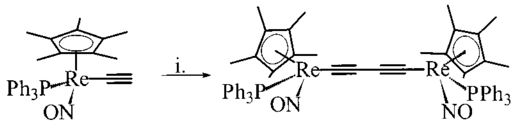


33

Bimetallic complexes of butadiyne can be obtained either through coupling of two organometallic terminal alkynes or through the reaction of an activated butadiyne with two equivalents of a metal complex. When the latter reaction is carried out stepwise, heterobimetallic species become accessible. The metals most commonly used are Fe and Re.

Terminal alkyne coupling was used by Gladysz and his group[109] to form binuclear Re complexes **34** (Scheme 10), by Lapinte and his group[110] to prepare binuclear Fe complexes **35** (Scheme 11), and by Yam and his group[111,112] who prepared the complex **36** (Scheme 12) whose extended linear O≡C−Re−C≡C−C≡C−Re−C≡O unit displayed a rich photophysical behavior.

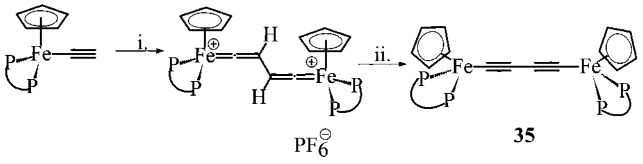
Scheme 10



34

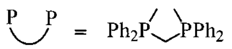
i. $Cu(OAc)_2$, pyridine

Scheme 11



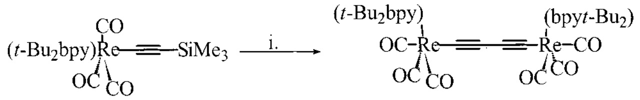
35

i. CH_2Cl_2, $[Fe(Cp)_2]PF_6$, -80°C; ii. THF, *t*-BuOK, -80°C.



Coupling of butadiyne to metal centers was used by Crescenzi and Lo Sterzo[113] to prepare both the mononuclear Fe complex **37** and the binuclear Fe complex **38** (Scheme 13) under very mild conditions.

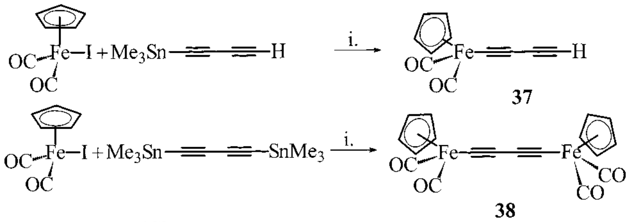
Scheme 12



36

i. 1. KOH, 2. $Cu(OAc)_2$, pyridine

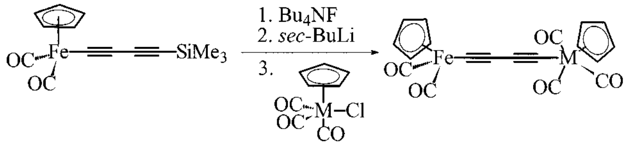
Scheme 13



i. $(CH_3CN)_2PdCl_2$

Complex **37** protected with a trimethylsilyl group was also obtained by Wong et al.,[114] and after desilylation, it was coupled with $Cp(CO)_2FeCl$ to obtain **38** or with $Cp(CO)_3MCl$ (M = W, Mo) to synthesize the heterobimetallic counterparts **39** and **40** (Scheme 14).

Scheme 14

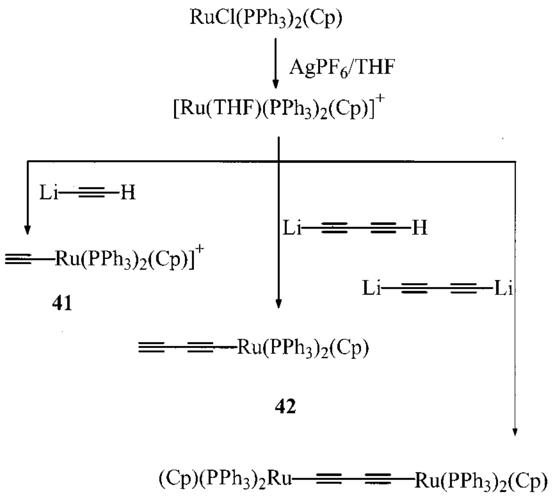


M = Mo, W

39, 40

Bruce and his group[115,116] obtained the mononuclear (**41** and **42**) and binuclear (**43**) Ru complexes by displacement of the weakly coordinated THF from the cation $[Ru(THF)(PPh_3)_2Cp]^+$ by the respective alkynyl anions and dianions (Scheme 15).

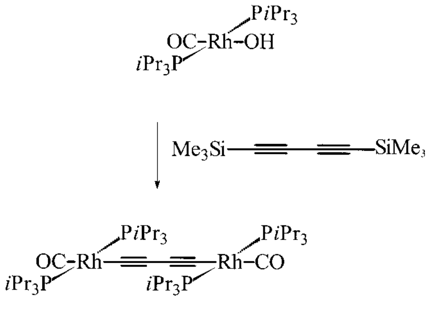
Scheme 15



43

A mononuclear $W(CO)_3Cp$ butadiyne complex was oxidatively coupled by the same group,[117] yielding an octatetrayne-bridged system. Werner and co-workers[118] reported the synthesis of a binuclear complex of Rh **44** (Scheme 16).

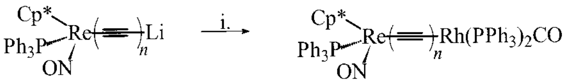
Scheme 16



44

Rods with a half-sandwich cap on one end and a purely μ-ligated metal on the other end, such as **45**, are also known (Scheme 17).[119]

Scheme 17

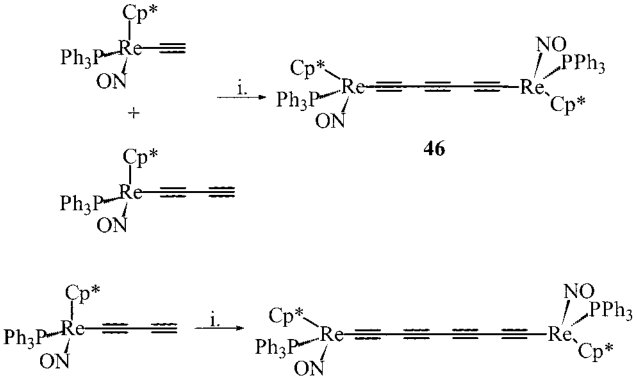


45

n = 1, 2

Terminal acetylene cross-coupling under Eglinton conditions[109] yielded primarily the binuclear Re complex of hexatriyne **46**, while homocoupling produced the octatetrayne analogue **47** (Scheme 18).

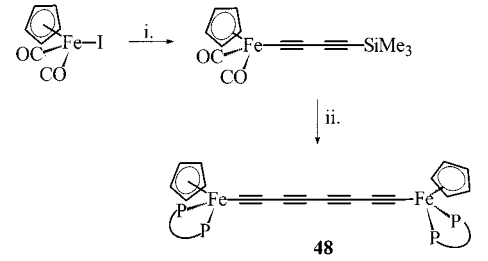
Scheme 18



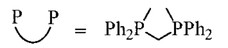
i. 1.5 equiv. $Cu(OAc)_2$, pyridine

A similar oxidative coupling[120] of $Fe(Cp)(dppe)(C{\equiv}C{-}C{\equiv}CH)$ yielded the analogous diiron complex **48** (Scheme 19), which is thermally

Scheme 19

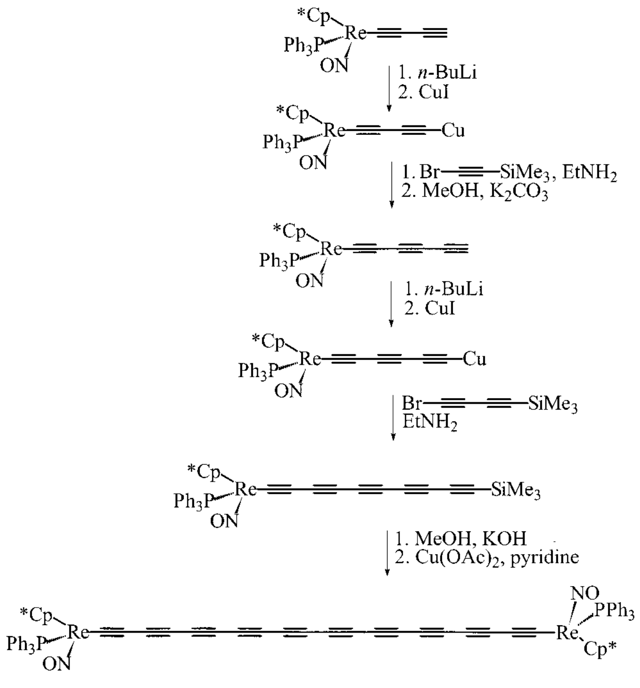


i. Me_3Si-C_4Li, THF; ii. 1. hν, dppe, 2. THF, n-Bu_4NF, 3. $Cu(OAc)_2$, pyridine



stable but air sensitive. The oligoyne growth methodology developed by Gladysz and co-workers[121,122] (Scheme 20) so far appears to be unlimited with respect to chain length and has been used to synthesize dirhenium complexes with chains of 12, 16, and 20 (**49**) sp-hybridized carbon atoms.

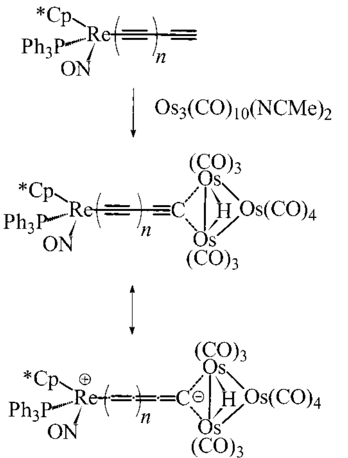
Scheme 20



49

Up to this point, only end groups with single metal atoms have been discussed. Gladysz[123,124] suggested that polymetallic end groups might provide additional features or enhance existing ones (greater capacitance, improved coupling and communication between the termini). The rhenium half-sandwich species with C_2, C_4, and C_6 oligoyne rods described above were treated with the triiosmium complex $[Os_3(CO)_{10}(NCMe)_2]$ under mild conditions to form the corresponding rhenium−triosmium carbon complexes $[(Cp^*)Re(NO)(PPh_3)(C{\equiv}C)_nOs_3(CO)_{10}H$ (**50**) (Scheme 21).

Scheme 21



50

Properties and Uses. The metal derivatives of oligoynes are generally fairly air stable at room temperature and quite soluble in polar aprotic organic solvents. However, the stability of the products **50** with metal clusters at the termini decreases significantly with increasing chain length, effectively limiting any practical application of such compounds.

Spectroscopic investigations of the neutral complexes and in some cases their radical ions provide evidence of strong electronic communication between the termini, not surprising for a fully conjugated chain. A detailed review of the electronic interactions in organometallic ethyne-bridged dimers has appeared recently.[125] An interesting comparison of the oxidation potentials for the two metal atoms has been made on the binuclear Re complexes of Gladysz and collaborators.[122] As the rod grows longer, the potentials approach each other until they merge at C_{20}, indicating an effectively independent behavior of the two rhenium centers. The group of Bruce has shown that the diruthenium butadiynyl complexes **43** undergo four stepwise one-electron oxidation−reduction processes, where only the last one is irreversible. The mixed-valence cations [Ru(II)/Ru(III) and Ru(III)/Ru(IV)] are thermodynamically stable and can be isolated.[126]

B. Oligomers of Cage Modules

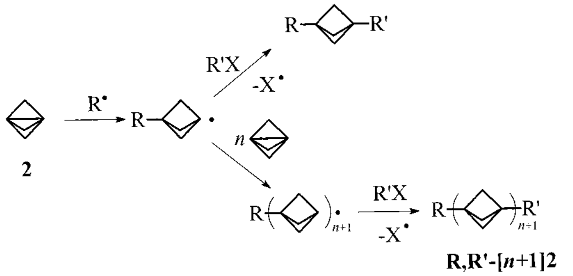
1. Staffanes

Among the monomers listed in Tables 1 and 2, bicyclo[1.1.1]pentane (**[1]2**)[127] is unique in that this module is also stable and readily available even in the absence of any terminal substituents, in the form of [1.1.1]propellane (**2**).[128−130] In this species, the two terminal dangling bonds do not dangle but instead mutually saturate through space and form a bond that has approximately the strength of the π bond in ethylene.[128,131,132] Despite its forbidding-looking structure, [1.1.1]propellane (**2**) is easily synthesized in the laboratory on a large scale from commercially available starting materials and is reasonably stable in solution. It can be stored indefinitely in the form of its iodine adduct, 1,3-diiodobicyclo[1.1.1]pentane, from which it is liberated as needed by treatment with NaCN.[133] Its oligomers, [*n*]staffanes (**[*n*]2**), are named for their characteristic shape, reminiscent of the staffs carried by medieval dignitaries, and their chemistry has been reviewed.[134]

Synthesis. The known [*n*]staffanes (**[*n*]2**) are all ultimately derived from [1.1.1]propellane (**2**).[135−138] This starting material can be oligomerized and the oligomer mixture separated or it can be inserted one cage at a time into a terminal C−I bond to yield short rods, and these can be coupled at the terminal positions to double the rod length. Selective terminus-to-terminus cross-coupling of [*n*]staffanes of different lengths has not been described.

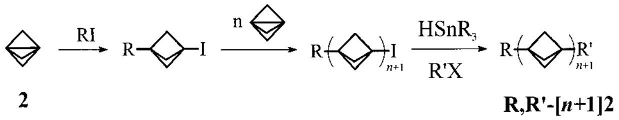
The first observation of [*n*]staffane formation by telomerization of **2** was reported by Wiberg et al. in 1986.[139] Subsequent work by his group and those of Szeimies and Michl showed that reagent and reaction conditions can be selected to direct the radical-induced insertion of **2** into a variety of single bonds either toward the formation of substituted bicyclo[1.1.1]pentanes[136] or toward the production of a mixture of [*n*]staffane oligomers[6,137,140,141] (Scheme 22). Although the lower oligomers are isolated fairly easily and some [2]staffanes, such as 3,3′-bis(acetylthio)[2]staffane, are thus accessible in high yields,[137] the yields of higher individual oligomers are modest.[136,137] Nevertheless, terminal dithiols and dicarboxylic acids have been fully characterized up to $n = 5$,[137] as have doubly terminal methyl sulfides up to $n = 4$.[141]

Scheme 22

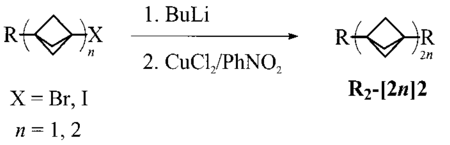


Light-induced insertion of [1.1.1]propellane (**2**) into a C−I bond is particularly facile (Scheme 23),[137,142] and a bicyclo[1.1.1]pentane unit and sometimes a longer [*n*]staffane chain can be grown on an iodinated site on a bicyclo[1.1.1]pentane (or another molecular module, see sections III.D.3 and III.D.4.a). The terminal C−I bonds in staffyl iodides tend to be stronger than most others, and solubility decreases with increasing rod length. As a result, it is often possible to stop the insertion after only one cage has been added. Thus, photoinsertion of **2** into 1,3-diiodobicyclo[1.1.1]pentane in pentane solution yields 3,3′-diiodo[2]staffane in high yield, and this provides easy access to [2]staffane-3,3′-dicarboxylic acid, while higher staffanes are not formed. A general method for the preparation of differentially terminally substituted [*n*]staffanes (**[*n*]2**) proceeds via 3-iodo-3$^{(n)}$-phenyl[*n*]staffanes, obtained from iodobenzene and **2**.[137] A number of specific methods have been developed for preparation of oligomers with a desired substitution pattern.[135−138] Rod length doubling by symmetric end-to-end coupling (Scheme 24) has been described by Michl's group.[143]

Scheme 23



Scheme 24



Properties and Uses. Despite their high strain content, the parent [*n*]staffanes (**[*n*]2**) are stable up to ∼300 °C and most derivatives are stable well above 200 °C.[137] Many form liquid crystals upon melting.[137,138,144−146] The [*n*]staffane skeleton resists acids, bases, strong oxidants, and reductants (forceful reduction of hexafluorinated bicyclo[1.1.1]pentane breaks the cage[147]). Radical abstraction of hydrogens is very difficult (chlorination[148,149] and fluorination[147] are possible). Certain synthetic manipulations must be avoided, however, since the bicyclo[1.1.1]pentane cage rearranges readily upon introduction of cationic character into the bridgehead position.[136,150] Bridgehead iodides solvolyze very readily and need to be handled with care. Hydrogens in these positions are about as acidic as those in ethene[134] and cannot be selectively removed by base.

The solubility of unsubstituted [*n*]staffanes (**[*n*]2**) decreases rapidly as their length increases, and some quantitative information has been reported.[137] Schlüter's group has shown that the introduction of even one alkyl substituent on the bridge per cage increases the solubility dramatically, and the high polymer is then soluble.[151]

The vibrations of [*n*]staffanes (**[*n*]2**) have been examined in considerable detail.[27,134] Their photoelectron spectra reveal a gradual decrease of the first ionization potential with increasing *n*, with convergence to a value of 8.5 eV, surprisingly low for a saturated hydrocarbon.[137] They do not absorb significantly above 200 nm.

For fully saturated species, the [*n*]staffanes (**[*n*]2**) offer surprisingly good communication between the termini,[138] as revealed in long-range NMR[137] and EPR[152] coupling constants and in photoelectron spectra of terminally disubstituted derivatives.[153] The interactions propagate both through bonds and through space, via backlobe-to-backlobe bridgehead-bridgehead transannular overlap.[152]

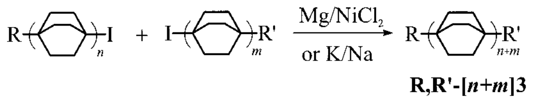
Terminally substituted [*n*]staffanes have been assembled into Langmuir−Blodgett films[154] and also into self-assembled monolayers on gold.[155] A staffane rod has also found use as a molecular rack for holding an otherwise flexible oligosilane chain stretched in an all-anti conformation for spectroscopic studies.[156] Staffane rods were used as components of a square grid holding molecular propellers in a computer simulation of their rotational behavior in a stream of helium atoms.[157]

2. Bicyclo[2.2.2]octane

Among the monomers of Tables 1 and 2, the long-known[158] bicyclo[2.2.2]octane (**[1]3**) comes the closest to bicyclo[1.1.1]pentane (**[1]2**) with regard to stability of the terminal substituent-free module, [2.2.2]propellane (**3**), in which the two terminal free valences are mutually saturated. Although the parent has never been characterized, a simple derivative has been known for decades.[159] It is relatively unstable (the cage opens with a half-life of 28 min at 25 °C) and difficult to prepare and has been of no significance in the synthesis of oligomeric bicyclo[2.2.2]octanes (**[*n*]3**). As a result, these are much less readily accessible than the analogous [*n*]staffanes (**[*n*]2**). This can change overnight if an efficient synthetic route to [2.2.2]propellane is discovered.

Synthesis. The only published route to the oligomers of bicyclo[2.2.2]octane (**[*n*]3**) is the bridgehead-to-bridgehead coupling of prefabricated terminally substituted modules. Up to four monomer units were linked by Zimmerman et al. in moderate yields (Scheme 25)[7,160] using reductive coupling of bridgehead iodinated bicyclo[2.2.2]octanes. An alternative route by electrolytic decarboxylative coupling of carboxylate salts (Kolbe reaction) proposed by Vögtle and co-workers gives much lower yields.[161] Additional efforts will be required before these rods become generally accessible.

Scheme 25



Properties and Uses. Oligo(bicyclo[2.2.2]octane)s (**[*n*]3**) contain little strain and have outstanding thermal stability (the tetramer $4,4'''$-diol melts above 525 °C[160]). The oligomers **[*n*]3** are much better insulators of electronic effects than staffanes (**[*n*]2**) because the σ bonds in the bicyclo[2.2.2]octane cage are less strained and the distance between the bridgeheads is much larger than that in the bicyclo[1.1.1]pentane cage, preventing significant transannular interactions.[160]

3. Cubane

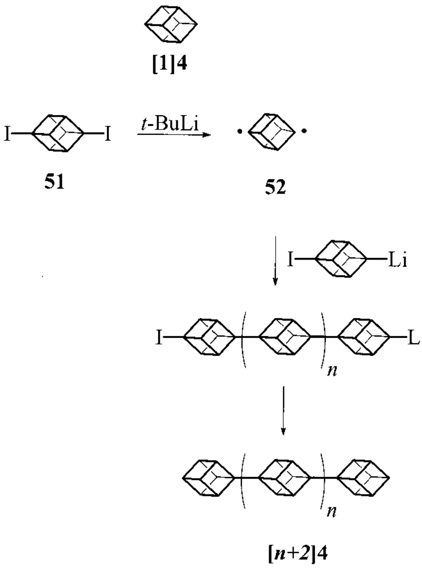
Cubane (**[1]4**) was first synthesized by Eaton and Cole,[162] and its chemistry has since been elaborated extensively, primarily in Eaton's laboratory.[163,164]

The formal monomeric module of the oligocubyl series, free of terminal substituents, is 1,4-cubanediyl. It is a highly reactive biradical that has been observed directly only in matrix isolation (argon, 12 K) by the group of Michl.[165] The spectroscopic evidence in the matrix and ab initio calculations performed by them[165] and Borden and Hrovat[166] suggest that this very reactive intermediate is a singlet ground-state biradical with the singlet a little over 10 kcal/mol below the triplet, in agreement with the lack of reactivity toward Diels–Alder dienes.[167] The mutual saturation of the terminal free valences is thus fairly minimal; it takes place by through-bond rather than through-space interactions, differently than in [1.1.1]propellane (**2**) and [2.2.2]propellane (**3**). Free 1,4-cubanediyl is generated in the reaction of 1,4-diiodocubane with *t*-BuLi at low temperatures, as demonstrated by Eaton and his group[167,168] using isotopic labeling, and is thus quite readily available, although it cannot be stored.

Synthesis. Oligocubyls (**[*n*]4**) have been prepared by nucleophilic addition of lithium compounds to 1,4-cubanediyl[164,165,169] (Scheme 26). Cubane-1,4-dicarboxylic acid is synthesized industrially on a large scale and represents the usual synthetic entry point. Its conversion to 1,4-diiodocubane (**51**), a direct precursor of 1,4-cubanediyl (**52**), was achieved by treatment with I_2/PhI(OAc)$_2$.[163]

Alkyllithium reagents do not react as easily with 1,4-cubanediyl as the corresponding aryl compounds (see section III.D.4.b), and Grignard reagents had to be utilized to obtain alkylated oligocubyls from 1,4-diiodocubane and RLi (R = alkyl) (Scheme 27).[164] The resulting Grignard products **[*n*]53** are capable of reacting further, allowing for a wide variety of substitution patterns.

Scheme 26



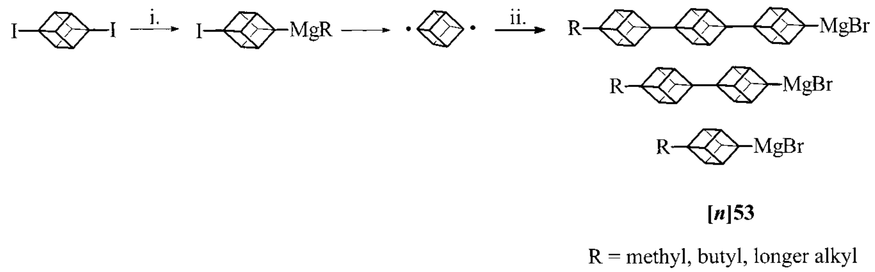
Properties and Uses. Cubane (**[1]4**), though highly strained, is kinetically surprisingly stable, surviving temperatures up to 200 °C. Its chemistry has been investigated thoroughly, and methods for systematic substitution of its skeleton have been developed.[163,164] As with most other linear rigid-rod molecules, low solubilities hinder the synthesis of longer oligomers. Unsubstituted oligocubyls containing more than two cubane units are quite insoluble in common organic solvents. However, when alkyl substituents are present in positions 2 and 7 of each cubane unit, the solubility increases sufficiently for polymers with up to 40 cubane units to be obtained.[164]

The X-ray single-crystal structure of the 4-bromo-substituted cubyl dimer reveals that all endocyclic CCC valence angles are within 1° of 90° and that the central CC bonds are perfectly staggered.[165]

4. Carboranes

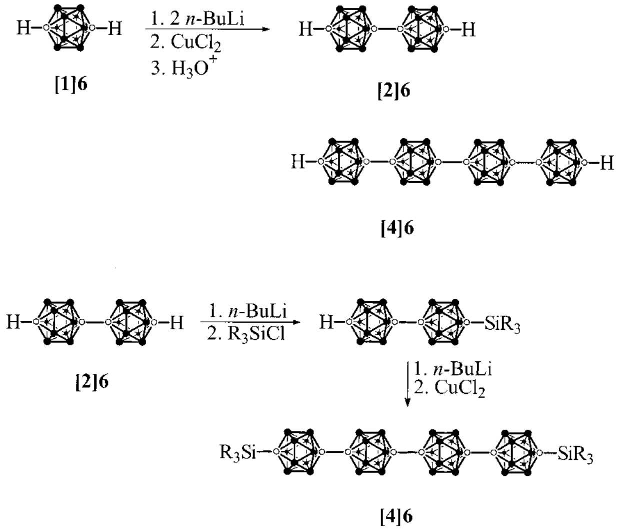
Deltahedral *closo*-boranes represent a little-known large class of rigid cage structures. Many possess axially directed terminal bonds and are suitable for use as elementary modules. The parent species, $B_nH_n^{2-}$, carry a double negative charge in their stable oxidation state, but if some of the boron atoms are replaced by heteroatoms, singly charged (e.g., $CB_{11}H_{11}^-$) or uncharged (e.g., $C_2B_{10}H_{12}$ or $NB_{11}H_{12}$) cages are formed. So far, only the neutral dicarbaboranes ($C_2B_{n-2}H_n$) have been used as modular components for rigid-rod construction, and Hawthorne has proposed that they be called carborods.[170] The 10-vertex carboranes ($C_2B_8H_{10}$) and 12-vertex carboranes ($C_2B_{10}H_{12}$) are the only ones that have been used to date, but the smaller 6-vertex $C_2B_4H_6$[171a] and 5-vertex $C_2B_3H_5$[171b] carboranes are known as well and would offer a wider variation of length increments. At least two positional isomers of each cluster are possible, but the *para*-isomers have attracted the most attention for the development of rigid rods. There is no reason the negatively charged *closo*-

Scheme 27



i. RMgBr, RLi; ii. RMgBr

Scheme 28

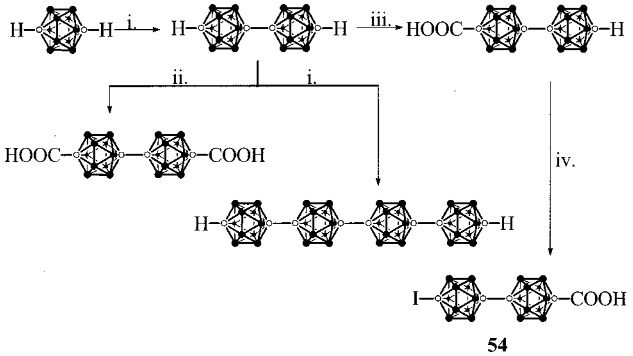


carboranes, e.g., $CB_{11}H_{12}^-$ or $B_{12}H_{12}^{2-}$,[171] could not be used as well, and charged rods may offer their own set of advantages, such as enhanced solubilities. A common disadvantage of all the carborane modules is their relatively high cost.

The formal modules devoid of terminal substituents are only known in the dianion form of *p*-carboranes, such as $^-CB_{10}H_{10}C^-$, obtained readily by deprotonation of both terminal CH groups with strong base. Their neutral analogues such as $^\bullet CB_{10}H_{10}C^\bullet$ are not known. Through-space separation of the termini is too large for bonding, and the degree of interaction through bonds of the cage is unknown but undoubtedly insufficient for effective stabilization of the parent modules.

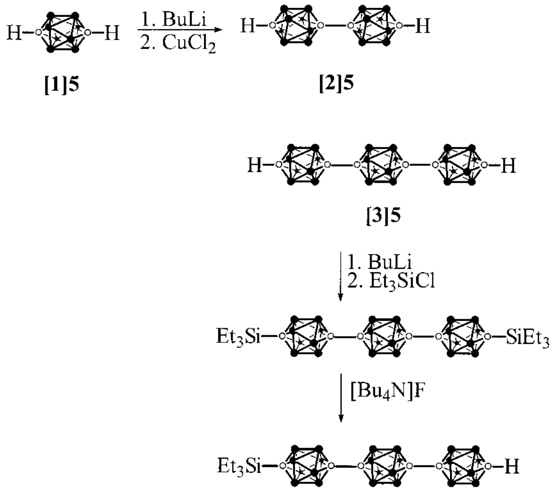
Synthesis. Oxidative coupling of deprotonated parent *p*-carboranes to a mixture of oligomers followed by separation and oxidative dimerization of singly terminally protected *p*-carborane monoanions have both been used to produce oligomeric *p*-carboranes. Zakharkin and co-workers were the first to produce the underivatized dimers[8,9] of *p*-$C_2B_{10}H_{12}$ and *p*-$C_2B_8H_{10}$. More recently, the groups of Hawthorne[170] and Michl[172] independently developed syntheses of oligomeric 12-vertex carboranes (**[*n*]6**, Schemes 28 and 29), and the latter group also synthesized oligomeric 10-vertex carboranes (**[*n*]5**, $C_2B_8H_{10}$, Scheme 30). Oligomers containing up to four carborane cages have been obtained,[170,172] with lengths of up to 17 Å.[170] The acidity of the terminal CH groups permitted subsequent functionalization with groups such as halogen and carboxyl (Scheme 29).[172]

Scheme 29



i. 1. BuLi, 2. $CuCl_2$; ii. 1. BuLi (exc), 2. CO_2, 3. HCl; iii. 1. BuLi, 2. CO_2, 3. HCl; iv. 1. BuLi, 2. I_2, 3. HCl

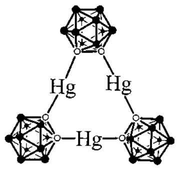
Scheme 30



Properties and Uses. The anticipated usefulness of carborods for incorporation in nanostructures is based on their thermal stability (the parent 12-vertex *p*-carborane can be heated to 700 °C without decomposition), general chemical inertness including resistance to oxidation and reduction, UV transparency, acidity of the terminal CH groups, and the specific reactivity of the B−H vertices.

Since the longer parent oligomers of the neutral carboranes are poorly soluble, modifications on the cages appear to be necessary in order to increase the rod length significantly. One attractive possibility is offered by Hawthorne's group's discovery[173] of peralkylation of the neutral carboranes with methyl triflate and triflic acid and Michl's group's discovery[174] of peralkylation of carborane anions with methyl triflate and base. Another is the use of two or more different modules, which seems to improve solubility significantly (see section III.D).

The availability of terminal substitution, e.g., with −COOH, allows the attachment of the carborods to other molecules in order to produce larger structures (cf. Scheme 29). The iodinated acid, I-*p*-$C_2B_{10}H_{10}$-*p*-$C_2B_{10}H_{10}$−COOH (**54**), assembles into Langmuir−Blodgett films.[172] Hawthorne and his group have synthesized a number of host-molecule mercury-linked carborane macrocycles, such as [9]-mercuracarborand-3 (**55**).[175]



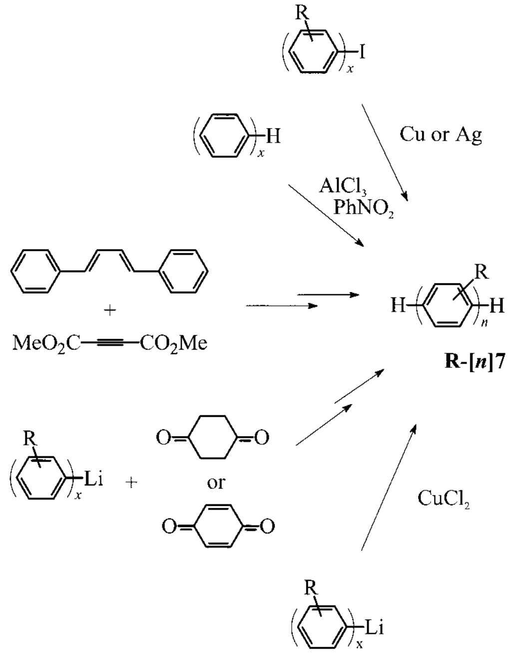
55

C. Oligomers of Planar Modules

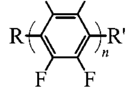
1. Benzene

Along with ethyne, *p*-phenylene represents the oldest and cheapest monomer for the construction of rigid rods. Unlike the modules discussed so far, it only has a 2-fold symmetry axis along the rod direction and is strongly anisotropic, both in shape and in other properties. The parent module devoid of terminal substituents, *p*-benzyne, has been observed indirectly[176] and more recently in matrix isolation by the group of Sander.[177,178] The through-bond interaction of its two free-valence centers is relatively weak[179] but it is expected to be less reactive than the free phenyl radical, say in hydrogen abstraction reactions,[180] as is known for 9,10-bisdehydroanthracene (section III.C.2.b). Nevertheless, *p*-benzyne is still much too reactive to be of synthetic utility as a precursor for oligophenyl oligomers. At elevated temperatures, its ring opens to yield *cis*-hexenediyne (cf. the Bergman rearrangement).[181,182] *p*-Oligophenylenes are, however, readily accessible by coupling reactions.

Scheme 31



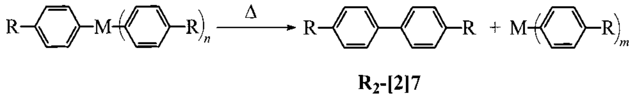
Synthesis. Earlier methods of synthesis of *p*-oligophenylenes (**[*n*]7**, Scheme 31)[183] include reductive coupling of 4-iodophenylarenes with copper[184,185] or silver[186] powder, oxidative coupling of unsubstituted arenes with $AlCl_3$ in nitrobenzene,[187] addition of 4-arylphenyllithium to quinone[188] or 1,4-cyclohexanedione[189] with subsequent dehydration and oxidation, oxidative coupling of 4-arylphenyllithium reagents with $CuCl_2$[190] and Diels−Alder addition of dimethyl acetylenedicarboxylate to 1,4-diphenylbutadiene with subsequent hydrolysis, decarboxylation, and oxidation.[191] Recently, an Ullmann-like reductive coupling of 1,4-diiodo-2,3,5,6-tetrafluorobenzene has been used to prepare a series of oligo(tetrafluorophenylene)s **[2]56**−**[6]56**.[192] Reductive elimination of biphenyl has been reported for polyphenyl derivatives of many nonmetals (Scheme 32).[193] All these reactions are potentially applicable to the synthesis of the rods **[*n*]7**. Statistical reductive coupling of *p*-dihalobenzenes on palladium[194] or nickel[195] catalysts yields mixtures of oligomers (Scheme 33).



R, R' = H, I
n = 2 - 5

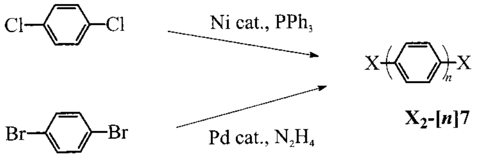
[*n*]56

Scheme 32



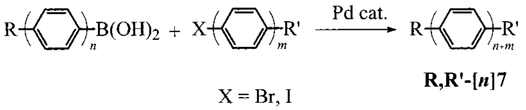
M = Br, I, S, S$_2$, SO$_2$, Se, P, Sb, As

Scheme 33



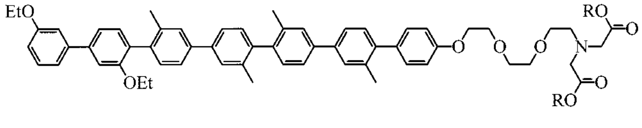
Presently, the most versatile step-by-step approach to *p*-oligophenylenes includes a palladium-catalyzed unsymmetrical coupling of arylboronic acids with aryl bromides or aryl iodides (Suzuki coupling, Scheme 34).[30,37,196−200] Using this reaction and an iterative approach to the coupling of oligomers, Schlüter's group was able to synthesize individual oligomers up

Scheme 34



X = Br, I

to $n = 16$ with lengths of up to ~68 Å in excellent yields.[37] The same reaction was used by Galda and Rehahn to prepare a series of oligomers up to $n = 15$.[200] A series of biphenyls was proposed for use as a construction kit for substituted oligophenylenes.[201] Recently, Matile[202–205] and his group succeeded in the synthesis of a series of *p*-oligophenylenes with up to 8 modules substituted with branched aliphatic diol groups along the chain and of amphiphilic *p*-oligophenylenes with various terminal substituents consisting of up to 10 modules and with lengths of up to 44 Å by applying the Giroux–Suzuki[206] coupling method (e.g., **57**). *p*-Oligophenylene rods with siloxy end groups were reported by Corriu[207] as molecular precursors for the synthesis of monophasic organic–inorganic hybrid materials by polycondensation.

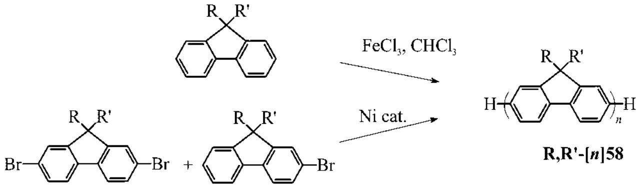


R = H, Et

57

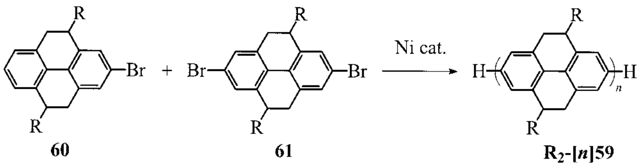
A mixture of oligofluorene rods (**[*n*]58**) with an average of 10 units per oligomer was synthesized by an oxidative coupling of alkyl-substituted fluorenes with $FeCl_3$ by Fukuda et al.[208] and by Yamamoto coupling by Klaerner and Miller[209] (Scheme 35), but they were not separated.

Scheme 35



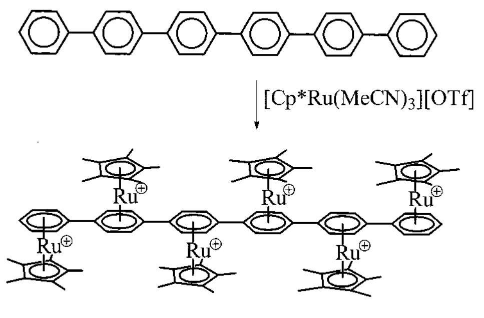
Oligo(tetrahydropyrene)s (**[*n*]59**) were obtained from 2-bromo- and 2,7-dibromo-4,9-dialkyl-4,5,9,10-tetrahydropyrene (**60** and **61**) in the group of Müllen[210] using statistical reductive coupling on a nickel(0) reagent (Yamamoto coupling, Scheme 36), and individual oligomers up to $n = 12$ were separated by size-exclusion chromatography.

Scheme 36

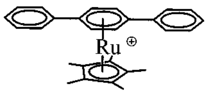


Substituents can be attached not only to the four free positions of each benzene ring, but also to the π face. Thus, long *p*-oligophenylene chains up to the hexamer **62** decorated with ruthenium Cp* groups were synthesized by Fagan et al.[211] (Scheme 37). Harre et al.[212] showed that Suzuki coupling conditions can be applied to the reaction of ruthenium-complexed aryl halides with aromatic boronic acids without decomposition of the organometallic moiety and obtained the *p*-terphenyl **63** with a RuCp* group located on the central ring.

Scheme 37



62



63

Properties and Uses. *p*-Oligophenylenes (**[*n*]7**) are among the most thermally stable rods in the molecular kit, and the high molecular weight polymers were reported to be stable up to 800 or 900 °C.[213] Unsubstituted oligomers **[*n*]7** with more than five units melt above 300 °C.

The planes of the rings of adjacent phenylene moieties in *p*-oligophenylenes (**[*n*]7**) form an angle of 20–40° because of the steric repulsion between the ortho hydrogens.[214–217] Substitution of the rings leads to an increase in the twist angles. This twist reduces π-orbital delocalization between the aromatic rings. Even a single benzene ring twisted out of conjugation may work as an insulator between two conducting parts of a molecular rod.[218] The twisted geometry and the reduced conjugation also enhance the flexibility of the backbone. The repulsion, however, is not strong enough to prevent rapid rotation around the single bond between the units, and an average planar structure of the parent oligomers **[*n*]7** at room temperature in crystals, as confirmed by crystallographic studies, is the result.[219] The twist angle is a sensitive function of substitution and molecular environment.[220] Planarization may be achieved by introduction of suitable ring-forming substituents. For example, in oligofluorenes (**[*n*]58**)[209] every other intermodule junction is planar (the related ladder oligomers are treated in Part 2[19]). The degree of conjugation in the variously planarized oligophenylenes is reflected in their photophysical properties. The inter-ring torsion angles in oligo(tetrahydropyrene)s (**[*n*]59**) are comparable to those in the parent oligophenylenes,[221] and thus, the conjugation through the backbone is not very efficient. The maximum of the first absorption band converges to about 385 nm as the length of the oligomer increases.[210] The effective conjugation length is estimated to be approximately 10 units or 20 benzene rings.[222] In the partially planarized oligofluorenes, the convergence limit is ~380 nm. Like the corresponding polymers,[223] they are extremely efficient fluorophores in solution with λ_{max} of emission converged for oligomers with more than six units.[209]

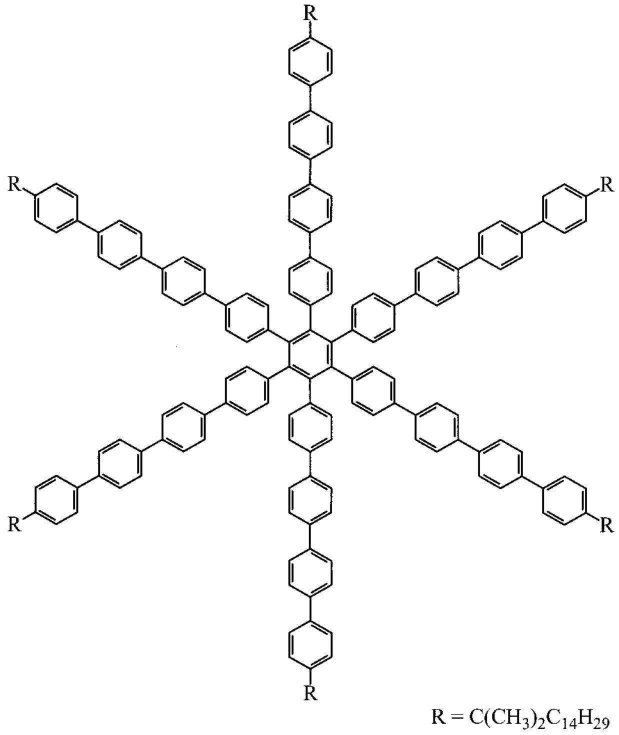
Analysis of the absorption spectra of **[*n*]59** revealed an effective conjugation length of approximately 12 units or a total of 24 aromatic rings.[209]

The solubility of the unsubstituted oligomers rapidly decreases with the degree of oligomerization. *p*-Sexiphenyl (**[6]7**) has a solubility less than 10 mg/L^{-1} in toluene.[189] One central 2,5-dihexylphenylene unit makes the corresponding heptamer soluble, but a larger number of long alkyl side chains is required for longer oligomers.[37,200]

Depending on their length and substitution pattern, Matile's oligophenylene rods, such as **57**, self-assemble as hydrophobic guests in lipid bilayers and form non-peptide proton channels or short-lived nanopores.[224,225] Their use as synthetic cell-surface receptors is under investigation.[226]

The *p*-oligophenylenes complexed to RuCp* groups are crystalline, air-stable solids with very high melting points. The Cp* complexed *p*-terphenyl derivative **63** is very soluble in common organic solvents. In its crystal, two adjacent phenyl rings are nearly coplanar while the third is twisted by about 40°, most likely because of interactions with the methyl groups on the Cp ring. The tetramer and hexamer **62** are very soluble in nitromethane. In the tetramer, the central phenyl rings are coplanar and the ones on the ends are twisted by about 28°.[211]

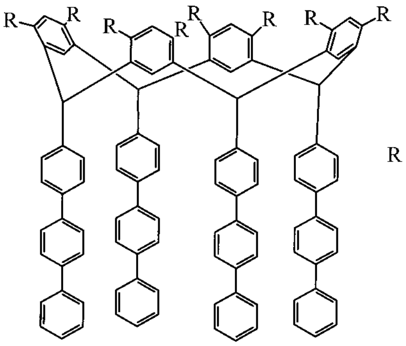
Müllen's group[227] has accomplished the synthesis of hexa-*p*-quaterphenylylbenzene **64**, a large star-shaped molecule, by Pd-mediated [2+2+2] cyclization of the corresponding acetylene precursors. This is of interest as a potential material for light-emitting diodes.



$R = C(CH_3)_2C_{14}H_{29}$

64

Lewis and Strongin[228] reported the synthesis of resorcinarenes **65** with four terphenyl substituents in the lower cavity. These molecules, if extended, could be used as rod bundles, thus increasing mechanical stiffness, especially if the individual rod components could be further connected laterally.



R = OH

65

2. Other Arenes

Many polynuclear aromatic hydrocarbons may be used in place of benzene as modules for molecular rods, and much of what has been said about benzene applies to them as well.

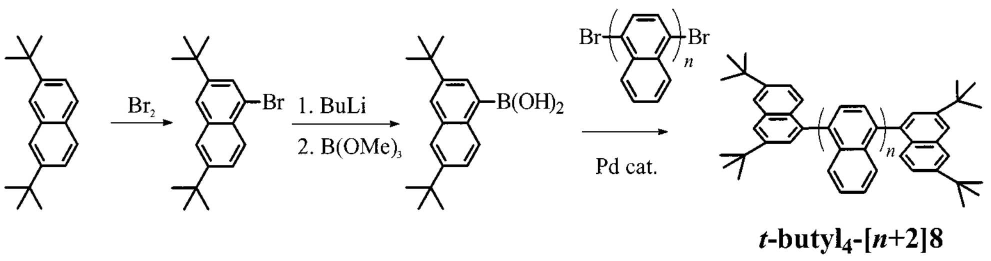
a. Naphthalene. Much attention has been paid to 1,1′-binaphthyls in other contexts, but this work is not covered here. It has been comprehensively reviewed recently.[229]

Synthesis. Müllen and co-workers have prepared a series of soluble oligo(1,4-naphthylene)s (**[2]8**−**[6]8**) by Suzuki coupling of appropriate bromonaphthalene and naphthaleneboronic acid precursors (Scheme 38).[230−232] An alternative route to the ter- and quaternaphthols **[3]66** and **[4]66** has been described by Bělohradský et al.[233] The reaction of the dibromide **67** with the 2-naphthoxide ion **68** proceeds under mild conditions and yields all possible isomers of **[3]66** and **[4]66** in yields up to 53% for **[3]66** and 11% for **[4]66**. The proposed mechanism for the formation of the ternaphthol **[3]66** involves nucleophilic substitution of bromines in the reactive keto isomer of **67** by the naphthoxide ion (Scheme 39). Electron transfer and concomitant loss of a bromide anion or bromine−halogen exchange are believed to compete with the former reaction and lead to the quaternaphthol **[4]66**.

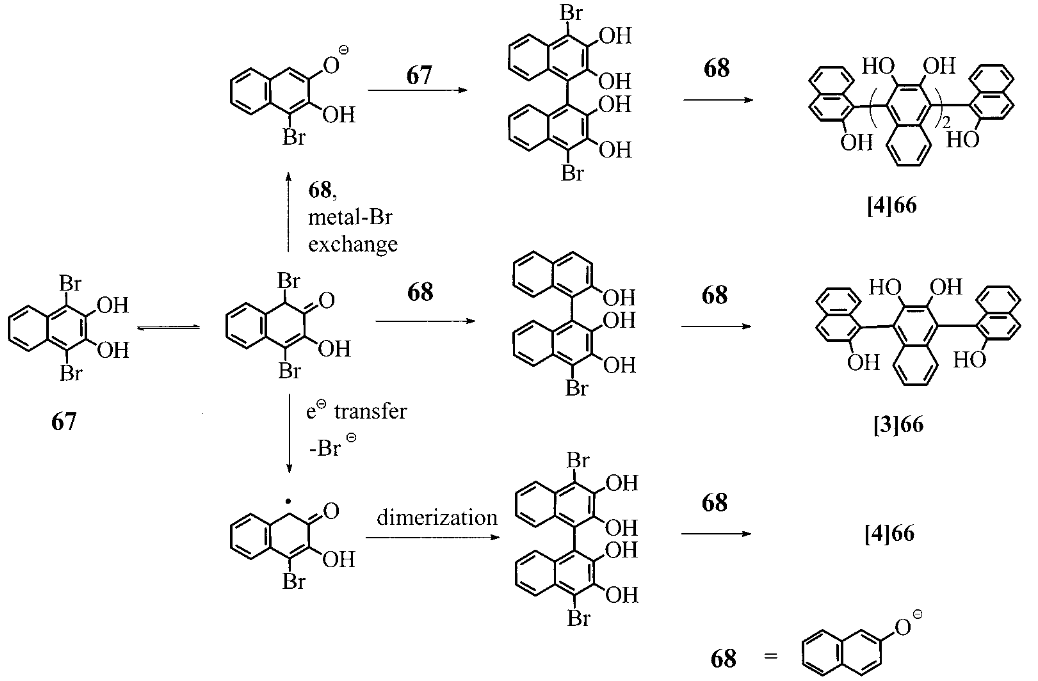
Properties and Uses. Rotation around the bonds connecting 1,4-naphthylene units in a homo-oligomer is hindered in the uncharged ground state, and the oligomers **[3]8**−**[6]8** form as a mixture of nonplanar diastereomers.[230] Presumably because of the limited conjugation, the first oxidation potential in **[*n*]8** is essentially independent of the chain length.[232] However, a single-electron oxidation or reduction causes some flattening of the π system and thus a stronger interaction between the units.[234] The spin density in the radical anion of **[*n*]8** is delocalized over the entire π system.[232] This is not in contradiction with a very minor effect of the chain length on the redox potentials, since the delocalization on the EPR time scale need not be associated with significant energetic effects.

b. Anthracene. The formal monomer, 9,10-bisdehydroanthracene, has been generated in solution and

Scheme 38



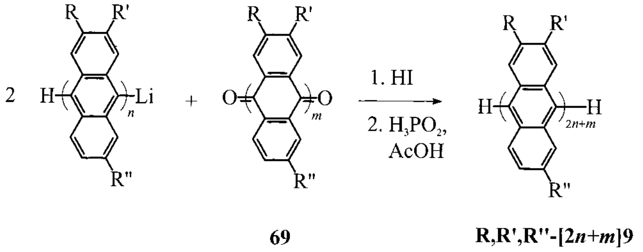
Scheme 39



found to be remarkably unreactive in hydrogen abstraction reactions. This has been attributed to singlet coupling on the two radical centers.[235] Much work has been done on 9,9′-bianthryl, chiefly on its photophysical properties,[236] but we shall deal with the higher oligomers only.

Synthesis. Oligo(9,9′-anthrylene)s (**[*n*]9**) with up to seven monomer units have been synthesized by Müllen's group by addition of 9-lithioanthracene precursors to substituted anthraquinones or bianthrylidenones (**69**) and subsequent treatment with hydrogen iodide and hypophosphorous acid in glacial acetic acid (Scheme 40).[237]

Scheme 40

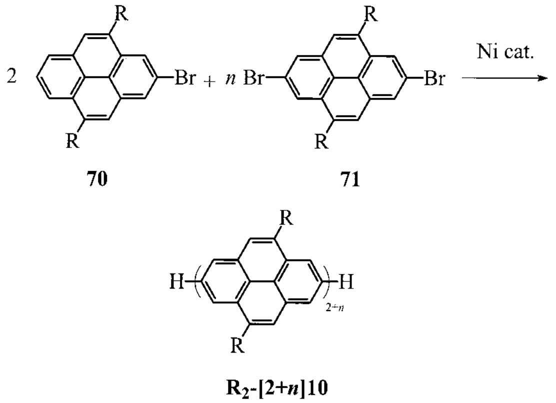


Properties and Uses. In **[*n*]9**, the rotation of the units is hindered even more strongly than in oligo(1,4-naphthylene)s (**[*n*]8**).[234] X-ray diffraction values for the dihedral angles between the central and terminal anthracene units in teranthracenes vary between 74.5° and 82.7°.[237] This leads to an extremely weak electronic coupling between units in ground, excited, oxidized, and reduced states.[234] Thus, the rods based on **9** can be charged with one and even two electrons per anthracene unit upon subsequent one-electron reductions.[238] The tetraanion of the tetraanthrylene **[4]9** has a quintet ground state.[239] When irradiated in solution, oligoanthrylenes undergo transitions into a charge-transfer or an excitonic state, depending on their substitution pattern and the polarity of the solvent.[240]

c. Pyrene. *Synthesis. p*-Bipyrenyls (**[2]10**) and *p*-terpyrenyls **[3]10** have been prepared in Müllen's group using the Yamamoto coupling of 2-bromo- and 2,7-dibromopyrene precursors (**70** and **71**, Scheme 41).[241]

Properties and Uses. Two alkyl substituents per monomer unit are required to make the *p*-oligopyrenes (**[*n*]10**) soluble.[241] The pyrenyl units are electronically very poorly coupled because the HOMO and LUMO coefficients at the bridgehead centers vanish. The interaction between the pyrenyl units is so weak that stepwise reduction of the oligomers **[*n*]10** increases not only the negative charge but also the spin multiplicity of the ground states.[241] Despite the greatly decreased steric problems, interactions

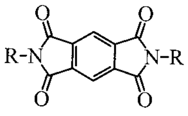
Scheme 41



between the frontier orbitals of the pyrene units are even smaller than those between the frontier orbitals in oligoanthrylenes (**[*n*]9**).[239]

d. Arenedicarboximides. The arene modules described so far had their termini at opposed ring atoms. It is also possible to use them rotated such that the axial positions correspond to midpoints of ring edges, but it is then necessary to fuse an odd-membered ring to the edge in order to provide an axial bond. Five-membered rings are optimal in providing stability as well as rigidity. In a similar fashion, a six-membered ring can be *peri*-fused to the two six-membered rings of naphthalene to provide a central axial bond. Favorite rings used for this purpose have been those containing dicarboximide groups. Benzene-1,2:4,5-bis(dicarboximide) (**[1]72**), anthracene-2,3:6,7-bis(dicarboximide) (**[1]73**), naphthalene-1,8:4,5-bis(dicarboximide) (**[1]74**), and perylene-3,4:9,10-bis(dicarboximide) (**[1]75**) have been employed to date for the construction of axial rods (Schemes 42 and 43).

Synthesis. Tandem Diels−Alder aromatization reaction was applied by Morris et al.[242] for the preparation of *N*,*N*′-diphenylanthracene-2,3:6,7-bis(dicarboximide) (**[1]73**, Scheme 42a). The linear oligomers are obtained from the corresponding bis(dicarboxanhydride)s upon condensation either with hydrazine hydrate or hydrazinium salts to form homo-oligomers, with the bis(dicarboximide) units directly linked through an N−N bond. Oligomers of naphthalene-1,8:4,5-bis(dicarboximide) (**[*n*]74**, Scheme 42b) were also reported. Langhals and Jona[243] have achieved the synthesis of bi- and trichromophoric perylene rods **[2]75** and **[3]75** utilized as dyes by condensation of perylene anhydride imides **76** with amino imides **77** (Scheme 43).



[1]72

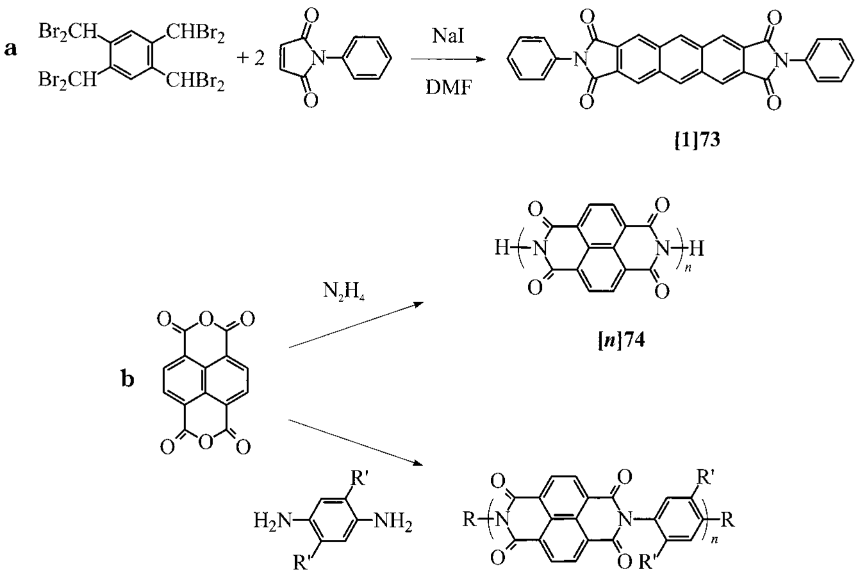
Properties and Uses. The oligo[bis(dicarboximide)]s are extremely stable chemically, thermally, and photochemically.[244,245] They are usually moderately soluble in common organic solvents. They are strongly fluorescent in solution and have very high extinction coefficients. Chromophore−chromophore interactions in di- and tri[perylene-3,4:9,10-bis(dicarboximide)]s (**[2]75** and **[3]75**) increase the extinction coefficient per monomer unit compared to that of the monomer **[1]75**.[243] Rotation around the single bonds is possible, but the rods cannot fold. Electrochemical studies showed that the naphthalenediimide group can be reduced to form anion radicals and dianions which are stable in oxygen-free solution.[246]

3. Pyridine

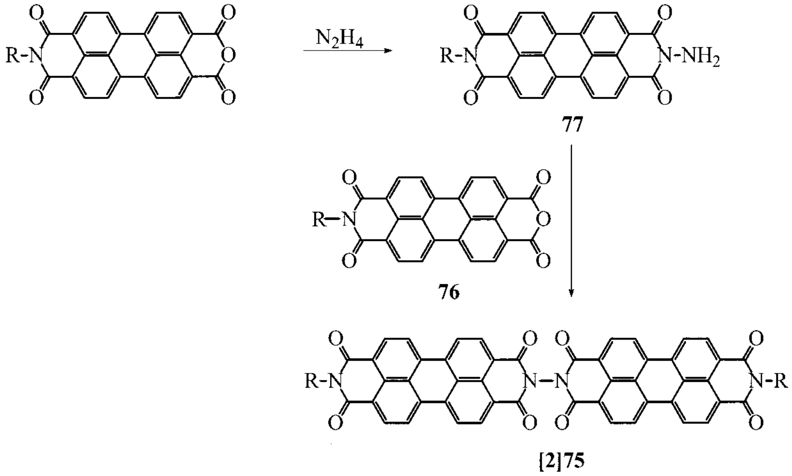
Although the replacement of a CH group in an aromatic ring by an aza nitrogen (or a C atom by an azonia nitrogen, >N$^+$=) could be viewed as a particular kind of substitution and oligomers of pyridine and other azabenzenes could be lumped with oligophenylenes, their importance is such that we place them in a separate section.

The reason molecular rods consisting of pyridine and other azabenzene units have attracted large interest is mainly their coordinating ability to metal centers but also their easy conversion to salts with

Scheme 42



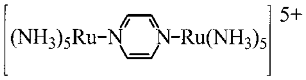
Scheme 43



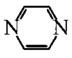
R = CH(C_nH_{2n+1})$_2$
n = 4, 6, 7, 8 ,9

the accompanying solubility and facilitated reduction compared to oligophenylenes. There are two ways in which pyridine can be used as an axial module: either through positions 2 and 5 or through positions 1 and 4. The latter, which necessarily forms positively charged azonia centers, is well known from work on polymers,[247] but we have not found any information on well-defined longer homo-oligomers. Only the dimer is known.[248] Turning to the 2,5-coupling mode, we note that mono-, bi-, and tridentate ligating sites can be created, depending on the relative position of the azabenzene units in the rod. Such chelating ligands separated by various modules have seen much utility as linear spacers used to hold complexed metal centers at distinct distances. Presently, however, these molecules are classified according to the rod structure and not according to the nature of the chelating termini.

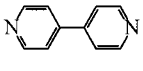
The Creutz–Taube ion[249] (**78**) has evoked large interest in the study of the electronic interaction of two or more metal centers through a pyrazine bridging ligand. Systems with rigid and coplanar conjugated backbones have displayed the strongest metal–metal interactions. The simplest such systems are pyrazine (**79**) and 4,4′-bipyridyl (**80**) where the coplanarity of the aromatic rings can be affected by introduction of substituents in the 3 and 3′ positions,[250] as in 3,3′-dimethyl-4,4′-bipyridyl (**81**) and compounds **82** and **83**. Various metal complexes, for example, those of Ru (**78** and **84**), have been reported and used for electron-transfer studies. Placing pyridyl substituents at the terminal pyridine rings in the rod, the tridentate ligand *o*-terpyridyl (**85**) can be constructed. This provides an opportunity to connect complexed metal ions linearly along the rod axis.



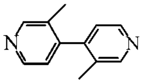
78



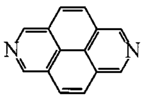
79



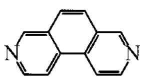
80



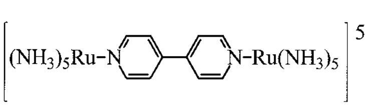
81



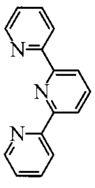
82



83



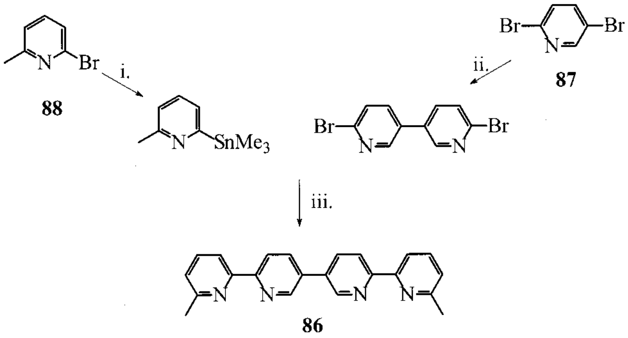
84



85

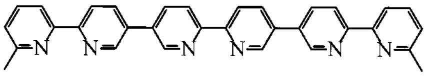
Synthesis. Lehn's group synthesized a variety of oligopyridines for use in supramolecular assemblies.[251−253] The quaterpyridine **86** was obtained in four steps from 2,5-dibromopyridine (**87**) and 2-bromo-6-methylpyridine (**88**), using the Stille reaction in the last step (Scheme 44).[254] The corresponding hexapyridyl **89** was also prepared. A rigidized quaterpyridine **90** was reported in which the two central pyridine units are bridged by an ethylene group.[255]

Scheme 44

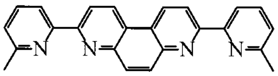


i. 1. BuLi, 2. SnMe$_3$Cl; ii. 1. n-BuLi, 2.CuCl$_2$, 3. O$_2$; iii. [Pd(PPh$_3$)$_4$]

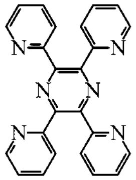
The shortest member of the group of terpyridyl-terminated doubly functionalized rods is 2,3,4,5-tetrapyridylpyrazine (**91**), synthesized by Goodwin and Lions.[256] The closely related fully planar tetrapyrido[2,3-*a*:3′,2′-*c*:2″,3″-h:3‴,2‴-*j*]phenazine (**92**) has been known for a considerable time as well.[257,258]



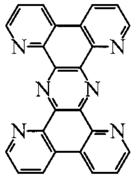
89



90



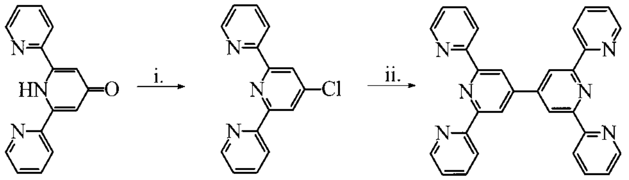
91



92

Constable and Ward[259] have prepared 6′,6″-bis(2-pyridyl)-2,2′:4′,4″:2″,2‴-quaterpyridine (**93**), effectively connecting two 4′-chloro-2,2′:6′,2″-terpyridyl molecules (**94**) back-to-back in a Ni(0)-promoted coupling reaction (Scheme 45).

Scheme 45



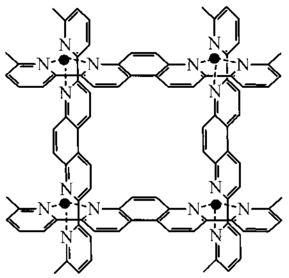
94 **93**

i. PCl_5, $POCl_3$; ii. 1. $[Ni(PPh_3)_2Cl_2]$, Zn, PPh_3, DMF; 2. NaCN

Properties and Uses. The compounds are all thermally and chemically very stable. The melting points are often above 250 °C. The solubility in nonpolar solvents is low but can be enhanced by methyl groups at the terminal pyridine rings. Complexation to metals has a solubilizing effect, and the protonated forms dissolve readily in aqueous media.

The most interesting and extensively investigated feature of oligopyridines is their ability to complex various metals at their monodentate, bidentate, and tridentate binding sites. From an electronic viewpoint, the bidentate 2,2′-bipyridyl unit is best suited for metal binding in an octahedral coordination, and its metal complexes show a strong and long-lived luminescence.[260] The ligand-field strength of the *o*-terpyridyl-based units is significantly weaker, and luminescence of their metal complexes can only be observed at very low temperatures.[260] However, since the *o*-terpyridyl ligand complexes the metal at the rod axis, it excludes any stereoisomerism that is present in 2,2′-bipyridyl-based rods.

The spontaneous complexation of oligopyridine ligands to transition metals such as copper was used to assemble distorted grid complexes, for example **95**, that contain a hole with a defined size for the trapping of guest molecules.[261] The longer bipyridyl rods **89** have been utilized to assemble ladder-type structures.[262]



95

● = Cu

Stang and his group used 4,4′-bipyridyl as a construction element in the preparation of a large number of metallacyclic polygons and polyhedra, and this work has been recently reviewed.[4]

4. Porphyrin

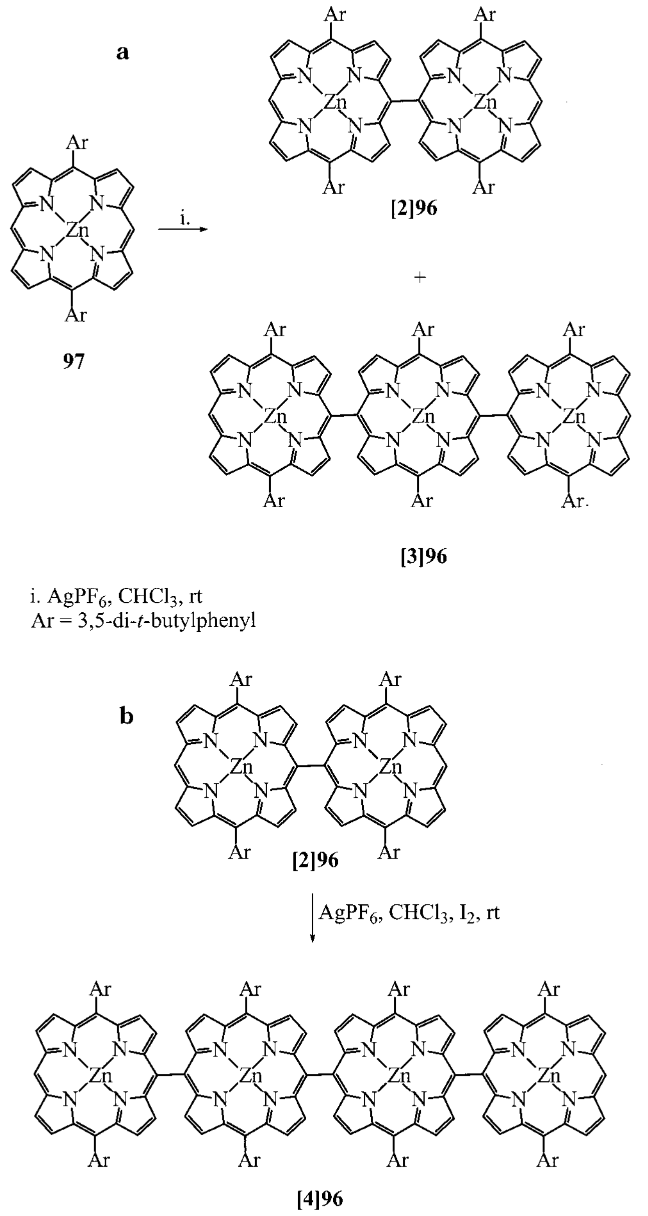
Exocyclic bonds in opposite meso positions are collinear and well suited for use in modular rod construction. Many examples of porphyrins connected by various linear spacers are known and treated in the chapters of the respective co-oligomers. However, examples of porphyrin units directly linked to form linear arrays **[*n*]14** have only been recently reported. They are of interest particularly as biomimetic systems but could also lead to the development of new photonic materials and molecular devices.[263,264]

Synthesis. Several methods for the preparation of directly meso−meso-linked porphyrin arrays have been reported. Zinc(II) porphyrins can be oxidatively coupled using Ag(I) salts. The reaction is accelerated in the presence of I_2. Osuka and Shimidzu[265] thus obtained the dimer **[2]96**, trimer **[3]96**, and tetramer **[4]96** of zinc(II) 5,15-di(3,5-di-*tert*-butylphenyl)porphyrin (**97**, Schemes 46a and 46b). The composition of the product mixture is a function of both reaction time and amount of silver salt added. The dimer **[2]96** was exclusively formed in high yield from a monomeric porphyrin with only a single *meso*-position available for coupling.[266] Such dimers were prepared with Cl and Br substituents in the 15 and 15′ positions that might be usable for further coupling with other modules (Scheme 47).

Electrochemical oxidative coupling yielded various oligomer mixtures in a one-step procedure through extended electrolysis.[267] The longest array formed was the octamer **[8]96**, obtained in an extremely low yield. The method was successfully applied to systems with differently substituted aryl groups, extending the scope beyond that of the silver salt method (Scheme 48).

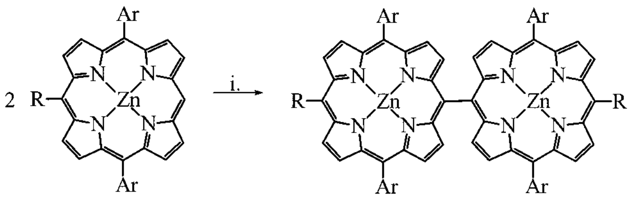
The directly meso−meso-linked free-base trimer **[3]98** was also synthesized by Susumu et al.,[268] using

Scheme 46



i. AgPF$_6$, CHCl$_3$, rt
Ar = 3,5-di-*t*-butylphenyl

Scheme 47

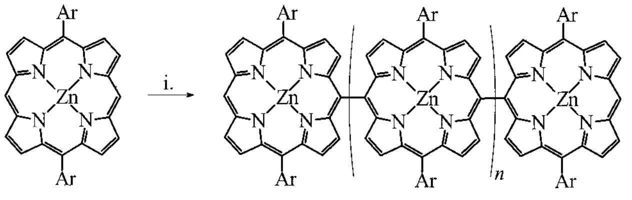


i. AgPF$_6$, CHCl$_3$, rt

Ar = 3,5-di-*t*-butylphenyl
R = Cl, Br, CHO

acid-catalyzed [2+2]-condensation between free-base *meso*-formylporphyrin **99** and *meso*-(3,5-di-*tert*-butylphenyl)dipyrrylmethane (**100**) (Scheme 49). However, the isolated yields were very low. An alternate route to meso−meso-coupled dimers was reported by the group of Smith.[269] 1,1,2,2-Tetra(2-pyrrolyl)ethene (**101**) was tetraformylated and cyclized with a dihydrodipyrrin to yield the porphyrin dimer **[2]102** with free positions 15 and 15′ after oxidation (Scheme 50).

Scheme 48

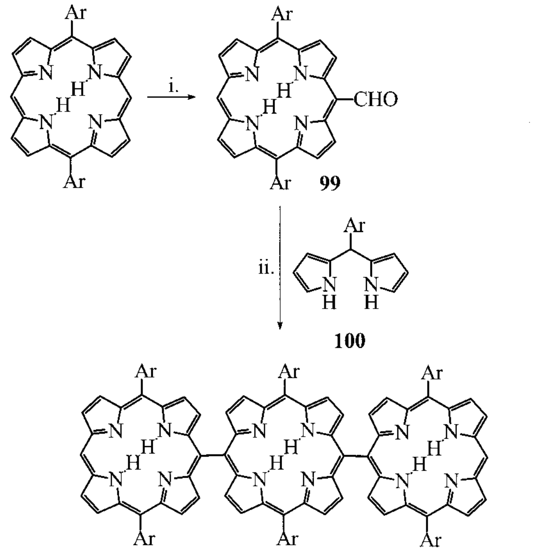


[8]96 (*n*=6) $n = 0, 1, 2, 3, 4, 5, 6$

Ar = phenyl; 3,5-di-*t*-butylphenyl, 4-methoxycarbonylphenyl, pentafluorophenyl

i. Anodic oxidation, Pt net as working electrode, Pt as counter electrode in benzonitrile, 0.1 M NBu$_4$ClO$_4$

Scheme 49



i. 1. Cu(OAc)$_2$, CH$_3$OH/CHCl$_3$, reflux; 2. POCl$_3$, DMF, dichloroethane; 3. aq. NaOAc; 4. 10% H$_2$SO$_4$/THF, rt; ii. 1. BF$_3$ Et$_2$O, CHCl$_3$ 2. chloranil, rt

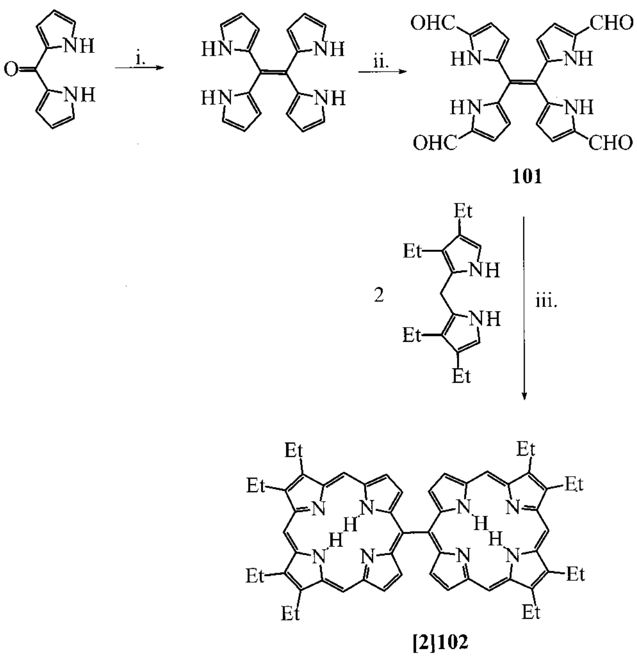
Ar = 3,5-di-*t*-butylphenyl

Holmes et al.[270] demonstrated the synthesis of bistetrapyrrol systems **103** from porphyrinyl *β*-ketoesters by radical dimerization. Crescenzi et al.[271] very recently proposed a pathway to oligomeric porphyrinogens illustrated by the oxidative dimerization of a *meso*-octaalkyl substituted mono(pyridine)tris(pyrrole) macrocycle **104** through the pyrrol units.

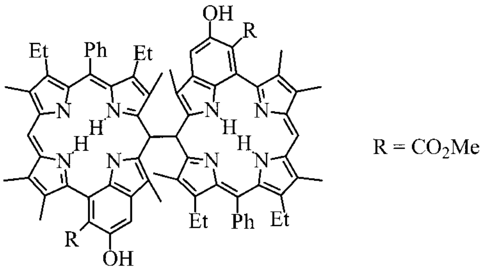
Properties and Uses. The meso positions are the most reactive centers toward both electrophilic and nucleophilic reagents, if steric hindrance is not too severe. This allows meso-to-meso coupling of porphyrin monomers that are unsubstituted at least in positions 3 and 7. The resulting arrays **[*n*]96** have a linear rigid structure and high thermal and chemical stability. The solubility in chloroform, including that of the higher oligomers, is high when di-*tert*-butylphenyl substituents are present in positions 5 and 15.[265]

X-ray structrures of the dimer **[2]102** of tetraethylporphyrin reveal an angle of 65−84° between the

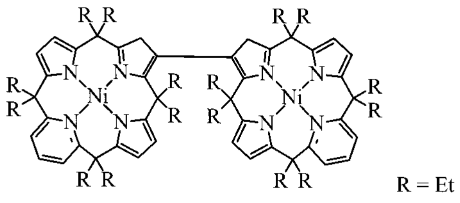
Scheme 50



i. Ti ii. 1. $POCl_3$-DMF; 2. aq. K_2CO_3 iii. H^+, then DDQ.



103



104

two planar porphyrin rings, depending on the crystallization solvent.[269] The NMR data of the oligomers derived from 5,15-diarylporphyrins suggest a perpendicular arrangement of the neighboring porphyrins.[265] Osuka and Shimidzu[265] reported a large excitonic splitting in the Soret bands but only small changes in the low-energy Q-band region of the dimer **[2]96**. Compared to the monomer, the fluorescence spectra exhibit slightly broadened and shifted peak positions and virtually unchanged quantum yields. These observations are compatible with an approximately orthogonal orientation of the two porphyrin rings. In contrast, Susumu et al.[268] reported distinct red shifts both in the Q-bands and the fluorescence maxima of the trimer **[3]98**, thus detecting a significant electronic interaction between the porphyrin rings despite their orthogonal geometry.

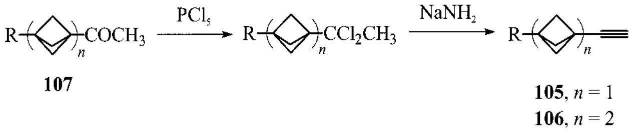
D. Co-Oligomers

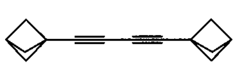
Often different modules are combined in a single molecular rod to facilitate the synthesis or to optimize rod properties such as length and solubility. The module that is most popular in co-oligomer rods is the ethyne group.[272] Triple bonds introduce flexibility and often increase solubility. The acidity of the terminal acetylenes and the stability of various metal acetylide intermediates offer opportunities for a variety of acetylene coupling reactions and provide a means of attachment of acetylene-terminated rods to other organic and organometallic modules. If introduced into a conjugated backbone, oligoethyne links decrease conjugation relative to oligoenes because of the stronger bond length alternation. In contrast to benzene and other arene rings, however, the ethyne unit has minimal steric demands and does not introduce any ambiguity with regard to twisting. The rigidity of the rods deteriorates fast with the increasing number of acetylene groups in the backbone, and only one or two adjacent triple bonds are normally used.

1. Ethyne/Cage

a. Ethyne/Bicyclo[1.1.1]pentane. Only a few rods of this class have been prepared, and few of their properties have been examined. Bunz and Szeimies prepared bicyclo[1.1.1]pentane (**105**) and [2]staffane (**106**) derivatives with one or two ethynyl substituents in the bridgehead positions from the corresponding methyl bicyclo[1.1.1]pentyl ketones (**107**, Scheme 51).[153,273,274] 1-Ethynylbicyclo[1.1.1]pentane (**[1]105**) was coupled oxidatively under Hay conditions into the diyne **108**.[274]

Scheme 51



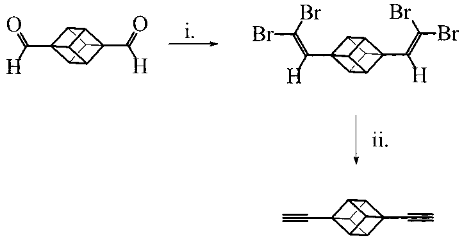


108

b. Ethyne/Cubane. Alkynylcubanes seem to be the most versatile structures for modular building blocks containing cubane units and have received considerable attention.

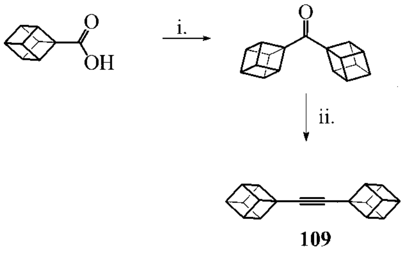
Synthesis. Ethynylcubane was originally synthesized by Eaton's group from methyl cubyl ketone[275] in low yield, and from iodocubane.[276] A more recent synthesis (Scheme 52) is general and gives excellent yields of various substituted and unsubstituted alkynylcubanes, which are useful monomeric building blocks.[276] Dicubylacetylene (**109**) was prepared from dicubyl ketone via the vinyl diazo compound (Scheme 53). Terminal cubylacetylenes were dimerized to diynes through copper-catalyzed oxidative coupling reactions.[276] Longer rods such as **110** were obtained from coupling of the monosilylated 1,4-diethynylcubane (Scheme 54).[276] Cross-coupled ethynylcubanes,

Scheme 52



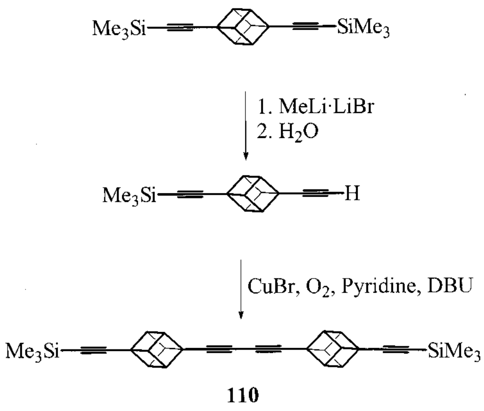
i. CBr_4, PPh_3; ii. 1. *n*-BuLi or MeLi; 2. H_2O

Scheme 53



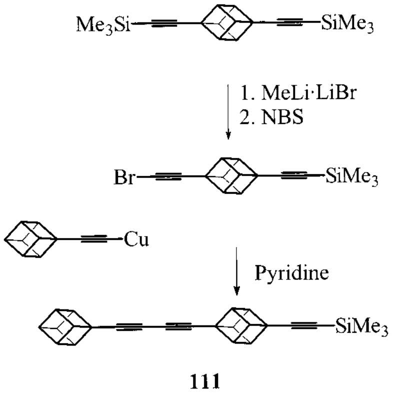
i. 1. EtMgBr, THF, -10 °C; 2. cubyllithium; ii. 1. *n*-BuLi, $Me_3Si\text{-}CHN_2$, THF, -78 °C; 2. H_2O

Scheme 54



for example **111**, are accessible via the reaction of bromoacetylenes with cuprous acetylides (Scheme 55).[276]

Scheme 55

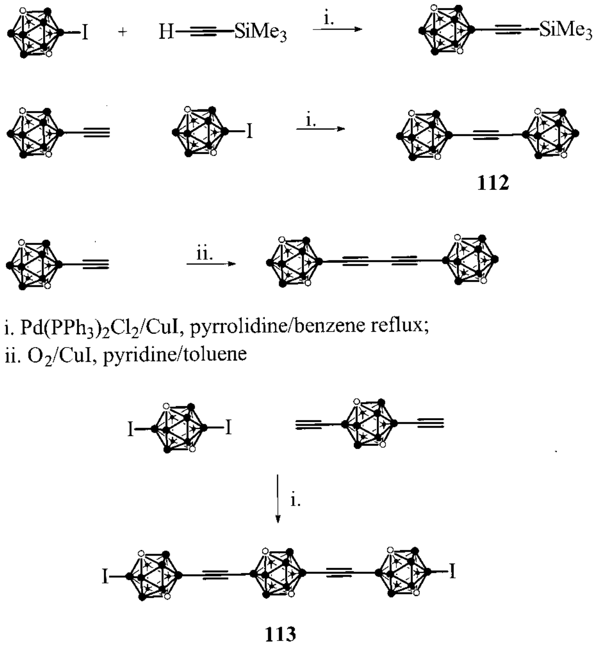


Properties and Uses. Dicubylacetylene (**109**) forms air- and light-stable crystals with high thermal stability but low solubility. Other ethynylcubanes are only moderately air stable, and the shorter oligomers are quite volatile. Their trimethylsilyl derivatives are easier to handle because they are crystalline, air-stable, and nonvolatile. 1,4-Bis[(trimethylsilyl)ethynyl]cubyl-1,3-butadiyne (**110**) is the longest rigid rod characterized within this family (the carbon backbone is 17.4 Å long). Since this compound and compounds with larger silyl groups show moderate to good solubilities, extension of the rods via further sequential coupling should be possible.

c. Ethyne/Carborane. A fair number of mixed rods of this class are known.

Synthesis. Zakharkin et al.[277] reported the synthesis of C-ethynylated 12-vertex carborane derivatives by coupling a terminally brominated acetylene with C-lithiocarboranes under copper mediation. A number of B-substituted *p*-carborane derivatives have also been described.[278] Of these, only the B-ethynylated compounds have been developed into mixed carborods. Twelve-vertex B-alkynyl-*p*-carboranes **112** were obtained by Hawthorne's group[279] through a Pd-catalyzed coupling reaction of terminal alkynes with *p*-carboranes iodinated in position 2 or the antipodal positions 2 and 9. This synthetic pathway allows for the sequential extension of the rods, with the longest rod **113** reported so far containing three carborane cages and two acetylene units with a length of approximately 18.7 Å (Scheme 56).[279]

Scheme 56



i. $Pd(PPh_3)_2Cl_2$/CuI, pyrrolidine/benzene reflux;
ii. O_2/CuI, pyridine/toluene

Properties and Uses. The B-ethynylated compounds are thermally very stable, with melting points over 250 °C. The linearity of the molecular structures was confirmed by X-ray diffraction.[279]

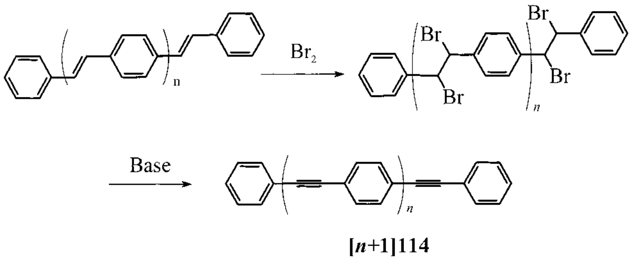
2. Ethyne/Planar Module

a. Ethyne/Benzene. This has been one of the most popular choices for molecular rods, and the longest individually characterized molecular rods are of this type.

Once again, we find it expedient to separate rods with organic terminal groups from those with metal substituents.

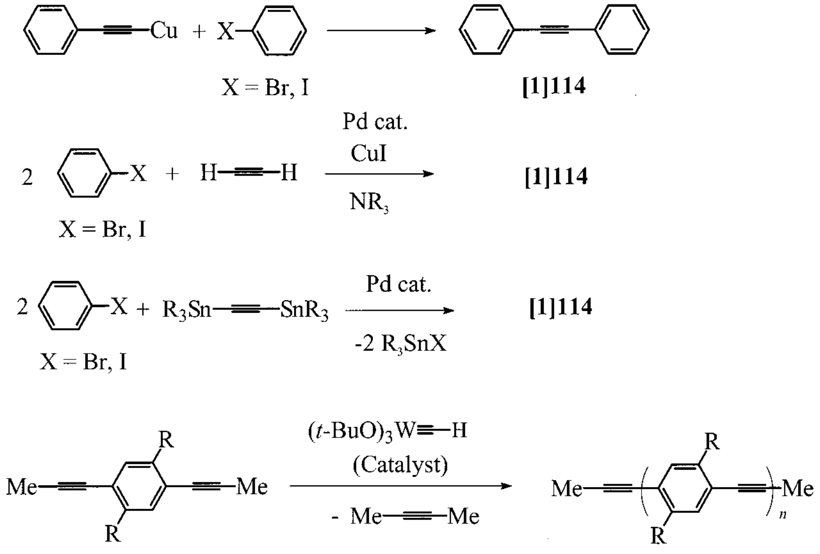
i. Organic Terminal Substitution. Synthesis. Ethyne/benzene co-oligomers with a regularly repeated modular pattern, oligo(phenyleneacetylene)s (**[*n*]114**), are among the most easily prepared and handled molecular rods. Originally, the oligomers **[*n*]114** were prepared by dehydrobromination of the corresponding oligo(phenylenevinylene)s with a bromine atom on each vinylene group (Scheme 57).[280] Modern synthetic approaches proceed via transition-metal intermediates (Scheme 58). The Stephens–Castro[281,282] reaction requires the preparation of copper(I) arylacetylenides and vigorous conditions for the coupling with aryl bromides or iodides. The palladium-catalyzed reaction reported by Cassar[283] and by Hagihara's[284,285] and Heck's[286] groups proceeds under milder conditions and gives better yields. This method requires cuprous iodide as a cocatalyst. The Stille reaction employed by the Tamao group[287] uses stannylacetylene derivatives and does not require the presence of copper salts. The acyclic diyne metathesis reaction used by Müllen's group is a potentially useful alternative method of the synthesis of the rods **[*n*]114**.[288] However, so far it has been applied only to the preparation of polymers.[288]

Scheme 57

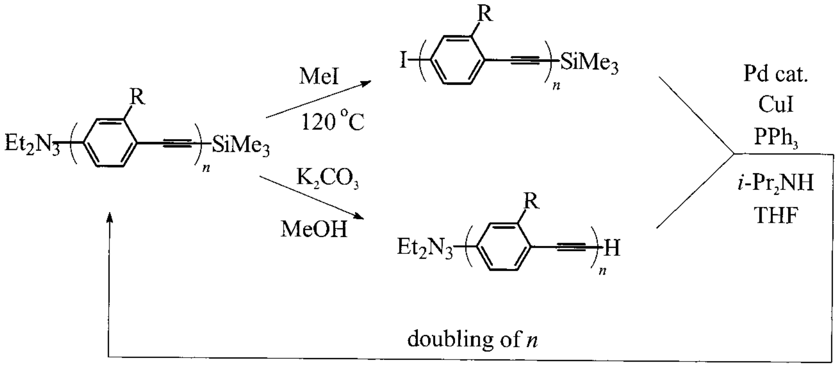


To streamline the synthesis of phenylacetylene oligomers of different lengths and substitution patterns, a divergent–convergent approach described in Scheme 1 was developed in Tour's group (Scheme 59).[38] An AB-type monomer is protected with the trimethylsilyl group on the acetylene side and with the diethyltriazine group on the phenylene side. Either of the protective groups can be selectively converted into a reactive group and coupled with a corresponding acetylene or aryl iodide. Iterative cross-coupling of the oligomers allows the chain length to double in each cycle. Oligo(phenyleneacetylenes)s with up to 16 repeating units and a length

Scheme 58

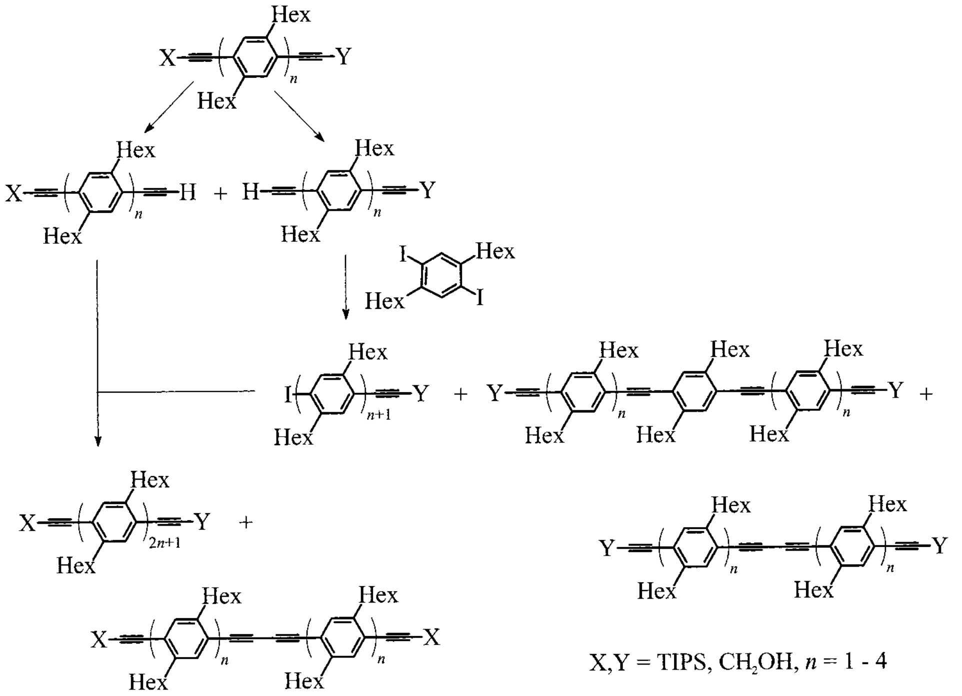


Scheme 59



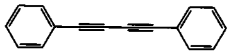
R = Et, 3-ethylheptyl; *n* = 1 - 16

Scheme 60



X,Y = TIPS, CH_2OH, n = 1 - 4

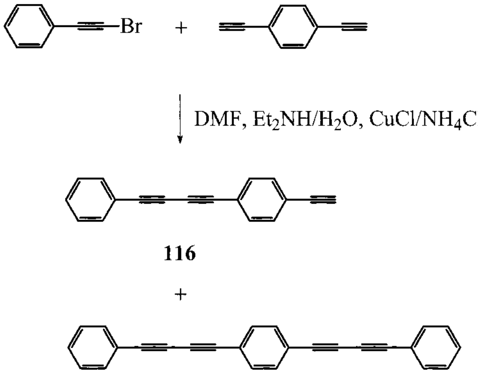
of 128 Å have been prepared by this method with yields ranging from good to excellent.[38] The procedure has been adapted for solid-phase synthesis.[289] An alternative set of orthogonal protective groups on two sides of a growing phenylacetylene chain has been proposed by Kukula et al.[290] (Scheme 60). Their approach yields phenyleneacetylenes terminated with acetylene units on both ends.



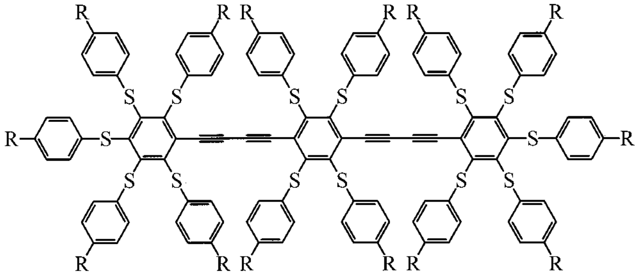
115

Ethyne/benzene rods of less regular patterns are also known but have received less attention. 1,4-Diphenylbutadiyne (**115**) was first reported by Hay[47] and has since been synthesized in many model reactions during the development of aryl−ethynyl and ethynyl−ethynyl coupling procedures. 4-(Phenylbutadiynyl)phenylacetylene (**116**) and 1,4-bis(phenylbutadiynyl)benzene (**117**) were obtained by White and Quinn from 1-bromo-2-phenylacetylene and *p*-diethynylbenzene under Cu mediation (Scheme 61).[291] Poly(phenylthio) substituted 1,4-diphenylbutadiene and 1,4-bis(phenylbutadiene)benzene **118** have been prepared by Lehn's group.[292]

Scheme 61

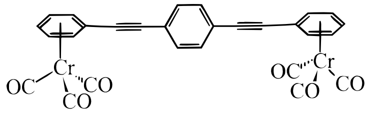


117



118 R = *t*-butyl

Tricarbonylchromium complexed alkynylarenes were shown by Müller et al.[293] to react easily with iodoarenes to yield tricarbonyl-η^6-phenylacetylenechromium(0) arenes **119**. The regioselective introduction of the complexed phenylacetylene fragments with the electron-withdrawing $Cr(CO)_3$ unit could lead to interesting new chromophores.



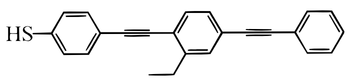
119

Properties and Uses. Oligo(phenylacetylene)s are very stable compounds. 4,4′-Bis(phenylethynyl)tolan (**[3]114**) has a sharp melting point at 278 °C.[280] 1,4-Bis(phenylbutadiynyl)benzene (**117**) melts slightly lower at 254 °C.[291] The presence of at least one ethyl group per phenylene unit is required for the oligomers **[*n*]114** up to the tetramer to be soluble.[289]

Larger substituents, such as 3-ethylheptyl or dodecyl, are necessary to solubilize the higher oligomers. The rigidity of the oligomers **[*n*]114** increases their hydrodynamic volume, and the number-average molecular weights for $n > 2$ determined by size-exclusion chromatography with polystyrene standards are significantly inflated.[289] The thermal reactivities for a number of phenylacetylenes have been measured.[291]

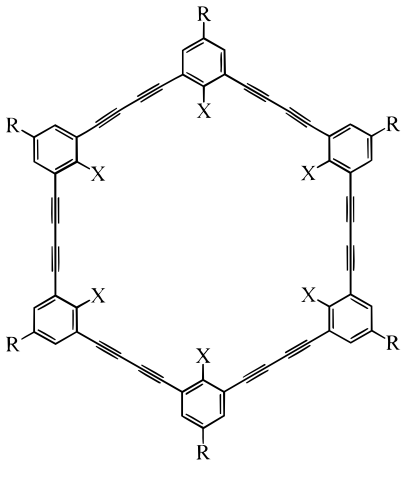
An increase in the length causes a bathochromic shift of the optical absorption and fluorescence of oligo(phenylacetylene)s. The maximum of the low-energy absorption band shifts from ~ 280 nm for tolan (**[1]114**) to 340 nm for **[3]114**. For oligomers **[*n*]114** with $n > 8$, this shift becomes very small, with the absorption maximum at 375 nm and emission maxima at 415 and 440 nm.

Conductivity of the thiol-terminated oligomer **120** is significantly higher than that of *n*-dodecanethiol molecules, as assessed by microwave frequency alternating current STM, even though the calculated length of the former molecules (21.3 Å) is 7.3 Å larger than that of the latter.[294] In this experiment, the molecules of **120** were imbedded into a self-assembled monolayer of *n*-dodecanethiol on gold, such that they extended above the surface of the monolayer and could be probed by the STM tip.



120

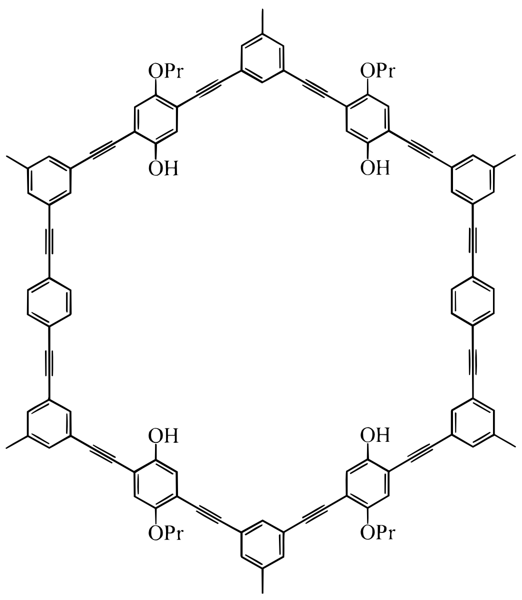
Quite a few large macrocyclic systems have been assembled from the phenylacetylene rods. Tobe et al.[295] reported the synthesis of a butadiyne-linked hexagon **121** with functionalized benzene units in the corners creating interior binding sites. Similarly,



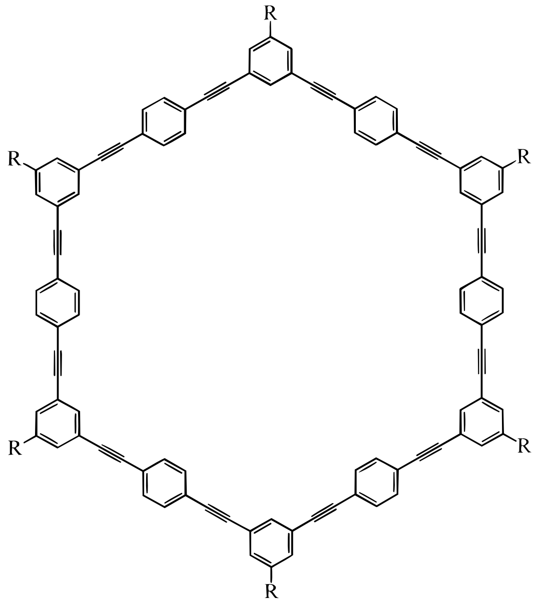
$R = H, CO_2C_8H_{17}$

$X = H, CN$

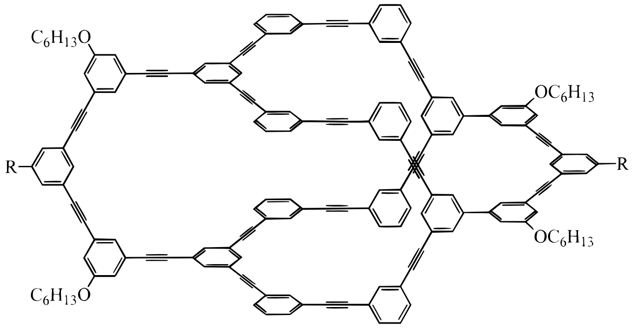
121



122



123 R = *t*-butyl

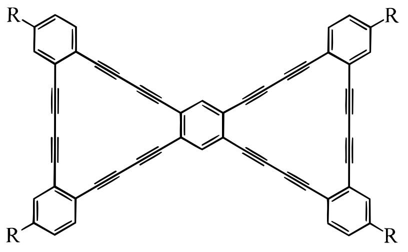


124

R = *t*-Butyl

Höger and Enkelmann[296] reported a large macrocyclic metaparacyclophane (**122**). Moore and collaborators[297] have accomplished the preparation of the hexagonal structure **123** with alternating benzene and acetylene modules and even more complex bicyclic and tricylic systems such as **124** by double cyclization of the appropriate branched precursors. Over the recent years, this group has published the synthesis of many shape-persistent molecular architectures based on the phenylacetylene unit.[298] Extended dendrimers, among them a 255-mer monodendron, were prepared by a double-exponential dendrimer growth methodology. These systems exhibit interesting structural and photophysical[299] features, making them candidates for liquid crystals[300] and nanotechnological applications such as antenna supermolecules.[301]

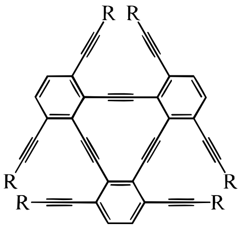
The quest for all-carbon networks has attracted much attention lately, and considerable progress has been reported. Haley et al.[302] succeeded in the synthesis of a annulenic substructure **125** of graphdiyne, which is considered to be the most stable carbon allotrope containing diacetylenic linkages and is thought to have many fascinating properties, such as superconductivity and enhanced redox activity.



R = *t*-Butyl, *n*-Decyl

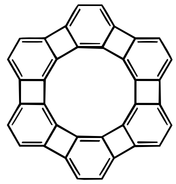
125

The group of Vollhardt[303] synthesized the hexaethynyltribenzocyclyne **126** as a subunit of a graphyne framework and as a precursor for antikekulene **127**, a member of the as yet unknown circular phenylenes.



126

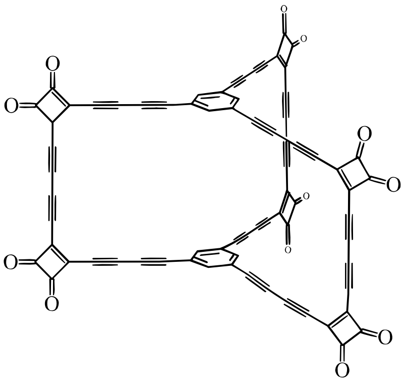
R = H, $Si(CH_3)_2[C(CH_3)_2CH(CH_3)_2]$, Pr, $CH_2C_6H_{11}$



127

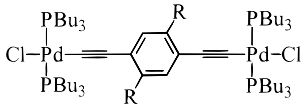
Acetylenic cyclophanes have been proposed as fullerene precursors. Rubin et al.[304] synthesized the large macrocycle **128** and indeed observed the formation of C_{60} in the gas phase in laser desorption mass spectroscopic experiments. The cyclobutenedione moiety apparently releases acetylenic bonds effectively with the loss of carbon monoxide.

ii. Metal Terminal Substitution. Like oligoynes, ethyne/benzene co-oligomers with ethyne termini are easily provided with terminal metal substituents, and these structures have received much attention.



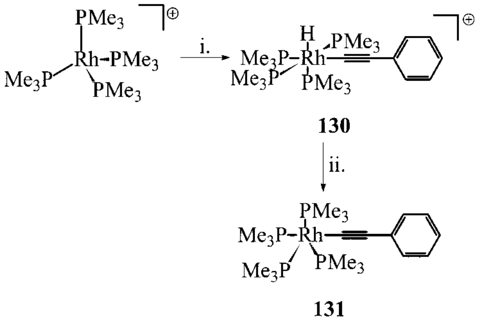
128

Synthesis. The first σ-acetylide complex of a transition metal was synthesized by the group of Hagihara[305] who obtained Pt^{2+}- and Pd^{2+}-containing rods (**129**) from transition metal dichlorides and a terminal acetylene. Marder's group[306] prepared cationic complexes **130** by oxidative addition of terminal alkynes to $[Rh(PMe_3)_4]Cl$ (Scheme 62). Subsequent deprotonation yielded the corresponding neutral counterparts **131**. Davies et al.[307] isolated the same complex **131** directly from $[Rh(PMe_3)_4]Cl$ and stannylated phenylacetylene (Scheme 63). Bianchini et al.[308] found that the complexes $[\{N(PPh_2Et)_3\}RhC\equiv CPh]$ are formed by reacting $[\{N(PPh_2Et)_3\}RhH]$ with $PhC\equiv CH$ with a concomitant loss of H_2. Crescenzi and Lo Sterzo[113] reported a Pd-catalyzed carbon−metal bond formation. They reacted $CpFe(CO)_2I$ with various trimethylstannylated acetylenes to give the



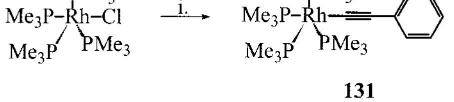
129 R = H, CH_3, C_2H_5

Scheme 62



i. phenylacetylene; ii. BuLi

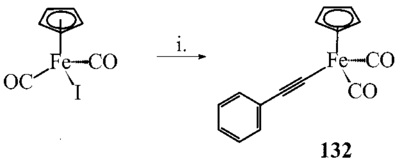
Scheme 63



i. $Me_3SnC\equiv CPh$

corresponding σ-alkynyliron complexes **132** (Scheme 64). The Ru analogue was prepared by Haquette et al.[309] via the vinylidene intermediate.

Scheme 64

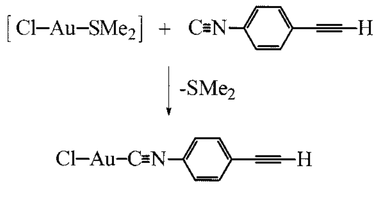


132

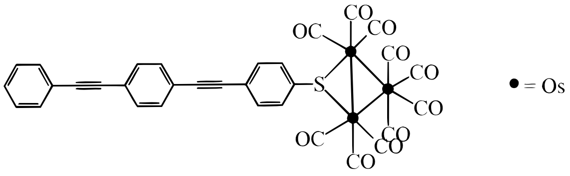
i. phenylacetylene, $PdCl_2(PPh_3)_2$

Puddephatt and his group[310] are pursuing the synthesis of new rigid-rod organometallic polymers with an ethyne/benzene backbone. *p*-Ethynylaryl isocyanides HC≡CArN≡C, prepared from *p*-iodoanilines by Pd-catalyzed coupling with a protected acetylene, deprotection, and a phase-transfer Hofmann carbylamine reaction, react rapidly with [AuCl-(SMe_2)] to yield [AuCl(CN)ArC≡CH)] (**133**, Scheme 65).[310] Adams et al.[311] synthesized the thiol-terminated oligophenylacetylene rod **134** connected to a triosmium cluster, mimicking the attachment of thiol-terminated molecular rods to metal surfaces. Yu et al.[312] accomplished the synthesis of 4-cyanobenzylidyne and 4-iodobenzylidyne tungsten complexes **135** from $[W(CO)_6]$ and phenyllithium derivatives (Scheme 66). The iodo group of these benzylidyne complexes can be used in standard Pd-catalyzed cross-coupling reactions with aromatic acetylenes, while the cyano group can act as a ligand to metal complexes. The complexes were proposed as monomeric building blocks for the synthesis of extended unsaturated alkylidyne ligands.

Scheme 65

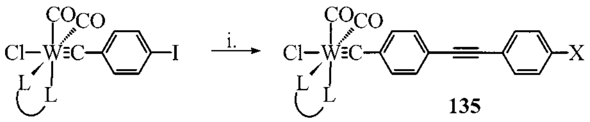


133



134

Scheme 66

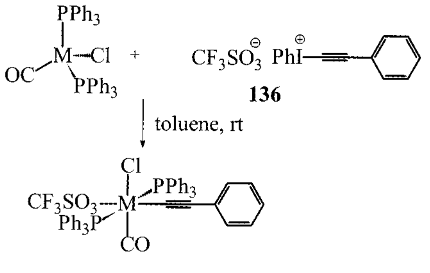


i. 1. $XC_6H_4(CCH\text{-}4)$, THF; 2. NEt_3, Pd(II), Cu(I)

L = tmeda, X = H, CHO, CN

The reactions described so far utilize either conventional nucleophilic acetylide chemistry or oxidative addition reactions to form the metal–carbon bond. Stang and Crittell[313] complemented these methods by developing electrophilic acetylene reagents, alkynyl(phenyl)iodonium triflates **136**. With this umpolung, electrophilic substitution on organometallic systems became possible and Rh(III) and Ir(III) σ-acetylide complexes **137** were obtained in a single step and in excellent yield (Scheme 67).[314]

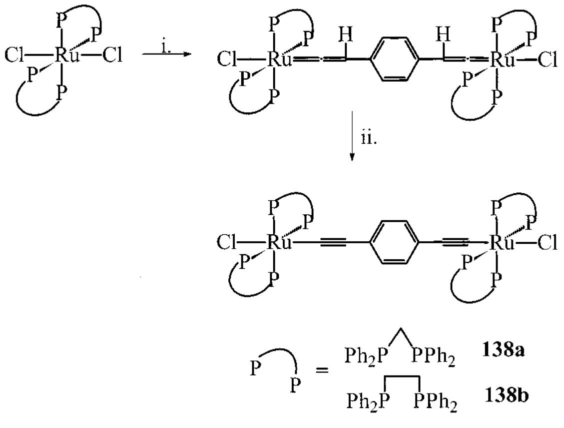
Scheme 67



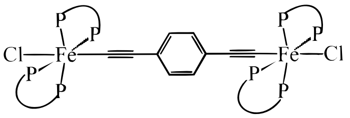
M= Ir, Rh

Rods carrying a terminal acetylene on each end can carry two transition-metal substituents (Scheme 68), as shown by Lavastre et al.[315] and Faulkner et al.,[316] who obtained the Ru-containing rods **138a** and **138b**. An analogous iron derivative **139** has been reported by Field et al.[317] Rods carrying one electron-acceptor metal atom with π-acidic ligands and one electron-donor metal atom with Lewis basic ligands have been produced by the group of Lewis.[318] Bis(trimethylstannyl)-1,4-diethynylbenzene was treated with [Mn-$(CO)_5Br$] to give the bis(acetylide) **140**, and subsequent treatment with *trans*-$[Pd(PBu_3)_2Cl_2]$ yielded

Scheme 68



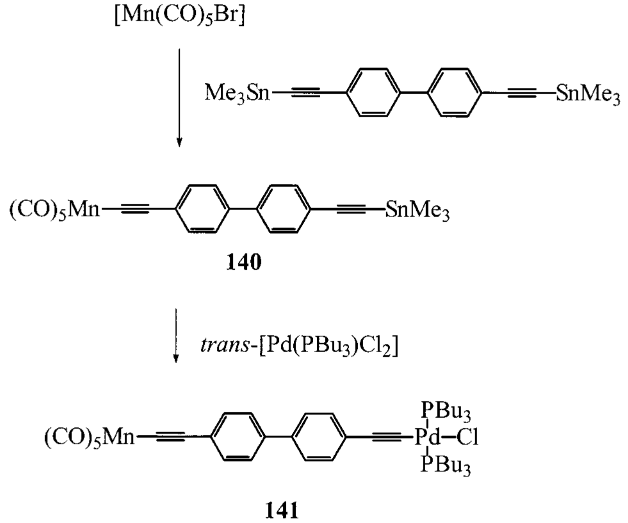
i. 0.5 eq 1,4-diethynylbenzene, 2 eq $NaPF_6$; ii. DBU



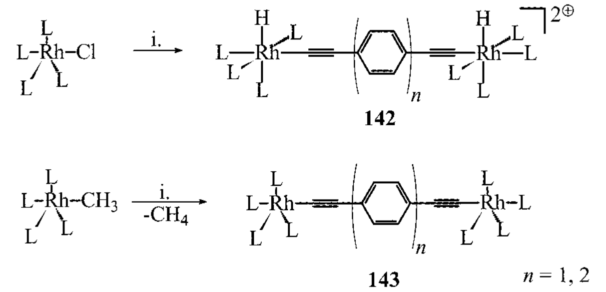
139

the donor−metal acceptor−metal-terminated rod **141** (Scheme 69). The group of Marder[319] synthesized dinuclear rhodium dications **142** directly from the appropriate terminal dialkynes, such as butadiyne or *p*-bisethynylbenzene, and two equivalents of [Rh(PMe$_3$)$_4$]Cl. The corresponding neutral complexes **143** were obtained in similar oxidative additions of the dialkynes to [Rh(PMe$_3$)$_4$(Me)] with a loss of methane (Scheme 70). The oligomeric [(AuC≡CArC≡CAu)$_x$], prepared in very high yield from two equivalents of [AuCl(SMe$_2$)] with the appropriate diethynylarenes in the presence of base, yielded [Me$_3$PAuC≡CArC≡CAuPMe$_3$] (**144**) upon treatment with PMe$_3$ (Scheme 71) and [XyNCAuCCRCCAuCNXy] upon reaction with 2,6-dimethylphenyl isocyanide.[320]

Scheme 69



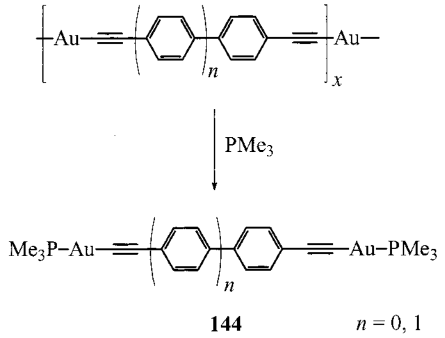
Scheme 70



i. 1,4-diethynylbenzene or 4,4'-diethynylbiphenyl

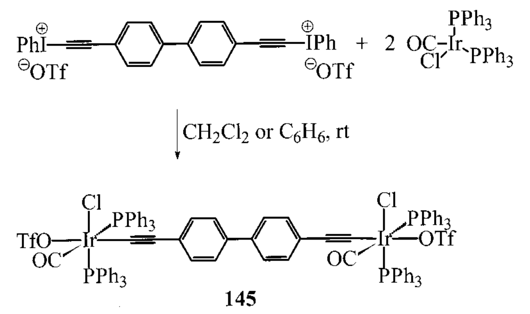
L = PMe$_3$

Scheme 71

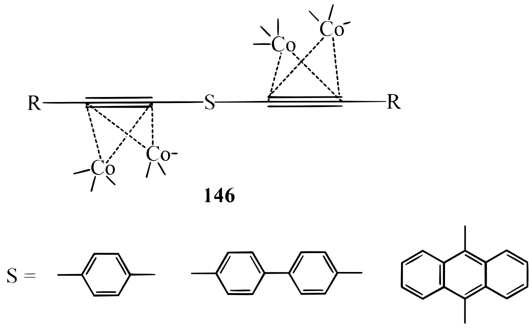


Stang and Tykwinski[314,321] used single-step alkynyl(phenyl)iodonium chemistry[313] to prepare doubly iridium(III)-**145** and rhodium(III)-substituted acetylene-terminated rods (Scheme 72).

Scheme 72



A large series of oligoarylacetylenes **146** *μ*-complexed to Co$_2$(CO)$_6$ and Co$_2$(CO)$_4$(dppm) clusters on the ethyne moieties was prepared by Osella et al.[322]



R = Ph, H

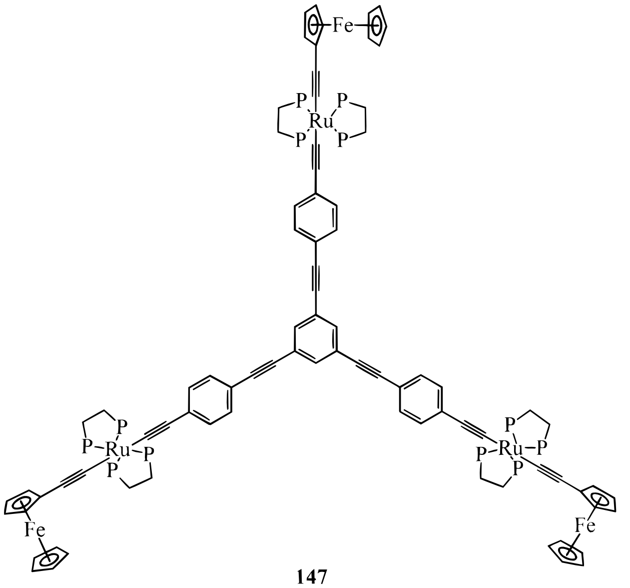
Properties and Uses. Most of the reported metal acetylide complexes are air sensitive, especially in solution. The use of bis(diphenylphosphine)methane and 1,2-bis(diphenylphosphine)ethane as auxiliary ligands stabilizes them and increases their solubility in common organic solvents.[316]

Tykwinski and Stang[314] reported that the cationic species obtained from **145** by displacement of the triflate ligands with acetonitrile were more soluble and easier to characterize. The solids are thermally quite stable with melting points around 200 °C and are also stable to air and moisture.

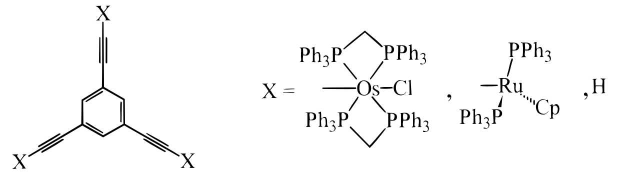
The Ru complexes **138** exhibit considerable delocalization along the rod and also offer interesting electrochemical properties due to the potential accessibility of the Ru(II)/Ru(III) couple.[316] The electrochemical investigation by Field et al.[317] shows that there is electronic communication between the iron centers in **139** through the bridge.

The highly soluble gold complexes such as **144** are air-stable but decompose slowly at room temperature, presumably due to polymerization. Many of them are luminescent.[323] The emission spectra show a significant red shift upon going from mononuclear to binuclear species and from solution to the solid state. The red shift observed upon going from mononuclear to binuclear gold complexes indicates at least some conjugation in the molecule. The red shift between solution and the solid state is due to stacking in the crystal, sometimes leading to Au−Au interactions and sometimes to π stacking.[323]

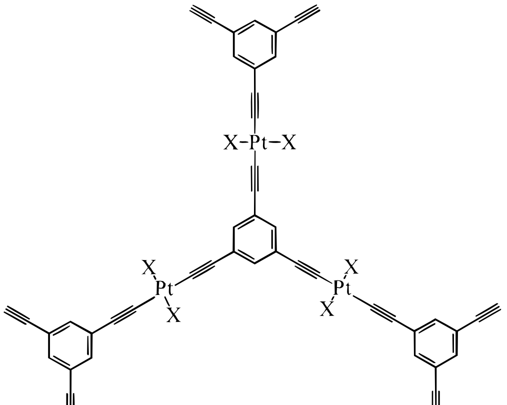
Interesting and aesthetic star-shaped molecules based on 1,3,5-triethynylbenzene have been reported very recently. Organometallic linkages were utilized to extend the length of the arms in the work of Uno and Dixneuf[324] (**147**) and Long et al.[325](**148**). Stang's group[326] used a step-by-step divergent strategy to obtain similar transition-metal dendrimers, such as **149**.



147



148

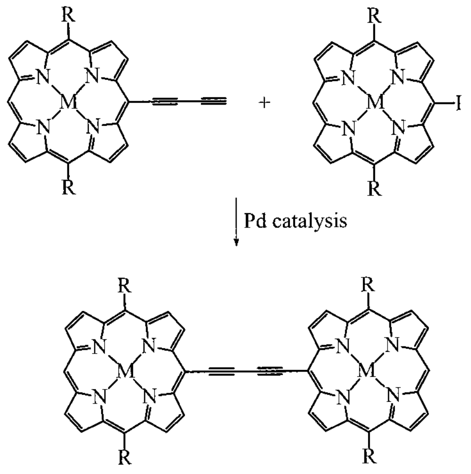


149

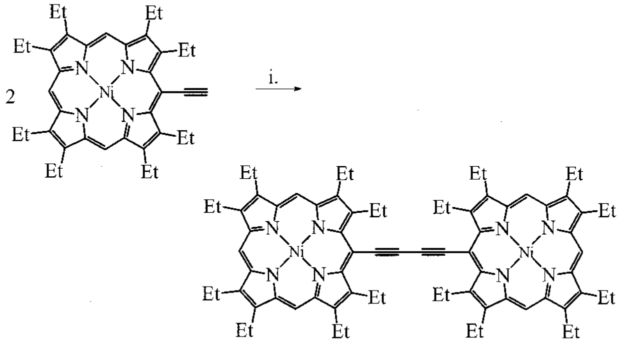
X = PEt_3

b. Ethyne/Porphyrin. *Synthesis.* Co-oligomers of porphyrin with ethyne offer an opportunity to connect several porphyrin rings without forcing them to be twisted strongly out of coplanarity. These co-oligomers were prepared by Pd-catalyzed coupling of iodoporphyrins with terminal alkynes (Scheme 73)[327,328] and alkyne to alkyne oxidative coupling using $Cu(OAc)_2$,[329,330] CuCl,[331] or $Pd(PPh_3)_4/CuI$[332,333] as catalysts (Scheme 74). A copper-free Pd-mediated coupling method has been developed by Lindsey.[334]

Scheme 73

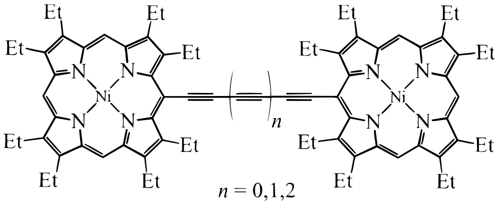


Scheme 74



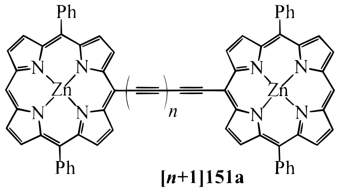
i. $Cu(OAc)_2$ or CuCl or $Pd(PPh_3)_4/CuI$

The group of Arnold[335] prepared the co-oligomer porphyrin dimer series **[*n*]150**. Therien and co-workers[336−338] synthesized the co-oligomeric dimers (**151a** and **151b**) and trimers (**152a** and **152b**) with both meso-to-meso and β-to-β connectivity. Anderson[339] reported the preparation of a porphyrin−ethyne co-oligomer **153** capable of further transformation to a *meso*-butadiyne-linked porphyrin polymer (Scheme 75).



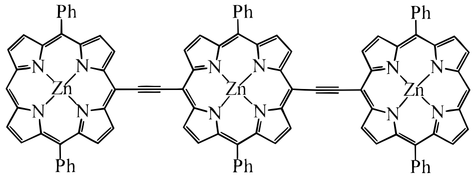
[*n*+2]150

Properties and Uses. The compounds are chemically and thermally stable, and most exhibit good solubility in common solvents. The dimers form bimolecular aggregates even at low concentrations.[339] The longest rod, Anderson's dimer **153**, measures 38 Å.[339] Complexation with 1,4-diazabicyclo[2.2.2]octane results

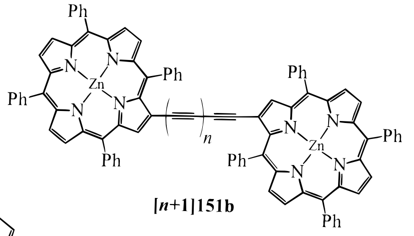


[n+1]151a

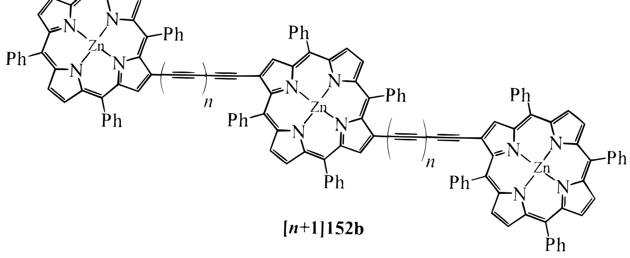
n = 0, 1



152a



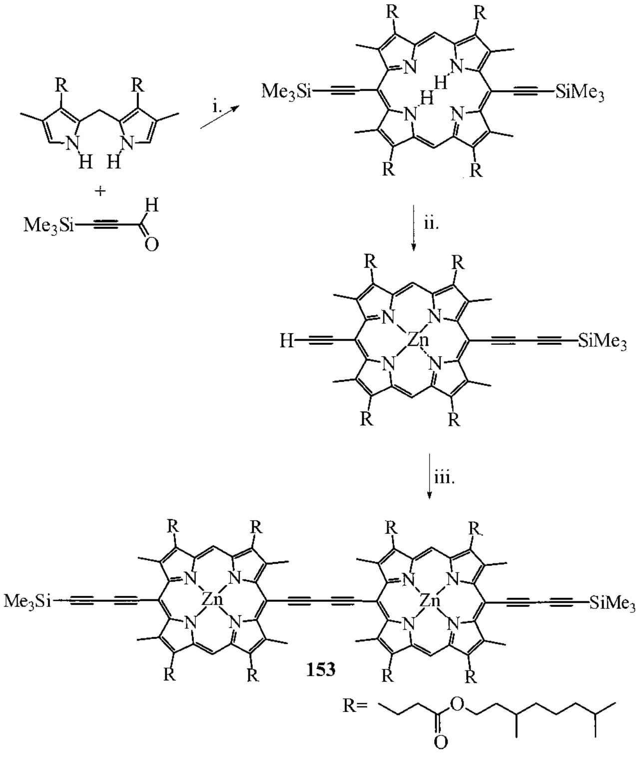
[n+1]151b



[n+1]152b

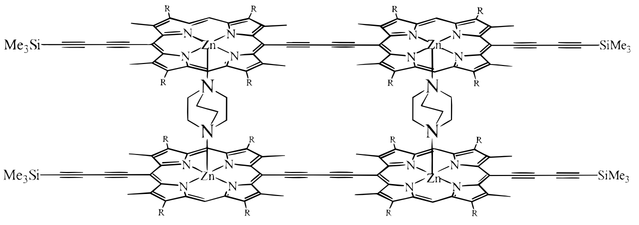
n = 0, 1

Scheme 75



i. 1. CF$_3$CO$_2$H, 2. DDQ; ii. 1. Zn(OAc)$_2$, 2. Bu$_4$NF, 3. CuCl/TMEDA Me$_3$SiC$_2$H, Air; iii. CuCl/TMEDA, Air

in the formation of a 2:2 ladder complex **154** which can twist significantly.[339]



154

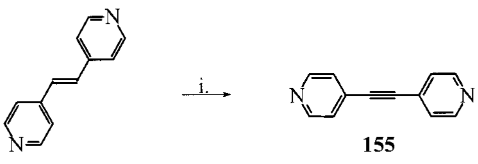
The dependence of the electronic and electrochemical spectra of the porphyrin dimers on the length of the bridging unit and the substitution pattern has been investigated. Attachment of *meso*-alkynyl substituents to a porphyrin ring causes a significant red shift of the porphyrin absorption peaks. In the dimers **150**, very little additional red shift of the Q bands occurs but their intensities increase markedly.[335] The major effect of the bridging ethyne module is the extraordinarily large excitonic coupling in the Soret band.[336,339,340] The splitting and red shift of the bands indicate a strong inter-porphyrin interaction. This interaction can be enhanced or inhibited by the incorporation of other aromatic spacers into the bridge (cf. section III.D.2.g).[341]

Electrochemical data revealed a dramatic decrease of the HOMO−LUMO gap of the dimeric systems **151** relative to the monomer (1.78 V in the dimer versus 2.21 V in the monomer).[338]

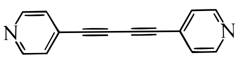
In the trimer, **152a**, the effects in the electronic spectra reported for the dimer are further amplified.[338] The information obtained from the UV−vis spectrum suggests a strong ground-state electronic interaction and some cumulenic character in the excited state. The porphyrin rings in the trimer, therefore, appear to be essentially coplanar.[338]

c. Ethyne/Pyridine. *Synthesis.* The simplest ethyne/pyridine rod, 1,2-bis(4-pyridyl)acetylene (**155**), was first synthesized by Sutton and Taube (Scheme 76).[342] The butadiyne-bridged analogue **156**, providing for a separation of two transition metals by about 15 Å, was obtained by Della Ciana and Haim[343] by oxidative coupling of 4-ethynylpyridine. The group of Ziessel[344] reported ethyne-bridged (Scheme 77) and butadiyne-bridged (Scheme 78) 2,2′-bipyridyls **157** and **158**. Two equivalents of 5-bromo-2,2′-bipyridyl (**159**) were coupled with 5,5′-diethynyl-2,2′-bipyridyl

Scheme 76

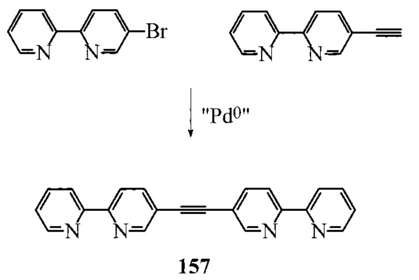


i. 1. Br$_2$/HBr/H$_2$O, 2. KO-*t*-Bu

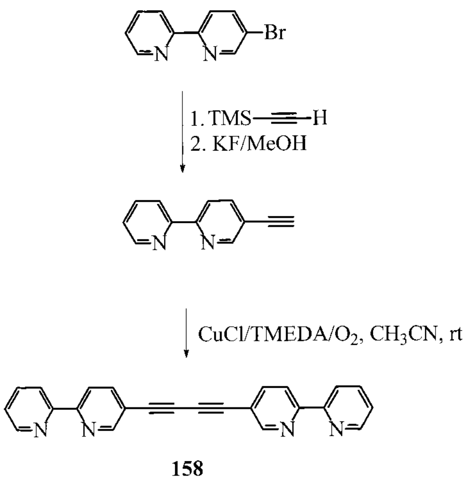


156

Scheme 77

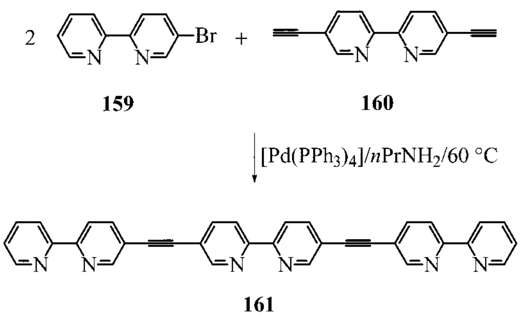


Scheme 78

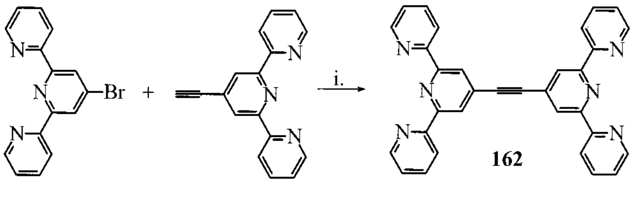


(**160**) under Pd(0) catalysis to yield 5,5′-bis(2,2′-bipyrid-5-ylethynyl)-2,2′-bipyridyl (**161**) (Scheme 79).

Scheme 79

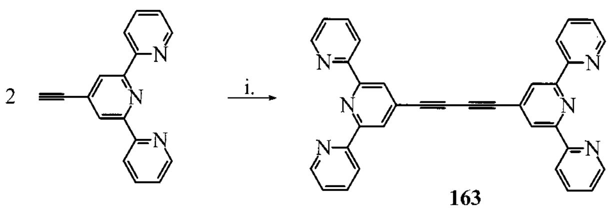


Scheme 80



i. [Pd(PPh$_3$)$_4$], nPr$_2$NH, 60 °C

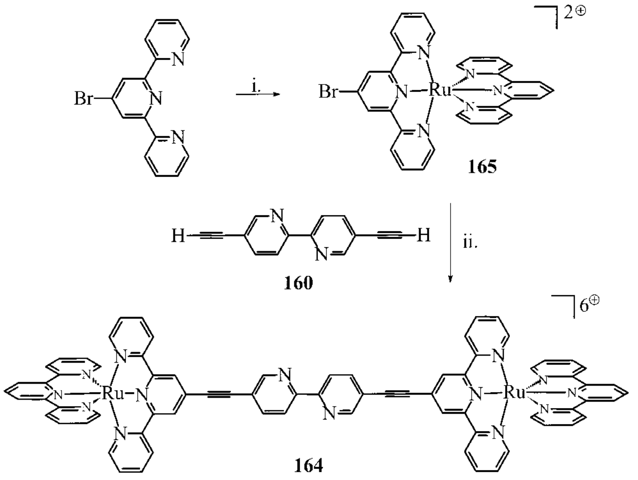
Scheme 81



i. CuCl/TMEDA/O$_2$

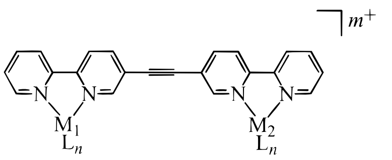
The same group[345] obtained two ethyne-containing terpyridyl-based rods **162** and **163** by Pd-catalyzed coupling reactions and the corresponding butadiyne-bridged rods by oxidative dimerization (Schemes 80 and 81, respectively). They have been converted into mononuclear ruthenium(II) bis(terpyridyl) subunits containing a free terpyridyl ligand.[346] Ziessel's group[347] also reported the preparation of a Ru(terpy)-based binuclear complex **164** in which the butadiynylene bridge is interspersed with a 5,5′-(2,2′-bipyridylene) unit, using a Sonogashira-type cross-coupling reaction between 5,5′-diethynyl-2,2′-bipyridyl (**160**) and a bromoterpyridyl complexed to the metal (**165**, Scheme 82).

Scheme 82



i. [Ru(terpy)(DMSO)Cl$_2$], Ag$^+$/Methanol; ii. [Pd(PPh$_3$)$_2$Cl$_2$] CH$_3$CN/C$_6$H$_6$, (i-Pr)$_2$NH, rt

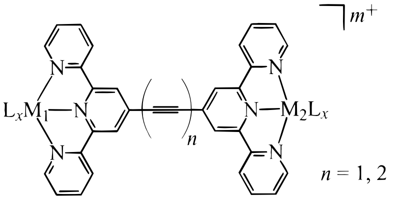
Properties and Uses. The compounds are air-stable solids with high melting points, reasonably soluble in polar organic solvents. Mono-, bi-, and some trinuclear metal complexes were prepared to study electron and energy transfer through these bridges and their distance dependence.[348] The 2,2′-bipyridyl-based Ru(II)/Os(II) mixed-metal complexes, such as **166a**, exhibit a rapid triplet energy transfer almost independent of the length of the bridging spacer (one or two ethyne modules).[349] For the symmetrical Ru and Os complexes **166b**, transient depolarization measurements showed that the excitation shuttles between chromophores several thousand times during the triplet lifetime. For the trinuclear complexes



166a: M$_1$= Ru(II), M$_2$ = Os(II)
166b: M$_1$= M$_2$ = Ru or Os

derived from **161**, quantitative triplet energy transfer from peripheral to central units was observed.[349]

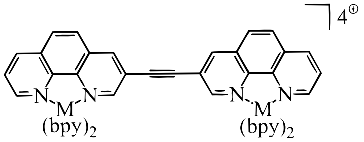
Much more information has been gathered on the terpyridyl-based systems. Ziessel's group's measurements[350] on binuclear Ru(II) complexes **[*n*]167a** revealed that the attachment of an ethyne module to the terpyridyl unit dramatically increases the yield of phosphorescence, the wavelength of the emission maximum, and the triplet lifetime (by about 1000-fold), thus converting a poor sensitizer into a more effective one. Addition of another ethyne module enhances these effects. Significant electronic coupling is observed between the terpyridyl and ethyne units as well as among the ethyne modules. Intense absorption bands in the NIR are present and attributed to electron delocalization between the terpy units along the bridge. In the mixed-metal Os(II)/Ru(II) species **[*n*]167b**,[351] the absorption spectra for the systems both with one and two ethyne modules retain the characteristics of the individual units. The triplet lifetime and energy decrease in the longer system **[2]167b**. Rapid, quantitative intramolecular triplet energy transfer takes place from the Ru(II) to the Os(II) unit even at room temperature. The rate increases significantly at lower temperatures and decreases significantly when going from fluid medium to a frozen glass.[345] The rate decrease observed upon addition of the second ethyne module is surprisingly small. These observations point toward the Dexter mechanism[352] for the energy transfer. Additionally, high transfer efficiency along the ethyne modules was deduced. However, since the transfer rates are faster for oligophenylene-bridged systems (cf. section III.D.5.b), it was concluded that the electronic coupling between terpyridyl and ethyne is relatively ineffective.[350] A more detailed account can be found in a recent review by Balzani et al.[260]



[*n*]167a: M_1= M_2= Ru(II)
[*n*]167b: M_1= Ru(II); M_2= Os(II)

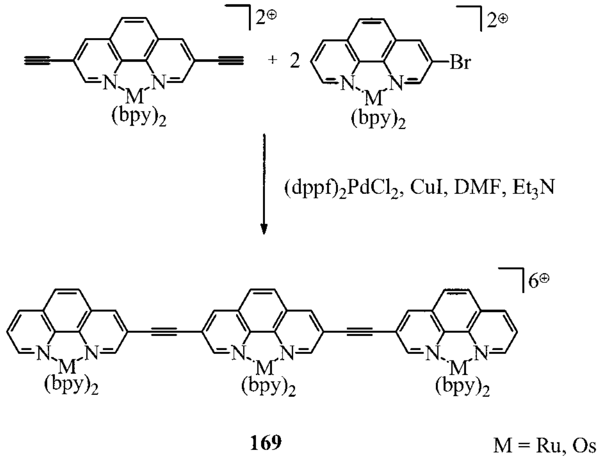
The homobinuclear Ru complexes **164** built from the rod interspersed with a bipyridyl unit reveal a decreased triplet lifetime and luminescence quantum yield compared to the counterparts containing only ethyne bridges.[347] The system spaces the terminal metals by about 23 Å and provides a free binding site for cations. Its N atoms can be easily quaternized or protonated. Quaternization quenches the luminescence, presumably due to electron transfer from the excited triplet of the Ru(terpy) chromophore to the cation. Protonation enhances the conjugation along the bridge by lowering the LUMO localized on the bipyridyl module, but the effect is miniscule. Cations show similar effects depending on the strength of their binding. Overall, these modifications allow for fine-tuning of the electronic properties of the bridge, as well as adjustments in solubility and overall charge.[347]

d. Ethyne/Phenanthroline. *Synthesis.* Linear rods **168** and **169** comprised of metal-complexed phenanthroline units and ethyne modules were prepared by Connors et al.[353] using Pd-catalyzed cross-couplings of metal-complexed bromophenanthrolines with metal-complexed 3-ethynylphenanthroline (Scheme 83). The coupling reactions proceeded in good yields and without any ligand exchange on the complexation sites, thus providing full control over the composition of the assembled metal-complexed rod in a single step. Bi- and trimetallic systems of Os and Ru with identical or different metal atoms were obtained.



168

Scheme 83

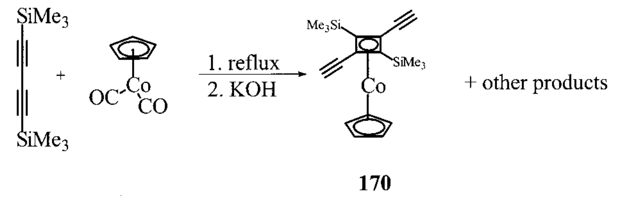


Properties and Uses. Since the rods were assembled with the building blocks already complexed to metals, no information was obtained on the "naked" rods. The cation-complexed systems **168** and **169** are soluble in polar organic solvents and in water. Absorption spectra show the conjugation of the phenantroline ligands and the expected intense metal to ligand charge-transfer (MLCT) bands. Voltammetry was used to confirm the locations of the metal centers.[353]

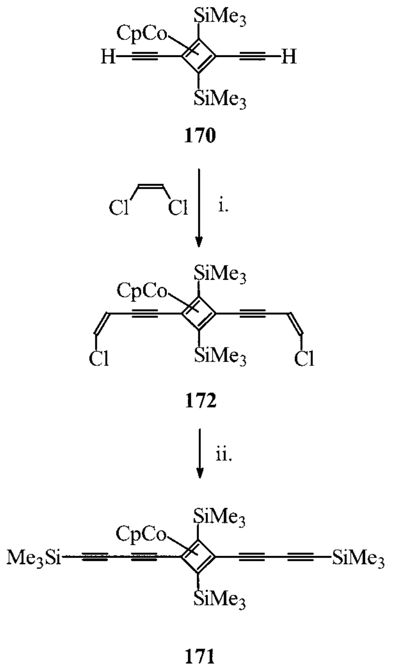
e. Ethyne/Cyclobutadiene. Free cyclobutadiene is too reactive for use in molecular rods, but as noted in section II.B.1.b, it can be stabilized in several ways. One of them is π complexation with a transition metal atom that removes the biradicaloid nature of the ring. The other ligands on the transition metal usually are carbonyls or cyclopentadienyl. Homo-oligomeric rods built from metal–cyclobutadiene complexes alone have not been prepared, but co-oligomers with other modules are known.

Synthesis. Co-oligomers of ethyne and cyclobutadiene modules complexed to either (cyclopentadienyl)cobalt or (tricarbonyl)iron were reported by Bunz and his group.[354–360] In the (cyclopentadienyl)cobalt series, 1,3-diethynyl-2,4-bis(trimethylsilyl)cyclopentadienylcobalt (**170**), accessible in moderate yield and multigram quantities (Scheme 84),[361] was used as the primary building block for the synthesis of longer rods. To obtain the 1,3-butadiynyl derivative **171**, **170** was coupled with *cis*-1,2-dichloroethene in a Heck–Cassar–Sonoshigara–Hagihara reaction followed by elimination on the doubly chlorovinylated intermediate **172** (Scheme 85).[360] The diacetylene **170** was also subjected to Hay conditions yielding a mixture of linear oligomers **173** (Scheme 86). The dimer to nonamer were isolated in moderate yields.[362] The trimethylsilyl groups on the cyclobutadiene ring were subsequently easily removed (Scheme 87). Following the route described in Scheme 85, 1-ethynyl-2,3,4-tris(trimethylsilyl)cyclopentadienylcobalt was extended by one ethyne module and after desilylation oxidatively coupled to produce the octatetrayne-linked cyclobutadiene dimer **174** as a model compound for the respective polymer.[358]

Scheme 84

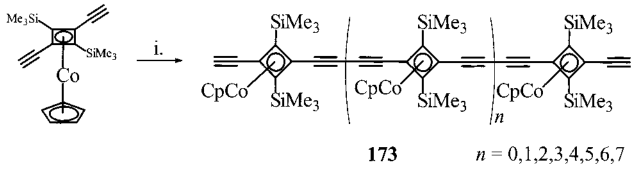


Scheme 85



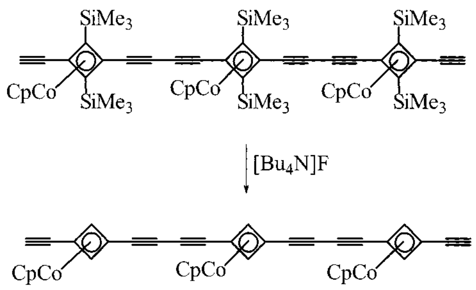
i. $Pd(PPh_3)_4$/CuI/piperidine; ii. 1. *sec*-BuLi/THF, 2. $ClSiMe_3$

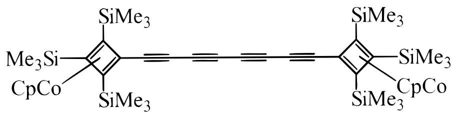
Scheme 86



i. $CuCl/TMEDA/O_2$

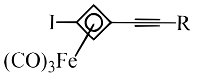
Scheme 87



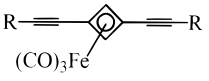


174

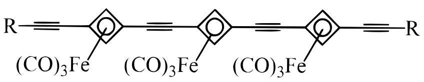
In the (tricarbonyl)iron series, cyclobutadiene(tricarbonyl)iron itself was used as the starting material. A metalation–iodination–coupling (MIC) scheme was developed which lead to stepwise alkynylation of the ring.[356] Hereby, lithiation takes place regioselectively in the ortho position only at low temperature. The monoethynylated isomer **175** iodinated in the para position was isolated from a mixture obtained at higher temperatures and used along with the 1,3-diethynyl derivative **176** as monomeric building blocks. Thus, two equivalents of **175** were coupled under Pd catalysis with **176** to obtain moderate yields of the ethyne-brigded cyclobutadiene(tricarbonyl)iron trimer **177** and with bis(trimethylstannyl)acetylene to produce the corresponding dimer **178**.[354] Wiegelmann-Kreiter and Bunz[363] developed a stepwise synthetic route to the peralkynylated dumbbell-shaped dinuclear cyclobutadieneirontricarbonyl complexes **179a** and **179b** from the 1,2-isomer **180**, using stepwise iodination, Pd-catalyzed coupling with (trimethylsilyl)(trimethylstannyl)ethyne and bis(trimethylstannyl)ethyne or -butadiyne after desilylation (Scheme 88). A few mixed rods containing both (tricarbonyl)iron and CpCo complexed cyclobutadiene rings were also reported.[354]



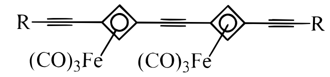
175



176



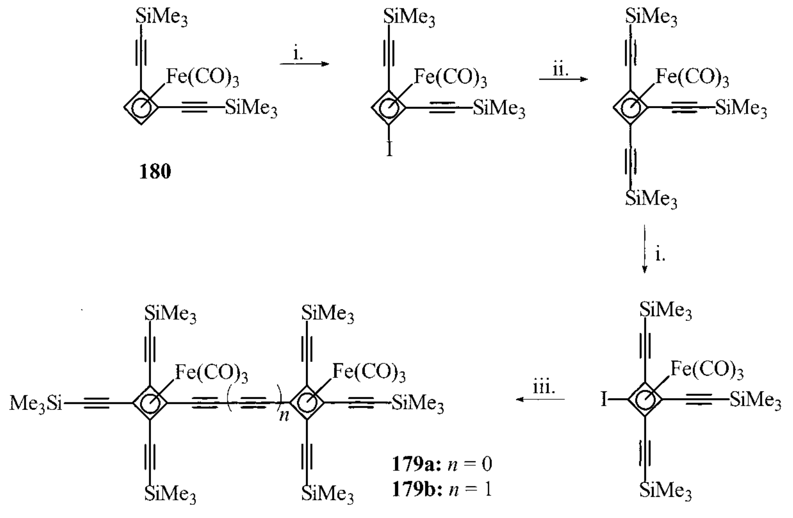
177



178

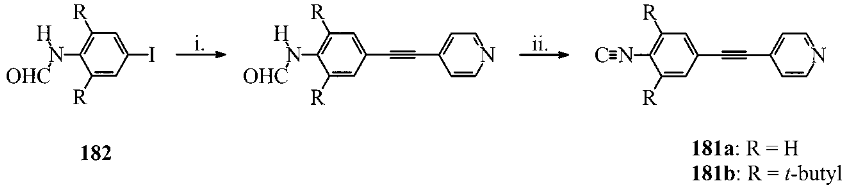
R = $SiMe_3$, H

Scheme 88



i. *sec*-BuLi, THF, -78 °C, diiodoethane; ii. $Me_3SiCCSnMe_3$, $PdCl_2(CH_3CN)_2$, DMF; iii. $Me_3SnCCSnMe_3$, $PdCl_2(CH_3CN)_2$, DMF

Scheme 89



i. 4-ethynylpyridine/$Pd(dba)_2/PPh_3/CuI/NEt_3$; ii. phosgene/$NEt_3$

The compounds carrying two terminal acetylene funtionalities were used for the synthesis of polymers.

Properties and Uses. Since the cyclobutadienecobalt(cyclopentadienyl) complexes are completely stable to standard conditions and contain terminal alkynes, they are excellent candidates as building blocks for the construction of larger organometallic structures. The octatetrayne-bridged dimer **174**, for example, decomposes above 300 °C without melting.[360] Analyses of X-ray data show that the cyclobutadiene ring is distorted from a square to a parallelogram with angles of 85−87° and 93−94°. The bisbutadiyne-substituted monomer **171** is not exactly linear, as the ligands are pointing away from the CpCo unit at an angle of about 7°.[360]

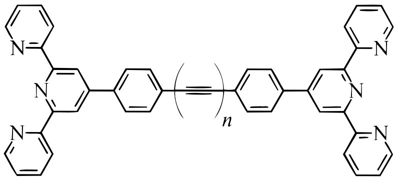
The UV−vis spectra of the oligomeric series **[*n*]173** indicate that the hydrocarbon ligand allows considerable electron delocalization.[362] The monomer and dimer show only two bands, while the trimer and higher oligomers have three bands. The third band (at about 350 nm) increases in intensity up to the heptamer, indicating that the effective conjugation length has been reached there. The spectra of all longer oligomers are virtually superimposable with the spectrum of the polymer. The third band is therefore attributed to the interaction of the diyne units with the complexed cyclobutadiene ring. In addition, variable-temperature ^1H NMR spectroscopy revealed free rotation of the organometallic moieties around the C−C bonds of the linkers down to at least −100 °C.[362]

The cyclobutadieneiron(tricarbonyl) complexes **179** are moderately sensitive under normal atmospheric conditions but are stable at low temperatures and exhibit good solubility in nonpolar and polar organic solvents.[363]

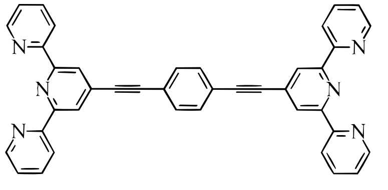
f. Ethyne/Benzene/Pyridine. *Synthesis.* Two linear pyridylethynylphenylisocyanides **181a** and **181b** were reported by Mayr and Guo[364] as building blocks in coordination polymers and supramolecular assemblies. Pd-catalyzed cross-coupling of the respective formamidophenyl iodides **182** with 4-ethynylpyridine followed by dehydration of the resulting formamides yielded the desired rods in good yields (Scheme 89).

The group of Ziessel[344] prepared a number of molecular rods based on terpyridyl termini bridged by spacers consisting of phenylene and ethynyl modules. The system **183** with the phenyl groups directly attached to the terpyridyl units containing a single ethyne module was synthesized by Pd-catalyzed cross-coupling, and the corresponding system with two ethyne modules was prepared by oxidative coupling of the terminal acetylene precursors. The rod **184** with a benzene ring in the center was prepared by Pd-catalyzed Sonogashira-type cross-coupling of the metal-complexed bromoterpyridyl with 1,4-diethynylbenzene.[347]

Properties and Uses. The pure isocyanides **181** have melting points around 100 °C but are not stable at room temperature and have to be stored at low temperature in methylene chloride solution.[364] They can be stabilized by complexation to a transition



[*n*]183 $n = 1, 2$



184

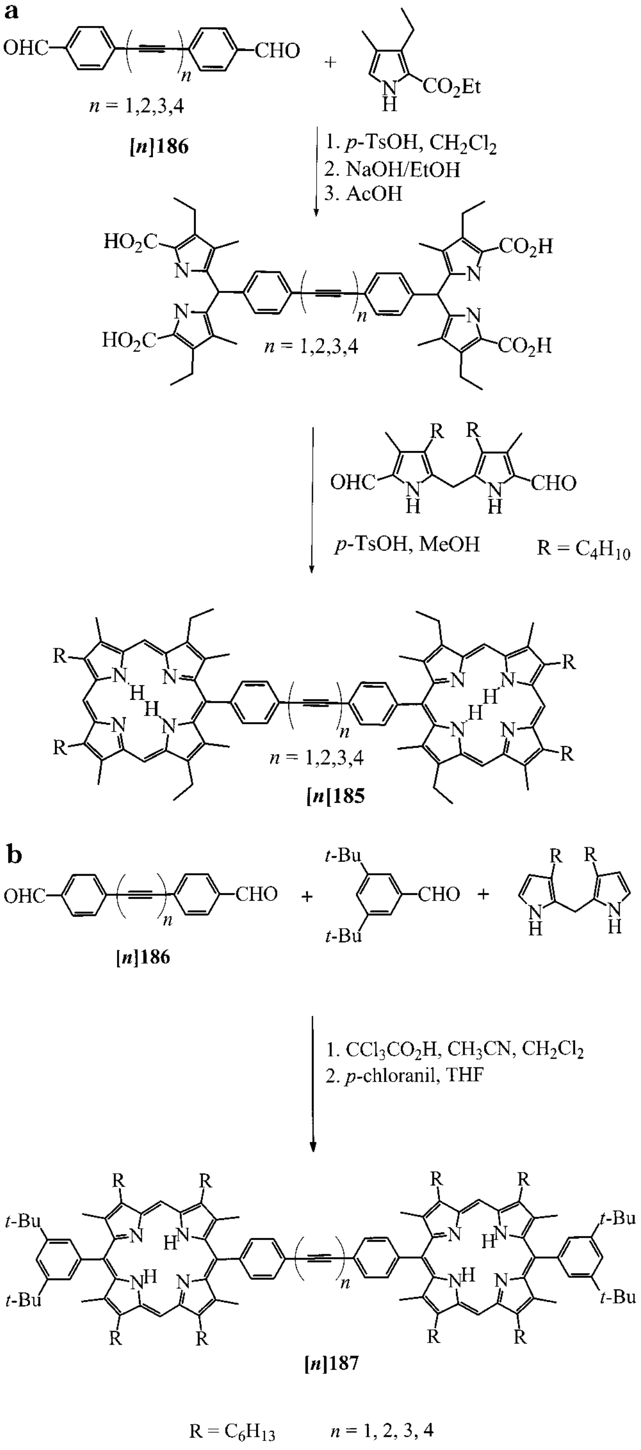
metal (cf. Part 2[19]). The rods **181** are versatile ligands because they can bind with a metal–pyridine-type interaction at one end and with a metal–isocyanide system at the other. The partial triple bond character of the carbon–metal bond on the isocyano terminus should enhance long-range electronic interactions.[364]

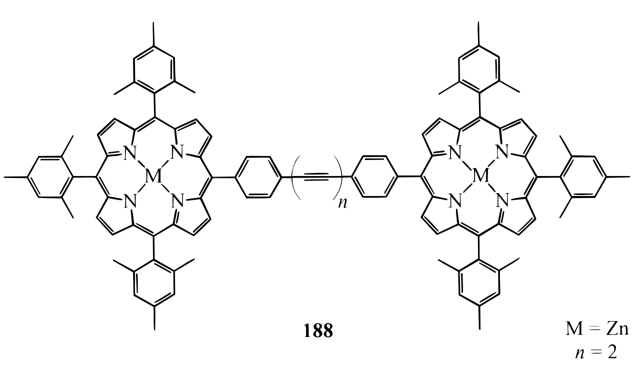
The terpyridyl-based systems **183** and **184** have been used to assemble mono- and dinuclear metal complexes in order to investigate their usefulness as bridging ligands.[349,350,365] For the bis-Ru(II) system, the insertion of the phenyl rings between the terpyridyl units and the ethyne modules leads to a dramatic decrease in the triplet lifetime, luminescence yields, and magnitude of the coupling between the metal centers.[349] However, the incorporation of the phenylene module into the center of the rod **184** has rather minute effects on the triplet lifetime and the luminescence quantum yields.[347] It appears, therefore, that the decreased energy-transfer capabilities of **183** are due to a poor orbital overlap between phenyl and pyridine modules. However, this is in stark contrast to the observation of very rapid energy transfer through a pure oligophenylene spacer (cf. section III.D.5.b).[366] Further investigations are needed to elucidate the effects governing the transfer rates. The central benzene ring in rod **184** offers an easily functionalizable site to modulate energetics and to attach secondary groups.[349]

g. Ethyne/Benzene/Porphyrin. *Synthesis.* Two types of rods were prepared based on porphyrin, phenylene, and ethyne modules. Murayama and Kawabata[367] originally synthesized dimeric arylporphyrins **[*n*]185** spaced by a series of ethyne linkers up to the octatetrayne from the corresponding dialdehydes **186** by a stepwise cyclization route in low yield (Scheme 90a). Kawabata et al.[368] obtained differently substituted diarylporphyrins **[*n*]187** with the same spacers in a one-pot reaction with improved yields (Scheme 90b). Lindsey's group[334] reported the ethyne- and butadiyne-bridged tetraarylporphyrins **188** using oxidative coupling of the terminal acetylene.

The second type of rod features alternating porphyrin, ethyne, and benzene modules and has attracted more attention. Lindsey's[334,369] synthesis is based on mild copper-free coupling conditions for

Scheme 90

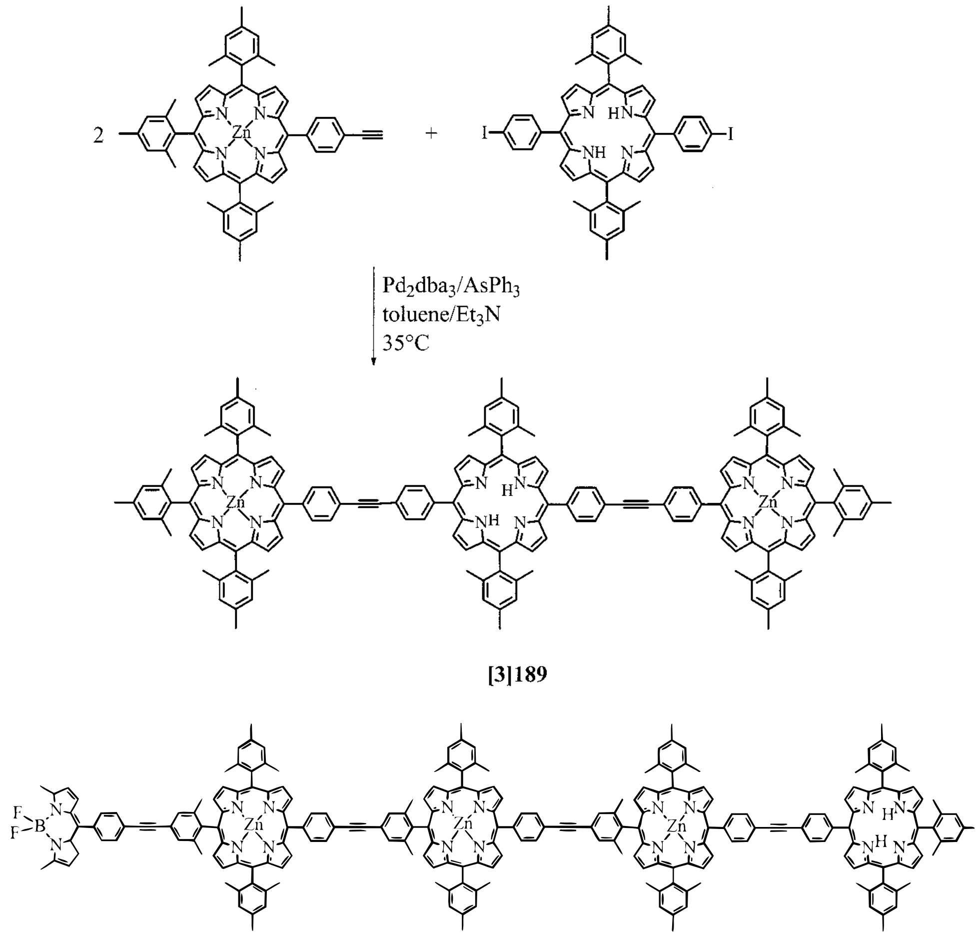




188

M = Zn
$n = 2$

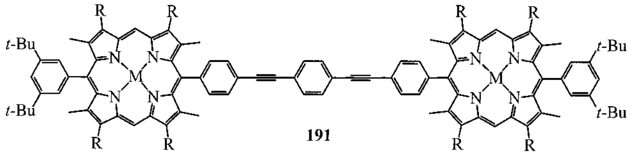
Scheme 91



[3]189

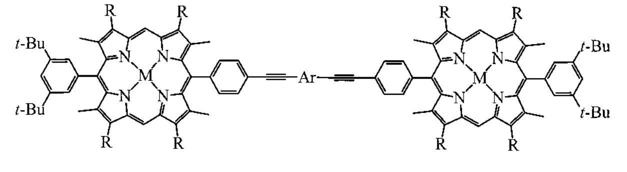
190

iodoarylporphyrins and terminal acetylenes. His group produced a number of porphyrin dimers **[2]189** and trimers **[3]189** bridged by tolan derivatives (Scheme 91) and a 90 Å long molecular photonic wire **190** endcapped by a fluorescent dye.[370] Kawabata et al.[371] coupled a phenylacetylene-substituted porphyrin, which was obtained from a double condensation reaction, with 1,4-diiodobenzene under Pd-catalysis to produce the bis(phenylethynyl)phenylene bridged diporphyrin **191**. Applying Lindsey's methodology[334] with minor modifications, Kajanus et al.[372] recently reported a series of bis(phenylethynyl)arylene-linked porphyrin dimers with 1,4-phenylene **192**, 1,4-naphthylene **193**, and 9,10-anthrylene **194** spacers for a systematic study of the influence of bridge energetics on the electron and energy transfer. Anderson's group[341] has synthesized a set of rods in which the porphyrin modules are connected directly to ethyne units using Pd-catalyzed cross-coupling of metalated ethynylporphyrins and arene dihalides. Thus, the porphyrin dimers are spaced by 1,4-diethynylbenzene (**195**) and 9,10-diethynylanthracene spacers (**196**).



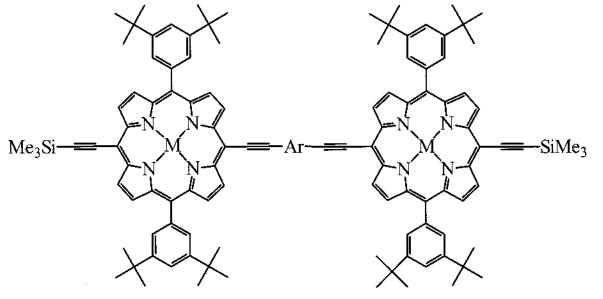
191

R = C$_6$H$_{13}$
M = H$_2$, Zn



192: Ar = 1,4-phenylene
193: Ar = 1,4-naphthylene
194: Ar = 9,10-anthrylene

R = C$_2$H$_5$
M = H$_2$, Zn



195: Ar = 1,4-phenylene
196: Ar = 9,10-anthrylene

M = Zn

Properties and Uses. The compounds described in this section are solids stable under normal atmospheric conditions. The oligoyne-bridged series **[*n*]187** is very soluble in polar organic solvents, but sensitivity to acid is suspected, especially with increasing length of the bridge. The systems containing alternating modules display good solubility in polar organic solvents and in toluene, except for the trimer **[3]189**.[334]

The oligoyne-bridged dimers **[*n*]187** with center-to-center distances between 16.9 and 26.6 Å were transformed into zinc/free-base hybrids to investigate intramolecular excitation energy transfer and into the zinc/ferric hybrids to measure photoinduced intramolecular electron transfer by picosecond time-resolved fluorescence spectroscopy.[371] Both transfer rates were found to be very fast and nearly independent of the distance. The energy transfer was shown to be more consistent with the Dexter mechanism.[352] The oligoyne spacers are less efficient than polyene spacers (Part 2[19]) in providing through-bond electronic coupling between the donor and the acceptor, presumably because of stronger bond length alternation, but enhance electronic interactions compared to oligophenyl bridges which suffer from twisting.[371]

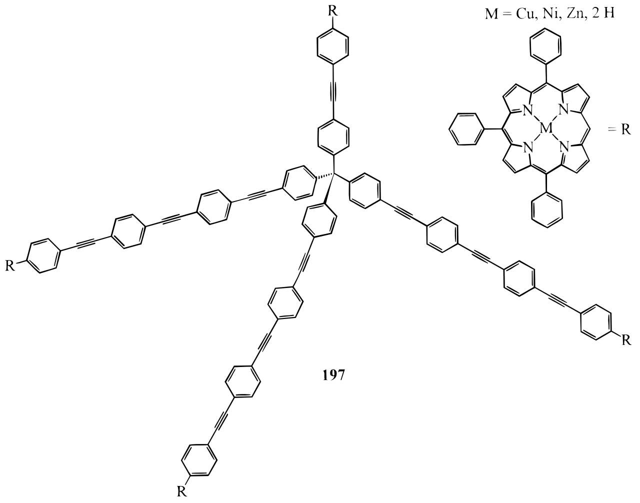
The rods with alternating modules were selectively metalated. Singlet energy transfer in the Zn/free-base hybrid of the bis(phenylethynyl)phenylene-bridged dimer **191** was investigated.[371,373] The fluorescence spectra show efficient singlet excitation energy transfer from the zinc porphyrin to the free-base porphyrin. Energy transfer seemed to proceed by the Dexter mechanism,[352] and the rate was quite rapid but slower than the rate through the diphenyloligoyne-bridged hybrid dimer of comparable length.

Strachan et al.[374,375] examined the energy transfer rates and efficiency across the Zn/free-base tolan-bridged dimers **[2]189** as a function of the substitution pattern on both the linker and the porphyrin rings. The rates and efficiencies decrease significantly when the rotation of the bridge is hindered by large substituents or when the benzene rings are perfluorinated, both leading to diminished orbital interaction between the linker and the porphyrins.[375] The substitution pattern on the porphyrins had an even greater impact on the transfer rate. Alkyl substituents in the β positions and fluorination of the porphyrins caused a 10−20-fold decrease in the rate.[374] The absorption spectra of these dimers are generally almost exactly a superposition of the constituents, indicating only weak interactions between the porphyrin units.

Comparison of the emission spectra of Anderson's group's[341] porphyrin dimers **196** spaced with diethynylnaphthalene and diethynylbenzene reveals a large red shift for the former, indicating stronger porphyrin−porphyrin conjugation. Furthermore, the addition of the naphthalene spacer increases the electronic coupling compared to the butadiyne-linked analogue (cf. section III.D.2.b), despite the longer distance. An explanation might be the anthrylene unit's ability to stabilize quinoidal/cumulenic resonance structures.[341] This behavior could lead to longer rods with strong third-order NLO behavior. In MO terms, the difference reflects the increased energetic proximity of the orbitals of the polycyclic spacer.

The photophysics of **190** has been investigated thoroughly.[370] The Q bands represent the sum of the individual components, while the porphyrin Soret band is split. As anticipated, the input dye absorbs most of the light (62%) under illumination at 485 nm. The integrated fluorescence quantum yield is 0.1, and 92% of the emission originate from the free-base porphyrin. This is about 7 times higher than could be expected from its absorption, pointing to efficient energy transfer across the diarylethyne linker.[370]

Rods comprised of porphyrin, benzene, and ethyne modules with lengths of up to 6.5 nm have been connected to a central methane unit by Mongin and Gossauer,[376,377] creating tripodaphyrins such as **197**, with edge lengths at the base of up 6.5 nm. The same group[378] synthesized a dendridic porphyrin hexamer with an external diameter of about 10 nm based on benzene centers substituted in 1,3,5 positions by porphyrin-endcapped oligophenylacetylene arms. Lindsey's group[379] has recently reported the synthesis of a molecular square **198** with four porphyrin units in the corners connected by tolan linkers. More complicated star-shaped light-harvesting arrays built around a central porphyrin unit connected on all *meso* carbons through biphenylacetylene spacers to four more porphyrin moieties were also assembled.[380] A smaller, more strained square system **199** with two porphyrins held in a face to face orientation by two bisphenylbutadiene rods was realized in the group of Sanders.[381]

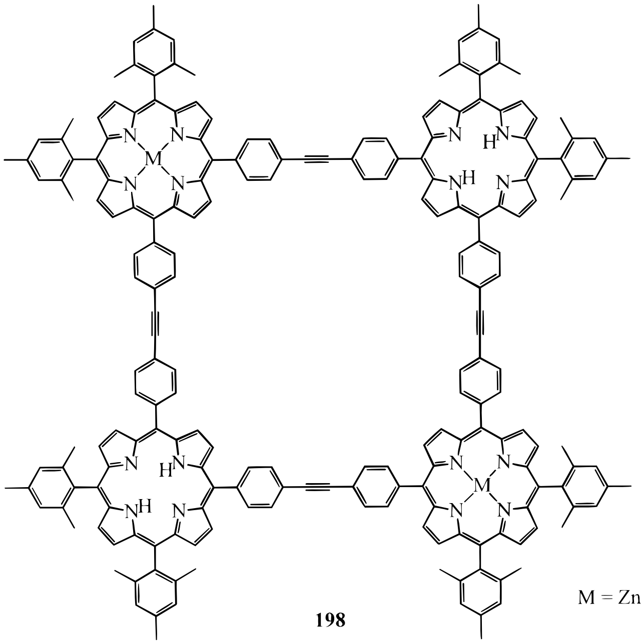


197

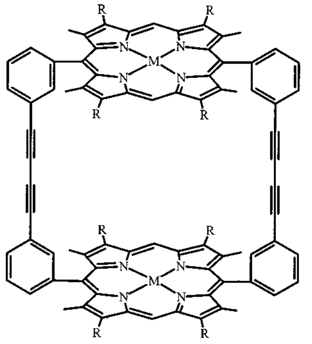
3. Bicyclo[1.1.1]pentane/Other Cages

a. Staffane/Bicyclo[2.2.2]octane. *Synthesis.* Michl's group[142] showed that one or two molecules of [1.1.1]propellane can be inserted into 1,4-diiodobicyclo[2.2.2]octane under UV irradiation to form two- or three-unit oligomers, depending on the length of the irradiation (Scheme 92). No further insertion into the terminal bicyclo[1.1.1]pentyl iodide bonds takes place. The iodo derivatives were converted to the parent hydrocarbons (e.g., **200**).[142]

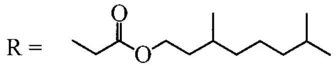
Properties and Uses. The bicyclo[1.1.1]pentane/bicyclo[2.2.2]octane co-oligomers are stable up to



198

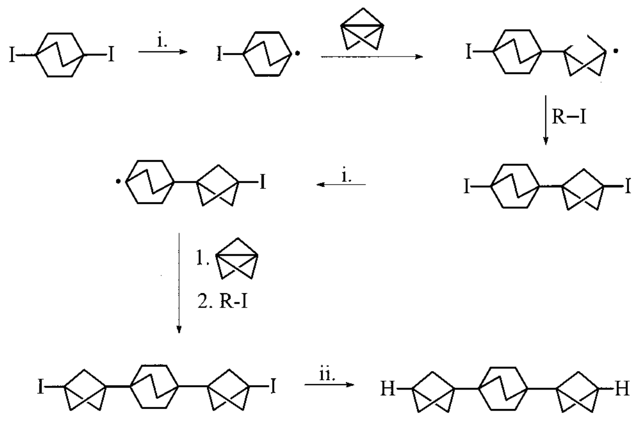


199



M = 2H, Zn

Scheme 92



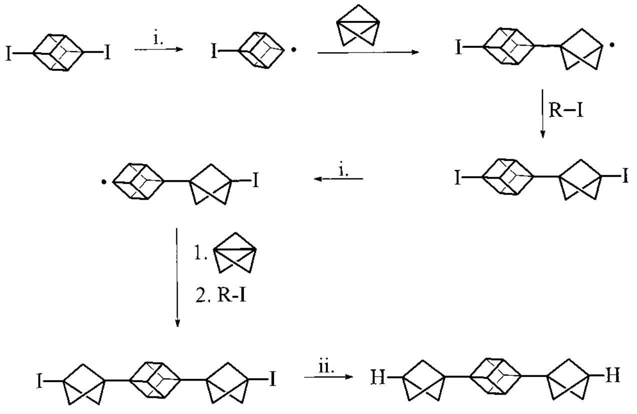
200

i. hν; ii. 1. BuLi 2. MeOH

280–300 °C and transparent in the UV at least down to 200 nm. The units behave quite independently as judged by the virtually unchanged IR bands and NMR shifts compared to the values for the homo-oligomers.[142]

b. Staffane/Cubane. *Synthesis.* The synthesis of mixed bicyclo[1.1.1]pentane/cubane and bicyclo[1.1.1]-pentane/cubane/bicyclo[1.1.1]pentane rods was accomplished in a similar fashion by irradiation of 1,4-diiodocubane in the presence of [1.1.1]propellane (Scheme 93).[142] Again, 1,4-bis(3-iodobicyclo[1.1.1]-pent-1-yl)cubane did not react further with [1.1.1]-propellane, and the products were reduced to the parent hydrocarbons (e.g., **201**).

Scheme 93



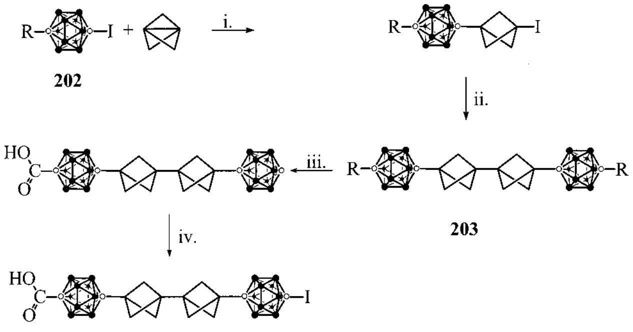
201

i. hν; ii. 1. BuLi 2. MeOH

Properties and Uses. The staffane/cubane rods melt below 200 °C and are thermally somewhat less stable than the parent homo-oligomers. A crystal structure of 1,4-bis(3-iodobicyclo[1.1.1]pent-1-yl)cubane confirmed its linearity and a very short exocyclic bridgehead-to-bridgehead distance (1.474 Å), anticipated from Bent's rules,[382] given the high s character of the exocyclic hybrid orbitals at the termini of the modules. The compounds are transparent in the UV and show the characteristic IR bands and NMR shifts of the individual modules.[142]

c. Staffane/Carborane. Photochemical insertion of [1.1.1]propellane into the C–I bond of monoiodinated, trihexylsilyl-protected 12-vertex carborane **202** followed by copper-mediated bridgehead-to-bridgehead coupling yielded the mixed carborane/staffane rod **203** (Scheme 94).[143]

Scheme 94



i. hν; ii. 1. *t*-BuLi, 2. CuI, PPh$_3$, 3. *p*-C$_6$H$_4$(NO$_2$)$_2$
iii. 1. Bu$_4$NF 2. BuLi 3. CO$_2$ 4. HCl; iv. 1. BuLi 2. I$_2$

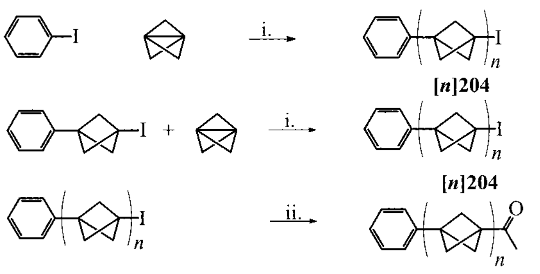
R = (C$_6$H$_{15}$)$_3$Si

Properties and Uses. Compound **203** is thermally quite stable and transparent in the UV. The trihexylsilyl groups provide for very good solubility in common organic solvents. After desilylation, the terminal C−H bonds provide sites for further functionalization and rod extension.

4. Benzene/Cage

a. Benzene/Staffane. *Synthesis.* Michl's group showed that [1.1.1]propellane (**2**) reacts with iodobenzene under irradiation to form 1-iodo-3-phenylbicyclo[1.1.1]pentane (**[1]204**), 3-iodo-3′-phenyl[2]staffane (**[2]204**), and a small amount of higher oligomers (Scheme 95).[137] The iodo derivatives reacted with biacetyl under irradiation in the presence of a tin hydride to yield the corresponding 3-acetyl-3′-phenyl[*n*]staffanes, which were oxidized to the 3-carboxylic acids and further to [*n*]staffane-3,3$^{(n-1)}$-dicarboxylic acids (section III.B.1). Compound (**[1]204**) can also be converted to higher co-oligomers by further irradiation in the presence of **2** in pentane. Oligomers with up to four bicyclo[1.1.1]pentane units have been isolated and characterized. Oxidative bridgehead-to-bridgehead coupling of the cuprate permitted the dimerization of (**[1]204**) to 3,3′-diphenyl-[2]staffane **205**, which can also be performed under Ni or Pd mediation (Scheme 96).[143]

Scheme 95



i. hν, pentane; ii. 1. biacetyl, benzene, 2. *n*-Bu$_3$SnH n = 1, 2, 3, 4

Scheme 96

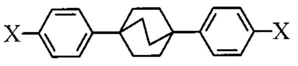
205

i. 1. *t*-BuLi, 2. CuI, 2 PPh$_3$, 3. *p*-C$_6$H$_4$(NO$_2$)$_2$

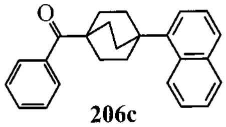
ii. 1. *t*-BuLi, 2. NiBr$_2$[P(*n*-Bu)$_3$]$_2$ or PdCl$_2$(PPh$_3$)$_2$

Properties and Uses. The compounds with an iodine substituent on the bridgehead decompose if irradiated or heated. The acetyl derivatives are chemically and thermally much more stable and can be functionalized further.[137]

b. Benzene/Bicyclo[2.2.2]octane. *Synthesis.* 1,4-Diphenylbicyclo[2.2.2]octane (**206a**), its *para*-substituted analogues **206b**, and the corresponding naphthalene/bicyclo[2.2.2]octane co-oligomers, such as **206c**, were synthesized by Zimmerman and McKelvey[383] in a multistep synthesis starting from aryl acetones. The bicyclic system was formed in an acid-catalyzed intramolecular aldol reaction in the key step. After chlorination of the free bridgehead position, a Friedel−Crafts reaction with benzene afforded the products. Chapman et al.[384] reported a similar pathway for the preparation of **206a**.



206a: X = H
206b: X = NO$_2$, CN

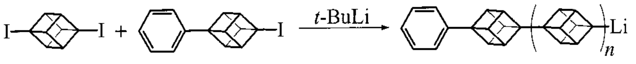


206c

Properties and Uses. The rods **206** were used in the investigation of electron and energy transfer across the saturated spacer. Reduction of one aromatic ring in the symmetrical systems produced a localized radical anion. It was concluded from EPR line widths that the rate of charge shift between the rings is less than 3×10^6 s^{-1} (the role of the counterion was not investigated). In the unsymmetrical species **206c**, singlet excitation energy is transferred from the naphthalene to the benzoyl chromophore by the Förster mechanism[385] and triplet energy is transferred in the opposite direction.[7,383]

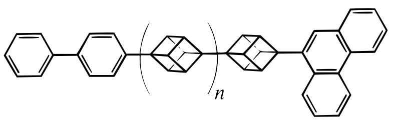
c. Benzene/Cubane. *Synthesis.* Symmetric and asymmetric arylated [*n*]oligocubyls have been prepared[164] by reaction of 1,4-diiodocubane and 1-iodo-4-phenylcubane with *t*-BuLi and subsequent trapping of the resulting lithiocubane **[*n*]207a** with an electrophile (Scheme 97).[169] Applying this chemistry, Paulson et al.[386] synthesized a series of [*n*]oligocubyls (n = 1, 2, 3) **[3]207b** with a biphenyl unit at one terminus and a naphthyl unit at the other in order to investigate the intramolecular electron transfer between the two aryl substituents through an oligocubyl rod. Two *n*-hexyl substituents were introduced on one of the cubane units in the trimeric rod **[3]207c** to improve the solubility of the compound.

Scheme 97

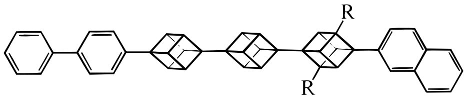


[*n*]207a

n = 1,2,3



[*n*]207b n = 0, 1, 2



[3]207c

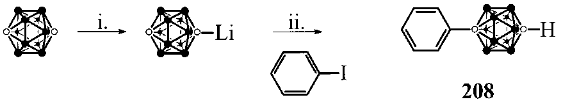
R = *n*-hexyl

Properties and Uses. The cubane spacers enhance the rate of electron transfer by a factor of 10 compared to spacers based on cyclohexane.[386] Apparently, through-bond coupling provides the main interaction pathways between donor and acceptor. The rate of electron transfer decreases exponentially with increasing distance at a rate similar to those observed in other saturated spacers.

Interestingly, the absorption spectra of the radical anions of biphenyl and naphthalene are more perturbed by cubyl substitution than by ordinary alkyl substitution, suggesting a stronger hyperconjugative interaction.[386]

d. Benzene/Carboranes. *Synthesis.* Zakharkin and Kovredov obtained the C-arylated 12-vertex *p*-carborane **208** by Pd-catalyzed coupling (Scheme 98).[387] Even though various disubstituted and trisubstituted analogues and cyclic structures are known,[278,388] longer linear C-phenylated carborane oligomers have not been reported. Using Pd-free coupling conditions, Wade's group recently reported the synthesis of a series of C-phenyl-*p*-carboranes and symmetric and unsymmetric C,C′-diphenyl-*p*-carboranes **209** with the phenyl groups substituted in the para position by various electron-withdrawing (NO_2, OH, CF_3) and electron-releasing (NMe_2, Me, NH_2) groups (Scheme 99).[389] In addition, the Michl group[390] used Pd-catalyzed coupling to prepare a B-phenylated monocarba-*closo*-dodecacarborane anion **210** (Scheme 100).

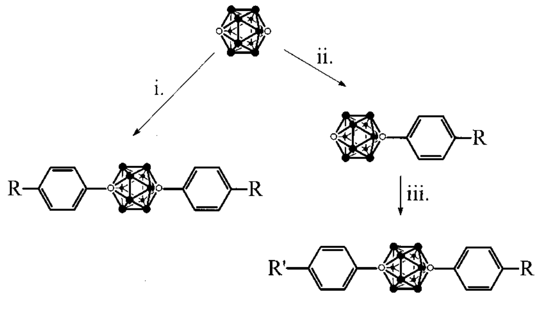
Scheme 98



208

i. 1 eq. *n*-BuLi, ether; ii. 1. CuCl/THF 2. NMP, $Pd(PPh_3)_2Cl_2$

Scheme 99

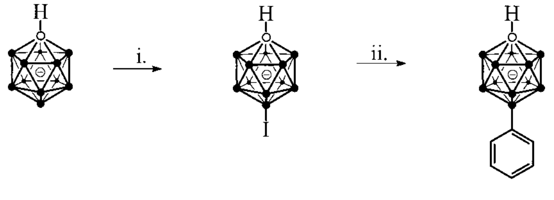


209

i. 1. 2 eq BuLi, CuCl, $(MeOCH_2)_2$, 2. R-Ph-I, C_5H_5N
ii. 1. 1 eq BuLi, CuCl, $(MeOCH_2)_2$ 2. R-Ph-I, C_5H_5N
iii. 1. 1 eq BuLi, CuCl, $(MeOCH_2)_2$ 2. R'-Ph-I, C_5H_5N

R = $-NO_2$, $-NH_2$, -OMe, -OH
R' = $-NO_2$, $-NH_2$, -OMe, -OH

Scheme 100

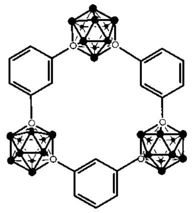


i. I_2, CH_3COOH; ii. PhMgI, [Pd]

210

Properties and Uses. Phenylcarboranes are chemically and physically extremely robust. The melting points of the parent phenylcarborane and diphenylcarborane are over 200 °C.[387] Their solubility in common organic solvents is high. From their ^{13}C NMR spectra, it appears that the aryl group transfers electron density to the antipodal carbon atom in the *p*-carborane cage.[389] The UV−vis spectra reveal substantial shifts of the arene ^1L_a transition to longer wavelength, indicating that the *p*-carboranyl group has a significant influence on the π-energy levels of the aryl groups. Furthermore, in the case of *para* substitution on the aryl groups, especially in examples with push−pull patterns, an interaction between the two aryl chromophores through the carborane bridge is observed.[389] This electronic connection between terminal π-systems was suggested to be similar to that reported in [*n*]staffanes and distinct from resonance interaction through π-electron bridges.[389]

Phenylcarboranes were used in the Wade group as building blocks for macrocyles such as **211**.[391]



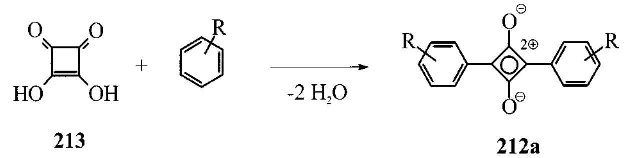
211

5. Benzene/Other Planar Module

a. Squaraines. As noted in section II.B.1.b, one of the ways in which the highly reactive 4 π-electron antiaromatic cyclobutadiene can be stabilized is push−pull substitution that removes its biradicaloid character. One strongly perturbed derivative is the dianion of squaric acid, which can be viewed as a $C_4H_4^{2+}$ ring carrying four $-O^-$ substituents.[392] When the negatively charged $-O^-$ donors in positions 1 and 3 are replaced by uncharged π-electron-donating substituents, overall electroneutral rods result.[393]

Synthesis. 1,3-Disubstituted squaric acid derivatives **212a** (squaraines) have been known for over 30 years.[394] They are usually prepared by a condensation of squaric acid (**213**) with two equivalents of electron-rich aromatic compounds and azeotropic water removal (Scheme 101). Common substrates are *N*,*N*-disubstituted anilines,[395−398] stilbenes,[399] azulenes,[400] pyrroles,[394,401] thiophenes,[402] 2-methylbenzothiazolium salts,[403] 2-methylindolinium salts,[404] and 2-methylquinolinium salts.[405] Unsymmetrical squaraines **212b** are also accessible, as shown in Scheme 102.[406−409] For our purposes, aryl- and azulyl-substituted squaraines are modules for axial rods while other squaraines (e.g., bis(benzothiazolylidene)squa-

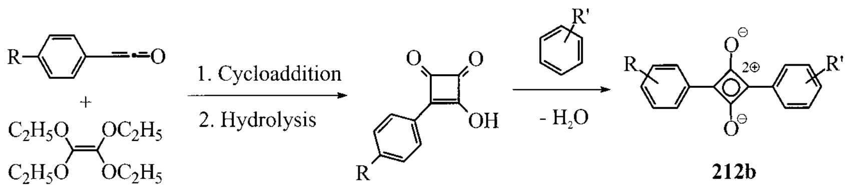
Scheme 101



213

212a

Scheme 102



212b

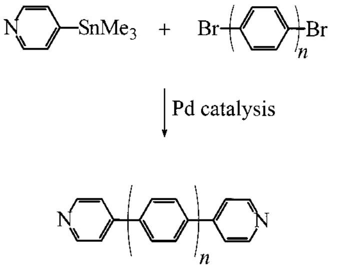
raine) are modules for zigzag rods (cf. Part 2[19]). Hydrogen-donor groups on adjacent benzene rings in the *ortho* position form strong hydrogen bonds with the oxygens of the squaraine group,[410] which leads to a ladder-type structure, enhanced conjugation, and increased rod rigidity. Aza-crown-appended squaraines have been prepared for sensor applications.[410]

Properties and Uses. The parent squaric acid (**213**) decomposes above 293 °C.[411] The UV–vis absorption of **212** is unusual with very high extinction coefficients (log $\epsilon > 5$) and a very long wavelength of absorption ($\lambda > 600$ nm).[395,411] The compounds exhibit large photoconductivity[395] and optical nonlinearity.[412,413] Squaraine molecules interact strongly with each other in the solid state and in solution. The aggregates are nonfluorescent, but if the chromophores are separated, they fluoresce strongly.[397,398]

b. Benzene/Pyridine. In most of these rods, the pyridine ligands are in terminal positions and are used for metal complexation.

Synthesis. 1,4-Bis(4-pyridyl)benzene (**[1]214**), the shortest member of the phenyl-bridged 4-pyridyl family, was synthesized by Ward's group.[414] Kim and Lieber[415] prepared the next higher homologue (**[2]214**) by Pd-catalyzed coupling of 4-(trimethylstannyl)pyridine with 4,4′-dibromobiphenyl (Scheme 103). A similar rod **215** with two bidentate 2,2′-bipyridyl complexation sites connected by a benzene module was prepared by Lehn's group.[416] Stille coupling conditions with $Pd(PPh_3)_4$ were used for the cross-coupling step (Scheme 104).

Scheme 103

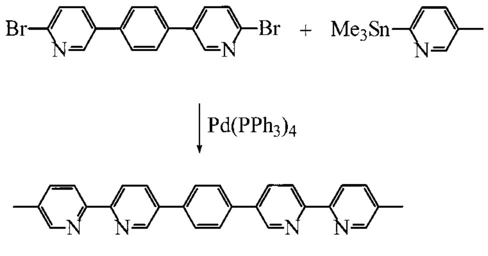


[n]214

n = 1, 2

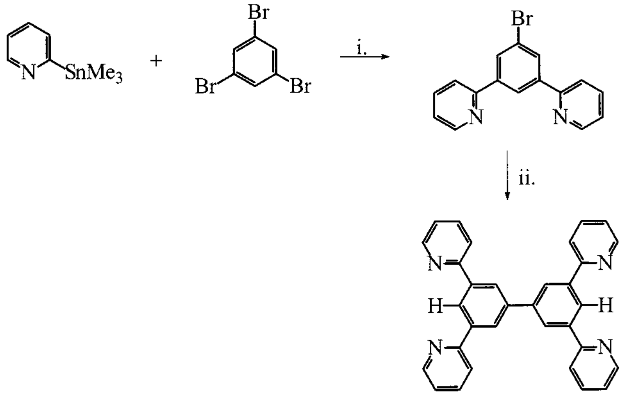
Pyridine/benzene rods with biscyclometalating binding sites were reported by Sauvage and collaborators,[417,418] who prepared 3,3′,5,5′-tetra(2-pyridyl)biphenyl (**216**, Scheme 105). This group[419,420] also extended this rod by incorporating one, two, or three phenylene spacers (**[*n*]217**, *n* = 1, 2, 3) using aromatic cross-coupling reactions between the diboronic acid derivatives of the respective phenylene bridge and the brominated bipyridylbenzene **218** or its ruthenium complex yielding the assembled dinuclear complex directly (Scheme 106).[421]

Scheme 104



215

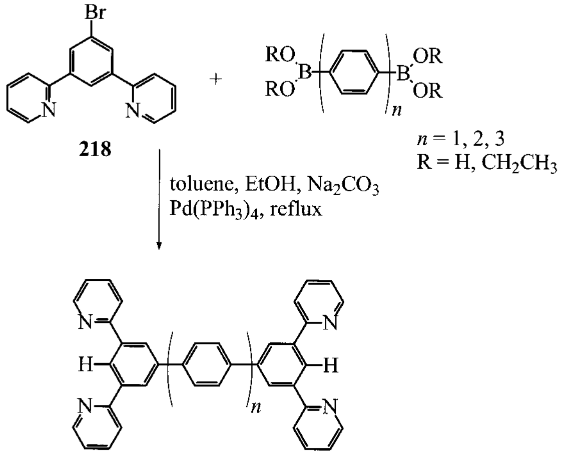
Scheme 105



216

i. THF, reflux, $PdCl_2(PPh_3)_2$
ii. DMF, $Ni(PPh_3)_4$, 50 °C

Scheme 106

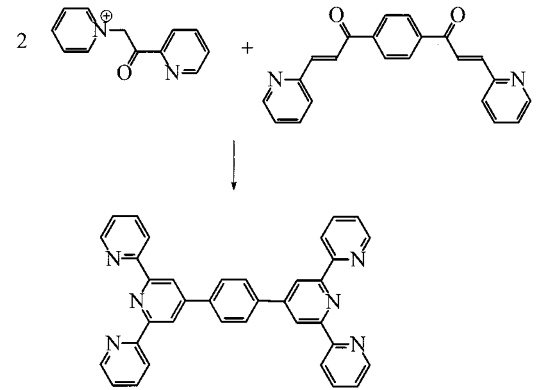


[n]217

n = 1, 2, 3

Two rods based on *p*-phenylene carrying terpyridyl ligands on both ends have been reported. Kröhnke[422] described the synthesis of **[1]219** (Scheme 107).

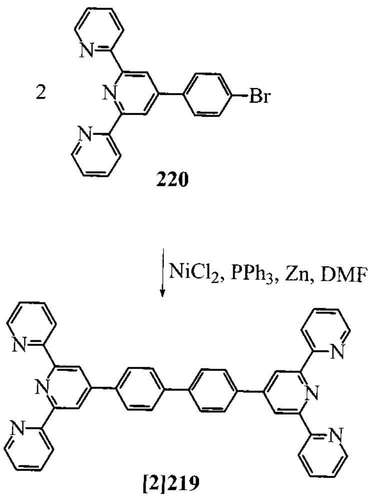
Scheme 107



[1]219

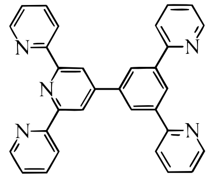
Sauvage's group synthesized the homologous compound **[2]219** with two benzene rings via Ni(0)-promoted homocoupling of 4′-*p*-bromophenyl-2,2′:6′,2″-terpyridyl (**220**) (Scheme 108).[423] The asymmetric

Scheme 108



220

[2]219



221

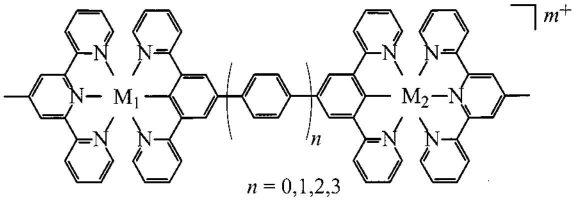
rod **221** with an *o*-terpyridyl unit directly connected to 3,5-di(2-pyridyl)benzene was recently reported as well.[365]

Properties and Uses. All these compounds are chemically and physically very stable. They can be dissolved easily in aqueous acids and in polar organic solvents.

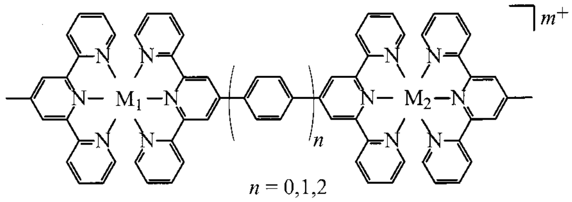
Doubly monodentate ligands, such as **214**, have been used in the preparation of mononuclear and binuclear Mo and Ru complexes to study long-range electron-transfer reactions.[250] The two metal atoms that are coordinated to the terminal nitrogens are separated by ~11–20 Å depending on the number of phenylene spacers. The UV–vis spectra of the binuclear Ru complexes show π–π* and metal-to-ligand charge-transfer (MLCT) absorptions. The addition of one phenylene spacer results in a 36 nm blue shift in the dπ–π* MLCT transition and the addition of the second one in an additional 18 nm shift.[415] These shifts can be explained by a decrease in the splitting of the π* pyridine energy levels caused by the electronic coupling between the terminal pyridines as the distance between the centers increases. Cyclic voltammograms revealed a small stabilization of the mixed-valence state compared to the fully oxidized and reduced species. However, the mixed-valence ion does not exhibit an intervalence peak in the UV–vis/NIR.[415] Overall, the data show that the electronic interaction between the metal centers through the aromatic spacers is quite weak.

The diastereomeric diruthenium complexes of the doubly bidentate bipyridyl–phenylene rod **215** were prepared similarly, but no electronic communication between the metal centers was observed in the electronic spectra or the cyclic voltammograms.[416]

Among the biscyclometalated species, diosmium and diruthenium complexes **222a** and **222b** were prepared by the Sauvage group from 3,3′,5,5′-tetra-(2-pyridyl)biphenyl (**216**) and **[*n*]217** in which the metals are attached to the 4 and 4′ positions of biphenyl and stabilized by the surrounding pyridine units.[417,418,420,421] The interaction between metal centers has been investigated. Strong electronic coupling is observed in the mixed-valence state [Ru(III)/Ru(II) or Os(III)/Os(II)] up to metal–metal distances of 20 Å and has been attributed to the strong electron-donating character of the bridge.[366] Besides an intense MLCT band in the UV–vis, the NIR spectrum reveals an intense intervalence transfer (IT) band. The intensity decreases with increasing length of the bridge but remains high even in the longest rod. The narrow bandwidth suggests significant delocalization in the mixed-valence species. These are most stable when the ligand is shortest and less so when it is longer.[417]



[*n*]222a: $M_1 = M_2 = Os$
[*n*]222b: $M_1 = M_2 = Ru$
[*n*]222c: $M_1 = Os$, $M_2 = Ru$



[*n*]223a: $M_1 = M_2 = Ru(II)$
[*n*]223b: $M_1 = Ru(II)$, $M_2 = Ru(III)$
[*n*]223c: $M_1 = Os$, $M_2 = Ru$

In the mixed-metal rod **222c** [Os(II)/Ru(II)], no energy transfer was observable at room temperature.[424] At low temperatures, it occurs by the Dexter[352] mechanism. The reduced energy transfer rate was attributed to a longer transfer pathway since the MLCT excited states are directed toward the terminal ligands.[418]

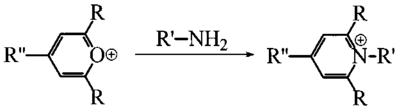
Both the dinuclear Ru(II)/Ru(II) complexes **[*n*]223a** and the mixed-valence species **[*n*]223b** Ru(II)/Ru(III) were prepared for the complete tridentate terpyridyl-based series **[*n*]219** with metal-to-metal distances of 7–20 Å.[366] Electrochemical studies show that in the Ru(II)/Ru(II) species, the metal centers behave as electrochemically isolated subunits. However, in the mixed-valence species, significant electronic coupling is observed as evidenced by a strong MLCT band and a pronounced IT band in the NIR. The coupling is less pronounced compared to the analogous biscyclometalated series **222**, but the extent of the coupling decreases only slightly with increasing length of the bridge.[423] Barigelletti et al.[425] used these rods to assemble the mixed-metal complexes (**[*n*]223c**, $n = 0, 1, 2$) and investigated both their luminescence and electrochemical properties. The substituents on the end-capping terpyridyl units were used for tuning these properties. Fast energy transfer was observed and attributed to the Dexter[352] mechanism.[426]

From these results, it was concluded that the phenylene spacers are very efficient transmitters of intermetal electronic communication. However, the orientation of the MLCT excited states involved in the transfer process has to be taken into account for the prediction of the rate of energy transfer. For further details we refer to a recent microreview.[366]

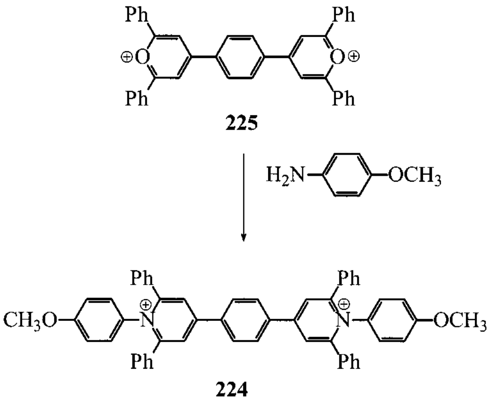
c. Benzene/Pyridinium. Poly(pyridinium salt)s are a well-known class of rigid-rod polymers which attract interest as potential ionic conductors, ion- and electron-exchange membranes,[427] and semiconducting materials.[428] However, reports of well-defined oligomers are comparatively rare.

Synthesis. The main route to the synthesis of phenyl-substituted pyridinium salts is the reaction of aromatic amines with pyrylium salts,[429] pyrones,[430] or dehydroacetic acid.[431] This ring transformation reaction usually proceeds in high yields if the pyrylium salt is sterically hindered in positions 2 and 6 (Scheme 109).[429,432,433] The reaction resulted in the formation of an oligomeric mixture when 2,2′,6,6′-tetraphenyl-4,4′-bis(pyrylium perchlorate) was treated with aromatic diamines in an attempt to obtain polymers.[434,435] However, no individual rods were isolated and characterized. More recently, Harris et al.[436] obtained oligomeric dipyridinium salts such as **224** in model studies for polymerizations (Scheme 110). Similarly, Sun and co-workers[437,438] prepared a series of diamino-substituted pyridinium/benzene rods as monomeric units when the aromatic diamine was used in large excess. Pyrylium salts such as **225** used as precursors are accessible from dehydroacetic acid or from aromatic aldehydes and acetophenone[436,439,440] (Scheme 111).

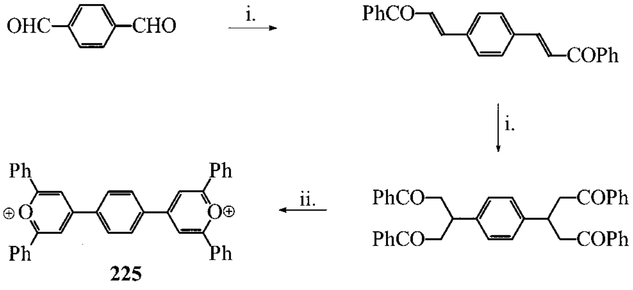
Scheme 109



Scheme 110



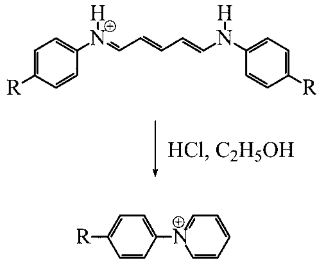
Scheme 111



i. 2 CH_3COPh; ii. tetraphosphoric acid, 70 °C or $Ph_3C^+BF_4^-$/HOAc

Another pathway is the ring closure of dianilide hydrochlorides in acidic medium (Scheme 112).[441]

Scheme 112

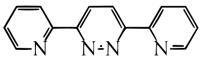


Magonov et al.[442] thus prepared a series of substituted phenyl and biphenyl pyridinium salts. However, the rods obtained by this method were short, and no method for increasing the length further was described.

Properties and Uses. Investigation of the polymers has received much more attention than that of the oligomers described above. The oligomers are generally thermally and chemically very stable and dissolve well in organic and aqueous solvents. They show one-dimensional ionic conductivity.[436] NMR studies show that the N-aryl group is orthogonal to the pyridinium ring if it is substituted in positions 2 and 6, and conjugation is therefore minimal.[438]

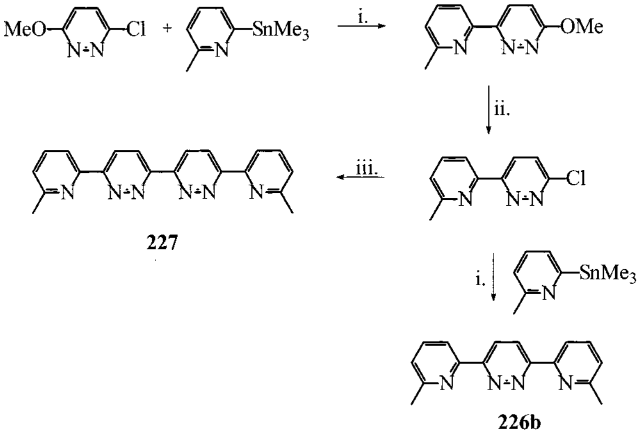
d. Benzene/Azabenzenes. These rods belong to the general class of aza analogues of oligophenyls and many are known.

Synthesis. 3,6-Bis(2-pyridyl)pyrazine (**226a**) was first synthesized by Butte and Case.[443] The methyl-substituted derivative **226b** and the corresponding bispyridylbipyrazines **227** were synthesized by Lehn and co-workers (Scheme 113)[444] and used in the self-assembly of noncovalent architectures. The preparation of the bispyridine-substituted tetrazine ligand **228** was accomplished by Lewis and Johnson,[445] and the analogous bispyrimidine-substituted tetrazine **229** was reported by Kaim and Fees.[446]

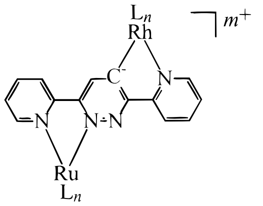


226a

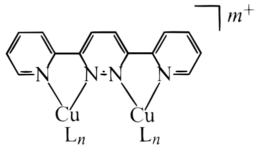
Scheme 113



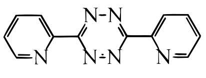
i. $Pd(PPh_3)_4$/toluene; ii. 1. HBr/CH_3COOH, reflux, 2. $POCl_3$
iii. $n$$Bu_4NI$, Zn, $[NiBr_2(PPh_3)_2]$/DMF



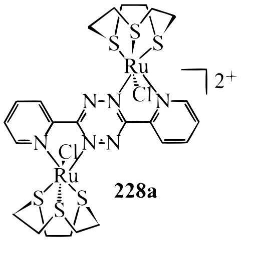
226c



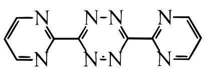
226d



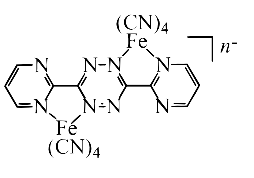
228



228a



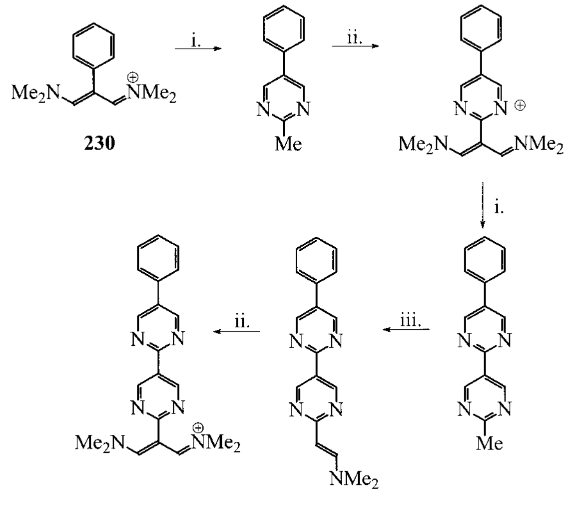
229



229a

An important advance in the synthesis of aza analogues of oligophenyls has been accomplished by Gompper et al.[447] Condensation of vinamidinium salts (**230**) with amidines (**231**) (Scheme 114) or *N*,*N*,*N*′-tris(trimethylsilyl)amidines (**232**) (Scheme 115) has yielded terminally functionalized rods with up to 12 aromatic rings arranged in an unsymmetrical or symmetrical fashion (Chart 2). The scope of this “pyrimidine method” is very general, and many functional groups are tolerated. Terminal amino groups were reacted further with 2,4,6-triphenylpyrylium tetrafluoroborate to yield the corresponding bispyridinium salts such as **233** with two additional aromatic rings (Scheme 116).[447]

Scheme 114



i. $MeC(=N^+H_2)NH_2$ (**231**), pyridine, heat; ii. 1. DMF-$(COCl)_2$, heat 2. H_2O, $NaClO_4$; iii. t-$BuOCH(NMe_2)_2$

Scheme 115

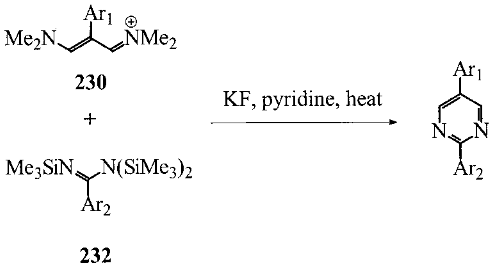
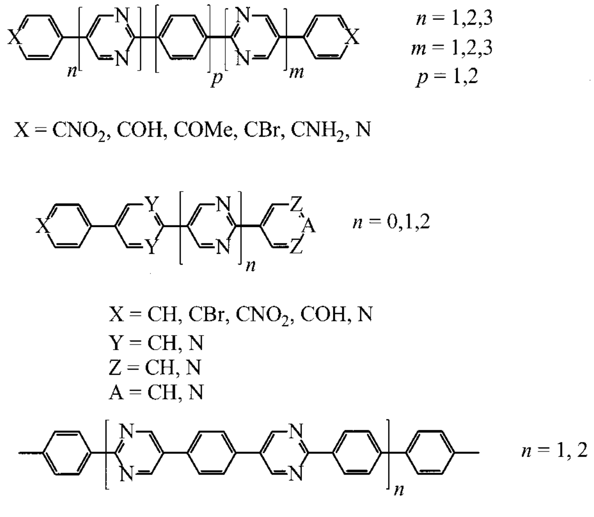


Chart 2



$n = 1,2,3$
$m = 1,2,3$
$p = 1,2$

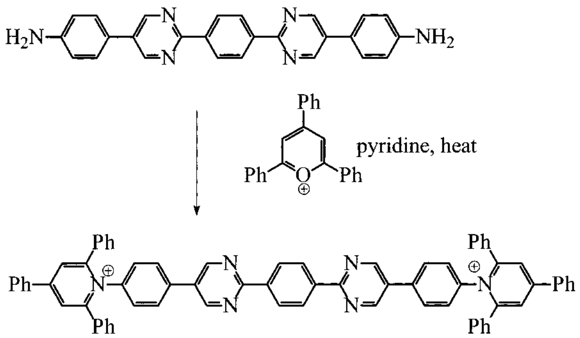
X = CNO_2, COH, COMe, CBr, CNH_2, N

$n = 0,1,2$

X = CH, CBr, CNO_2, COH, N
Y = CH, N
Z = CH, N
A = CH, N

$n = 1, 2$

Scheme 116



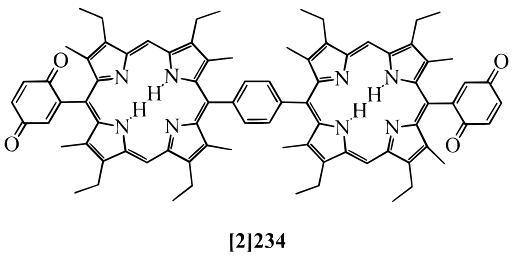
233

Properties and Uses. Pyridylpyrazines are chemically and physically very stable compounds with high melting points. They can be used both to bind two metals on the same side through the N−N chelating moieties and to bind two metals on opposite sides by means of N−N and C^-−N chelating moieties after deprotonation. They have been investigated as chromophoric ligands in Ru,[448] Ir,[449] Cu,[450] and other transition metal complexes. Mixed-metal complexes **226c** with Ru(II) on the N−N and Rh(III) on the C^-−N coordination sites were reported by the Balzani group.[451] The electrochemical investigation of the Cu pyridylpyrazine complex **226d** revealed two sets of reversible waves with seven one-electron processes. The complexed metal significantly lowers the reduction potential of the ligand. The bimetallic Ru[452] complex **228a** and the cyanodiiron[453] complex **229a** have recently been prepared, and both display very strong coupling between the metal centers in the mixed valence species.

Oligopyrimidylenes (Chart 2) are thermally stable and have melting points over 200 °C, in many cases over 300 °C.[447] Their solubility depends on the length, but even the longest rods are very soluble at least in strong acids. UV spectra are similar to those of oligophenyls, and deviations are attributed primarily to different degrees of coplanarity.[447] The compounds display strong blue fluorescence both in solution and in the solid state, and its wavelength can be tuned by changing the number and position of the nitrogen atoms in the rod. The heterocycles are easier to reduce than oligophenyls. They show NLO activity when donor−acceptor substituted.[447]

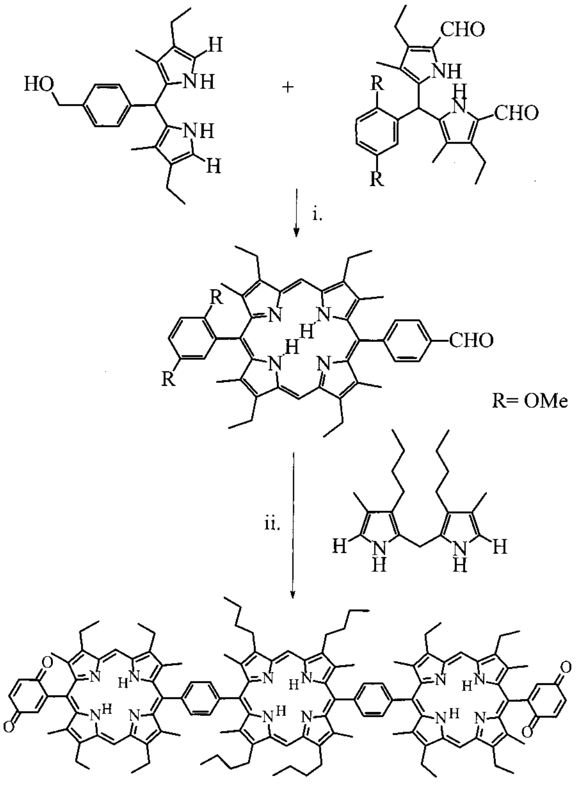
Lehn and his group have assembled pseudorotaxane racks and metal-complexed ladder structures from pyrazine-pyridine rods.[454]

e. Benzene/Porphyrin. *Synthesis.* The group of Sessler produced singly[455,456] and doubly[457] quinone-substituted porphyrin dimers **[2]234** directly linked through a 1,4-phenylene spacer as model systems for natural photosynthesis. These arrays hold the key biomimetic components, a metalloporphyrin, a free-base porphyrin, and a quinone unit, in a well-defined spatial arrangement. A similar trimeric porphyrin **[3]234** has also been prepared by the same group (Scheme 117).[458]



[2]234

Scheme 117



[3]234

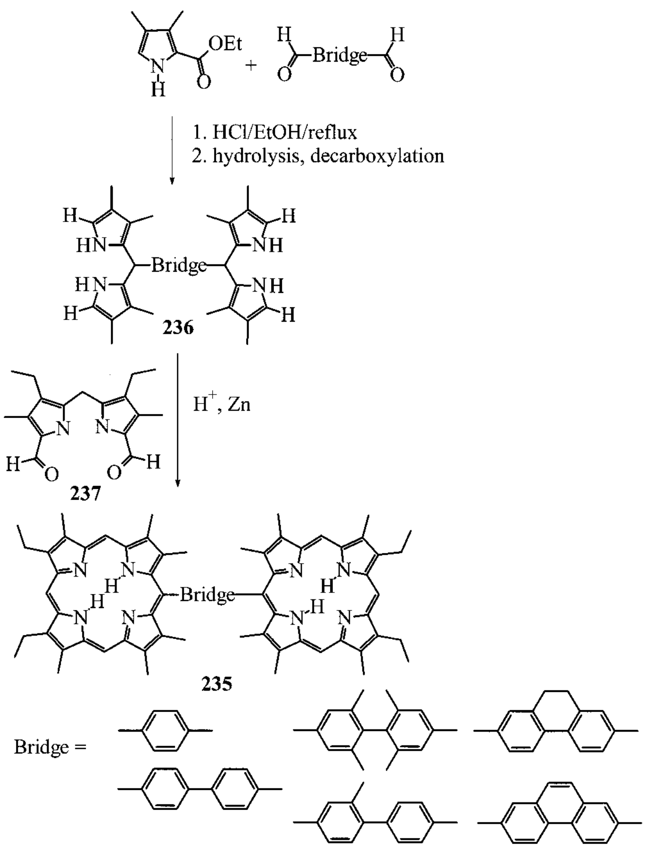
i. 1. $HClO_4$, THF/CH_3OH, rt, 2. *o*-chloranil, 3. Pd/C, CH_2Cl_2
ii. 1. TFA, CH_2Cl_2, rt, 2. *o*-chloranil, 3. BI_3, 0 °C, 3. DDQ

The McLendon group[264d] synthesized a series of dimeric porphyrins **235** connected through differently 2-substituted biphenyl units as a model system mimicking intramolecular electron transfer in proteins (Scheme 118). The critical step was the Zn-mediated coupling of **236** with 3,3′-diethyl-4,4′-dimethyl-5,5′-diformyl-2,2′-dipyrromethane (**237**), followed by air oxidation.

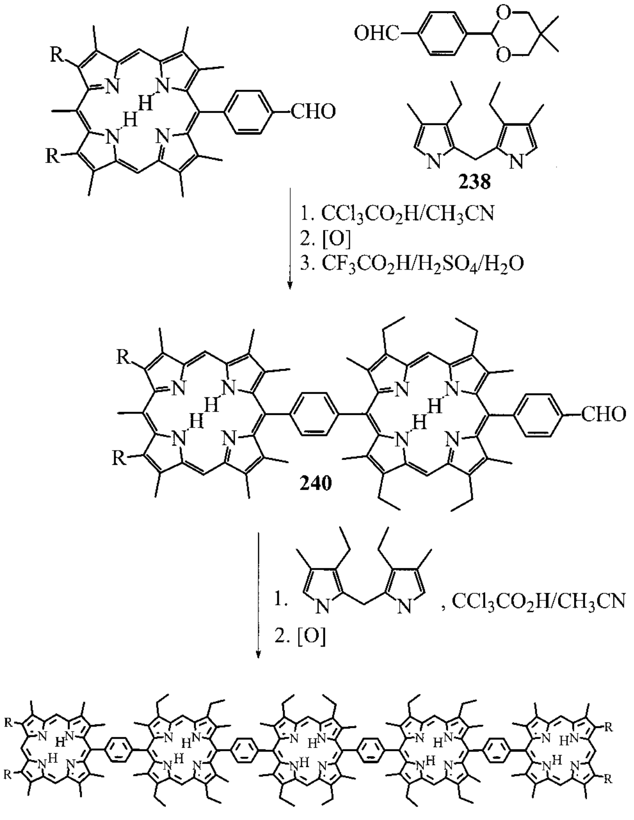
Maruyama's group[459] reported a generally applicable method for the preparation of conformationally constrained oligomeric porphyrins sequentially linked by a 1,4-phenylene or 4,4′-biphenyl unit. By condensation of 5-(4-formyl)dihexylhexamethylporphyrin and bis(3-ethyl-4-methyl-2-pyrrolyl)methane **238** and subsequent oxidation, they synthesized a trimeric phenylene-linked porphyrin array. Pentameric porphyrins **239** bridged by 1,4-phenylene were obtained when formyl-substituted dimeric porphyrins **240** were subjected to these conditions (Scheme 119). The compounds were proposed as models for photosynthetic charge separation.

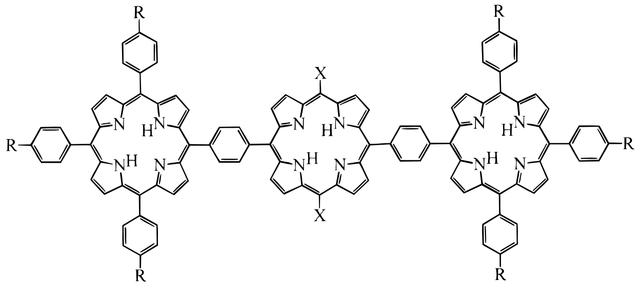
Müllen's group[460] showed that alkyl- and aryl-substituted dipyrromethanes can be converted into the 1,4-phenylene-bridged trisporphyrin **241** in one

Scheme 118



Scheme 119

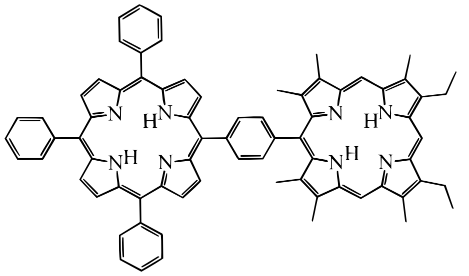




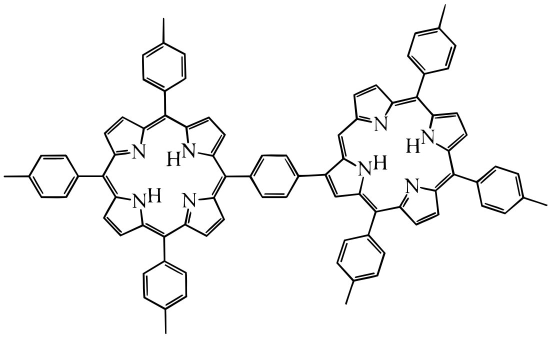
241

$R = C_3H_7$

$X = (CH_2)_4CH_3$, p-$C_6H_4CH_3$



242



243

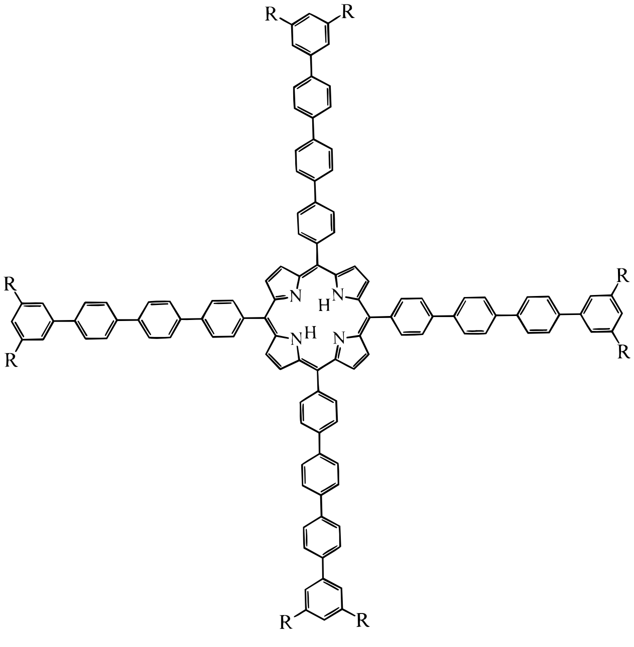
step by a [2+2] cyclization with a monoformylated tetraarylporphyrin. An unsymmetrical 1,4-phenylene-bridged porphyrin dimer **242** with meso substitution on one ring and *β* substitution on the other was synthesized by Kadish et al.[461] Suzuki-type cross-coupling was utilized by Zhou and Chan[462] in their synthesis of a *β*-to-meso porphyrin dimer **243** linked by a 1,4-phenylene unit.

Properties and Uses. All rods mentioned above are very stable under atmospheric conditions. The photophysical data for **[2]234** and **[3]234** have been collected.[456] The Soret band splitting in the UV increases with the number of porphyrin units. The higher oligomers have a lower quantum yield of fluorescence. Excitation energy is transferred rapidly from one pigment to another prior to trapping at the redox-active site. In McLendon's group's study,[264d] the biphenyl spacers were modified to systematically investigate the electron-transfer rate dependence on the overall porphyrin−porphyrin dihedral angle. The maximum transfer rate is highest at $\theta = 0°$ and 90° and lowest at 45°.[463]

The trimers **241** reported by Müllen's group[460] were metalated, and the interaction of the porphyrin rings was examined by electronic absorption spectroscopy, revealing a weak coupling between the coplanar chromophores via the phenylene spacers which are twisted out of the porphyrin plane by 65°. In addition, cyclic voltammetry showed that the Zn_3 trimer can be charged reversibly to the dodecaanion, with each unit carrying four charges. Apparently, the phenylene spacers effectively decouple the individual porphyrin units, thus increasing the charge storage capacity.[460]

The electrochemical and photophysical investigation of the heterodimer **242** showed very weak electronic interactions between the rings in the neutral, oxidized and reduced forms.[461] However, in the excited state emission and excitation spectra demonstrate a very efficient energy transfer process between the subunits of both free-base and metalated systems whose mechanism is in agreement with the Förster[385] theory.

A cross-shaped structure **244** was assembled by Mikami et al.[464] by substitution of a central porphyrin ring at the *meso* positions with four oligophenyl arms.

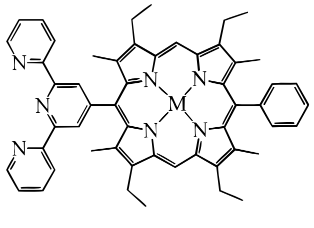


244

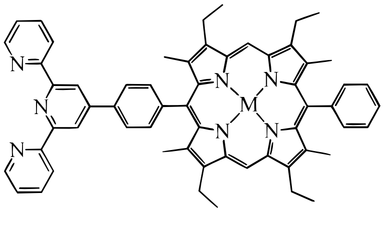
R = *t*-butyl

A crystal structure shows the molecule to be ~42 Å across.

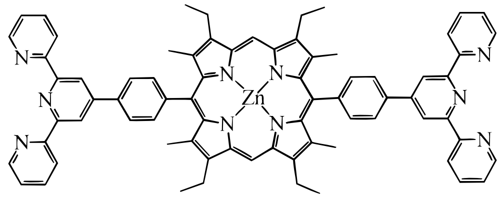
f. Benzene/Pyridine/Porphyrin. *Synthesis.* Rods consisting of pyridine, benzene, and porphyrin modules were reported by the Sauvage group.[465−468] Porphyrins **245** with a terpyridyl unit directly attached to a meso carbon were prepared from formylterpyridyl, a substituted benzaldehyde, and a substituted pyrrole in very low yield following Lindsey's[469] modified version of MacDonald's[470] methodology. Similarly, mono- and 5,15-bis-substituted systems **246a** and **246b** with a phenyl spacer between the terpyridyl units and an octaalkylporphyrin ring were synthesized from terpyridylbenzaldehyde in low to moderate yields.



245

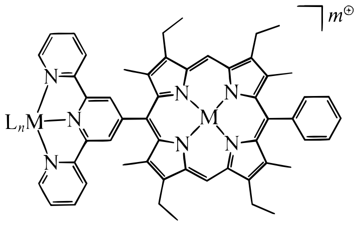


246a

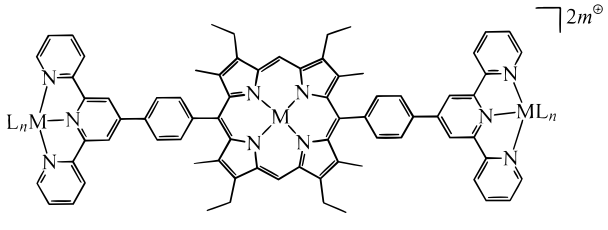


246b

Properties and Uses. The compounds described in this section are very stable under normal atmospheric conditions and soluble in polar organic solvents. Photophysical investigations of the porphyrin−terpyridyl diads prepared from the metalated porphyrin rods and Ru(II) or Rh(III) salts revealed a quenching of the porphyrin fluorescence due to extremely rapid intramolecular electron transfer in the case of the directly linked systems **247**.[465,466] The incorporation of the phenyl spacer, however, slows the electron transfer process considerably. Charge recombination is especially slow, leading to a charge-separated state with an extended lifetime.[466] Systems **248** are of interest for use as molecular bridges in multicomponent arrays for photosynthetic simulation. In the Ru(II) bisterpyridyl species, light energy absorbed by the metal complex is transferred via the Dexter[352] mechanism to the triplet excited state of the porphyrin.[468]



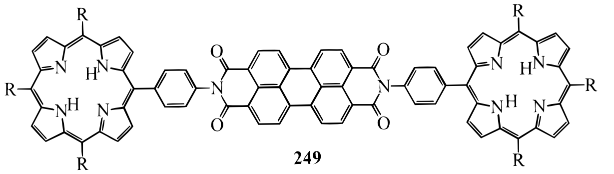
247



248

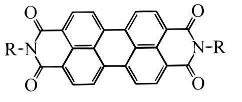
M = Ru(II), Rh(III)

g. Benzene/Porphyrin/Arenedicarboximide. *Synthesis.* The group of Wasielewski[471] reported the synthesis of a molecular rod **249** consisting of two porphyrin modules connected by a rigid *N*,*N*′-diphenyl-3,4,9,10-perylenebis(dicarboximide) (**250**). The porphyrin building block was prepared in moderate yield by condensation of hexanal, *p*-nitrobenzaldehyde, and pyrrol following Lindsey's protocol,[469] and after reduction to the amine, it was condensed with perylenetetracarboxydianhydride to yield **249**. Similar systems have been produced by Osuka and his group[472,473] to mimic the primary charge separation in natural photosynthesis, but they contain methylene linkages and are thus not entirely rigid. The methylenechlorin/porphyrin/pyromellitimide rod **251** was synthesized by condensing the methylenechlorin unit with dipyrrylmethane and the pyromellitimide-linked benzaldehyde. Imahori et al.[474] incorporated a fullerene unit at the terminus of a porphyrin/phenyl/pyromellitimide rod as a building block in the proposed construction of a solar energy conversion system. The pyromellitimide-substituted porphyrin **252** was obtained by cross condensation between aminoporphyrin, pyromellitic anhydride, and a protected formylaniline and reacted with *N*-methylglycin and C_{60}, followed by metalation of the porphyrin.

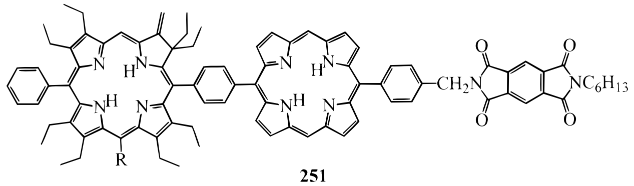


249

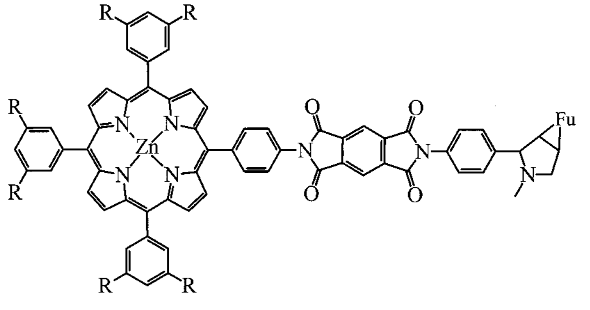
R = C_5H_{11}



250



251



252

R = *t*-butyl Fu = C_{60}

Several arenedicarboximides have been combined in the synthesis of a molecular switch **253** (Scheme 120).[218]

Properties. Wasielewski's group[471] showed that **250** serves as an excellent electron acceptor comparable in its reduction potential to benzoquinone and that rods such as **249** can be reversibly reduced with either one or two electrons. The resulting mono- and dianions feature characteristic well separated intense absorption peaks. The ion pairs in the monoanionic species recombine on a time scale of about 100 ps, and the lifetime of the dianionic species is about 50 times longer. Depending on the intensity of the light used in the excitation, the system switches between being a strong transient absorber at the monoanion and at the dianion wavelengths, thus constituting a light-intensity-dependent optical switch. It was postulated that two different excitation wavelengths could be used for the switching, the first one at the absorption peak of **250** to produce the monoanion and the second one at the absorption of the remaining ground-state porphyrin to initiate the second electron transfer. This would in principle allow the performance of logic operations.[471]

Osuka's[472] rod **251** displays weak interactions between the macrocycles in the ground state. Steady-state fluorescence spectra show emission only from the methylenechlorin unit, indicating efficient intramolecular electron transfer. Transient absorption spectroscopy was used to elucidate the excited-state dynamics both of the free base and the metalated species. The system containing the free-base porphyrin follows a stepwise electron-transfer relay, while in the metalated counterpart, a direct superexchange mechanism seems to be involved as well. The ion-pair states are long-lived in a nonpolar environment and can be observed directly.[472]

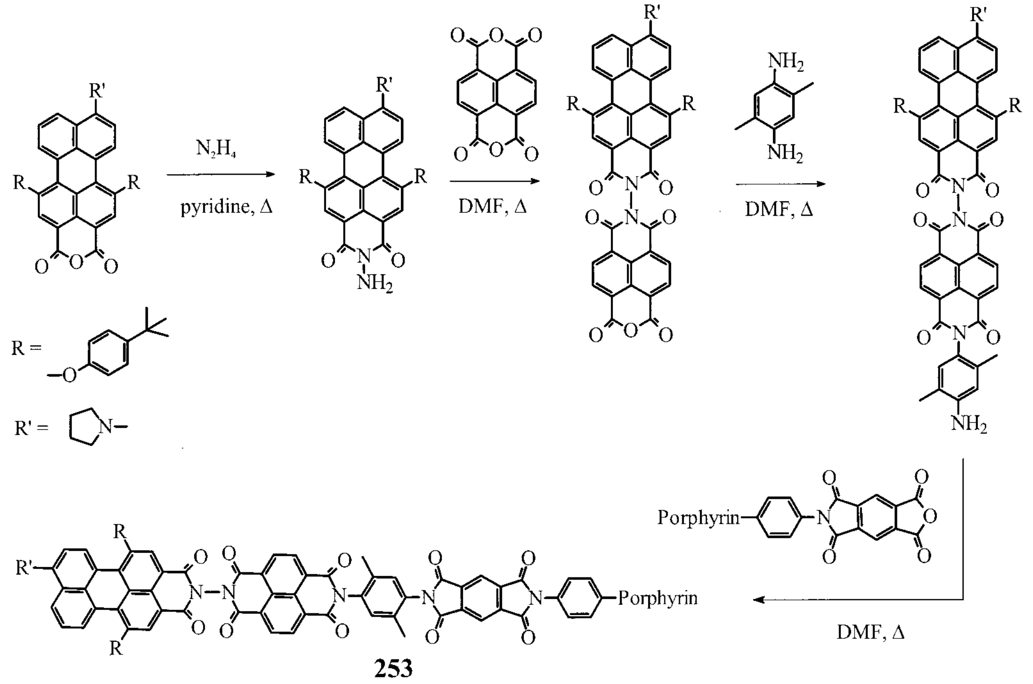
The fullerene-containing triad **252** features a sequential electron-transfer relay with a charge-separated species with a lifetime in the picosecond range.[474]

6. Cage/Other/Other

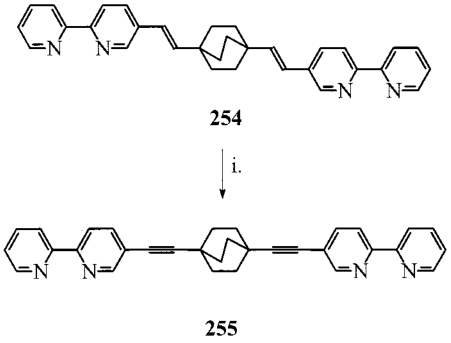
a. Bicyclo[2.2.2]octane/Pyridine/Other. *Synthesis.* Vögtle et al.[475] converted the two ethylene units of 1,4-bis[2,2′-bipyridin-5-yl)ethenyl]bicyclo-[2.2.2]octane (**254**, cf. Part 2[19]) into two acetylene units by addition of Br_2 and subsequent double dehydrobromination to obtain the bicyclo[2.2.2]octane/ethyne/pyridine co-oligomer **255** (Scheme 121). Barigeletti et al.[476] synthesized a terpyridyl-terminated rod **256** using a Suzuki-type aryl−aryl coupling in the key step (Scheme 122).

Properties and Uses. The rods are thermally and chemically stable under ambient conditions. Mono- and dinuclear complexes of both rods with Ru and Os have been prepared.[366,475] The bipyridyl-based species **255** separates the metal centers by 17 Å and the terpyridyl-capped system **256** by 24 Å. Each metal unit behaves independently with regard to absorption and electrochemical properties. It is noteworthy that the superimposed absorption spectra of the three dinuclear compounds (Os/Os, Ru/Ru and Os/Ru) derived from **255** exhibit two isosbestic points.[475] Apparently, the bicyclo[2.2.2]octane unit effectively inhibits electronic communication between the metal centers in the ground state, virtually isolating the two chromophoric units.

Scheme 120

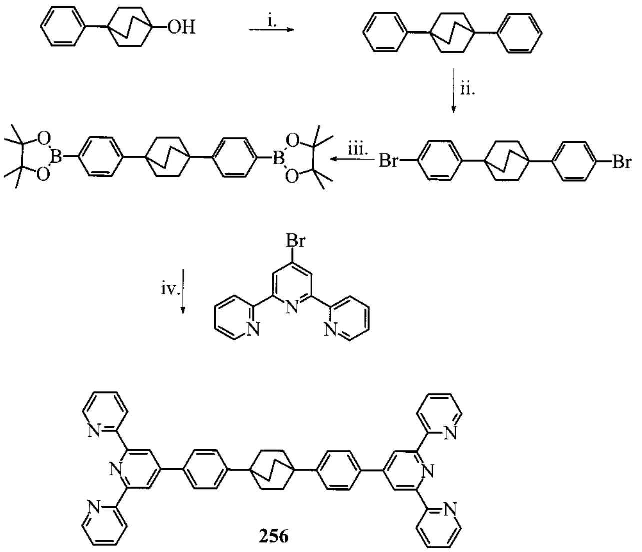


Scheme 121



i. 1. Br_2, CCl_4 2. KOH/ethanol/dioxane, reflux

Scheme 122



i. benzene, H_2SO_4; ii. Br_2, Fe, CCl_4; iii. 1. *t*-BuLi, THF 2.$(RO)_2BOMe$ iv. $Pd(dppb)Cl_2$, Na_2CO_3, ethanol, toluene

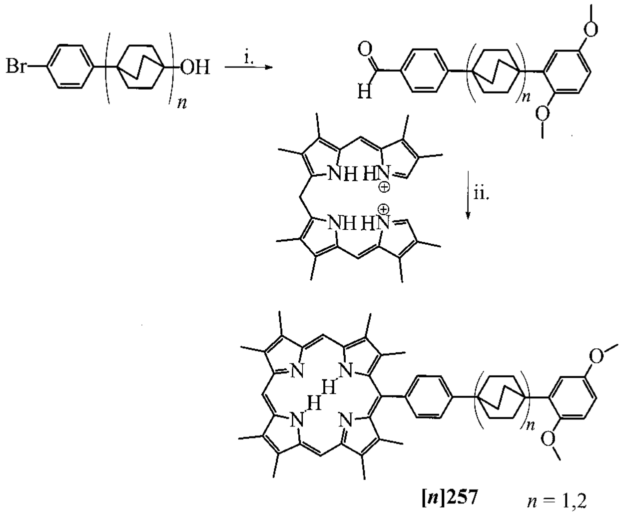
In the mixed-metal complex [Os(II)/Ru(II)] of **255**, a very efficient energy transfer with a small transfer rate takes place after excitation at room temperature, causing the sensitized emission of the Os-based unit.[476] The results can be accounted for quantitatively by assuming the Förster mechanism.[385] Energy transfer in the heterometallic derivative of **256** [Os(II)/Ru(II)] was observed only in a rigid matrix at 77 K but with an even smaller rate than in that of **255** at room temperature.[476] The short excited-state lifetime of the Ru-based moiety prevents energy transfer at higher temperatures. Electron transfer in the oxidized species [Os(III)/Ru(II)] does not occur even at 77 K.[366]

The examples show nicely that saturated hydrocarbon fragments are effective electronic insulators between metal centers in the ground state. Since energy transfer in the excited state remains a possibility depending on rod length, binding site, and oxidation states, the incorporation of bicyclo[2.2.2]octane into nanostructures offers an important way of electronically fine-tuning the device. It would be very interesting to compare the behavior and effects of other cage modules in similar systems systematically.

b. Bicyclo[2.2.2]octane/Porphyrin/Other. *Synthesis.* Porphyrin/phenylene/bicyclo[2.2.2]octane rods **257** have been synthesized by the Dervan group[477] via condensation of tetrapyrroles with aldehydes to form *meso*-substituted porphyrins (Scheme 123).

Properties and Uses. The compounds are thermally and air stable. Fluorescence yield measurements showed a marked distance dependence of the intramolecular electron-transfer rate from the porphyrin excited singlet state to the quinone moiety.[477] The temperature dependence of electron-transfer rates was found to be weak both in polar and nonpolar solvents.[478]

Scheme 123



i. 1. 1,4-Dimethoxybenzene, BF_3, p-TsOH, CCl_2CHCl, heat 2. n-BuLi, THF, -78°C 3. DMF, -78°C; ii. 1. HBr, HOAc, CH_3OH, heat 2. BF_3, p-TsOH, benzene, 60°C

IV. Doubly Linked Axial Rods

A. Cumulenes

In cumulenes, adjacent ethylene modules share carbon atoms. Like oligoynes, these are rods of pure carbon. Terminal substituents can be attached by one or two single bonds or a double bond. When redox-active groups are located at the termini, particularly metals, a close relation between cumulenes and oligoynes becomes apparent: whether the rod should be classified as a cumulene or an oligoyne depends on the oxidation state, e.g., Gladysz's[479] and Lapinte's[110] complexes of C_4 chains can exist both in a butadiyne and a butatriene form depending on the degree of oxidation, and the two electron reduction of tetraarylbutatrienes causes a shift of bonds and the formation of acetylenic dianions.[480]

As in the case of oligoynes, we find it expedient to treat separately cumulene rods with organic terminal substituents and those with metal terminal substituents.

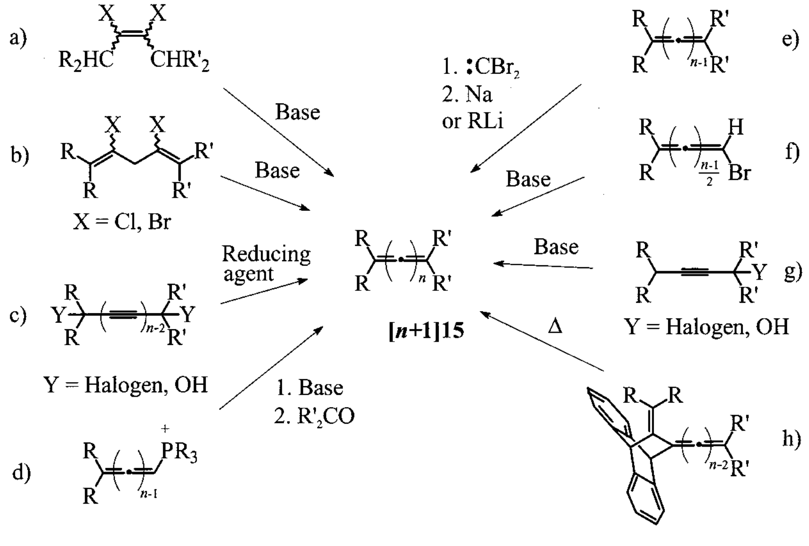
1. Organic Terminal Substitution

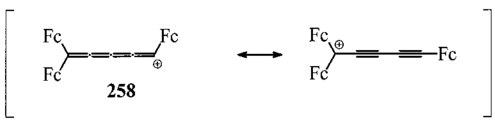
Synthesis. The history of cumulenes (**[n]15**) started in 1887 when Burton and Pechmann prepared the first allene derivative, which they mistook for the corresponding acetylene derivative.[481] Cumulenes with up to 10 carbon atoms in the chain are now known.

Methods of synthesis of **[n]15** are discussed in great detail in several reviews[482,483] and in a compilation of synthetic procedures.[50] The most general methods include the elimination reactions of suitable halides (Scheme 124a–c), vinylogous propargylic rearrangements (Kuhn's method, Scheme 124c), and the Wittig reaction of cumulenic ylids (Scheme 124d).[482] Addition of bromocarbene and subsequent dehalogenation of the resulting *gem*-dibromocyclopropane extends the chain by one carbon atom (Doering–Moore–Skattebøl synthesis, Scheme 124e).[482] The procedure, however, requires drastic conditions and the use of strong bases and is not generally applicable to the synthesis of the parent and alkyl-substituted cumulenes.[482] Dimerization of carbenoids obtained from two types of precursors doubles the length of cumulenes (Scheme 124f,g).[482] Retro-Diels–Alder reaction has also been used to prepare these structures (Scheme 124h).[482] Bildstein et al.[484] accomplished the synthesis of the first air-stable C_5-cumulenic salt **258** from 1,1-diferrocenyl-1-methoxypropyne applying a metalation, iodination, cross-coupling and dehydration scheme. The neutral tetraferrocenyl-C_5-cumulene **259** was prepared by treating the protonated C_5-cumulenic salt precursor with a "superbase".[484] Dua et al.[485] produced the carbenoid cumulene C_6CH_2 **260** in the gas phase by charge stripping of the corresponding radical anion, which is generated in the reaction of HO^- with DC_6CH_2OEt and subsequent loss of EtO•.

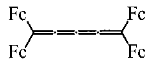
Properties and Uses. Parent cumulenes and those substituted with small alkyls are not stable thermally.[482] However, their stability is significantly

Scheme 124



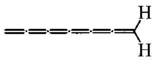


258

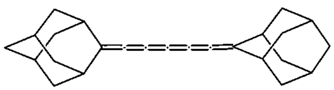


259

Fc = Ferrocenyl



260



261

increased upon introduction of *tert*-butyl and aryl substituents or when the terminal carbons are part of a cage or a cycle.[482] For example, bis(adamantylene)pentatetraene (**[5]261**) is stable up to 360 °C.[486]

The flexibility of the cumulenic backbone is considerable (Table 3). Several macrocycles containing cumulene fragments have been reported, but the limiting ring size for incorporating such units is not known.[482]

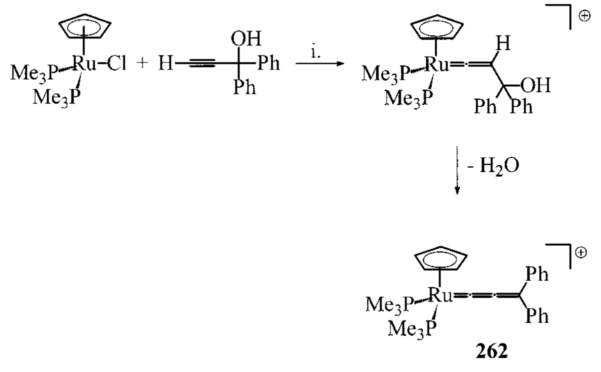
Chemical instability is one of the major factors limiting application of cumulene rods in supramolecular assembly. Cumulenes react readily with strong acids, bases, and many other reagents. They are strong π donors.[487]

2. Metal Terminal Substitution

A fair number of known cumulene rods carry a metal atom at the terminus. In addition to possible applications in material science, their catalytic potential has recently been recognized.[488] Vinylidene complexes have been investigated extensively, and their chemistry has been reviewed elsewhere.[489]

Synthesis. After the discovery of allenylidene metal complexes,[490] various methods[489] have been developed for their synthesis. Most convenient is the synthesis from terminal alkynols, a reaction that has been discovered by Selegue[491] when he treated the electron-rich ruthenium complex [CpRu(PMe$_3$)$_2$(Cl)] with HC≡CCPh$_2$OH to obtain the cation **262** (Scheme 125).

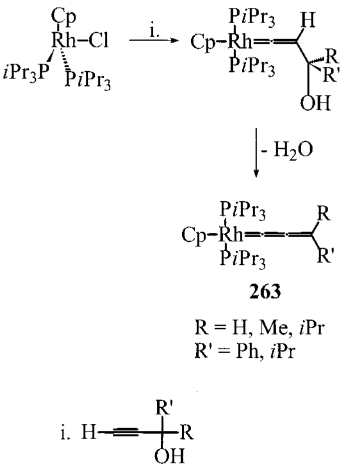
Scheme 125



i. NH$_4$PF$_6$, EtOH

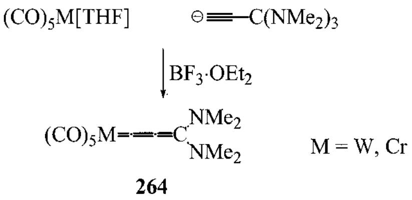
Another example is due to Werner et al.,[492] who prepared the first (allenylidene)rhodium complex **263** with a hydrogen substituent on the γ carbon and obtained the first X-ray structure of a compound with a Rh=C=C=CRR′ chain (Scheme 126). The corresponding Ir-containing complexes are also known.[493] Diaminoallenylidene complexes **264** were reported by Roth and Fischer[494] (Scheme 127).

Scheme 126



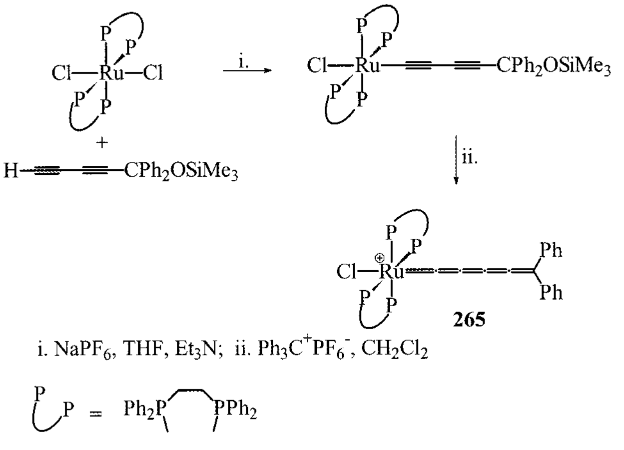
R = H, Me, *i*Pr
R' = Ph, *i*Pr

Scheme 127



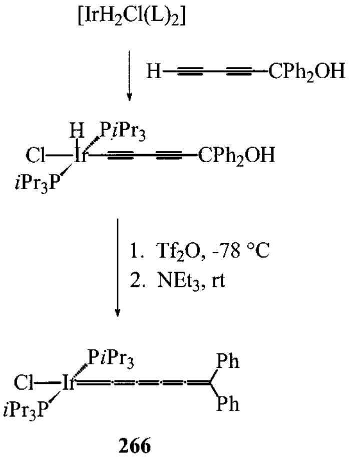
The higher cumulogues have attracted interest recently, and the Dixneuf[495] group isolated the first metalated C$_5$ cumulene **265** (Scheme 128). A similar Ir-containing rod **266** was synthesized by Werner and co-workers (Scheme 129).[496] Roth and Fischer[494] reported the counterparts **267** with electron-poor group 6 metal–ligand fragments (Scheme 130). These authors[497] also attempted the synthesis of the next higher homologues, the heptahexaenylidene complexes, but were unable to isolate and characterize them. It appears that the intermediate C$_6$ cumulene added dimethylamine to the C$_4$–C$_5$ bond.

Scheme 128

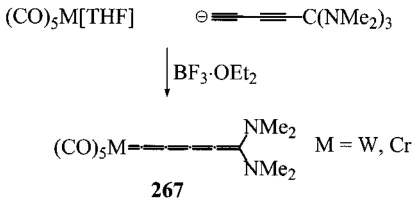


i. NaPF$_6$, THF, Et$_3$N; ii. Ph$_3$C$^+$PF$_6^-$, CH$_2$Cl$_2$

Scheme 129

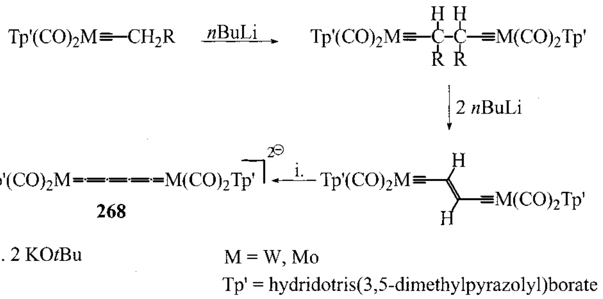


Scheme 130

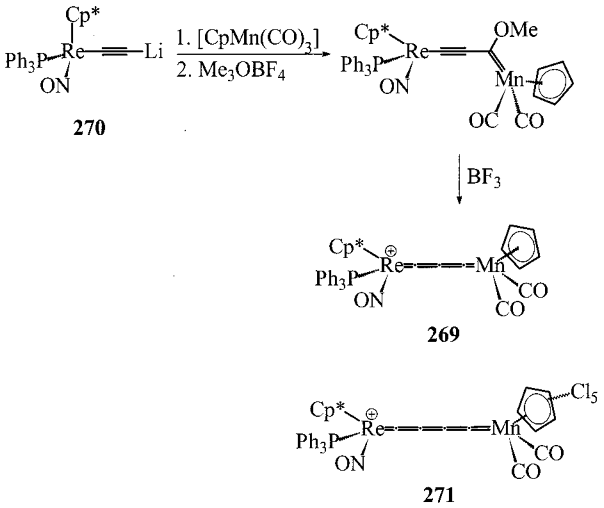


Some known cumulene rods carry metal atoms at both termini. Woodworth et al.[107] reported the synthesis of a dianionic C_4-bridged dimer **268** (Scheme 131). Gladysz and co-workers[498] showed that the abstraction of methoxide from bimetallic Fischer carbene species yields C_3 and C_5 cumulene rods with metalated termini (Scheme 132). Of the compounds characterized, only the heterobimetallic sandwich complexes with Re and Mn centers were linear. The Fischer carbenes of the C_3 series, such as **269**, were obtained[498] from the lithiated rhenium monoacetylides **270** by treatment with the metal carbonyls, $Fe(CO)_5$, $CpMn(CO)_3$, and $Re(CO)_5$. For the C_5 homologues, only the pentachlorinated Mn half-sandwich complex proved to be reactive enough for the nucleophilic addition, yielding **271**.

Scheme 131



Scheme 132



Properties and Uses. The isolated W and Cr pentacarbonyltetranylidenes **267** are stable in air and decompose only above 100 °C.[494] Their chemical reactivity is dominated by the electrophilicity of the central carbon atom. The linear complex **265** is stable in THF, but slight modifications of the ligands drastically increases its lability.[495] The remaining Cl ligand offers a site for further elaboration. The stability of the pure Ir-based compound **266** is very high both in nonpolar solutions and in the solid state, and the melting point is over 100 °C.[496]

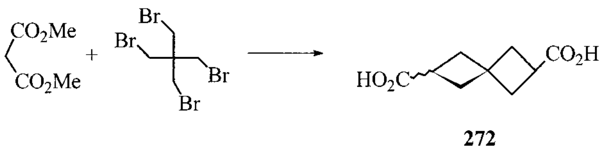
The C_5 cumulene rod **271** is extremely light sensitive and decomposes in solution within hours even in the dark, while the C_3 analogue **269** shows no unusual photochemical or thermal reactivity.[498]

B. Carbocyclic Spiro Rods

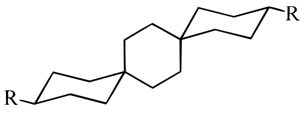
Homooligomers of the doubly linked modules other than ethene are connected by shared spiro carbons. Relatively few axial rods of this type are known.

Synthesis. The original synthesis of Fecht's acid (**272**, Scheme 133),[499] the first reported compound containing the spiro[3.3]heptane unit, has been significantly improved by Rice and Grogan[500] and Buchta and Geibel.[501] The latter group pursued the synthesis of the oligo[spiro(cyclobutane)] rods **[*n*]16** with up to 11 cycles (Scheme 134).[502] Synthesis of a rod series with dendrimer substituents has been reported more recently by Newkome et al.[503]

Scheme 133



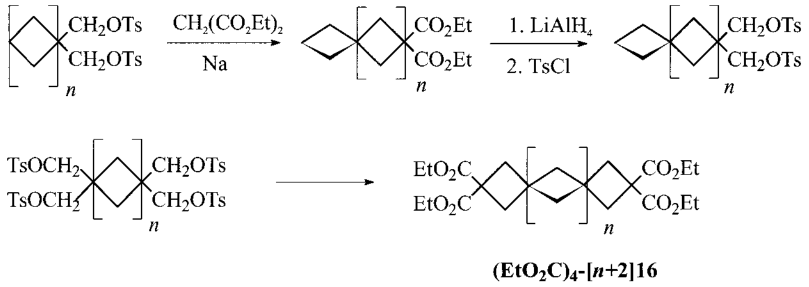
Three cyclohexane modules are spiro connected in **[3]17**, obtained by an iterative synthesis by Feuerbacher and Vögtle.[36] Spiro[5.5]undeca-1,4,7,10-tetraene-3,9-dione (**273**) has been prepared from the spirodienone **274** in five steps (Scheme 135).[504]



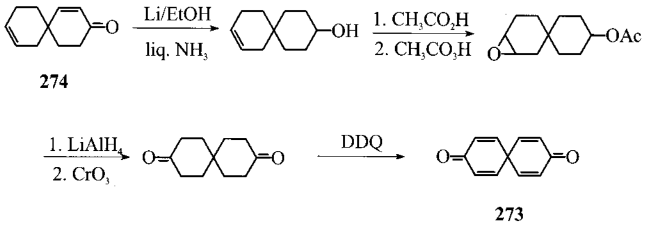
[3]17

Properties and Uses. Unsubstituted spiro rods are thermally stable, e.g., higher oligo[spiro(cyclobutane)]s melt without decomposition at 250−275 °C.[502] The rods containing only sp^3-hybridized carbons are expected to be transparent in the UV and

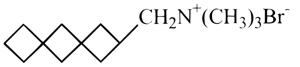
Scheme 134



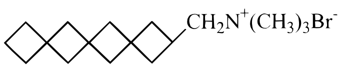
Scheme 135



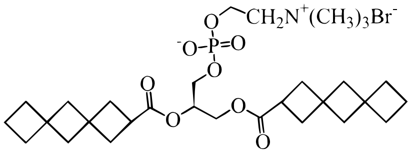
visible regions in the absence of chromophoric substituents. The oligomers with an even number of cyclobutane rings and unsymmetric substitution of both termini are chiral and weakly optically active.[500] The relative rigidity of the tri- and tetra[spiro(cyclobutane)] moieties was suggested as a possible rationalization for the low propensity of the spiro surfactants **275** and **276** to form micelles and for the lack of expected phase transitions in vesicles formed by the spiro phospholipids **277** and **278**.[505]



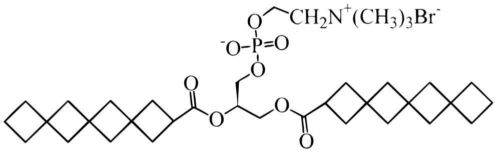
275



276



277

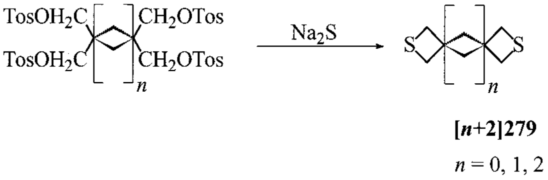


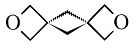
278

C. Heterocyclic Spiro Rods

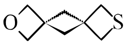
Synthesis. Spirocyclic sulfides **[2]279**, **[3]279**, and **[4]279** were synthesized by Seitz and Mikulla[506] by double cyclization of the corresponding tetramethanol derivatives (Scheme 136). The oxygen analogues **280** were also prepared along with the mixed oxygen–sulfur rods **281**.[507]

Scheme 136





280



281

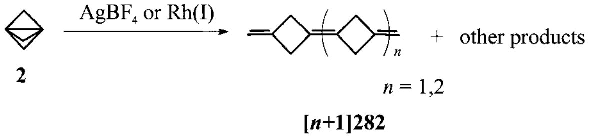
Properties and Uses. These compounds are air-stable, low-melting solids. The double thioethers were used as ligands in Ru(II) complexes,[508] with metal–metal through-bond distances from 11.3 to 17.5 Å. Intervalence transfer bands were observed for the series of the mixed valence binuclear Ru compounds and were used to deduce high electron-transfer rate constants. Apparently, electrons tunnel fairly effectively through the σ framework. CNDO/2 calculations showed that the orbitals were ideally set up for "sideways π overlap" providing a hyperconjugative pathway for the electron transfer. Photoelectron spectra indicate that the spiro ligands with an odd number of rings interact differently with metal atoms than those with an even number of rings.[508]

D. Co-Oligomers

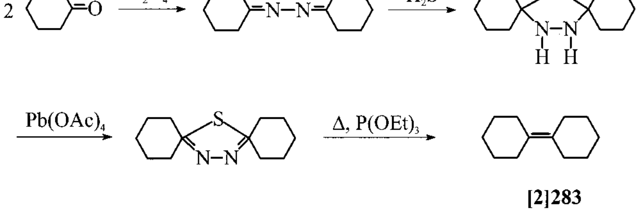
1. Ethene//Cycloalkane

In oligomeric cyclobuta-1,3-diylidenes (**[*n*]282**, Scheme 137) and cyclohexa-1,4-diylidenes (**[*n*]283**, Scheme 138), puckered aliphatic cycles are linked by

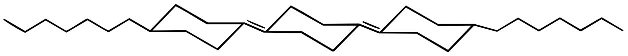
Scheme 137



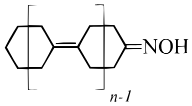
Scheme 138



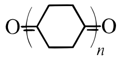
double bonds. Rigidity is moderate and is provided by the conformational stability of the puckered rings, which is presumably higher in the six-membered rings of **283**.



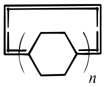
[3]283a



[*n*]283b



[*n*]284



[*n*]285

Synthesis. The dimer **[2]282** and the trimer **[3]282** result from transition-metal-catalyzed reaction of [1.1.1]propellane (Scheme 137).[136] Oligomers **[2]283**–**[5]283** have been prepared by the group of Jenneskens[509] by nitrogen extrusion from the corresponding diazo precursors (Barton–Kellogg olefin synthesis) (Scheme 138). The same method was used earlier by Vögtle et al.[510] and McMurry et al.[511–513] to prepare the terminal diones of **[4]284** and **[5]284**, respectively.

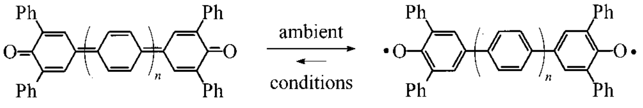
Properties and Uses. The oligomers are stable to air and organic solvents.[509] Thermal stability increases with length.[509] The higher oligomers **[*n*]283** are marginally soluble in common solvents, but introduction of alkoxy substituents at the termini improves solubility markedly. The expected all-trans conformation has been confirmed by an X-ray study of **[3]283a**.[509] The terminal diones **[4]284** and **[5]284** cyclize under McMurry coupling conditions into the compounds **[4]285**[510] and **[5]285**,[511,512] respectively, but in extremely low yields. Clearly, the rods are relatively flexible.

No evidence for any chemical instability of oligomers **283** has been reported, but an excess of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone oxidizes oligo(cyclohex-1,4-ylidene)s into the corresponding *p*-oligophenylenes.[509] An oxime group in the terminal position of **[*n*]283b** detectably affects the chemical shift of a carbon atom located 7 Å away along the rod.[514]

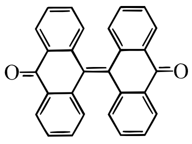
2. Ethene//Cyclohexadiene

Oligoquinylidenes (**[*n*]286**) are expected to have low-lying biradical states with aromatic benzene rings. Indeed, at ambient conditions, the trimer and the tetramer of 1,4-quinylidene terminated by carbonyl groups (**[3]286a** and **[4]286a**) exist as the corresponding *p*-oligophenylenedioxy biradicals **287** (Scheme 139).[515] Aromatic stabilization of the central ring in anthracene derivatives is much smaller than that in phenylenes. Presumably this is the reason bianthrone **[2]288** is stable at ambient conditions.[515] Bianthrone (**[2]288**) was used by Müllen's group[237] as an intermediate in the synthesis of oligoanthrylenes (section III.C.2.b).

Scheme 139



[*n*]286 **287**



[2]288

3. Ethene//Stellane

Synthesis. Tricyclo[3.3.0.0$^{3.7}$]hexane (stellane) modules are the smallest hydrocarbon cages that can be used as axial units connected by double bonds. The cage can be prepared in two steps from cyclopentadiene precursors.[516–522] Spiro-type homo-oligomers are not known, but co-oligomers of stellane with ethene **289** have been synthesized by the McMurry coupling of the appropriate ketones (Scheme 140).[523]

Properties and Uses. Electronic interaction between different π moieties through the stellane bridge has been evaluated by means of photoelectron spectroscopy and is much larger than the interaction through the 1,4-cyclohexylidene bridge.[524–526]

4. Ethene//Adamantane

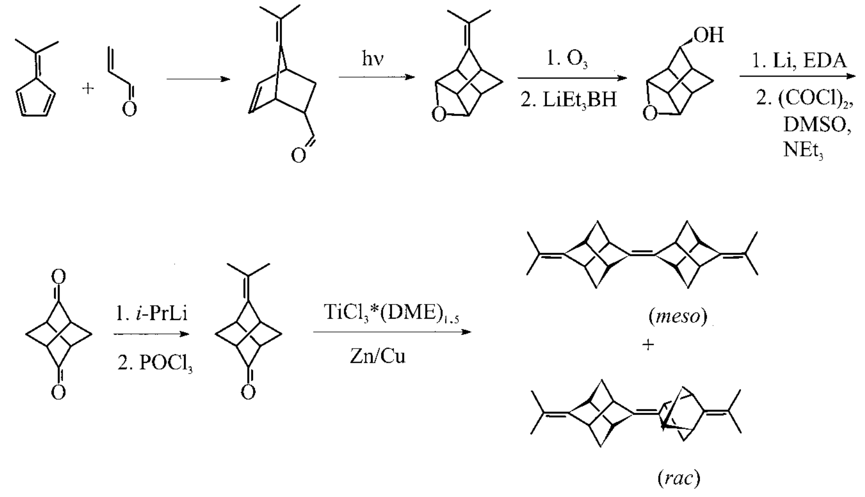
The spiro oligomers of adamantane are not known, but the co-oligomers with ethene, **[2]290a**–**[4]290a**, as well as the terminal diketals **[2]290b**–**[4]290b** and diones **[2]290c**–**[4]290c**, were prepared by McMurry coupling (Scheme 141).[527] The dimer **[2]290c** is linear, while the trimer **[3]290c** is bent 22.4° in a crystal because of a distortion of one of the terminal adamantane cages.[527]

5. Ethene//Diazafluorene

Synthesis. The co-oligomer **291** of two bidentate 4,5-diazafluorene ligands with a single ethene is known. It was synthesized by Riklin and von Zelewsky (Scheme 142).[528] Mono- and dinuclear Ru complexes have been prepared, and the latter exist in two diastereoisomeric forms.[528]

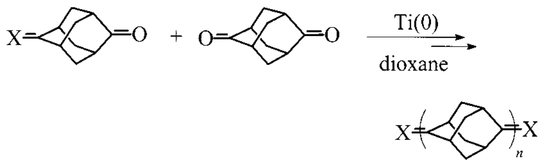
Properties and Uses. The compound is very stable under normal atmospheric conditions. The molecule was calculated to adopt a twisted conformation and consequently shows axial chirality. The UV–vis spectrum shows a strong absorption band at 417 nm, which was attributed to a TICT state, as in 9,9′-bifluorenylidene. The cyclic voltammogram shows two successive one-electron reduction steps. Compared to *o*-phenanthroline, the 4,5-diazafluorenone molecule is distorted, resulting in a reduced nitrogen–

Scheme 140



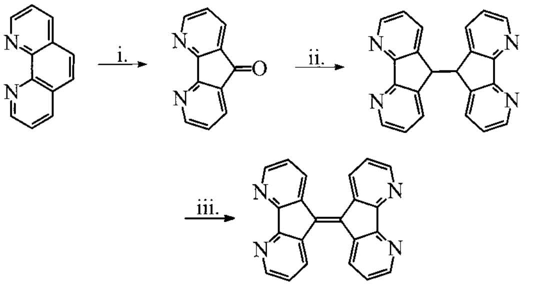
289

Scheme 141



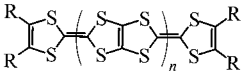
n = 2 - 4
[*n*]290a, X = H$_2$
[*n*]290b, X = -OCH$_2$CH$_2$O-
[*n*]290c, X = O

Scheme 142

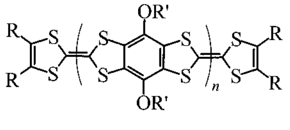


291

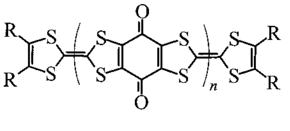
i. KMnO$_4$, KOH; ii. H$_2$NNH$_2$; iii. DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone)



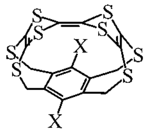
[*n*]292a



[*n*]292b



[*n*]292c



292d

metal overlap. However, the metal coordination ability is maintained.[528]

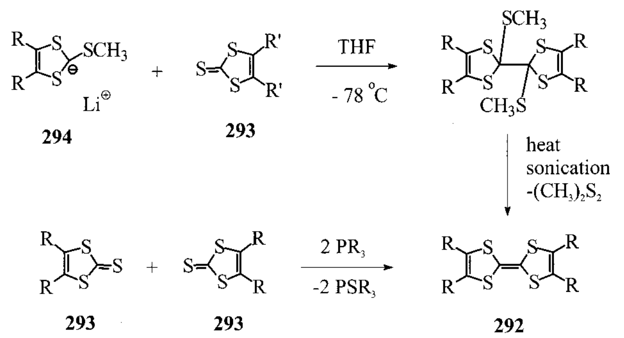
6. Tetrathiafulvalenes

Among numerous oligotetrathiafulvalenes (**[*n*]292**),[529] only those with fused monomer units possess sufficient rigidity to be considered as molecular rods. The tetrathiafulvalene (TTF) groups may be fused to each other directly, as in the oligomers **[*n*]292a**,[530] and through benzene or quinone rings, as in **[*n*]292b** and **[*n*]292c**.[531] In our classification scheme, the fused rings linked by C═C modules, not the TTF groups, must be considered as the other module in these co-oligomers.

Synthesis. Individual oligomers **[*n*]292a**[530] and **[*n*]292b**[532−535] with up to three TTF groups and a mixture of oligomers **[*n*]292b** with 15−20 monomers[532] have been prepared. The oligomers are formed by a trialkyl phosphite-mediated coupling of bis-1,3-dithiol-2-thiones (**293**)[532,536] or by a reaction of the lithium salt **294** with the fused ring precursor thiones **293** with subsequent oxidative extrusion of dimethyl disulfide (Scheme 143).[532,533,537,538] The latter method permits unsymmetrical coupling and gives higher yields.

Properties and Uses. Oligo(tetrathiafulvalene)s are strong electron donors and can reversibly transfer up to two electrons per monomer unit. They can be used as electroactive conducting rods. Conductivity of up to 160 S cm^{-1} and metallic behavior up to 120 K have been observed for some radical−cation salts of TTF rods with Au(CN)$_2$.[539] The TTF group permits the rods to bend easily in the direction perpendicular to the ring plane, as illustrated by the synthesis of a cyclic compound **292d** by Müllen's group.[532,540,541] The

Scheme 143

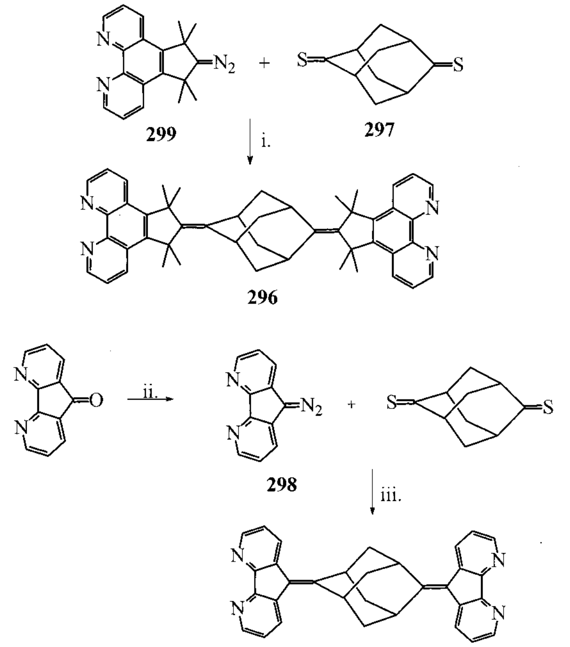


unsubstituted tetrathia-*s*-indacene precursor is not soluble in organic solvents,[542] but two 3,5-di-*tert*-butylbenzyloxy substituents per indacene unit make the oligomers **[*n*]292b** very soluble.[533]

7. Ethene//Adamantane//Other

Synthesis. Bernhard and Belser[543] prepared adamantane-2,6-bis(4,5-diazafluorenenylidene) (**295**) and 2,6-adamantanebis(1,3-dihydro-1,1,3,3-tetramethyl-7,8-diazacyclopenta[1]phenanthren)-2-ylidene (**296**) by condensing adamantane-2,6-dithione (**297**) with 9-diazo-4,5-diazafluorene (**298**) and 2-diazo-1,3-dihydro-1,1,3,3-tetramethyl-7,8-diazacyclopenta[1]phenanthrene-2-hydrazone (**299**), respectively (Scheme 144).

Scheme 144



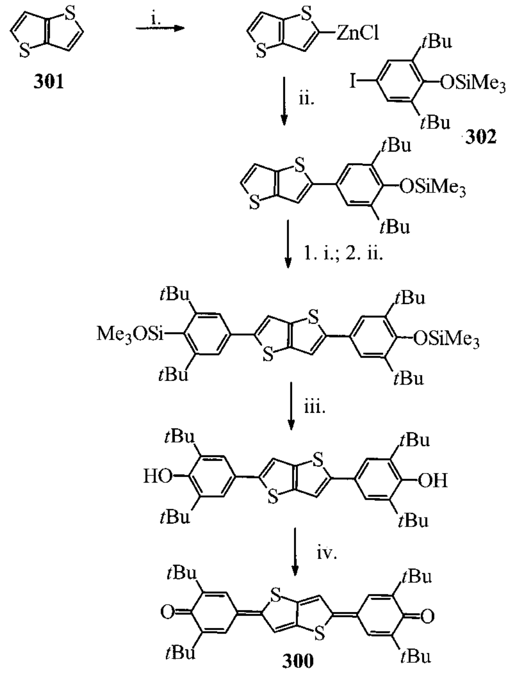
i. 1. THF/pyridine, rt 2. P(Bu)$_3$/pyridine, 140°C; ii. 1. tosylhydrazide, EtOH, rt 2. aq. NaOH, MeOH, CHCl$_3$, reflux; iii. PPh$_3$, CHCl$_3$, reflux

Properties and Uses. Both compounds are stable under normal atmospheric conditions. The bridging ligands are rigid and binuclear complexes have been prepared.[543] While **295** displays a reduced ligand field strength compared to an unsplayed 2,2′-bipyridyl, **296** combines both the electronic qualities of phenanthroline and the structural advantage of connecting metal centers along the coordination axis.[260]

8. Ethene//Cyclohexadiene//Other

Synthesis. A tetra-*tert*-butyl derivative **300** of the dihydrodithiapentalenediylidene-extended diphenoquinone was synthesized by Takahashi and Ogiyama[544] in five steps from dithiapentalene **301** using Pd-catalyzed cross-coupling reactions between the organozinc derivatives of **301** and 1-iodo-4-(trimethylsilyl)methoxybenzene **302** in the key steps (Scheme 145).

Scheme 145



i. 1. *t*-BuLi, ether, 0 °C, 2. ZnCl$_2$, THF; ii. PdCl$_2$(PPh$_3$)$_2$, THF, *i*-BuAlH$_4$, hexane; iii. 12 M HCl, THF, RT; iv. K$_3$[Fe(CN)$_6$], benzene, aq. KOH, RT

Properties and Uses. The rod is quite stable in the solid state and in solution in common organic solvents. At ordinary temperatures, rotation around the intercyclic bonds is sufficiently hindered. Cyclic voltammography reveals the occurrence of a two-stage one-electron reduction and a two-stage one-electron oxidation. The second oxidation wave is irreversible. The compound is the first closed-shell amphoteric four-stage redox system involving different redox-active units. Both its radical anion and radical cation are stable, characterizable species.[544]

V. Concluding Remarks

Although we anticipate a more comprehensive commentary at the end of Part 2,[19] a few comments seem in place.

The very large number of studies dedicated to the synthesis of axial rods and to the examination of their properties has made it possible to choose rods according to need to a degree that is amazing in some parts but still somewhat disappointing in others. The variety of axial modules available presently permits the design of rods of arbitrary length tailored to the nearest angstrom or even more finely, and rod thickness can be adjusted by the addition of substituents. The remaining synthetic challenges have been mentioned along the way, selective end-to-end cross-coupling of cage modules being perhaps the most pressing. All the axial rod modules are quite similar with regard to the flexibility of the resulting rods, and it is clear that stiffer rods will have to be sought either in bundles of axial rods of the types available today or in altogether different types of structures, such as fused polycyclic cages or carbon nanotubes.

With regard to electronic properties, the modules used to build axial rods are of two types: insulating and conducting, with little if anything in between. The transmission of electronic effects through a rod falls off roughly exponentially with its length. A single insulating module included in a set of well conducting modules suffices to suppress conduction by about an order of magnitude. Structurally, this division of rod modules in two classes corresponds well to saturated and conjugated hydrocarbons. Although the carborane modules have not yet been investigated sufficiently to make a definitive statement, they appear to belong to the aliphatic family. Despite considerable recent advances, we are still far from being able to make general predictions of energy and charge transfer rates and even farther from being able to control them by reversible chemical transformations, as would be desirable for a molecular field-effect transistor.

VI. Acknowledgments

Our work on molecular rods has been supported by NSF Grant CHE-9819179 and USARO Grant DAAG55-98-1-0310.

VII. References

(1) *Comprehensive Supramolecular Chemistry*; Lehn, J.-M., Chair Ed.; Atwood, J. L., Davis, J. E. D., MacNicol, D. D., Vögtle, F., Exec. Eds.; Pergamon Press: Oxford, U.K., 1996; Vols. 1−11.
(2) *Supramolecular Chemistry*; Balzani, V., De Cola, L., Eds.; NATO ASI Series; Vol. 320; Kluwer: Dordrecht, 1992.
(3) *Modular Chemistry*, Michl, J., Ed.; Kluwer: Dordrecht, 1997.
(4) Stang, P. J.; Olenyuk, B. *Acc. Chem. Res.* **1997**, *30*, 502.
(5) Michl, J. in *Chemical Synthesis: Gnosis to Prognosis*; Chatgilialoglu, C.; Snieckus, V., Eds.; NATO ASI Series 371; Kluwer: Dordrecht, 1996; p 429.
(6) Kaszynski, P.; Michl, J. *J. Am. Chem. Soc.* **1988**, *110*, 5225.
(7) Zimmerman, H. E.; Goldman, T. D.; Hirzel, T. K.; Schmidt, S. P. *J. Org. Chem.* **1980**, *45*, 3933.
(8) Zakharkin, L. I.; Kovredov, A. I. *Zh. Obshch. Khim.* **1974**, *44*, 1840.
(9) Zakharkin, L. I.; Kovredov, A. I. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1973**, 1428.
(10) Tour, J. M. *Chem. Rev.* **1996**, *96*, 537.
(11) *Electronic Materials: The Oligomeric Approach*; Müllen, K., Wegner, G., Eds.; Wiley-VCH: Weinheim, 1998.
(12) Batchelder, T. L.; Fox, R. J., III; Meier, M. S.; Fox, M. A. *J. Org. Chem.* **1996**, *61*, 4206.
(13) Schneider, J. P.; Kelly, J. W. *Chem. Rev.* **1995**, *95*, 2169.
(14) Nolte, R. J. M. *Chem. Soc. Rev.* **1994**, 11.
(15) Yasumoto, T.; Murata, M. *Chem. Rev.* **1993**, *93*, 1897.
(16) Li, X.; Dias, J. R. *Chem. Rev.* **1997**, *97*, 283.
(17) Storhoff, J. J.; Mirkin, C. A. *Chem. Rev.* **1999**, *99*, 1849.
(18) Piguet, C.; Bernardinelli, G.; Hopfgartner, G. *Chem. Rev.* **1997**, *97*, 2005.
(19) Schwab, P. F. H.; Levin, M. D.; Michl, J. Manuscript in preparation.
(20) Murakami, Y.; Kikuchi, J.; Hisaeda, Y.; Hayashida, O. *Chem. Rev.* **1996**, *96*, 721.
(21) Breslow, R.; Dong, S. D. *Chem. Rev.* **1998**, *98*, 1997.
(22) Marchand, A. P. *Chem. Rev.* **1989**, *89*, 1011.
(23) Paquette, L. A. *Chem. Rev.* **1989**, *89*, 1051.
(24) Arnold, B. R.; Michl, J. In *Kinetics and Spectroscopy of Carbenes and Biradicals*; Platz, M. S., Ed.; Plenum Press: New York, 1990; p 1.
(25) Bonacic-Koutecky, V.; Koutecky, J.; Michl J. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 170.
(26) Fleischhauer, J.; Höweler, U.; Michl, J. *Spectrochim. Acta, Part A* **1999**, *55A*, 585.
(27) Gudipati, M. S.; Hamrock, S. J.; Balaji, V.; Michl, J. *J. Phys. Chem.* **1992**, *96*, 10165.
(28) Delnoye, D. A. P.; Sijbesma, R. P.; Vekemans, J. A. J. M.; Meijer, E. W. *J. Am. Chem. Soc.* **1996**, *118*, 8717.
(29) Cuff, L.; Kertesz, M.; Scherf, U.; Müllen, K. *Synth. Met.* **1995**, *69*, 683.
(30) Lamba, J. J. S.; Tour, J. M. *J. Am. Chem. Soc.* **1994**, *116*, 11723.
(31) Frey, H. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2193 and references therein.
(32) Wenz, G. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 803 and references therein.
(33) Harada, A.; Li, J.; Kamachi, M. *Nature* **1993**, *364*, 516.
(34) Born, M.; Ritter, H. *Macromol. Chem. Rapid Commun.* **1996**, *17*, 197.
(35) Geerts, Y.; Klärner, G.; Müllen, K. In *Electronic Materials: The Oligomeric Approach*; Müllen, K., Wegner, G.; Eds.; Wiley: Chichester, 1998; Chapter 1, p 1.
(36) Feuerbacher, N.; Vögtle, F. *Top. Curr. Res.* **1998**, *197*, 1. Feuerbacher, N.; Vögtle, F.; Windscheidt, J.; Pötsch, E.; Nieger, M. *Synthesis* **1999**, 117.
(37) Liess, P.; Hensel, V.; Schlüter, A.-D. *Liebigs Ann.* **1996**, 1037.
(38) Schumm, J. S.; Pearson, D. L.; Tour, J. M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1360.
(39) Hegedus, L. S. *Transition Metals in the Synthesis of Complex Organic Molecules*; University Science Books: Mill Valley, CA, 1994.
(40) *Metal-Catalyzed Cross-Coupling Reactions*; Diederich, F., Stang, P. J., Eds.; Wiley-VCH: Weinheim, 1998.
(41) Diederich, F.; Rubin, Y.; Knobler, C. B.; Whetten, R. L.; Schriver, K. E.; Houk, K. N.; Li, Y. *Science* **1989**, *245*, 1088.
(42) Iwamura, H.; Matsuda, K. In *Modern Acetylene Chemistry*; Stang, P. J., Diederich, F., Eds.; VCH: Weinheim, 1995; p 385.
(43) Glaser, C. *Ber. Dtsch. Chem. Ges.* **1869**, *2*, 422.
(44) Glaser, C. *Ann. Chem.* **1870**, *154*, 137.
(45) Behr, O. M.; Eglinton, G.; Galbraith, A. R.; Raphael, R. A. *J. Chem. Soc.* **1960**, 3614.
(46) Eglinton, G.; Galbraith, A. R. *Chem. Ind.* **1956**, 737.
(47) Hay, A. S. *J. Org. Chem.* **1962**, *27*, 3320.
(48) Wright, M. E.; Porsch, M. J.; Buckley, C.; Cochran, B. B. *J. Am. Chem. Soc.* **1997**, *119*, 8393.
(49) Cadiot, P.; Chodkiewicz, W. In *Chemistry of Acetylenes*; Viehe, H. G., Ed.; Marcel Dekker: New York, 1969; p 597.
(50) Brandsma, L.; Verkruijsse, H. D. *Synthesis of Acetylenes, Allenes and Cumulenes*; Elsevier: Amsterdam, 1981.
(51) Bohlmann, F.; Herbst, P.; Gleinig, H. *Chem. Ber.* **1961**, *94*, 948.
(52) Berscheid, R.; Vögtle, F. *Synthesis* **1992**, 58.
(53) Chodkiewicz, W. *Ann. Chim. (Paris)* **1957**, *2*, 819.
(54) Eglinton, G.; McRae, W. *Adv. Org. Chem.* **1963**, *4*, 225.
(55) Black, H. K.; Horn, D. H. S.; Weedon, B. G. L. *J. Chem. Soc.* **1954**, 1704.
(56) Miller, J. A.; Zweifel, G. *Synthesis* **1983**, 128.
(57) Kitamura, T.; Lee, C. H.; Taniguchi, H.; Masumoto, M.; Sano, Y. *J. Org. Chem.* **1994**, *59*, 8053.
(58) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508.
(59) Rubin, Y.; Lin, S. S.; Knobler, C. B.; Anthony, J.; Boldi, A. M.; Diederich, F. *J. Am. Chem. Soc.* **1991**, *113*, 6943.
(60) Eastmond, R.; Johnson, T. R.; Walton, D. R. M. *Tetrahedron* **1972**, *28*, 4601.
(61) Lagow, R. J.; Kampa, J. J.; Wei, H.-C.; Battle, S. L.; Genge, J. W.; Laude, D. A.; Harper, C. J.; Bau, R.; Stevens, R. C.; Haw, J. F.; Munson, E. *Science* **1995**, *267*, 362.
(62) Lagow, R. J.; Kampa, J. J.; Wei, H.-C.; Battle, S. L.; Genge, J. W.; Laude, D. A.; Harper, C. J.; Mitchell, D. R.; Bau, R.; Stevens, R. C.; Haw, J. F.; Munson, E. *Tanso* **1998**, *181*, 27.
(63) Pasto, D. J.; Taylor R. T. *Org. React.* **1991**, *40*, 91.
(64) Gutmann, H.; Lindlar, H. In *Chemistry of Acetylenes*; Viehe, H. G., Ed.; Marciel Dekker: New York, 1969; p 355.
(65) House, H. O. *Modern Synthetic Reactions*; Cummings/Benjamin, Inc.: Menlo Park, CA, 1972.
(66) Bohlman, F.; Mannhardt, H. J. *Chem. Ber.* **1956**, *89*, 1307.
(67) Schulte, K. E.; Reisch, J.; Hörner, L. *Chem. Ber.* **1962**, *95*, 1943.
(68) Sternberg, H. W.; Greenfield, H.; Friedel, R. A.; Wotiz, J.; Markby, R.; Wender, I. *J. Am. Chem. Soc.* **1954**, *76*, 1457.
(69) Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Wilkinson, D. A. *J. Organomet. Chem.* **1991**, *408*, C9.
(70) Sly, W. G. *J. Am. Chem. Soc.* **1959**, *81*, 18.
(71) Hamilton, D. G.; Sanders, J. K. M. *Chem. Commun.* **1998**, 1749.
(72) Koreeda, M.; Yang, W. *J. Am. Chem. Soc.* **1994**, *116*, 10793.
(73) O'Brien, D. F.; Whitesides, T. H.; Klingbiel, R. T. *J. Polym. Sci., Polym. Lett. Ed.* **1981**, *19*, 95.
(74) Wegner, G. *Z. Naturforsch. B* **1969**, *24*, 824.
(75) Enkelmann, V. *Adv. Polym. Sci.* **1984**, *63*, 91.

(76) Zutaut, S. E.; McManus, S. P.; Jalali-Heravi, M. *Chem. Mater.* **1996**, *8*, 2223.

(77) Coates, G. W.; Dunn, A. R.; Henling, L. M.; Dougherty, D. A.; Grubbs, R. H. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 248.

(78) Storrs, R. W.; Tropper, F. D.; Li, H. Y.; Song, C. K.; Kuniyoshi, J. K.; Sipkins, D. A.; Li, K. C. P.; Bednarski, M. D. *J. Am. Chem. Soc.* **1995**, *117*, 7301.

(79) Kim, T.; Crooks, R. M.; Tsen, M.; Sun, L. *J. Am. Chem. Soc.* **1995**, *117*, 3963.

(80) Kim, T.; Chan, K. C.; Crooks, R. M. *J. Am. Chem. Soc.* **1997**, *119*, 189.

(81) Wolovsky, R.; Sondheimer, F. *J. Am. Chem. Soc.* **1962**, *84*, 2844.

(82) Wolovsky, R.; Sondheimer, F. *J. Am. Chem. Soc.* **1965**, *87*, 5720.

(83) Sondheimer, F.; Wolovsky, R.; Garrat, P. J.; Calder, I. C. *J. Am. Chem. Soc.* **1966**, *88*, 2610.

(84) Anthony, J.; Knobler, C. B.; Diederich, F. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 406.

(85) Hoffmann, R. *Tetrahedron* **1966**, *22*, 521.

(86) Hutter, J.; Lüthi, H. P.; Diederich, F. *J. Am. Chem. Soc.* **1994**, *116*, 750.

(87) Plattner, D. A.; Houk, K. N. *J. Am. Chem. Soc.* **1995**, *117*, 4405.

(88) (a) Gotts, N. G.; von Helden, G.; Bowers, M. T. *Int. J. Mass Spectrom Ion Processes* **1995**, *149/150*, 217. (b) von Helden, G.; Hsu, M. T.; Gotts, N. G.; Bowers, M. T. *J. Phys. Chem.* **1993**, *97*, 8182. (c) von Helden, G.; Gotts, N. G.; Bowers, M. T. *Nature* **1993**, *363*, 60.

(89) (a) Rubin, Y.; Kahr, M.; Knobler, C. B.; Diederich, F.; Wilkins, C. L. *J. Am. Chem. Soc.* **1991**, *113*, 495. (b) McElvany, S. W.; Ross, M. M.; Goroff, N. S.; Diederich, F. *Science* **1993**, *259*, 1594.

(90) Diederich, F.; Rubin, Y.; Chapman, O.; Goroff, N. S. *Helv. Chim. Acta* **1994**, *77*, 1441.

(91) Faust, R. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2825.

(92) Yamaguchi, M.; Park, H.-J.; Hirama, M. *Chem. Lett.* **1997**, 535.

(93) Lang, H. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 547.

(94) Bunz, U. H. F. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 969.

(95) Beck, W.; Niemer, B.; Wieser, M. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 923.

(96) Koutsantonis, G. A.; Selegue, J. P. *J. Am. Chem. Soc.* **1991**, *113*, 2316.

(97) (a) Listemann, M. L.; Schrock, R. R. *Organometallics* **1985**, *4*, 74. (b) Caulton, K. G.; Cayton, R. H.; Chisholm, M. H.; Huffman, J. C.; Lobkovsky, E. B.; Xue, Z. *Organometallics* **1992**, *11*, 321. (c) Gilbert, T. M.; Roger, R. D. *J. Organomet. Chem.* **1991**, *421*, C1.

(98) Ustynyuk, N. A.; Vinogradova, V. N.; Kravtsov, D. N.; Oprunenko, Y. F.; Piven, V. A. *Metalloorg. Khim. USSR* **1988**, *1*, 884.

(99) (a) Akita, M.; Terada, M.; Oyama, S.; Sugimoto, S.; Moro-oka, Y. *Organometallics* **1991**, *10*, 1561. (b) Akita, M.; Terada, M.; Oyama, S.; Moro-oka, Y. *Organometallics* **1990**, *9*, 816.

(100) St. Clair, M.; Schaefer, W. P.; Bercaw, J. E. *Organometallics* **1991**, *10*, 525.

(101) Ustynyuk, N. A.; Vinogradova, V. N.; Kravtsov, D. N. *Metalloorg. Khim. USSR* **1988**, *1*, 85.

(102) Binger, P.; Müller, P.; Philipps, P.; Gabor, B.; Mynott, R.; Herrmann, A. T.; Langhauser, F.; Krüger, C. *Chem. Ber.* **1992**, *125*, 2209.

(103) (a) Cross, R. J.; Davidson, M. F.; McLennan, A. J. *J. Organomet. Chem.* **1984**, *265*, C37. (b) Cross, R. J.; Davidson, M. F. *J. Chem. Soc., Dalton Trans.* **1986**, 411.

(104) (a) Beck, W.; Niemer, B.; Breimair, J.; Heidrich, J. *J. Organomet. Chem.* **1989**, *372*, 79. (b) Heidrich, J.; Steimann, M.; Appel, M.; Beck, W.; Phillips, J. R.; Trogler, W. C. *Organometallics* **1990**, *9*, 1296.

(105) Davies, J. A.; El-Ghanam, M.; Pinkerton, A. A.; Smith, D. A. *J. Organomet. Chem.* **1991**, *409*, 367.

(106) Southard, G. E.; Curtis, M. D.; Kampf, J. W. *Organometallics* **1996**, *15*, 4667.

(107) Woodworth, B. E.; White, P. S.; Templeton, J. L. *J. Am. Chem. Soc.* **1997**, *119*, 828.

(108) (a) Bullock, R. M.; Lemke, F. R.; Szalda, D. J. *J. Am. Chem. Soc.* **1990**, *112*, 3244. (b) Lemke, F. R.; Szalda, D. J.; Bullock, R. M. *J. Am. Chem. Soc.* **1991**, *113*, 8466.

(109) Brady, M.; Weng, W.; Gladysz, J. A. *J. Chem. Soc., Chem. Commun.* **1994**, 2655.

(110) (a) Le Narvor, N.; Toupet, L.; Lapinte, C. *J. Am. Chem. Soc.* **1995**, *117*, 7129. (b) Le Narvor, N.; Lapinte, C. *J. Chem. Soc., Chem. Commun.* **1993**, 357.

(111) Yam, V. W.-W.; Lau, V. C.-Y.; Cheung, K.-K. *Organometallics* **1995**, *14*, 2749.

(112) Yam, V. W.-W.; Lau, V. C.-Y.; Cheung, K.-K. *Organometallics* **1996**, *15*, 1740.

(113) Crescenzi, R.; Lo Sterzo, C. *Organometallics* **1992**, *11*, 4301.

(114) Wong, A.; Kang, P. C. W.; Tagge, C. D.; Leon, D. R. *Organometallics* **1990**, *9*, 1992.

(115) Bruce, M. I.; Hinterding, P.; Tiekink, E. R. T.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1993**, *450*, 209.

(116) Adams, C. J.; Bruce, M. I.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1993**, *450*, C9.

(117) Bruce, M. I.; Ke, M.; Low, P. J. *Chem. Commun.* **1996**, 2405.

(118) Gevert, O.; Wolf, J.; Werner, H. *Organometallics* **1996**, *15*, 2806.

(119) Weng, W.; Bartik, T.; Brady, M.; Bartik, B.; Ramsden, J. A.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1995**, *117*, 11922.

(120) Coat, F.; Lapinte, C. *Organometallics* **1996**, *15*, 477.

(121) Bartik, T.; Bartik, B.; Brady, M.; Dembinski, R.; Gladysz, J. A. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 414.

(122) Bartik, B.; Dembinski, R.; Bartik, T.; Arif, A. M.; Gladysz, J. A. *New J. Chem.* **1997**, *21*, 739.

(123) Falloon, S. B.; Arif, A. M.; Gladysz, J. A. *Chem. Commun.* **1997**, 629.

(124) Falloon, S. B.; Szafert, S.; Arif, A. M.; Gladysz, J. A. *Chem. Eur. J.* **1998**, *4*, 1033.

(125) Osella, D.; Milone, L.; Nervi, C.; Ravera, M. *J. Organomet. Chem.* **1995**, *488*, 1.

(126) Bruce, M. I.; Denisovich, L. I.; Low, P. J.; Peregudova, S. M.; Ustynyuk, N. A. *Mendeleev Commun.* **1996**, 200.

(127) Wiberg, K. B.; Connor, D. S.; Lampman, G. M. *Tetrahedron Lett.* **1964**, 531.

(128) Kaszynski, P.; Michl, J. In *The Chemistry of the Cyclopropyl Group*; Rappoport, Z., Ed.; Wiley: New York, 1995; Vol. 2, p 773.

(129) Wiberg, K. B.; Walker, F. H. *J. Am. Chem. Soc.* **1982**, *104*, 5239.

(130) (a) Belzner, J.; Gareiss, B.; Polborn, K.; Schmid, W.; Semmler, K.; Szeimies, G. *Chem. Ber.* **1989**, *122*, 1509. (b) Belzner, J.; Bunz, U.; Semmler, K.; Szeimies, G.; Opitz, K.; Schlüter, A. D. *Chem. Ber.* **1989**, *122*, 397.

(131) Feller, D.; Davidson, E. R. *J. Am. Chem. Soc.* **1987**, *109*, 4132.

(132) Wiberg, K. B.; Hadad, C. M.; Sieber, S.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1992**, *114*, 5820.

(133) (a) Alber, F.; Szeimies, G. *Chem. Ber.* **1992**, *125*, 757. (b) Alber, F.; Szeimies, G. *Tetrahedron Lett.* **1994**, *35*, 4093.

(134) Kaszynski, P.; Michl, J. In *Advances in Strain in Organic Chemistry*; JAI Press Inc.: London, 1995; Vol. 4, p 283.

(135) Della, E. W.; Lochert, I. J. *Org. Prep. Proc. Int.* **1996**, *28*, 411.

(136) Wiberg, K. B.; Waddell, S. T. *J. Am. Chem. Soc.* **1990**, *112*, 2194.

(137) Kaszynski, P.; Friedli, A. C.; Michl, J. *J. Am. Chem. Soc.* **1992**, *114*, 601.

(138) Levin, M. D.; Kaszynski, P.; Michl, J. Manuscript in preparation.

(139) Wiberg, K. B.; Waddell, S. T.; Laidig, K. *Tetrahedron Lett.* **1986**, *27*, 1553.

(140) (a) Szeimies, G. In *Strain and Its Implications in Organic Chemistry*; de Meijere, A., Blechert, S., Eds.; NATO ASI Series 273; Kluwer: Dordrecht, 1989; p 361. (b) Michl, J.; Kaszynski, P.; Friedli, A. C.; Murthy, G. S.; Yang, H.-C.; Robinson, R. E.; McMurdie, N. D.; Kim, T. In *Strain and Its Implications in Organic Chemistry*; de Meijere, A.; Blechert, S., Eds.; NATO ASI Series 273; Kluwer: Dordrecht, 1989; p 463.

(141) Schäfer, J.; Polborn, K.; Szeimies, G. *Chem. Ber.* **1988**, *121*, 2263.

(142) Hassenrück, K.; Murthy, G. S.; Lynch, V. M.; Michl, J. *J. Org. Chem.* **1990**, *55*, 1013.

(143) Mazal, C.; Paraskos, A. J.; Michl, J. *J. Org. Chem.* **1998**, *63*, 2116.

(144) Friberg, S. E.; Kayali, I.; Kaszynski, P.; Michl, J. *Langmuir* **1992**, *8*, 996.

(145) de Meijere, A.; Messner, M.; Vill, V. *Mol. Cryst. Liq. Cryst.* **1994**, *257*, 161.

(146) Ramireddy, C.; Reddy, V. S.; Munk, P.; Wu, C. N. *Macromolecules* **1991**, *24*, 1387.

(147) Levin, M. D.; Hamrock, S. J.; Kaszynski, P.; Shtarev, A. B.; Levina, G. A.; Noll, B. C.; Ashley, M. E.; Newmark, R.; Moore, G. G. I.; Michl, J. *J. Am. Chem. Soc.* **1997**, *119*, 12750.

(148) Wiberg, K. B.; Williams, V. Z., Jr. *J. Org. Chem.* **1970**, *35*, 369.

(149) Robinson, R. E.; Michl, J. *J. Org. Chem.* **1989**, *54*, 2051.

(150) Wiberg, K. B.; McMurdie, N. *J. Am. Chem. Soc.* **1994**, *116*, 11990.

(151) Schlüter, A.-D.; Bothe, H.; Gosau, J.-M. *Makromol. Chem.* **1991**, *192*, 2497.

(152) McKinley, A. J.; Ibrahim, P. N.; Balaji, V.; Michl, J. *J. Am. Chem. Soc.* **1992**, *114*, 10631.

(153) Gleiter, R.; Pfeifer, K.-H.; Szeimies, G.; Bunz, U. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 413.

(154) Yang, H. C.; Magnera, T. F.; Lee, C. M.; Bard, A. J.; Michl, J. *Langmuir* **1992**, *8*, 2740.

(155) Obeng, Y. S.; Laing, M. E.; Friedli, A. C.; Yang, H. C.; Wang, D.; Thulstrup, E. W.; Bard, A. J.; Michl, J. *J. Am. Chem. Soc.* **1992**, *114*, 9943.

(156) Mazieres, S.; Raymond, M. K.; Raabe, G.; Prodi, A.; Michl, J. *J. Am. Chem. Soc.* **1997**, *119*, 6682.

(157) Vacek, J.; Michl, J. *New J. Chem.* **1997**, *21*, 1259.

(158) Alder, K.; Stein, G. *Liebigs Ann.* **1934**, *514*, 1.

(159) Eaton, P. E.; Temme, G. H., III *J. Am. Chem. Soc.* **1973**, *95*, 7508.

(160) Zimmerman, H. E.; King, R. K.; Meinhardt, M. B. *J. Org. Chem.* **1992**, *57*, 5484.

(161) Nuding, G.; Vögtle, F.; Danielmeier, K.; Steckhan, E. *Synthesis* **1996**, 71.

(162) Eaton, P. E.; Cole, T. W., Jr. *J. Am. Chem. Soc.* **1964**, *86*, 962.

(163) Griffin, G. W.; Marchard, A. P. *Chem. Rev.* **1989**, *89*, 997.

(164) Eaton, P. E. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1421.

(165) Hassenrück, K.; Radziszewski, J. G.; Balaji, V.; Murthy, G. S.; McKinley, A. J.; David, D. E.; Lynch, V. M.; Martin, H.-D.; Michl, J. *J. Am. Chem. Soc.* **1990**, *112*, 873.
(166) Borden, W. T.; Hrovat, D. A. *J. Am. Chem. Soc.* **1990**, *112*, 875.
(167) Eaton, P. E.; Tsanaktsidis, J. *J. Am. Chem. Soc.* **1990**, *112*, 876.
(168) Gilardi, R.; Maggini, M.; Eaton, P. E. *J. Am. Chem. Soc.* **1988**, *110*, 7232.
(169) Eaton, P. E.; Pramod, K.; Emrick, T.; Gilardi, R. *J. Am. Chem. Soc.* **1999**, *121*, 4111.
(170) Yang, X. G.; Jiang, W.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1992**, *114*, 9719.
(171) Scholer, F. R.; Todd, L. J. In *Preparative Inorganic Reactions*; Jolly, W. L., Ed.; Wiley-Interscience: New York, 1971; (a) p 41, (b) p 40, (c) p 11.
(172) Müller, J.; Baše, K.; Magnera, T. F.; Michl J. *J. Am. Chem. Soc.* **1992**, *114*, 9721.
(173) Mortimer, M. D.; Hawthorne, M. F. *Chem. Brit.* **1996**, *32*, 32.
(174) (a) King, B. T.; Janoušek, Z.; Grüner, B.; Trammell, M.; Noll, B. C.; Michl, J. *J. Am. Chem. Soc.* **1996**, *118*, 3313. (b) Michl, J.; King, B. T.; Janousek, Z. U.S. Patent No. 5,731,470, March 24, 1998.
(175) Zinn, A. A.; Zheng, Z.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1996**, *118*, 70.
(176) Berry, R. S.; Clardy, J.; Schafer, M. E. *Tetrahedron Lett.* **1965**, 1003.
(177) Marquardt, R.; Balster, A.; Sander, W.; Kraka, E.; Cremer, D.; Radziszewski, J. G. *Angew. Chem.* **1998**, *110*, 1001.
(178) Marquardt, R.; Sander, W.; Kraka, E. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 746.
(179) Dewar, M. J. S.; Li, W.-K. *J. Am. Chem. Soc.* **1974**, *96*, 5569.
(180) Logan, C. F.; Chen, P. *J. Am. Chem. Soc.* **1996**, *118*, 2113.
(181) Jones, R. R.; Bergman, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 660.
(182) Bergman, R. G. *Acc. Chem. Res.* **1973**, *6*, 25.
(183) Ried, W.; Freitag, D. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 835.
(184) Ullmann, F. *Liebigs Ann. Chem.* **1904**, *332*, 38.
(185) Wirth, H. O.; Gönner, K. H.; Stück, R.; Kern, W. *Makromol. Chem.* **1963**, *63*, 30.
(186) Pummerer, R.; Bittner, K. *Ber. Dtsch. Chem. Ges.* **1924**, *57B*, 84.
(187) Dayal, S. K.; Rao, K. N. *Indian J. Chem.* **1967**, *5*, 122.
(188) Mayer, F.; Schiffner, R. *Ber. Dtsch. Chem. Ges.* **1932**, *65*, 1337.
(189) Kern, W.; Gruber, W.; Wirth, H. O. *Makromol. Chem.* **1960**, *37*, 198.
(190) Heitz, W.; Ullrich, R. *Makromol. Chem.* **1966**, *98*, 29.
(191) Lohaus, H. *Liebigs Ann. Chem.* **1935**, *516*, 295.
(192) Babudri, F.; Cardone, A.; Farinola, G. M.; Naso, F. *Tetrahedron* **1998**, *54*, 14609.
(193) Heldt, W. Z. *J. Org. Chem.* **1965**, *30*, 3897.
(194) Busch, M.; Weber, W.; Darboven, C.; Renner, W.; Hahn, H. J.; Mathauser, G.; Strätz, F.; Zitzmann, K.; Engelhart, H. *J. Prakt. Chem.* **1936**, *146*, 1.
(195) Yamamoto, T.; Hayashi, Y.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2091.
(196) Miyaura, N.; Yanagi, T.; Suzuki, A. *Synth. Commun.* **1981**, *11*, 513.
(197) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457.
(198) Scherf, U.; Müllen, K. *Synthesis* **1992**, 23.
(199) Goldfinger, M. B.; Swager, T. M. *J. Am. Chem. Soc.* **1994**, *116*, 7895.
(200) Galda, P.; Rehahn, M. *Synthesis* **1996**, 614.
(201) Hensel, V.; Schlüter, A.-D. *Liebigs Ann./Recl.* **1997**, 303.
(202) Ghebremariam, B.; Sidorov, V.; Matile, S. *Tetrahedron Lett.* **1999**, *40*, 1445.
(203) Weiss, L. A.; Sakai, N.; Ghebremariam, B.; Ni, C.; Matile, S. *J. Am. Chem. Soc.* **1997**, *119*, 12142.
(204) Sakai, N.; Brennan, K. C.; Weiss, L. A.; Matile, S. *J. Am. Chem. Soc.* **1997**, *119*, 8726.
(205) Ni, C.; Matile, S. *Chem. Commun.* **1998**, 755.
(206) Giroux, A.; Han, Y.; Prasit, P. *Tetrahedron Lett.* **1997**, *38*, 3841.
(207) (a) Corriu, R. *Polyhedron* **1998**, *17*, 925. (b) Corriu, R. *Coord. Chem. Rev.* **1998**, *180*, 1051.
(208) Fukuda, M.; Sawada, K.; Yoshino, K. *J. Polym. Sci., Polym. Chem.* **1993**, *31*, 2465.
(209) Klaerner, G.; Miller, R. D. *Macromolecules* **1998**, *31*, 2007.
(210) Kreyenschmidt, M.; Uckert, F.; Müllen, K. *Macromolecules* **1995**, *28*, 4577.
(211) Fagan, P. J.; Ward, M. D.; Calabrese, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 1698.
(212) Harre, K.; Enkelmann, V.; Schulze, M.; Bunz, U. H. F. *Chem. Ber.* **1996**, *129*, 1323.
(213) Wallenberger, F. T. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 460.
(214) Tour, J. M.; Lamba, J. J. S. *J. Am. Chem. Soc.* **1993**, *115*, 4935.
(215) Tsuzuki, S.; Tanabe, K. *J. Phys. Chem.* **1991**, *95*, 139.
(216) Farmer, B. L.; Chapman, B. R.; Dudis, D. S.; Adams, W. W. *Polymer* **1993**, *34*, 1588.
(217) Socci, E. P.; Forner, B. L.; Adams, W. W. *J. Polym. Sci., Part B* **1993**, *31*, 1975.
(218) Gosztola, D.; Niemczyk, M. P.; Wasielewski, M. R. *J. Am. Chem. Soc.* **1998**, *120*, 5118.
(219) Enkelmann, V. In *Electronic Materials: The Oligomeric Approach*; Müllen, K.; Wegner, G., Eds.; Wiley: Chichester, 1998; Chapter 5.1, p 295 and references therein.
(220) Murthy, P. S.; Michl, J. *Collect. Czechoslovak Chem. Commun.* **1988**, *53*, 2366.
(221) Grim, P. C. M.; De Feyter, S.; Gesquière, A.; Vanoppen, P.; Rücker, M.; Valiyaveettil, S.; Moessner, G.; Müllen, K.; De Schryver, F. C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2601.
(222) Grimme, J.; Kreyenschmidt, M.; Uckert, F.; Müllen, K.; Scherf, U. *Adv. Mater.* **1995**, *7*, 292.
(223) Pei, Q.; Yang, Y. *J. Am. Chem. Soc.* **1996**, *118*, 7416.
(224) Sakai, N.; Majumdar, N.; Matile, S. *J. Am. Chem. Soc.* **1999**, *121*, 4294.
(225) Sakai, N.; Ni, C.; Bezrukov, S. M.; Matile, S. *Bioorg. Med. Chem. Lett.* **1998**, *8*, 2743.
(226) Ghebremariam, B.; Matile, S. *Tetrahedron Lett.* **1998**, *39*, 5335.
(227) Keegstra, M.; De Feyter, S.; De Schryver, F.; Müllen, K. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 774.
(228) Lewis, P. T.; Strongin, R. M. *J. Org. Chem.* **1998**, *63*, 6065.
(229) Pu, L. *Chem. Rev.* **1998**, *98*, 2405.
(230) Koch, K.-H.; Müllen, K. *Chem. Ber.* **1991**, *124*, 2091.
(231) Fahnenstich, U.; Koch, K.-H.; Müllen, K. *Makromol. Chem. Rapid Commun.* **1989**, *10*, 563.
(232) Koch, K. H.; Fahnenstich, U.; Baumgarten, M.; Müllen, K. *Synth. Met.* **1991**, *41−43*, 1619.
(233) Bělohradský, M.; Buděšínský, M.; Günterová, J.; Hodačová, J.; Holý, P.; Závada, J.; Císařová, I.; Podlaha, J. *J. Org. Chem.* **1996**, *61*, 1205.
(234) Müllen, K. *Pure Appl. Chem.* **1993**, *65*, 89.
(235) Schottelius, M. J.; Chen, P. *J. Am. Chem. Soc.* **1996**, *118*, 4896.
(236) Lippert, E.; Rettig, W.; Bonacic-Koutecky, V.; Heisel, F.; Miehé, J. A. *Adv. Chem. Phys.* **1987**, *68*, 1.
(237) Müller, U.; Adam, M.; Müllen, K. *Chem. Ber.* **1994**, *127*, 437.
(238) Baumgarten, M.; Müller, U. *Synth. Met.* **1993**, *55−57*, 443.
(239) Baumgarten, M.; Müller, U.; Bohnen, A.; Müllen, K. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 448.
(240) Nishiyama, K.; Honda, T.; Reis, H.; Müller, U.; Müllen, K.; Baumann, W.; Okada, T. *J. Phys. Chem. A.* **1998**, *102*, 2934.
(241) Kreyenschmidt, M.; Baumgarten, M.; Tyutyulkov, N.; Müllen, K. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1957.
(242) Morris, J. L.; Becker, C. L.; Fronczek, F. R.; Daly, W. H.; McLaughlin, M. L. *J. Org. Chem.* **1994**, *59*, 684.
(243) Langhals, H.; Jona, W. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 952.
(244) Graser, F.; Hädicke, E. *Liebigs Ann. Chem.* **1980**, 1994.
(245) Graser, F.; Hädicke, E. *Liebigs Ann. Chem.* **1984**, 483.
(246) Baumgarten, M.; Anton, U.; Gherghel, L.; Müllen, K. *Synth. Met.* **1993**, *55−57*, 4807.
(247) Harris, F. W.; Chuang, K. C.; Huang, S. A. X.; Janimak, J. J.; Cheng, S. Z. D. *Polymer* **1994**, *35*, 4940.
(248) Reuss, R. H.; Winters, L. J. *J. Org. Chem.* **1973**, *38*, 3993.
(249) Creutz, C.; Taube, H. *J. Am. Chem. Soc.* **1973**, *95*, 1086.
(250) Ward, M. D. *Chem. Soc. Rev.* **1995**, 121.
(251) Sleiman, H.; Baxter, P. N. W.; Lehn, J.-M.; Rissanen, K. *J. Chem. Soc., Chem. Commun.* **1995**, 715.
(252) Baxter, P. N. W.; Hanan, G. S.; Lehn, J.-M. *Chem. Commun.* **1996**, 2019.
(253) Baxter, P. N. W.; Lehn, J.-M.; Fischer, J.; Youinou, M.-T. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2284.
(254) Baxter, P. N. W.; Lehn, J.-M.; DeCian, A.; Fischer, J. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 69.
(255) Sleiman, H.; Baxter, P. N. W.; Lehn, J.-M.; Airola, K.; Rissanen, K. *Inorg. Chem.* **1997**, *36*, 4734.
(256) Goodwin, H. A.; Lions, F. *J. Am. Chem. Soc.* **1959**, *81*, 6415.
(257) (a) Case, F. H. *J. Heterocycl. Chem.* **1967**, *4*, 157. (b) Pfeiffer, F.; Case, F. H. *J. Org. Chem.* **1966**, *31*, 3383.
(258) Bonhôte, P.; Wrighton, M. S. *Synlett* **1997**, 897.
(259) Constable, E. C.; Ward, M. D. *J. Chem. Soc., Dalton Trans.* **1990**, 1405.
(260) Balzani, V.; Juris, A.; Venturi, M.; Campagna, S.; Serroni, S. *Chem. Rev.* **1996**, *96*, 759.
(261) Baxter, P. N. W.; Lehn, J.-M.; Kneisel, B. O.; Fenske, D. *Chem. Commun.* **1997**, 2231.
(262) Marquis-Rigault, A.; Dupont-Gervais, A.; Baxter, P. N. W.; Van Dorsselaer, A.; Lehn, J.-M. *Inorg. Chem.* **1996**, *35*, 2307.
(263) Wasielewski, M. R. *Chem. Rev.* **1992**, *92*, 435.
(264) (a) Wasielewski, M. R. *Photo Chem. Photobiol.* **1988**, *47*, 923. (b) Gust, D.; Moore, T. A. *Science* **1989**, *244*, 35. (c) Kersey, K. M.; Minsek, D. W. *J. Am. Chem. Soc.* **1988**, *110*, 7219. (d) Heiler, D.; McLendon, G.; Rogalskyj, P. *J. Am. Chem. Soc.* **1987**, *109*, 604. (e) Kurreck, H.; Huber, M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 849.
(265) Osuka, A.; Shimidzu, H. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 135.
(266) Yoshida, N.; Shimidzu, H.; Osuka, A. *Chem. Lett.* **1998**, 55.
(267) Ogawa, T.; Nishimoto, Y.; Yoshida, N.; Ono, N.; Osuka, A. *Chem. Commun.* **1998**, 337.
(268) Susumu, K.; Shimidzu, T.; Tanaka, K.; Segawa, H. *Tetrahedron Lett.* **1996**, *37*, 8399.

(269) Khoury, R. G.; Jaquinod, L.; Smith, K. M. *Chem. Commun.* **1997**, 1057.
(270) Holmes, R. T.; Lin, J. J.; Khoury, R. G.; Jones, C. P.; Smith, K. M. *Chem. Commun.* **1997**, 819.
(271) Crescenzi, R.; Solari, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Inorg. Chem.* **1998**, *37*, 6044.
(272) Bunz, U. H. F. *Synlett* **1997**, 1117.
(273) Bunz, U.; Szeimies, G. *Tetrahedron Lett.* **1990**, *31*, 651.
(274) Bunz, U.; Szeimies, G. *Tetrahedron Lett.* **1989**, *30*, 2087.
(275) Eaton, P. E.; Stössel, D. *J. Org. Chem.* **1991**, *56*, 5138.
(276) Eaton, P. E.; Galoppini, E.; Gilardi, R. *J. Am. Chem. Soc.* **1994**, *116*, 7588.
(277) Zakharkin, L. I.; Kovderov, A. I.; Ol'shevskaya, V. A. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1986**, 1388.
(278) Bregadze, V. I. *Chem. Rev.* **1992**, *92*, 209.
(279) Jiang, W.; Harwell, D. E.; Mortimer, M. D.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1996**, *35*, 4355.
(280) Drefahl, G.; Plötner, G. *Chem. Ber.* **1958**, *91*, 1280.
(281) Stephens, R. D.; Castro, C. E. *J. Org. Chem.* **1963**, *28*, 3313.
(282) Burdon, J.; Coe, P. L.; March, C. R.; Tatlow, J. C. *Chem. Commun.* **1967**, 1259.
(283) Cassar, L. *J. Organomet. Chem.* **1975**, *93*, 253.
(284) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, 4467.
(285) Takahashi, S.; Kuroyama, Y.; Sonogashira, K.; Hagihara, N. *Synthesis* **1980**, 627.
(286) Dieck, H. A.; Heck, F. R. *J. Organomet. Chem.* **1975**, *93*, 259.
(287) Yamaguchi, S.; Iimura, K.; Tamao, K. *Chem. Lett.* **1998**, 89.
(288) Weiss, K.; Michel, A.; Auth, E.-M.; Bunz, U. H. F.; Mangel, T.; Müllen, K. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 506.
(289) Jones, L., II; Schumm, J. S.; Tour, J. M. *J. Org. Chem.* **1997**, *62*, 1388.
(290) Kukula, H.; Veit, S.; Godt, A. *Eur. J. Org. Chem.* **1999**, 277.
(291) White, D. M.; Quinn, C. B. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 2595
(292) Mayor, M.; Lehn, J.-M.; Fromm, K. M.; Fenske, D. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 21.
(293) Müller, T. J. J.; Lindner, H. J. *Chem. Ber.* **1996**, *129*, 607.
(294) Bumm, L. A.; Arnold, J. J.; Cygan, M. T.; Dunbar, T. D.; Burgin, T. P.; Jones, L., II; Allara, D. L.; Tour, J. M.; Weiss, P. S. *Science* **1996**, *271*, 1705.
(295) Tobe, Y.; Utsumi, N.; Nagano, A.; Naemura, K. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1285.
(296) Höger, S.; Enkelmann, V. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2713.
(297) (a) Zhang, J.; Pesak, D. J.; Ludwick, J. J.; Moore, J. S. *J. Am. Chem. Soc.* **1994**, *116*, 4227. (b) Bedard, T. C.; Moore, J. S. *J. Am. Chem. Soc.* **1995**, *117*, 10662. (c) Wu, Z.; Moore, J. S. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 297.
(298) Moore, J. S. *Acc. Chem. Res.* **1997**, *30*, 402.
(299) Devadoss, C.; Bharathi, P.; Moore, J. S. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1633.
(300) Pesak, D. J.; Moore, J. S. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1636.
(301) Shortreed, M. R.; Swallen, S. F.; Shi, Z.-Y.; Tan, W.; Xu, Z.; Devadoss, C.; Moore, J. S.; Kopelman, R. *J. Phys. Chem. B* **1997**, *101*, 6318.
(302) Haley, M. M.; Brand, S. C.; Pak, J. J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 836.
(303) Eickmeier, C.; Junga, H.; Matzger, A. J.; Scherhag, F.; Shim, M.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2103.
(304) Rubin, Y.; Parker, T. C.; Pastor, S. J.; Jalisatgi, S.; Boulle, C.; Wilkins, C. L. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1226.
(305) Takahashi, S.; Morimoto, H.; Murata, E.; Kataoka, S.; Sonogashira, K.; Hagashira, N. *J. Polym. Sci., Part A* **1982**, *20*, 565.
(306) Zargarian, D.; Chow, P.; Taylor, N. J.; Marder, T. B. *J. Chem. Soc., Chem. Commun.* **1989**, 540.
(307) Davies, S. J.; Johnson, B. F. G.; Khan, M. S.; Lewis, J. *J. Chem. Soc., Chem. Commun.* **1991**, 187.
(308) Bianchini, C.; Mealli, C.; Peruzzini, M.; Vizza, F.; Zanobini, F. *J. Organomet. Chem.* **1988**, *346*, C53.
(309) Haquette, P.; Pirio, N.; Touchard, D.; Toupet, L.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1993**, 163.
(310) Jia, G. C.; Payne, N. C.; Vittal, J. J.; Puddephatt, R. J. *Organometallics* **1993**, *12*, 4771.
(311) Adams, R. D.; Barnard, T.; Rawlett, A.; Tour, J. M. *Eur. J. Inorg. Chem.* **1998**, 429.
(312) (a) Yu, M. P. Y.; Cheung, K.-K.; Mayr, A. *J. Chem. Soc., Dalton Trans.* **1998**, 2373. (b) Yu, M. P. Y.; Mayr, A.; Cheung, K.-K. *J. Chem. Soc., Dalton Trans.* **1998**, 475.
(313) Stang, P. J.; Crittell, C. M. *Organometallics* **1990**, *9*, 3191.
(314) Tykwinski, R. R.; Stang, P. J. *Organometallics* **1994**, *13*, 3203.
(315) Lavastre, O.; Plass, J.; Bachmann, P.; Guesmi, S.; Moinet, C.; Dixneuf, P. H. *Organometallics* **1997**, *16*, 184.
(316) Faulkner, C. W.; Ingham, S. L.; Khan, M. S.; Lewis, J.; Long, N. J.; Raithby, P. R. *J. Organomet. Chem.* **1994**, *482*, 139.
(317) Field, L. D.; George, A. V.; Laschi, F.; Malouf, E. Y.; Zanello, P. *J. Organomet. Chem.* **1992**, *425*, 347.
(318) Davies, S. J.; Johnson, B. F. G.; Khan, M. S.; Lewis, J. *J. Chem. Soc., Chem. Commun.* **1991**, 187.
(319) Fyfe, H. B.; Mlekuz, M.; Zargarian, D.; Taylor, N. J.; Marder, T. B. *J. Chem. Soc., Chem. Commun.* **1991**, 188.
(320) Jia, G. C.; Puddephatt, R. J.; Scott, J. D.; Vittal, J. J. *Organometallics* **1993**, *12*, 3565.
(321) Stang, P. J.; Tykwinski, R. *J. Am. Chem. Soc.* **1992**, *114*, 4411.
(322) Osella, D.; Milone, L.; Nervi, C.; Ravera, M. *Eur. J. Inorg. Chem.* **1998**, 1473.
(323) Irwin, M. J.; Vittal, J. J.; Puddephatt, R. J. *Organometallics* **1997**, *16*, 3541.
(324) Uno, M.; Dixneuf, P. H. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1714.
(325) Long, N. J.; Martin, A. J.; Fabrizi de Biani, F.; Zanello, P. *J. Chem. Soc., Dalton Trans.* **1998**, 2017.
(326) Leininger, S.; Stang, P. J.; Huang, S. *Organometallics* **1998**, *17*, 3981.
(327) DiMagno, S. G.; Lin, V. S.-Y.; Therien, M. J. *J. Am. Chem. Soc.* **1993**, *115*, 2513.
(328) DiMagno, S. G.; Lin, V. S.-Y.; Therien, M. J. *J. Org. Chem.* **1993**, *58*, 5983.
(329) Lindsey, J. S.; Prathapan, S.; Johnson, T. E.; Wagner, R. W. *Tetrahedron* **1994**, *50*, 8941.
(330) Arnold, D. P.; Johnson, A. W.; Mahendran, M. *J. Chem. Soc., Perkin Trans. 1* **1978,** 366.
(331) Anderson, H. L.; Sanders, J. K. M. *J. Chem. Soc., Chem. Commun.* **1989**, 1714.
(332) Vidal-Ferran, A.; Müller, C. M.; Sanders, J. K. M. *J. Chem. Soc., Chem. Commun.* **1994**, 2657.
(333) Gosper, J. J.; Ali, M. *J. Chem. Soc., Chem. Commun.* **1994**, 1707.
(334) Wagner, R. W.; Johnson, T. E.; Li, F.; Lindsey, J. S. *J. Org. Chem.* **1995**, *60*, 5266.
(335) Arnold, D. P.; James, D. A. *J. Org. Chem.* **1997**, *62*, 3460.
(336) Angiolillo, P. J.; Lin, V. S.-Y.; Vanderkooi, J. M.; Therien, M. J. *J. Am. Chem. Soc.* **1995**, *117*, 12514.
(337) Lin, V. S.-Y.; Therien, M. J. *Chem. Eur. J.* **1995**, *1*, 645.
(338) Lin, V. S.-Y.; DiMagno, S. G.; Therien, M. J. *Science* **1994**, *264*, 1105.
(339) Anderson, H. L. *Inorg. Chem.* **1994**, *33*, 972.
(340) Stranger, R.; McGrady, J. E.; Arnold, D. P.; Lane, I.; Heath, G. A. *Inorg. Chem.* **1996**, *35*, 7791.
(341) Taylor, P. N.; Wylie, A. P.; Huuskonen, J.; Anderson, H. L. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 986.
(342) Sutton, J. E.; Taube, H. *Inorg. Chem.* **1981**, *20*, 3125.
(343) Della Ciana, L.; Haim, A. *J. Heterocycl. Chem.* **1984**, *21*, 607.
(344) Grosshenny, V.; Romero, F. M.; Ziessel, R. *J. Org. Chem.* **1997**, *62*, 1491.
(345) Grosshenny, V.; Harriman, A.; Ziessel, R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1100.
(346) Grosshenny, V.; Harriman, A.; Ziessel, R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2705.
(347) Hissler, M.; El-ghayoury, A.; Harriman, A.; Ziessel, R. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1717.
(348) Grosshenny, V.; Harriman, A.; Hissler, M.; Ziessel, R. *Platinum Met. Rev.* **1996**, *40*, 72.
(349) Harriman, A.; Ziessel, R. *Chem. Commun.* **1996**, 1707.
(350) Benniston, A. C.; Grosshenny, V.; Harriman, A.; Ziessel, R. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1884.
(351) Grosshenny, V.; Harriman, A.; Ziessel, R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1100.
(352) Dexter, D. L. *J. Chem. Phys.* **1953**, *21*, 836.
(353) Connors, P. J., Jr.; Tzalis, D.; Dunnick, A. L.; Tor, Y. *Inorg. Chem.* **1998**, *37*, 1121.
(354) Bunz, U. H. F.; Wiegelmann-Kreiter, J. E. C. *Chem. Ber.* **1996**, *129*, 785.
(355) Bunz, U. H. F. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 10.
(356) Wiegelmann, J. E. C.; Bunz, U. H. F. *Organometallics* **1993**, *12*, 3792.
(357) Wiegelmann, J. E. C.; Bunz, U. H. F.; Schiel, P. *Organometallics* **1994**, *13*, 4649.
(358) Bunz, U. H. F. *Synlett* **1997**, 1117.
(359) Altmann, M.; Roidl, G.; Enkelmann, V.; Bunz, U. H. F. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1107.
(360) Altmann, M.; Enkelmann, V.; Bunz, U. H. F. *Chem. Ber.* **1996**, *129*, 269.
(361) Fritsch, J. R.; Vollhardt, K. P. C. *Organometallics* **1982**, *1*, 590.
(362) Altmann, M.; Enkelmann, V.; Beer, F.; Bunz, U. H. F. *Organometallics* **1996**, *15*, 394.
(363) Wiegelmann-Kreiter, J. E. C.; Bunz, U. H. F. *Organometallics* **1995**, *14*, 4449.
(364) Mayr, A.; Guo, J. *Inorg. Chem.* **1999**, *38*, 921.
(365) Patoux, C.; Launay, J.-P.; Beley, M.; Chodorowski-Kimmes, S.; Collin, J.-P.; James, S.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1998**, *120*, 3717.
(366) Collin, J.-P.; Gaviña, P.; Heitz, V.; Sauvage, J.-P. *Eur. J. Inorg. Chem.* **1998**, 1.
(367) Maruyama, K.; Kawabata, S. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 170.
(368) Kawabata, S.; Tanabe, N.; Osuka, A. *Chem. Lett.* **1994**, 1797.

(369) Ravikanth, M.; Strachan, J.-P.; Li, F.; Lindsey, J. S. *Tetrahedron* **1998**, *54*, 7721.
(370) Wagner, R. W.; Lindsey, J. S. *J. Am. Chem. Soc.* **1994**, *116*, 9759.
(371) Kawabata, S.; Yamazaki, I.; Nishimura, Y.; Osuka, A. *J. Chem. Soc., Perkin Trans 2* **1997**, 479.
(372) Kajanus, J.; van Berlekom, S. B.; Albinsson, B.; Mårtensson, J. *Synthesis*, in press.
(373) Osuka, A.; Maruyama, K.; Yamazaki, I.; Tamai, N. *Chem. Phys. Lett.* **1990**, *165*, 392.
(374) Strachan, J.-P.; Gentemann, S.; Seth, J.; Kalsbeck, W. A.; Lindsey, J. S.; Holten, D.; Bocian, D. F. *Inorg. Chem.* **1998**, *37*, 1191.
(375) Strachan, J.-P.; Gentemann, S.; Seth, J.; Kalsbeck, W. A.; Lindsey, J. S.; Holten, D.; Bocian, D. F. *J. Am. Chem. Soc.* **1997**, *119*, 11191.
(376) Mongin, O.; Gossauer, A. *Tetrahedron* **1997**, *53*, 6835.
(377) Mongin, O.; Gossauer, A. *Tetrahedron Lett.* **1996**, *37*, 3825.
(378) Mongin, O.; Papamicaël, C.; Hoyler, N.; Gossauer, A. *J. Org. Chem.* **1998**, *63*, 5569.
(379) Wagner, R. W.; Seth, J.; Yang, S. I.; Kim, D.; Bocian, D. F.; Holten, D.; Lindsey, J. S. *J. Org. Chem.* **1998**, *63*, 5042.
(380) Prathapan, S.; Johnson, T. E.; Lindsey, J. S. *J. Am. Chem. Soc.* **1993**, *115*, 7519.
(381) Wylie, R. S.; Levy, E. G.; Sanders, J. K. M. *Chem. Commun.* **1997**, 1611.
(382) Bent, H. A. *Chem. Rev.* **1961**, *61*, 275.
(383) Zimmerman, H. E.; McKelvey, R. D. *J. Am. Chem. Soc.* **1971**, *93*, 3638.
(384) Chapman, N. B.; Sotheeswaran, S.; Toyne, K. J. *J. Org. Chem.* **1970**, *35*, 1970.
(385) Förster, T. *Discuss. Faraday Soc.* **1959**, *27*, 7.
(386) Paulson, B.; Pramod, K.; Eaton, P. E.; Closs, G.; Miller, J. R. *J. Phys. Chem.* **1993**, *97*, 13042.
(387) Zakharkin, L. I.; Kovredov, A. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1974**, 740.
(388) Schöberl, U.; Magnera, T. F.; Harrison, R. M.; Fleischer, F.; Pflug, J. L.; Schwab, P. F. H.; Meng, X.; Lipiak, D.; Noll, B. C.; Allured, V. S.; Rudalevige, T.; Lee, S.; Michl, J. *J. Am. Chem. Soc.* **1997**, *119*, 3707.
(389) Fox, M. A.; MacBride, J. A. H.; Peace, R. J.; Wade, K. *J. Chem. Soc., Dalton Trans.* **1998**, 401.
(390) Grüner, B.; Janousek, Z.; King, B. T.; Guan H.-W.; Wang, C. H.; Vsetecka, V.; Michl, J. *J. Am. Chem. Soc.* **1999**, *121*, 3122.
(391) Clegg, W.; Gill, W. R.; MacBride, J. A. H.; Wade, K. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1328.
(392) Michl, J.; West, R. In *Oxocarbons*; West, R., Ed.; Academic Press: New York, 1980; p 79.
(393) Schmidt, A. H. *The Chemistry of Squaraines* in *Oxocarbons*; West, R., Ed.; Academic Press: New Yoark, 1990; Chapter 10.
(394) Treibs, A.; Jacob, K. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 694.
(395) Law, K.-Y. *Chem. Rev.* **1993**, *93*, 449.
(396) Ashwell, G. J.; Bahra, G. S.; Brown, C. R.; Hamilton, D. G.; Kennard, C. H. L.; Lynch, D. E. *J. Mater. Chem.* **1996**, *6*, 23.
(397) Chen, H.; Law, K.-Y.; Perlstein, J.; Whitten, D. G. *J. Am. Chem. Soc.* **1995**, *117*, 7257.
(398) Liang, K.; Law, K.-Y.; Whitten, D. G. *J. Phys. Chem. B* **1997**, *101*, 540.
(399) Meier, H.; Dullweber, U. *J. Org. Chem.* **1997**, *62*, 4821.
(400) Ziegenbeimn, W.; Sprenger, H.-E. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 893.
(401) Treibs, A.; Jacob, K. *Liebigs Ann. Chem.* **1966**, *699*, 153.
(402) Keil, D.; Hartmann, H.; Moschny, T. *Dyes Pigm.* **1991**, *17*, 19.
(403) Das, S.; Thomas, K. G.; Thomas, K. J.; Madhavan, V.; Liu, D. Kamat, P. V.; George, M. V. *J. Phys. Chem.* **1996**, *100*, 17310.
(404) Sprenger, H.-E.; Ziegenbeim, W. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 530.
(405) Nakazumi, H.; Natsukawa, K.; Nakai, K.; Isagawa, K. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1001.
(406) Law, K.-Y.; Bailey, F. C. *Can. J. Chem.* **1993**, *71*, 494.
(407) Law, K.-Y.; Bailey, F. C. *J. Org. Chem.* **1992**, *57*, 3278.
(408) Law, K.-Y. *Chem. Mater.* **1992**, *4*, 605.
(409) Law, K.-Y.; Bailey, F. C. *J. Chem. Soc., Chem. Commun.* **1990**, 863.
(410) Oguz, U.; Akkaya, E. U. *J. Org. Chem.* **1998**, *63*, 6059.
(411) Maahs, G.; Hegenberg, P. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 888.
(412) Dirk, C. W.; Herndon, W. C.; Cervantes-Lee, F.; Selnau, H.; Martinez, S.; Kalamegham, P.; Tan, A.; Campos, G.; Velez, M.; Zyss, J.; Ledoux, I.; Cheng, L.-T. *J. Am. Chem. Soc.* **1995**, *117*, 2214.
(413) Meyers, F.; Chen, C.-T.; Marder, S. R.; Brédas, J.-J. *Chem. Eur. J.* **1997**, *3*, 530.
(414) Das, A.; Maher, J. P.; McCleverty, J. A.; Badiola, J. A. N.; Ward, M. D. *J. Chem. Soc., Dalton Trans.* **1993**, 681.
(415) Kim, Y.; Lieber, C. M. *Inorg. Chem.* **1989**, *28*, 3990.
(416) Wärnmark, K.; Baxter, P. N. W.; Lehn, J.-M. *Chem. Commun.* **1998**, 993. Cf. Henze, O.; Lehmann, U.; Schlüter, A. D. *Synthesis* **1999**, 683.
(417) Beley, M.; Collin, J.-P.; Sauvage, J.-P. *Inorg. Chem.* **1993,** 32, 4539.
(418) Beley, M.; Collin, J.-P.; Louis, R.; Metz, B.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1991**, *113*, 8521.
(419) Beley, M.; Chodorowski, S.; Collin, J.-P.; Sauvage, J.-P. *Tetrahedron Lett.* **1993**, *34*, 2932.
(420) Beley, M.; Chodorowski-Kimmes, S.; Collin, J.-P.; Lainé, P.; Launay, J.-P.; Sauvage, J.-P. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1775.
(421) Chodorowski-Kimmes, S.; Beley, M.; Collin, J.-P.; Sauvage, J.-P. *Tetrahedron Lett.* **1996**, *37*, 2963.
(422) Kröhnke, F. *Synthesis* **1976**, 1.
(423) Collin, J.-P.; Lainé, P.; Launay, J.-P.; Sauvage, J.-P.; Sour, A. *J. Chem. Soc., Chem. Commun.* **1993**, 434.
(424) Barigelletti, F.; Flamigni, L.; Collin, J.-P.; Sauvage, J.-P. *Chem. Commun.* **1997**, 333.
(425) Barigelletti, F.; Flamigni, L.; Balzani, V.; Collin, J.-P.; Sauvage, J.-P.; Sour, A.; Constable, E. C.; Thompson, A. M. W. C. *J. Am. Chem. Soc.* **1994**, *116*, 7692.
(426) Barigelletti, F.; Flamigni, L.; Collin, J.-P.; Sauvage, J.-P. *Chem. Commun.* **1997**, 333.
(427) Hiroyuki, O.; Naohiro, H.; Eishun, T. *Macromol. Chem.* **1983**, *184*, 1061.
(428) Anzai, H.; Tokumoto, M.; Ishiguro, T. *J. Phys.* **1983**, *44*, 1229.
(429) Baeyer, A.; Piccard, J. *Liebigs Ann. Chem.* **1911**, *384*, 208.
(430) Dimroth, K. *Angew. Chem.* **1960**, *72*, 331.
(431) (a) Michaelis, A.; Hölken, A. *Liebigs Ann. Chem.* **1904**, *331*, 245. (b) Hünig, S.; Köbrich, G. *Liebigs Ann. Chem.* **1958**, *617*, 181.
(432) Balaban, A. T.; Dinculescu, A.; Dorofeenko, G. N.; Fischer, G. W.; Koblik, A. V.; Mezheritskii, V. V.; Schroth, W. In *Pyrylium Salts: Syntheses, Reaction, and Physical Properties*; Academic Press: New York, 1982; p 85.
(433) Baeyer, A. *Chem. Ber.* **1910**, *43*, 2337.
(434) Katritzky, A. R.; Tarr, R. D.; Heilmann, S. M.; Rasmussen, J. K.; Krepski, L. R. *J. Polym. Sci., Part A* **1988**, *26*, 3323.
(435) Katritzky, A. R.; Manzo, R. H.; Lloyd, J. M.; Patel, R. C. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 306.
(436) Harris, F. W.; Chuang, K. C.; Huang, S. A. X.; Janimak, J. J.; Cheng, S. Z. D. *Polymer* **1994**, *35*, 4940.
(437) Sun, X. H.; Yang, Y.-K.; Lu, F. C. *Polymer* **1997**, *38*, 4737.
(438) Sun, X. H.; Yang, Y.-K.; Lu, F. C. *Macromolecules* **1998**, *31*, 4291.
(439) Ariyan, Z. S.; Mooney, B. *J. Chem. Soc.* **1962**, 1519.
(440) Dimroth, K.; Reichardt, C. *Liebigs Ann. Chem.* **1969**, *727*, 93.
(441) Kossmehl, G.; Kabbeck-Kupijai, D.; Magonov, S. N. *Synth. Met.* **1991**, *41*, 2565.
(442) Magonov, S. N.; Bar, G.; Cantow, H.-J.; Kabbeck-Kupijai, D.; Kossmehl, G. *Ber. Bunsen-Ges. Phys. Chem.* **1993**, *97*, 1478.
(443) Butte, W. A.; Case, F. H. *J. Org. Chem.* **1961**, *26*, 4690.
(444) Baxter, P. N. W.; Lehn, J.-M.; Fischer, J.; Youinou, M.-T. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2284.
(445) Lewis, E. S.; Johnson, M. D. *J. Am. Chem. Soc.* **1959**, *81*, 2070.
(446) Kaim, W.; Fees, J. *Z. Naturforsch., Teil B* **1995**, *50*, 123.
(447) Gompper, R.; Mair, H.-J.; Polborn, K. *Synthesis* **1997**, 696.
(448) Denti, G.; Sabatino, L.; De Rosa, G.; Bartolotta, A.; Di Marco, G.; Ricevuto, V.; Campagna, S. *Inorg. Chem.* **1989**, *28*, 3309.
(449) Lanfredi, A. M. M.; Tiripicchio, A.; Ugozzoli, F.; Ghedini, M.; Neve, F. *J. Chem. Soc., Dalton Trans.* **1988**, 651.
(450) Youinou, M.-T.; Rahmouni, N.; Fischer, J.; Osborn, J. A. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 733.
(451) Campagna, S.; Serroni, S.; Juris, A.; Venturi, M.; Balzani, V. *New J. Chem.* **1996**, *20*, 773.
(452) Roche, S.; Yellowlees, L. J.; Thomas, J. A. *Chem. Commun.* **1998**, 1429.
(453) Ketterle, M.; Fiedler, J.; Kaim, W. *Chem. Commun.* **1998**, 1701.
(454) Baxter, P. N. W.; Sleiman, H.; Lehn, J.-M.; Rissanen, K. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1294.
(455) Sessler, J. L.; Johnson, M. R.; Creager, S. E.; Fettinger, J. C.; Ibers, J. A. *J. Am. Chem. Soc.* **1990**, *112*, 9310.
(456) Sessler, J. L.; Johnson, M. R.; Lin, T.-Y.; Creager, S. E. *J. Am. Chem. Soc.* **1988**, *110*, 3659.
(457) Sessler, J. L.; Johnson, M. R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 678.
(458) Sessler, J. L.; Capuano, V. L.; Harriman, A. *J. Am. Chem. Soc.* **1993**, *115*, 4618.
(459) Nagata, T.; Osuka, A.; Maruyama, K. *J. Am. Chem. Soc.* **1990**, *112*, 3054.
(460) Hammel, D.; Erk, P.; Schuler, B.; Heinze, J.; Müllen, K. *Adv. Mater.* **1992**, *4*, 737.
(461) Kadish, K. M.; Guo, N.; Van Caemelbecke, E.; Froiio, A.; Paolesse, R.; Monti, D.; Tagliatesta, P.; Boschi, T.; Prodi, L.; Bolletta, F.; Zaccheroni, N. *Inorg. Chem.* **1998**, *37*, 2358.
(462) Zhou, X.; Chan, K. S. *J. Org. Chem.* **1998**, *63*, 99.
(463) Helms A.; Heiler, D.; McLendon, G. *J. Am. Chem. Soc.* **1991**, *113*, 4325.
(464) Mikami, S.; Sugiura, K.; Sakata, Y. *Chem. Lett.* **1997**, 833.
(465) Collin, J.-P.; Dalbavie, J.-O.; Heitz, V.; Sauvage, J.-P.; Flamigni, L.; Armaroli, N.; Balzani, V.; Barigelletti, F.; Montanari, I. *Bull. Soc. Chim. Fr.* **1996**, *133*, 749.

(466) Collin, J.-P.; Harriman, A.; Heitz, V.; Odobel, F.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1994**, *116*, 5679.

(467) Odobel, F.; Sauvage, J.-P. *New J. Chem.* **1994**, *18*, 1139.

(468) Harriman, A.; Odobel, F.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1995**, *117*, 9461.

(469) Lindsey, J. S.; Schreiman, J. C.; Hsu, H. C.; Kearney, P. C.; Marguerattaz, A. M. *J. Org. Chem.* **1987**, *52*, 827.

(470) Arsenault, G. P.; Bullock, E.; MacDonald, S. F. *J. Am. Chem. Soc.* **1960**, *82*, 4382.

(471) O'Neil, M. P.; Niemczyk, M. P.; Svec, W. A.; Gosztola, D.; Gaines, G. L., III; Wasielewski, M. R. *Science* **1992**, *257*, 63.

(472) Osuka, A.; Marumo, S.; Mataga, N.; Taniguchi, S.; Okada, T.; Yamazaki, I.; Nishimura, Y.; Ohno, T.; Nozaki, K. *J. Am. Chem. Soc.* **1996**, *118*, 155.

(473) Shiratori, H.; Ohno, T.; Nozaki, K.; Yamazaki, I.; Nishimura, Y.; Osuka, A. *Chem. Commun.* **1998**, 1539.

(474) Imahori, H.; Yamada, K.; Hasegawa, M.; Taniguchi, S.; Okada, T.; Sakata, Y. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2626.

(475) Vögtle, F.; Frank, M.; Nieger, M.; Belser, P.; von Zelewsky, A.; Balzani, V.; Barigelletti, F.; De Cola, L.; Flamigni, L. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1643.

(476) Barigelletti, F.; Flamigni, L.; Balzani, V.; Collin, J.-P.; Sauvage, J.-P.; Sour, A. *New J. Chem.* **1995**, *19*, 793.

(477) Joran, A. D.; Leland, B. A.; Geller, G. G.; Hopfield, J. J.; Dervan, P. B. *J. Am. Chem. Soc.* **1984**, *106*, 6090.

(478) Khundkar, L. R.; Perry, J. W.; Hanson, J. E.; Dervan, P. B. *J. Am. Chem. Soc.* **1994**, *116*, 1994.

(479) Brady, M.; Weng, W.; Zhou, Y. L.; Seyler, J. W.; Amoroso, A. J.; Arif, A. M.; Bohme, M.; Frenking, G.; Gladysz, J. A. *J. Am. Chem. Soc.* **1997**, *119*, 775.

(480) Zweig, A.; Hoffmann, A. K. *J. Am. Chem. Soc.* **1962**, *84*, 3278.

(481) Burton, B. S.; von Pechmann, H. *Chem. Ber.* **1887**, *20*, 145.

(482) Hopf, H. In *The Chemistry of Ketenes, Allenes, and Related Compounds*; Patai, S., Ed.; Wiley: Chichester, 1980; Vol. 2, p 779.

(483) Rutledge, T. F. *Acetylenes and Allenes*; Reinhold: New York, 1969.

(484) Bildstein, B.; Schweiger, M.; Kopacka, H.; Ongania, K.-H.; Wurst, K. *Organometallics* **1998**, *17*, 2414.

(485) Dua, S.; Blanksby, S. J.; Bowie, J. H. *Chem. Commun.* **1998**, 1767.

(486) Karich, G.; Jochims, J. C. *Chem. Ber.* **1977**, *110*, 2680.

(487) Komatsu, K.; Kamo, H.; Tsuji, R.; Takeuchi, K. *J. Org. Chem.* **1993**, *58*, 3219.

(488) Trost, B. M.; Flygare, J. A. *J. Am. Chem. Soc.* **1992**, *114*, 5476.

(489) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197.

(490) (a) Fischer, E. O.; Kalder, H. J.; Frank, A.; Köhler, F. H.; Huttner, G. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 623. (b) Berke, H. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 624.

(491) Selegue, J. P. *Organometallics* **1982**, *1*, 217.

(492) Werner, H.; Rappert, T.; Wiedemann, R.; Wolf, J.; Mahr, N. *Organometallics* **1994**, *13*, 2721.

(493) Lass, R. W. Ph.D. Thesis, Universität Würzburg, Würzburg.

(494) Roth, G.; Fischer, H. *Organometallics* **1996**, *15*, 1139.

(495) Touchard, D.; Haquette, P.; Daridor, A.; Toupet, L.; Dixneuf, P. H. *J. Am. Chem. Soc.* **1994**, *116*, 11157.

(496) Lass, R. W.; Steinert, P.; Wolf, J.; Werner, H. *Chem. Eur. J.* **1996**, *2*, 19.

(497) Roth, G.; Fischer, H. *Organometallics* **1996**, *15*, 5766.

(498) Weng, W.; Bartik, T.; Gladysz, J. A. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2199.

(499) Fecht, H. *Chem. Ber.* **1907**, *40*, 3883.

(500) Rice, L. M.; Grogan, C. H. *J. Org. Chem.* **1961**, *26*, 54.

(501) Buchta, E.; Geibel, K. *Liebigs Ann. Chem.* **1961**, *648*, 36.

(502) Buchta, E.; Merk, W. *Liebigs Ann. Chem.* **1966**, *694*, 1.

(503) Newkome, G. R.; Lin, X.; Yaxiong, C.; Escamilla, G. H. *J. Org. Chem.* **1993**, *58*, 3123.

(504) Farges, G.; Dreiding, A. S. *Helv. Chim. Acta* **1966**, *49*, 552.

(505) Menger, F. M.; Ding, J. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2137.

(506) Seitz, G.; Mikulla, W.-D. *Tetrahedron Lett.* **1970**, 615.

(507) Seitz, G.; Mikulla, W.-D. *Liebigs Ann. Chem.* **1974**, 1328.

(508) Stein, C. A.; Lewis, N. A.; Seitz, G. *J. Am. Chem. Soc.* **1982**, *104*, 2596.

(509) Hoogesteger, F. J.; Havenith, R. W. A.; Zwikker, J. W.; Jenneskens, L. W.; Kooijman, H.; Veldman, N.; Spek, A. L. *J. Org. Chem.* **1995**, *60*, 4375.

(510) Friederich, R.; Nieger, M.; Vögtle, F. *Chem. Ber.* **1993**, *126*, 1723.

(511) McMurry, J. E.; Haley, G. J.; Matz, J. R.; Clardy, J. C.; Van Duyne, G. *J. Am. Chem. Soc.* **1984**, *106*, 5018.

(512) McMurry, J. E.; Haley, G. J.; Matz, J. R.; Clardy, J. C.; Mitchell, J. *J. Am. Chem. Soc.* **1986**, *108*, 515.

(513) McMurry, J. E.; Haley, G. J.; Matz, J. R.; Clardy, J. C.; Van Duyne, G.; Gleiter, R.; Schäfer, W.; White, D. H. *J. Am. Chem. Soc.* **1986**, *108*, 2932.

(514) Hoogesteger, F. J.; Grove, D. M.; Jenneskens, L. W.; de Bruin, T. J. M.; Jansen, B. A. J. *J. Chem. Soc., Perkin Trans. 2* **1996**, 2327.

(515) Dimroth, K.; Umbach, W.; Blöcher, K. H. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 620.

(516) Naemura, K. In *Carbocyclic Cage Compounds: Chemistry and Applications*; Osawa, E., Yonemitsu, O., Eds.; VCH: Weinheim, 1992; p 61.

(517) Sauers, R. R.; Schinski, W.; Mason, M. M. *Tetrahedron Lett.* **1969**, 79.

(518) Sauers, R. R.; Rousseau, A. D. *J. Am. Chem. Soc.* **1972**, *94*, 1776.

(519) Sauers, R. R.; Henderson, T. R. *J. Org. Chem.* **1974**, *39*, 1850.

(520) Sauers, R. R.; Lynch, D. C. *J. Org. Chem.* **1980**, *45*, 1286.

(521) Nakazaki, M.; Naemura, K.; Kondo, Y. *J. Org. Chem.* **1976**, *41*, 1229.

(522) Nakazaki, M.; Naemira, K.; Harita, S. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 1907.

(523) Gleiter, R.; Fritzsche, G.; Borzyk, O.; Oeser, T.; Rominger, F.; Irngartinger, H. *J. Org. Chem.* **1998**, *63*, 2878.

(524) Gleiter, R.; Kissler, B.; Ganter, C. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1252.

(525) Gleiter, R.; Lange, H.; Borzyk, O. *J. Am. Chem. Soc.* **1996**, *118*, 4889.

(526) Lange, H.; Gleiter, R.; Fritzsche, G. *J. Am. Chem. Soc.* **1998**, *120*, 6563.

(527) Ayres, F. D.; Khan, S. I.; Chapman, O. L. *Tetrahedron Lett.* **1994**, *35*, 8561.

(528) Riklin, M.; von Zelewsky, A. *Helv. Chim. Acta* **1996**, *79*, 2176.

(529) Becher, J.; Lau, J.; Mørk, P. In *Electronic Materials: The Oligomeric Approach*; Müllen, K., Wegner, G., Eds.; Wiley: Chichester, 1998; Chapter 2.2, p 198 and references therein.

(530) Schumaker, R. R.; Engler, E. M. *J. Am. Chem. Soc.* **1980**, *102*, 6651.

(531) Adam, M.; Müllen, K. *Adv. Mater.* **1994**, *6*, 439.

(532) Adam, M.; Räder, H.-J.; Röhrich, J.; Scherer, U.; Wolf, P.; Müllen, K. *Synth. Met.* **1991**, *41*−*43*, 1623.

(533) Wolf, P.; Naarmann, H.; Müllen, K. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 288.

(534) Räder, H.-J.; Scherer, U.; Wolf, P.; Müllen, K. *Synth. Met.* **1989**, 32, 15.

(535) Adam, M.; Müllen, K.; Räder, H.-J.; Wolf, P. *J. Chem. Soc., Chem. Commun.* **1990**, 1624.

(536) Hansen, T. K.; Jørgensen, T.; Jensen, F.; Thygesen, P. H.; Christiansen, K.; Hursthouse, M. B.; Harman, M. E.; Malik, M. A.; Girmay, B.; Underhill, A. E.; Begtrup, M.; Kilburn, J. D.; Belmore, K.; Roepstorff, P.; Becher, J. *J. Org. Chem.* **1993**, *58*, 1359.

(537) Brown, C. A.; Miller, R. D.; Lindsay, C. M.; Smith, K. *Tetrahedron Lett.* **1984**, 991.

(538) Lindsay, C. M.; Smith, K.; Brown, C. A.; Betterton-Cruz, K. *Tetrahedron Lett.* **1984**, 995.

(539) Ashizawa, M.; Aragaki, M.; Mori, T.; Misaki, Y.; Yamabe, T. *Chem. Lett.* **1997**, 649.

(540) Röhrich, J.; Wolf, P.; Enkelmann, V.; Müllen, K. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1377.

(541) Röhrich, J.; Müllen, K. *J. Org. Chem.* **1992**, *57*, 2374.

(542) Wolf, P.; Müllen, K.; Przybylski, M. *Chimia* **1986**, *40*, 200.

(543) Bernhard, S.; Belser, P. *Synthesis* **1996**, 192.

(544) Takahashi, K.; Ogiyama, M. *J. Chem. Soc., Chem. Commun.* **1990**, 1196.

CR970070X