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Alkynes Between Main Group Elements: From Dumbbells via Rods to Squares and Tubes

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1. Introduction

Since its first reported synthesis from calcium carbide in 1862 by Friedrich Wöhler,[1] acetylene and its alkyl- or aryl derivatives have developed as key reagents in organic chemistry. The C≡C triple bond proved to be reactive toward electrophiles, nucleophiles, hydrogenation reagents, various catalysts, light, and heat. This high reactivity makes the C≡C triple bond an ideal reagent for the formation of new C−C bonds. It is therefore of high interest in industry and research laboratories. In the latter places very often main group elements play a pivotal role as reaction partner of the C≡C triple bond.

In Scheme 1, we list four examples for this role. In most protocols for alkylation of acetylene or monosubstituted triple bonds such as **1** alkali or alkali earth metal salts of an acetylide anion, usually generated in situ, are used as starting materials[2] (eq 1 in Scheme 1). Alkynyl 9-BBN derivatives (e.g., **4**) are utilized to prepare enynones by reacting them with alkyl ethers of β-ketoaldehydes[3] (eq 2 in Scheme 1). Trialkyl- or triarylsilyl groups are frequently used to protect one end of a triple bond when the other will be functionalized. These bulky groups play also an important role to synthesize and stabilize (oligo)alkynes. To couple two different alkyne units together to a diyne, it is effective to use a cross-coupling protocol suggested by Cadiot and Chodkiewicz with a monobrominated alkyne **8** as one component[4] (eq 3 in Scheme 1). Most recently, a nitrogen-substituted alkyne **10** was used to construct an aldol product **12** with a quaternary all-carbon stereocenter in a sequential one-pot procedure[5] (eq 4 in Scheme 1).

The important function of C≡C triple bonds in various fields of synthesis[6−12] and their occurrence in nature[13] has been documented in various monographs and reviews. The recent discovery of fullerenes[14,15] has added a new aspect to acetylene chemistry and has spurred the search for further stable allotropes of carbon[16,17] and several two- and three-dimensional networks.[18] A further allotrope of carbon could be imagined by assuming rods of sp-hybridized carbon atoms, called carbyne.[19] Closest to this goal were cyclic carbynes, which were generated in the gas phase.[20,21] As models of linear carbyne one can consider (oligo)alkynes,

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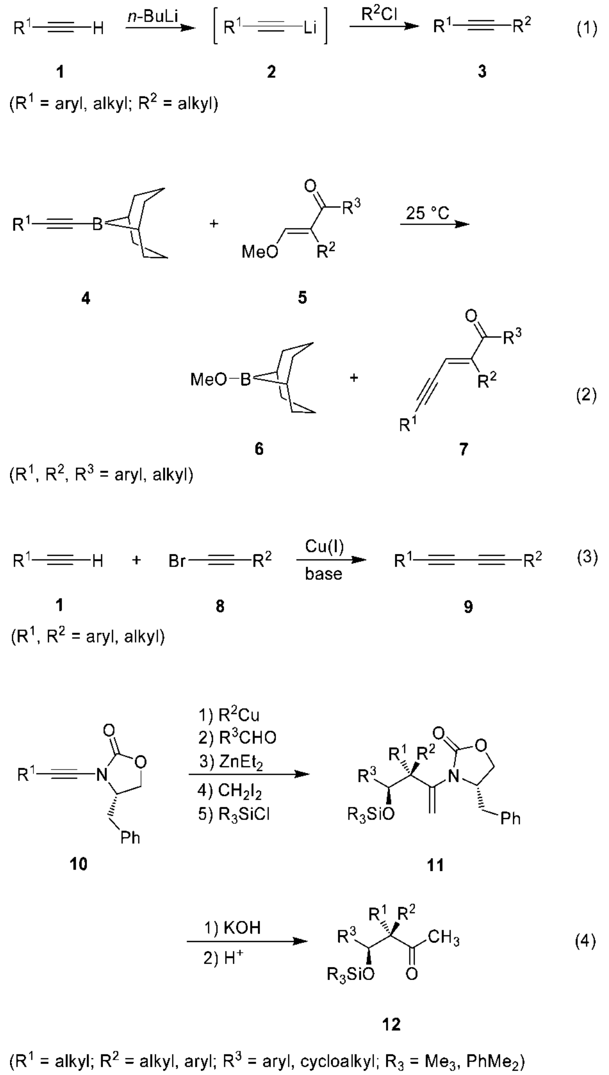
Rolf Gleiter received his Ph.D. from the University of Stuttgart with Franz Effenberger in 1964. As a postdoctoral fellow he joined the groups of Paul v. Ragué Schleyer at Princeton University and Roald Hoffmann at Cornell University. In 1968, he started independent research at the University of Basel, Switzerland, in Edgar Heilbronner's laboratory. In 1973, he was appointed full professor at the Technical University of Darmstadt, Germany. In 1979, he moved to the University of Heidelberg, Germany, where he retired in 2007 as professor emeritus. His main fields of interest were studies of intramolecular interactions by means of photoelectron spectroscopy, structural investigations concerning long chalcogen−chalcogen bonds, the synthesis of superphanes, strained hydrocarbons, cyclacenes, and structural studies on metallocenylmethylium ions. These investigations were accompanied by quantum chemical calculations (see also www.gleiter.uni-hd.de).

Daniel B. Werz (born 1975) studied chemistry at the University of Heidelberg, Germany, and at the University of Bristol, U.K., supported by a fellowship of the Studienstiftung des deutschen Volkes. In 2000, he received his diploma from University of Heidelberg, where he also earned his Ph.D. in organic chemistry under the guidance of Rolf Gleiter in 2003. His Ph.D. thesis dealt with chalcogen-substituted alkynes, which is also a part of this review. In 2004, he moved as a Feodor Lynen postdoctoral fellow of the Alexander von Humboldt Foundation (AvH) to Peter H. Seeberger's group at the Swiss Federal Institute of Technology (ETH) in Zürich, Switzerland. In December 2006, he joined the faculty of chemistry of the University of Göttingen as an Emmy Noether Fellow. Among several fellowships, such as the Emmy Noether Fellowship of the Deutsche Forschungsgemeinschaft (DFG) and the Liebig Fellowship of the Fonds der Chemischen Industrie, he received in 2004 the Ruprecht-Karls-Preis of the University of Heidelberg and the Klaus Grohe Award for medicinal chemistry of the GDCh (see also www.werz.chemie.uni-goettingen.de).

Scheme 1. Four Examples (1−4) for the Utilization of Alkynes Substituted by Main Group Elements in the Synthesis



which are capped at the end by metal fragments,[22,23] main group atoms, or groups such as aryl,[24] 1-adamantyl,[25] *t*-butyl,[26] or cyano moieties.[27] In this review, we present (oligo)alkynes capped with main group elements except carbon atoms. We do not consider (oligo)alkynes that are capped by transition metals or that are asymmetrically substituted by different elements such as the compounds **13−18** depicted exemplarily in Figure 1. Furthermore, we abstain from discussing alkynes capped by carbon with the

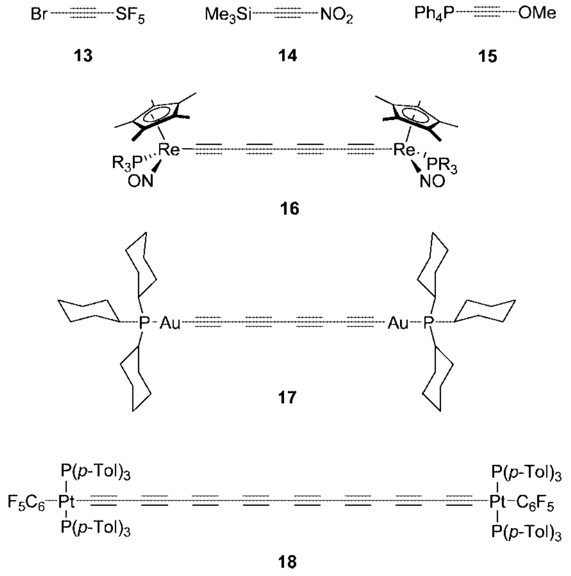


Figure 1. Examples of heterosubstituted alkynes **13−15** and (oligo)alkynes **16−18** capped by transition metal elements, which are not treated in this review.[28−30,22a,31,32]

exception of elucidating general properties of (oligo)alkynes. In those cases where no symmetrically capped species are available or are less informative than species with an unsymmetrical capping such as in the cases where atoms of main groups I, II, III, and VIII are involved we will deviate from this restriction.

2. Alkynes Substituted by Elements of Main Groups I−IV (Except Carbon)

2.1. Alkynes Substituted by Elements of Main Groups I and II

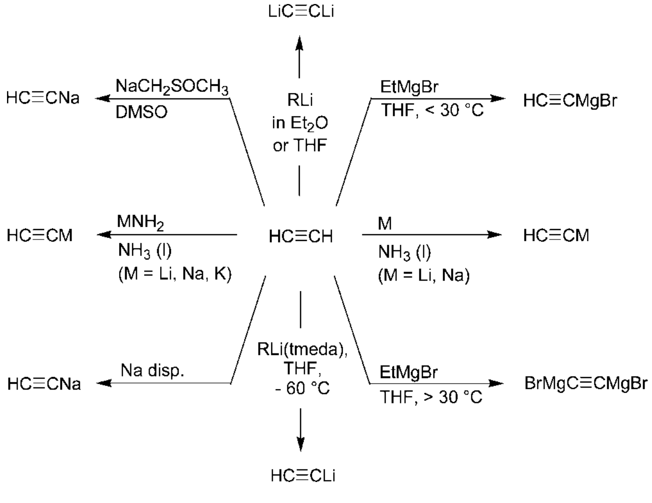
2.1.1. Alkali and Alkali Earth Metal Derivatives of Alkynes

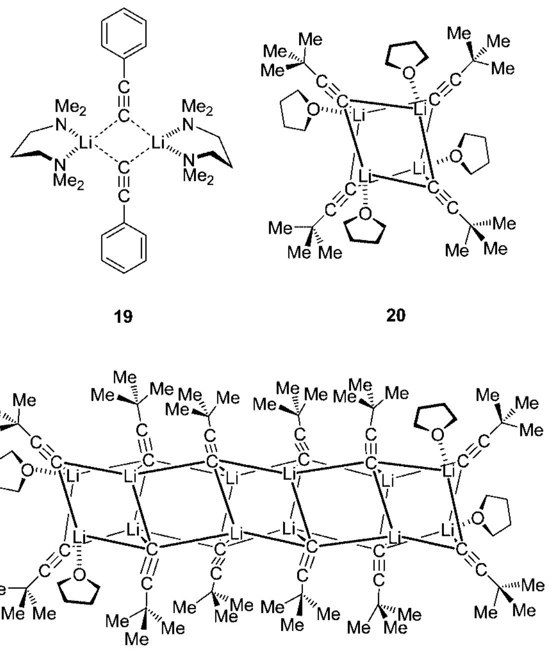
Alkali and alkali earth metal derivatives of organic compounds belong to the most reactive intermediates in synthetic organic chemistry. Therefore their preparation, structure and reactivity have deserved special attention.[33−38] As stated in the Introduction we restrict ourselves to alkynes substituted symmetrically on both ends with main group elements. However, in this chapter we will deviate from this intention because such an approach would limit us only to the alkali and alkali earth metal carbides, which play only a minor role in alkyne chemistry.

The functionalization of many species with a terminal alkyne group proceeds via metalation of the terminal C(sp) carbon ($R-C\equiv CM$; M = Li, Na, K, MgBr). These metal derivatives are readily available by abstracting the proton in $R-C\equiv CH$ with a strong base. The most frequently applied bases are alkali metal amides in liquid ammonia as solvent, alkyllithium in diethyl ether or tetrahydrofuran (THF) or by using alkyl Grignard compounds such as RMgBr. Detailed procedures for the preparation of monometalated terminal alkynes are given by Brandsma.[33] In Scheme 2, the various methods are summarized to derive mono- and dimetalated alkynes.

Most of the reagents shown in Scheme 2 are produced in situ and thus are utilized without further isolation or purification. Nevertheless, their structures and their associations with other molecules, such as solvents are of interest with respect to mechanistic discussions. In the past 30 years quite a number of structural data were made available by X-ray investigations on alkali and alkali earth organometallic compounds.[34−38] In the following, we will present some examples for monometalated alkynes. This overview will give an impression of the role of coligands such as ethers (THF, 18-crown-6) or amines [*N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmeda), *N*,*N*,*N*′,*N*′-tetramethyl-1,3-propanediamine (tmpda), *N*,*N*,*N*′,*N*′-tetramethyl-1,6-hexanediamine (tmhda)].

Scheme 2. Various Methods for the Metalation of Alkynes with Alkali and Alkali Earth Metals or Their Derivatives[33]





19 **20**

21

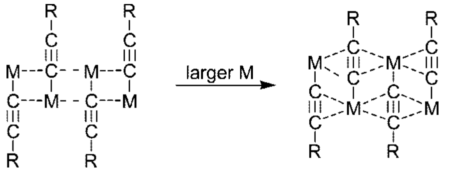
Figure 2. Molecular structures of $[(PhC\equiv CLi)(tmpda)_2]$ (**19**), $[(t\text{-}BuC\equiv CLi)_4(THF)_4]$ (**20**), and $[(t\text{-}BuC\equiv CLi)_{12}(THF)_4]$ (**21**).

The tmpda-adduct of phenyllithium was isolated as a dimer $[((PhC\equiv CLi)\cdot(tmpda))_2]$ (**19**).[39] The terminal carbon atoms of the two alkyne units are bridged by the lithium centers to form a rhombus with angles of 107° at the Li atoms and 73° at the carbon atoms (see Figure 2). The Li−C(sp) distances vary between 2.13 and 2.16 Å.[39] The bond lengths of the alkyne units amount to 1.241(9) Å. The THF adduct of *t*-butylethynyllithium was isolated as a tetramer $[(t\text{-}BuC\equiv CLi)_4\cdot(THF)_4]$ (**20**) and as dodecamer $[(t\text{-}BuC\equiv CLi)_{12}\cdot(THF)_4]$ (**21**)[40] as shown schematically in Figure 2. These structures arise by stacking of dimer units. The arithmetic mean of the Li−C(sp) bond lengths amounts to 2.19 (tetramer) and 2.22 Å (dodecamer). The C≡C bond lengths were reported to be 1.20 Å (average) for **20** and 1.15 Å (average) for **21**.[40] The tetrameric structure was first discovered by low temperature ^{13}C NMR studies in THF.[41] A coupling constant $J_{^{13}C-^{6}Li}$ of 6 Hz was found. The tmhda-adduct of the lithium salt of phenylacetylene reveals a tetrameric structure $[(PhC\equiv CLi)\cdot(tmhda))_2]$ (**22**) with a distorted cubic Li_4C_4 unit.[40] This unit is very similar to that found in $[(CH_3Li)_4]$.[37] The most relevant distances in **22** are Li−C (sp) with 2.20 Å, and C≡C with 1.24(2) Å, respectively.[42]

To complete the data of monoalkali salts of alkynes, we mention the structure of the alkali salts (Na, K, Rb) of acetylene and the Na, K, Rb and Cs salts of propyne.[43,44] The X-ray powder diffraction data show sheets with the H and CH_3 groups, respectively, pointing outward. With increasing size of the cation the $M-C_\alpha$ and $M-C_\beta$ distances are getting similar. This tendency is indicated in Scheme 3.

Alkali earth metal derivatives of terminal alkynes were reported from *t*-butylacetylene, trimethylsilyl-, and triphenylsilylacetylene, as well as from arylacetylenes. The corresponding metal salts were stabilized by coligands such

Scheme 3. Structural Changes of Monoalkali Salts of Alkynes as a Function of M



as cyclic ethers, tetramethylated α,ω-diaminoalkanes, or α,ω-disubstituted diketiminato ligands.[45−52] In Figure 3, we list six of the investigated magnesium complexes (**23**−**28**) and three complexes with calcium, strontium, and barium in the center (**29**−**31**).[46−48,52] The Mg−C(sp) distances were reported to be 2.176 and 2.220 Å for **23**,[46] 2.180(2), and 2.175(4) Å for **24**,[47−52] 2.202(6) and 2.198(6) Å for **25**,[52] 2.222(2) Å for **26**,[52] 2.239(1) Å for **27**,[52] and 2.214(4) Å for **28**.[52] The C≡C distances vary slightly between 1.207(5) Å for **24** and 1.226(2) Å for **27**.[52]

In all six magnesium complexes, a linear or nearly linear trans arrangement of the alkyne units was reported. The angle C−Mg−C was found to be 180° for **23**−**25**, **27**, and **28** (see Figure 4). For **26**, the C−Mg−C angle was found to be 174°.

In the cases of the calcium **29**, strontium **30**, and barium complexes **31**[48] the metal M-C(sp) distances were reported to be 2.523(7) and 2.558(7) Å for **29**, 2.692(4) and 2.723(4) Å for **30**, and 2.852(3) and 2.853(2) Å for **31**.[48] The lengths of the triple bonds vary only slightly between 1.22 and 1.23 Å. As shown in Figure 4, strong deviations from the linearity of the C−M−C angle were observed.[48] The values were 168.7(2)° for **29**, 166.0(1)° for **30**, and 162.7(1)° for **31**.[48] In line with these values were the M−C≡C angles, which reveal also that the ethynyl ligand is not linearly bound to the metal (see Figure 4). The strong deviation from linearity (**32**, **33**) was ascribed to the high s-character of the lone pair orbital at the terminal carbon atom of the triple bond.[48] The high s-character implies a low directionality of the orbital. Thus a deviation from linearity is associated only with a small increase of energy. A recent analysis[53] suggests that donor−acceptor interactions between the acetylenic unit and the crown ether are responsible for the deviations from ideal geometry.

$[(PhC{\equiv}C)_2Mg(tmeda)_2]$

23

$[(t\text{-}BuC{\equiv}C)_2Mg(tmeda)_2]$

24

$[(Me_3SiC{\equiv}C)_2Mg(tmeda)_2]$

25

$[(p\text{-}t\text{-}Bu\text{-}C_6H_4C{\equiv}C)_2Mg(15\text{-crown-}5)]$

26

$[(Ph_3SiC{\equiv}C)_2Mg(THF)_4]$

27

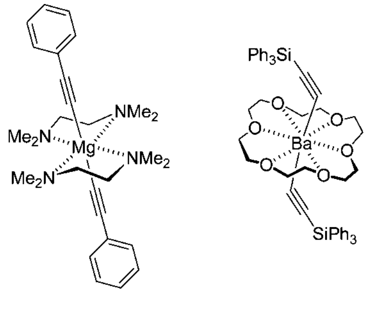
$[(Ph_3SiC{\equiv}C)_2Mg(tmeda)]$

28

$[(Ph_3SiC{\equiv}C)_2M(18\text{-crown-}6)]$

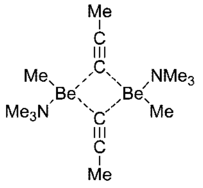
29-31 (M = Ca, Sr, Ba)

Figure 3. Six magnesium alkyne complexes and three alkyne complexes with Ca, Sr, and Ba.

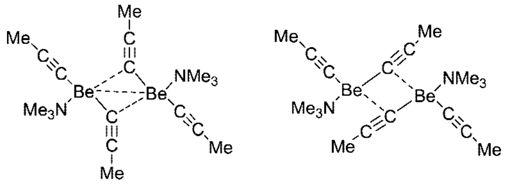


32 **33**

Figure 4. Molecular structure of *trans*-Mg(C≡C−Ph)$_2$(tmeda)$_2$ (**32**) and *trans*-Ba(C≡C−SiPh$_3$)$_2$(18-crown-6) (**33**).



34



35a **35b**

Figure 5. Structures of beryllium complexes with propyne.

Scheme 4. Preparation of Alkali Metal Carbides

$$\mathrm{HC{\equiv}CH} + \mathrm{M} \xrightarrow[\mathrm{NH_3\,(l)}]{} \mathrm{HC{\equiv}CM} \xrightarrow{180\ °\mathrm{C}} \mathrm{MC{\equiv}CM} + \mathrm{HC{\equiv}CH}$$

The reports on beryllium derivatives of alkynes are sparse and only data on the dimers **34** and **35** are available (see Figure 5).[54,55] In the case of **34**, the propynyl groups are only slightly tilted toward one of the Be centers. In the case of **35** two independent centrosymmetric dimers were obtained (**35a**, **35b**) in which the binding alkynyl groups exhibit quite different types of interactions with the metal. In **35a**, the bridging alkynyl groups function as one electron donors to each metal leading to a predominantly electron deficient Be$_2$C$_2$ ring system. As a result, a short transannular Be···Be contact is observed (2.319(6) Å). In **35b** the electron deficiency is compensated by an additional π type interaction between the metal and the triple bond. This increases the transannular Be···Be distance to 2.549(6) Å.[55]

2.1.2. Alkali and Alkali Earth Metal Carbides

In the solid state, the carbides of the alkali and alkali earth metals exist as discrete dianions and metal cations. There are two ways to prepare these species: (i) First from the elements by heating graphite and the metal in a high-pressure vessel at 800−1000 °C (Li$_2$C$_2$, CaC$_2$).[56,57] For the industrial production of CaC$_2$, a process from lime (CaO) and coke (C) is used. (ii) The second procedure utilizes the acidity of acetylene. In liquid ammonia (see also Scheme 2) acetylene reacts under monosubstitution to yield MC$_2$H. Heating this species in high vacuo above 180 °C affords the desired carbide and acetylene as shown in Scheme 4.[58] By this protocol, most alkali metal carbides were prepared.

The most simple structures are reported for CaC$_2$,[59a,b] SrC$_2$ and BaC$_2$.[60] At least four polymorphs of CaC$_2$ are known.[59c−f,61] In the common form CaC$_2$ crystallizes in a tetragonal NaCl lattice.[59a,b] The same holds for SrC$_2$ and BaC$_2$.[60] As shown in Figure 6 (top), the C$_2^{2-}$ dumbbell-shaped ions are oriented

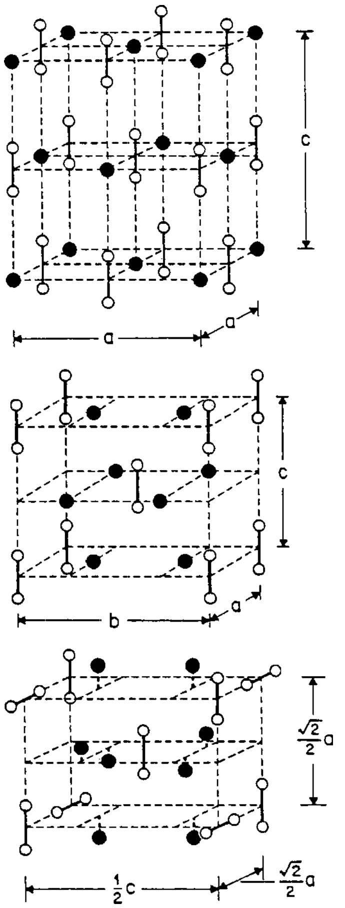


Figure 6. The tetragonal lattices of CaC_2, SrC_2 and BaC_2 (top), the RbO_2-type lattice of Li_2C_2 (center) and the distorted CaF_2-type lattice of Na_2C_2 (bottom).[66] Reprinted with permission from ref 66. Copyright 1989 American Chemical Society.

along the *c*-axis. The cations are situated on the axis defined by the C_2^{2-} units. In the orthorhombic Li_2C_2,[40,56,57,62] which is isotypic to Rb_2O_2, the C_2^{2-} units are also oriented along the *c*-axis, whereas no cations are situated on this axis (Figure 6, center). In the distorted CaF_2 lattice of the Na_2C_2,[63] successive C_2^{2-} units are rotated by 90° (Figure 6, bottom). At temperatures of about 500 °C for Li_2C_2, a reversible phase-transition to a cubic modification has been observed, which adopts an antifluorite structure with disordered C_2^{2-} units.[63] Similarly, a phase-transition to an undistorted antifluorite structure was reported for Na_2C_2 and K_2C_2.[64] For Rb_2C_2 and Cs_2C_2 two modifications were found.[65] A hexagonal and an orthorhombic modification were characterized by X-ray powder diffraction.

The anisotropy of the ^{13}C chemical shielding of Li_2C_2, Na_2C_2, CaC_2, SrC_2, and BaC_2 was measured utilizing ^{13}C nuclear magnetic resonance in the solid state.[66] The shielding perpendicular to the C≡C bond in the acetylides was found to be independent of the cation and amounts to 315 ppm relative to tetramethylsilane. However, it varies parallel to the C≡C bond by over 110 ppm and correlates with the distances to cations in the plane bisecting the C≡C bond. For acetylides with bonding along the C≡C axis (the alkaline earth metal acetylides and acetylene) the isotropic shift was found to be proportional to the acetylide-nearest neighbor distance and the ionization potential of the nearest neighbor.[66]

2.1.3. Quantum Chemical Calculations on the Metal-Alkyne Interaction of Group II Metals

In this paragraph, we list only a few examples of quantum chemical calculations on the bonding properties of alkali and alkali earth metals derivatives of alkynes. In some of the reviews cited above,[35] such calculations are discussed extensively. We mention here model calculations on the covalent character of simple organolithium compounds[67,68] that suggest that in comparison to alkyl and vinyl derivatives ethynyllithium has effectively lower electron density between the C_α and Li atoms. This corresponds to a high ionic character of the carbon lithium bond.

The discovery by computational chemistry that the Li_2C_2 prefers a double π-bridged structure over a linear structure in the gas phase has stimulated further calculations.[69] In the light of these results, the polymeric structures of the alkali metal acetylides shown in Scheme 3 have been discussed.[70] Computational chemistry was also used to explore the structures and energies of the binary beryllium compounds CBe_2, C_2Be, C_2Be_2.[71] Nonlinear geometries were predicted to be the global minima for CBe_2 ($^1A_1$) and C_2Be ($^1A_1$). For C_2Be_2, a linear triplet is favored ($^3\Sigma_u^+$). The results of the electron density analysis indicate that charge transfer from Be to C is responsible for the stabilities of the nonlinear isomers. It was also found that there is little covalent CBe bonding in the singlet nonlinear minima of CBe_2 and C_2Be.

2.2. Alkynes Substituted by Elements of Main Group III

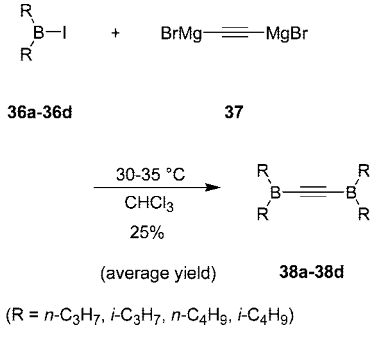
2.2.1. Diborylacetylenes

The bis(dialkylboron)acetylenes **38a**−**38d** were prepared by the reaction of dialkylboron iodide **36** with acetylene dimagnesiumdibromide (**37**) at 30−35 °C.[72] The resulting alkynes were obtained in moderate yields (~25%). All derivatives were found to be highly air-sensitive liquids (Scheme 5).

The thermal stability of alkynylboranes depends strongly on the substituents at the boron centers. If the alkyl groups in **38** were replaced by electron donor substituents, such as alkoxy or dialkylamino groups, their stability increased considerably.[73,74] On the basis of these findings, a variety of alkynylboranes was synthesized and investigated.[75−79] Wrackmeyer and Nöth prepared the alkynes **39**−**41** (Figure 7, top) and investigated their NMR spectra.[75] The yields of **40** and **41** were reported to be 60% and 70%, respectively.

These investigations revealed a conjugation between the π system of the triple bond and the boron center. The first X-ray data were available from **42** and **43** (Figure 7, bottom),

Scheme 5. Preparation of the Bis(dialkylboron)acetylenes 38a−38d



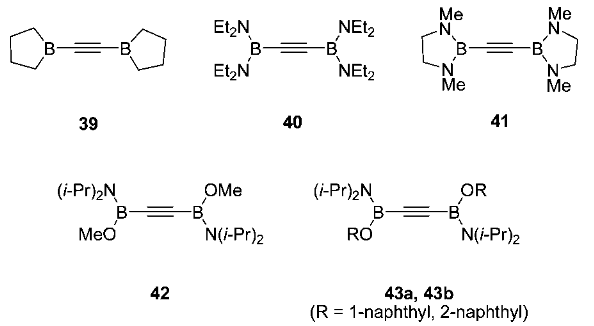
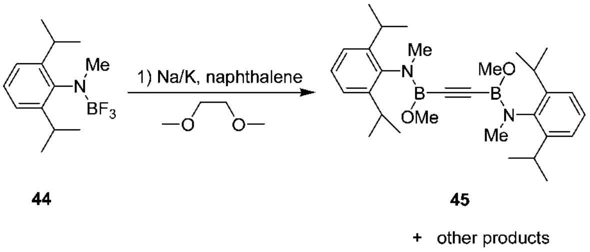
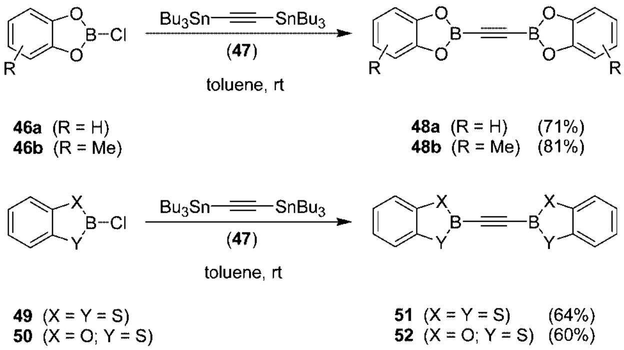


Figure 7. Diborylacetylenes **39**−**43**.

Scheme 6. Generation of Diborylethyne 45



Scheme 7. Preparation of the Diborylacetylenes 47, 51, and 52



which were obtained by Meller et al.[76] as side products during a dehalogenation reaction of dichloro(diisopropylamino)-borane using a Na/K alloy with dimethoxyethane and 1-methylnaphthalene (**42**)[76a] or aromatic ethers **43**.[76b] Starting from [(2,6-diisopropylphenyl)methylamino]difluoroborane (**44**) Na/K alloy, naphthalene in dimethoxyethane yielded as side product the diborylethyne **45** (Scheme 6).[76c]

A more straightforward synthesis of diborylacetylenes was published by Siebert et al.[77] by reacting 2-chloro-1,2,3-benzodioxaborole (**46**) or the congeners **49** and **50** with bis(trimethylstannyl)acetylene (**47**) (Scheme 7).

The structure of **48a** (R = H) was confirmed by X-ray investigations.[77] Further diborylacetylenes, which were prepared in high yields by the Siebert group are **53**, **54**, and **55** (Figure 8).[77a]

The reaction of 2-cyano-1,3-di-*t*-butyl-2,3-dihydro-1*H*-1,3,2-diazoborole (**56**) with lithium acetylide **57** afforded **58**, which can be transferred to the bis(diazaboryl)acetylene (**59**), as well as the unsymmetrically substituted alkynes **60** and **61** (Scheme 8).[78]

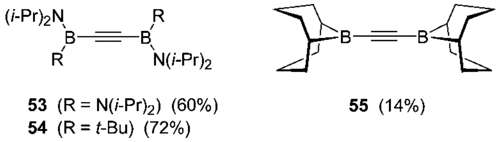
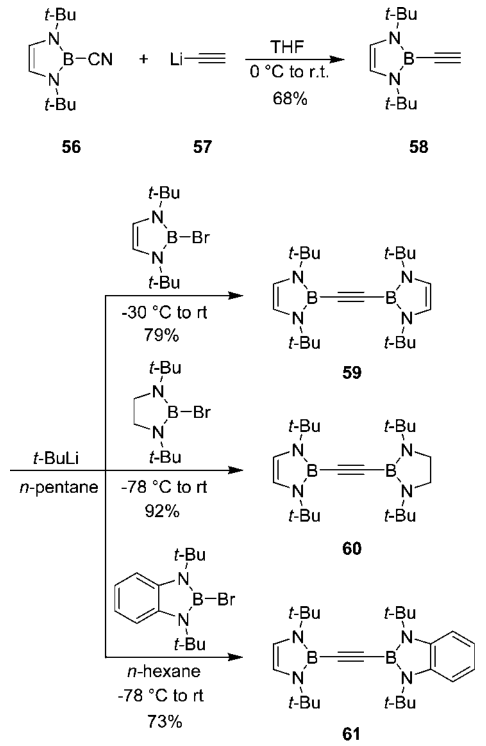
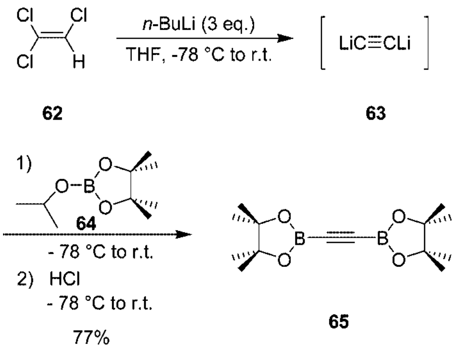


Figure 8. Diborylacetylenes **53**−**55**.

Scheme 8. Synthesis of Diborylacetylenes 59−61



Scheme 9. Synthesis of Diborylacetylene 65

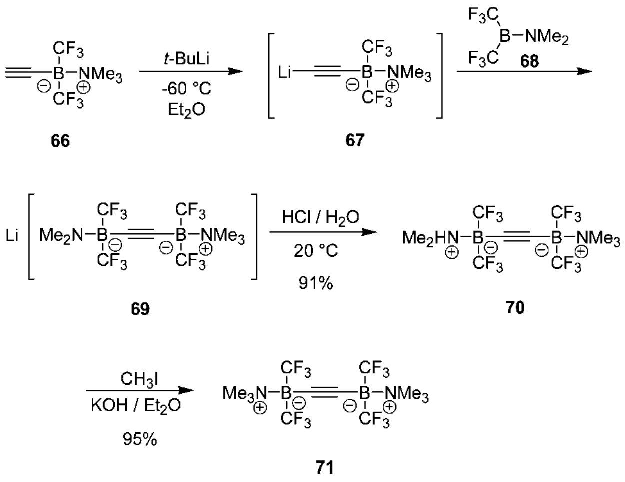


The synthesis of **65** makes use of a procedure developed by Brown et al.[80] to prepare in situ dilithium acetylide (**63**) from trichloroethylene and three equivalents of *n*-BuLi in THF/diethylether. Reaction of **63** with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**64**) followed by treatment with dry HCl affords **65** in high yield (Scheme 9).[79]

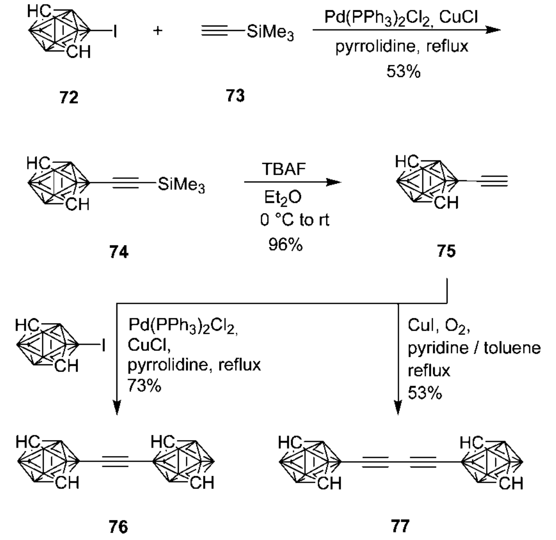
An acetylene capped with a tetravalent boron center, **71**, was recently reported.[81] Its synthesis starts with **66**. The corresponding lithium salt, **67**, generated in situ was reacted with **68** to afford **69** which was protonated to give **70** in 91% yield. After methylation the desired product **71** was isolated (Scheme 10). X-ray investigations on single crystals of **71** showed an B−C(sp) bond length of 1.565(4) Å.[81] This value is close to that reported for **42** with 1.553(3) Å,[77] for **53** with 1.564(4) Å, and for **54** with 1.557(4) Å.[77a]

A new variation of capping alkynes with boron derivatives was first published by Hawthorne et al.[82] The methodology to access rodlike *p*-carboranes makes use of a palladium-catalyzed cross-coupling reaction of the B-iodinated *p*-carborane, **72**, with terminal alkynes (Scheme 11). The first product, **74**, from the coupling reaction can be transformed to **75** by treatment with fluoride ions.[83] The reaction of **72** with an excess of the alkyne **75** and catalytic amounts of $Pd(PPh_3)_2Cl_2$ in presence of pyrrolidine afforded the 2-fold

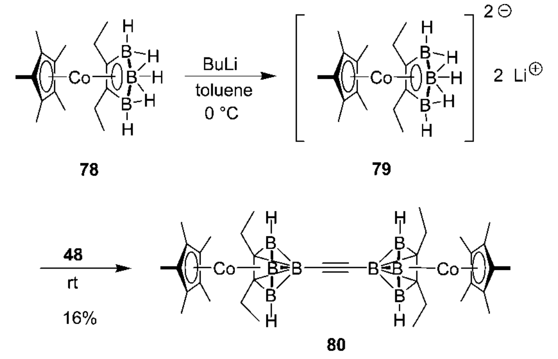
Scheme 10. Synthesis of Diborylacetylene 71



Scheme 11. Preparation of the Carborane-Capped Alkynes 76 and 77



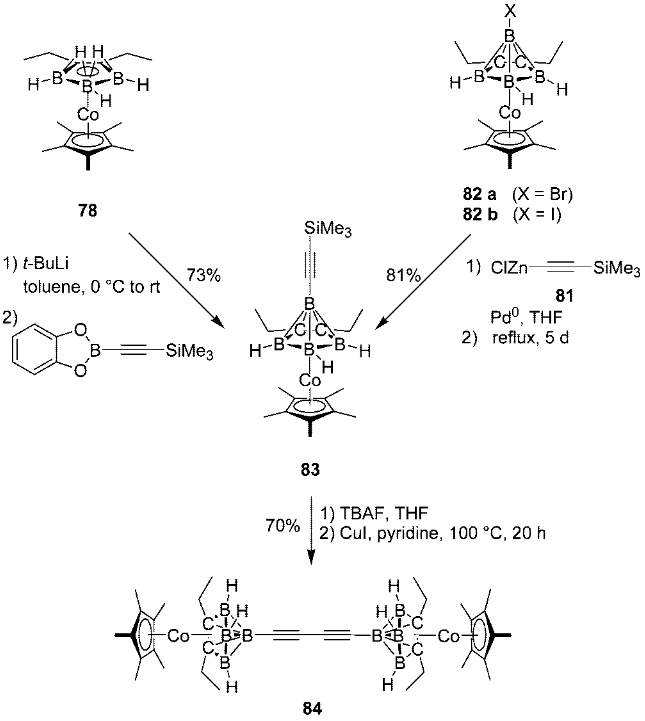
Scheme 12. Preparation of 80



capped alkyne **76**. The free alkyne **75** can be reacted to the dimer **77** by utilizing a Glaser coupling with CuI, oxygen and pyrrolidine. X-ray structural investigations on single crystals of **77** revealed a B−C(sp) distance of 1.528(10) Å and a C≡C distance of 1.209(9) Å.[83]

Grimes and Siebert et al.[84] made use of a recapitation approach via boron insertion into the dianion **79**.[85] This procedure (Scheme 12) furnishes a useful and versatile entry to apically substituted Cp*Co(2,3-$Et_2CB_4H_3$-7-X) compounds, including linked clusters.

Scheme 13. Preparation of 84 From 78 and 82



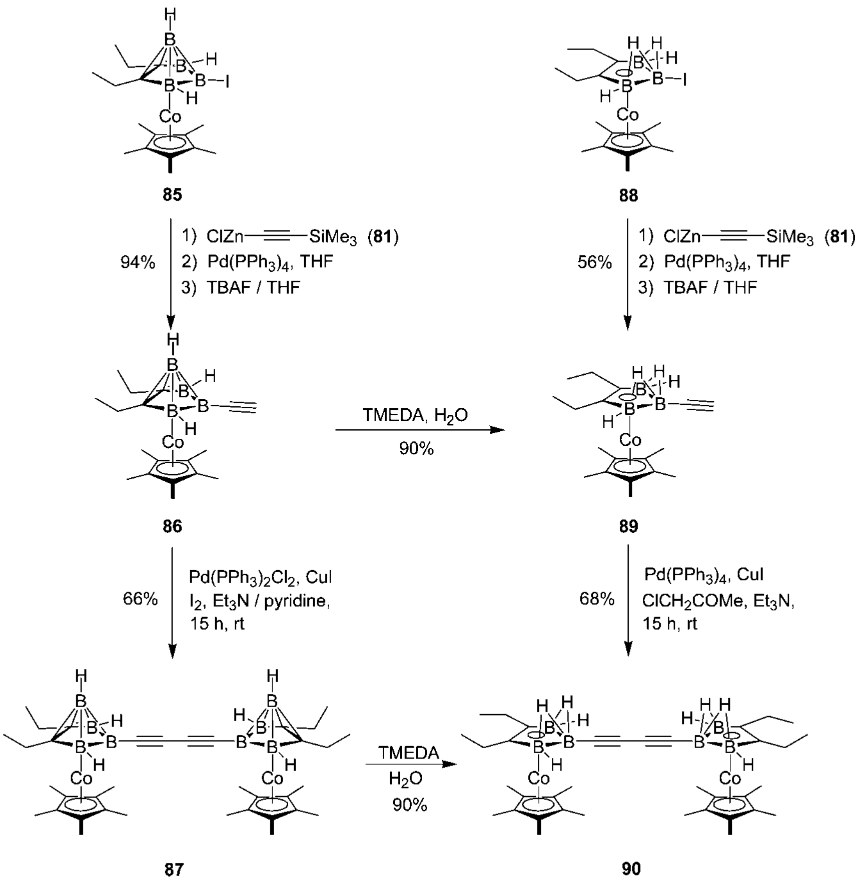
Treatment of the dianion **79** with **48** yielded the desired ethynyl bridged bis(cobaltacarboranyl)complex **80**. X-ray investigations revealed two independent molecules in the unit cell. One of them deviates strongly from the expected linearity of the B−C≡C−B unit with a calculated value of the Co-X-Co angle of 158°, where X represents the center of the C≡C bond. In the other molecule, this angle amounts to 172°. The authors interpret the observation that relatively weak intermolecular interactions can produce a substantial distortion from linearity indicating that the binding between the acetylenic carbons and the apical boron atom is mostly σ in character.

A route to a congener of **80** with a 1,3-butadiyne unit as bridge between the cobaltacarborane units was reported by Grimes et al.[86] In Scheme 13, there are two possibilities shown to introduce alkynyl substituents at the apex boron either by starting with the *nido*-MB_2C_3 species **78** (see also Scheme 12) and recapitation or by attack of the alkynylzinc reagent **81** at the B7 halogen atoms of **82a** or **82b**. The resulting product **83** was desilylated with fluoride ions and coupled with CuI/pyridine to afford dimer **84** in 69% yield. The molecular structure of **84**, derived by X-ray studies, revealed a linear 1,3-butadiynyl chain.[86]

Scheme 14 summarizes the conversion of B(5)-iodo*closo*- and *nido*-cobaltacarboranes **85** and **88**, respectively, to the corresponding B(5)-ethynyl derivatives **86** and **89** in two steps. In a first step, **85** and **88** are reacted with the alkynylzinc reagent, **81**. The resulting substitution products were desilylated in a second step with tetra(*n*-butylammonium)fluoride to afford the parent acetylenes **86** and **89**. The dimerization of **86** to **87** was achieved by treatment of **86** with Pd(II), CuI, I_2, and Et_3N. The yield of **87** was 66%. Compound **87** could be doubly deboronated with TMEDA to afford the *nido*-cobaltacarborane dimer **90** (Scheme 14). The latter species was also obtained from **89** by reaction with chloroacetone and trimethylamine.[86]

The substitution of the cobaltacarboranes at the 5- and 7-positions by halogen enabled Grimes et al. to prepare the

Scheme 14. Preparation of the Dimers 87 and 90 from 85 and 88



carbon wired planar octagon **97** as summarized in Schemes 15 and 16.[87] Starting point of this endeavor was the iodation of **83** by *N*-iodosuccinimide (NIS) to yield **91** (Scheme 15) Removal of the trimethylsilyl group afforded **92**. The iodine in the 5-position of **92** was substituted by **81** to afford **93**. Treatment of **93** with Pd(II), CuI, I_2, and Et_3N yields the dimer **95**.

This latter compound could also be obtained by first dimerization of **92** to **94** and then substitution at the 5-,5′-positions by **81**. From **95**, the path to the octagon **97** was straightforward: desilylation of **95** yielded the free bis-alkyne **96**, which was dimerized with $Cu(OAc)_2$, CuCl and pyridine to afford the red colored **97** (Scheme 16). X-ray investigations on **97** revealed discrete well-separated layers with the anticipated bond lengths and angles. The diagonally measured distance across the square is approximately 24 Å. Analysis of **97** by cyclic voltammetry revealed two separated one-electron reductions followed by a single two electron reduction. This indicates significant intramolecular electronic communication within the four cobalt centers.

2.2.2. Acetylenes Capped by Organometallic Groups with Aluminum, Gallium, Indium, and Thallium

There are only a few examples where two main group elements of Al or Tl are bound to an alkyne unit; therefore, we will deviate also in this chapter from our original intention expressed in the title and consider here also such examples where only one side of an alkyne is substituted by one organometallic group of the four elements.

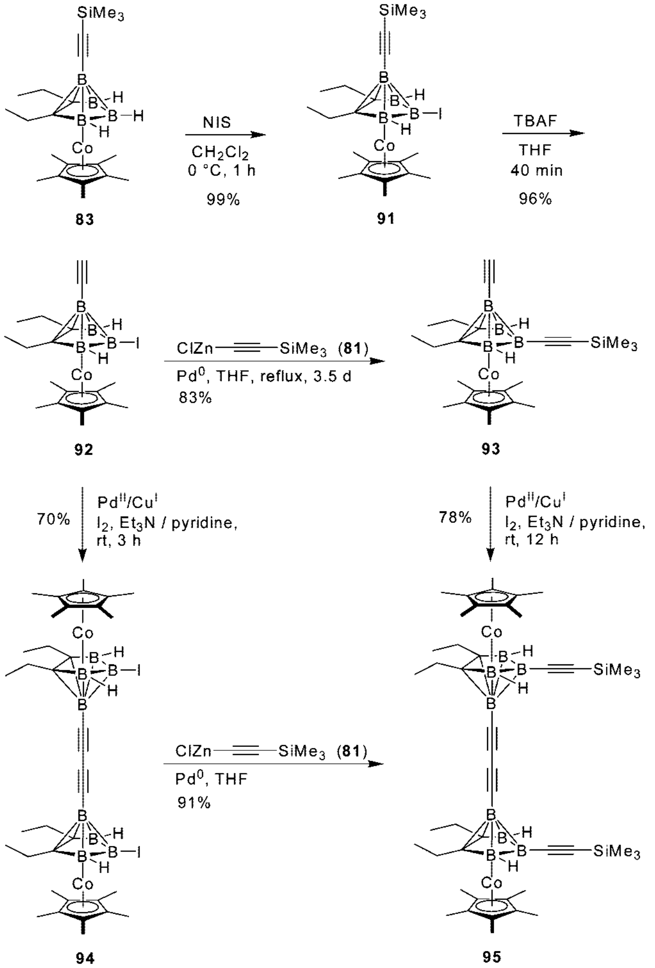
1,2-Bis(diphenylaluminium)ethyne was probably generated together with diphenylaluminiumethyne when diphenylaluminium bromide was reacted with monosodium acetylide.[88] Neither substance could be separated and isolated. However, when two equivalents of diethylaluminiumchloride (**98**) were reacted with 1,2-bis(trimethylstannyl)ethyne (**99**), 1,2-bis(diethylaluminium)ethyne (**100**) resulted in 95% yield (Scheme 17).[89] Compound **100** proved to be highly pyrophoric and insoluble in benzene and chloroform. However it dissolves in diethylether and THF and forms complexes with these solvents.[89] 1,2-Bis(dimethylthallium)ethyne (**104**) was prepared from trimethylthallium and acetylene (Scheme 17).[90] It is reported to be sensitive to air and explosive.

By treatment of R_2MHal (R = alkyl, aryl; M = Al, Ga, In, Tl; Hal = Cl, Br) with an alkali metal salt of a terminal alkyne one obtains readily the anticipated monosubstitution products.[88,89] The investigation of the structures of these species in the solid state revealed dimers. Similar to those reported for beryllium derivatives (see Figure 5) these structures can either have D_{2h} (**A**) or C_{2h} (**B**) symmetry (Figure 9).

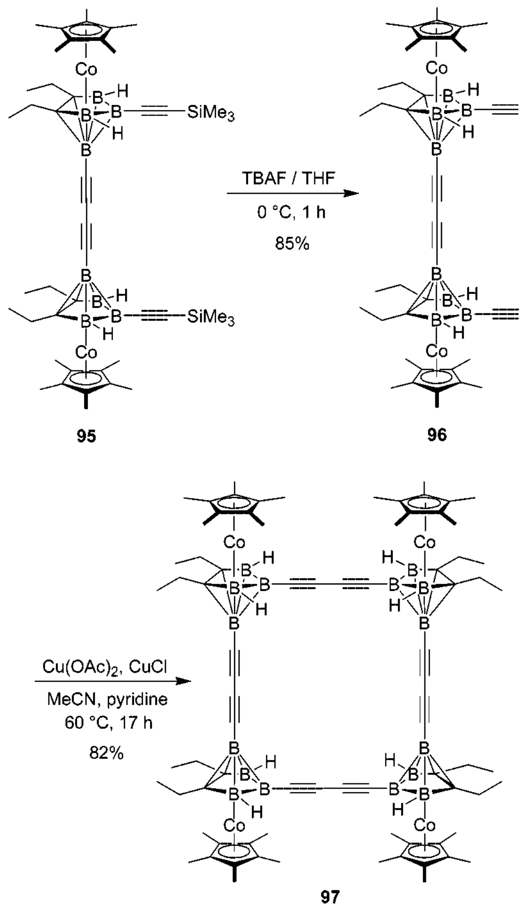
In Figure 9, we have depicted ten dimers. The formulas were drawn according to the results of X-ray investigations (**106** and **108**−**115**)[91−96] or electron diffraction studies (**107**).[97] It is seen that those dimers with bulky substituents at the metal prefer the D_{2h}-type structure (**112**−**114**), whereas all others choose the C_{2h} geometry. This observation can be rationalized by assuming that the electron-deficient (6e, 4c) bonding of the D_{2h} geometry can be stabilized by π-donor groups if there are no geometrical constraints.

To complete this chapter we mention that metals of group III can also be substituted with three alkyne units. In Scheme 18, two examples are depicted. The X-ray investigations confirm the structures of **118** and **121**.[98,99]

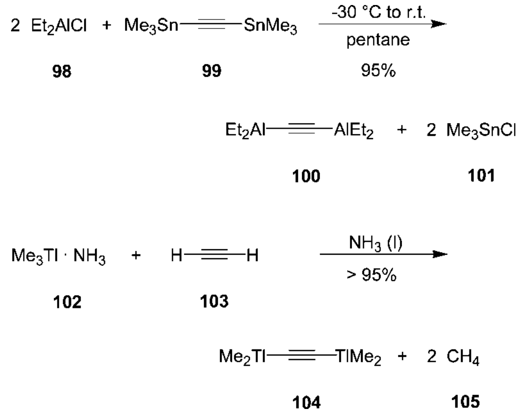
Scheme 15. Two Routes to Synthesize 95



Scheme 16. Synthesis of the Square 97



Scheme 17. Preparation of 100 and 104



$$\underset{\mathbf{98}}{2\ Et_2AlCl} + \underset{\mathbf{99}}{Me_3Sn{-}C{\equiv}C{-}SnMe_3} \xrightarrow[\text{pentane, 95\%}]{-30\ °C\ \text{to r.t.}} \underset{\mathbf{100}}{Et_2Al{-}C{\equiv}C{-}AlEt_2} + \underset{\mathbf{101}}{2\ Me_3SnCl}$$

$$\underset{\mathbf{102}}{Me_3Tl \cdot NH_3} + \underset{\mathbf{103}}{H{-}C{\equiv}C{-}H} \xrightarrow[> 95\%]{NH_3\ (l)} \underset{\mathbf{104}}{Me_2Tl{-}C{\equiv}C{-}TlMe_2} + \underset{\mathbf{105}}{2\ CH_4}$$

2.3. Alkynes Substituted by Group IV Elements

2.3.1. Alkynes Substituted by Silicon

The most examples for alkyne moieties capped by a main group element are definitely the ones with silicon, if we do not consider carbon. A variety of protecting groups, such as trimethylsilyl (TMS) and triisopropylsilyl (TIPS), ideally suited for the stabilization of long carbon rods, consist of silicon. A variety of them, such as the small TMS, are also easily removable, either by catalytic amounts of base or by the use of fluoride anions, to afford terminal alkyne moieties. The first example of a bis-silicon-substituted alkyne was $Me_3SiC{\equiv}CSiMe_3$ that was reported in 1952.[100] The first attempts to prepare longer alkyne chains were based on triethylsilyl (TES) groups as capping moieties.[101,102] Partial cleavage of the bis-TES-capped (oligo)ynes by aqueous sodium hydroxide solution and instantaneous oxidative coupling under Hay conditions led to the corresponding dimers (Scheme 19). A repetition of this sequence afforded (oligo)ynes up to a hexadecayne **131**. Mixed couplings led to (oligo)ynes with an odd number of alkyne units. The TES-protected (oligo)ynes **132(*n*)** served as starting material for the preparation of the parent (oligo)ynes $H(C{\equiv}C)_nH$ (**133(*n*)**) (Scheme 20).[101] However, when the latter compounds were synthesized a proper characterization was not possible; only UV data were recorded.

The much bulkier TIPS moiety employed by Tykwinski increased the solubility, as well as the stability of (oligo)-alkynes tremendously. With terminal TIPS groups even a crystallographic study of a hexadecaoctayne (see section 4.2.4) was possible. In addition, silicon as substituent next to the triple bond does not dramatically alter the electronic properties of the oligoynes (see section 4.2.2) and may serve therefore as the most appropriate model of an sp-hybridized polymeric carbon chain.

Silicon-substituted alkyne moieties have received further interest due to several aspects. Polymeric acetylene silicon systems showing interesting properties have been studied by macromolecular chemists. This journey started by incorporating acetylene units in strained silacycles that can undergo ring-opening or ring-contraction reactions when heated. Physical organic chemists gained interest because of the strong σ/π interaction of the Si−Si single bond with the triple bond next to it.[103,104] The first syntheses of cyclosilaalkynes were performed mid of the 1980s. The bis-Grignard reagent of **134** was reacted with a dichlorotrisilane **135** to yield **136**

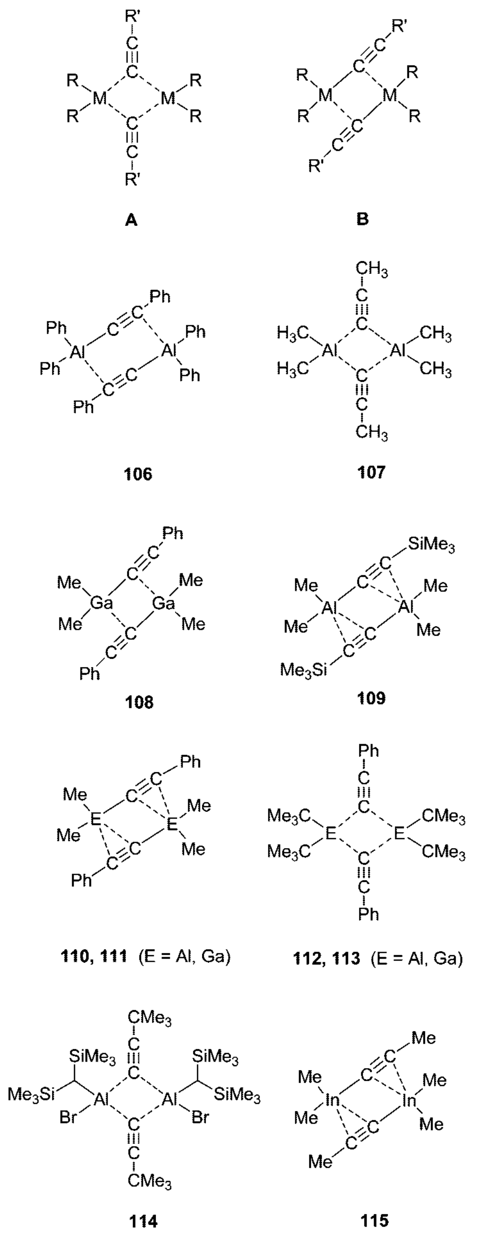
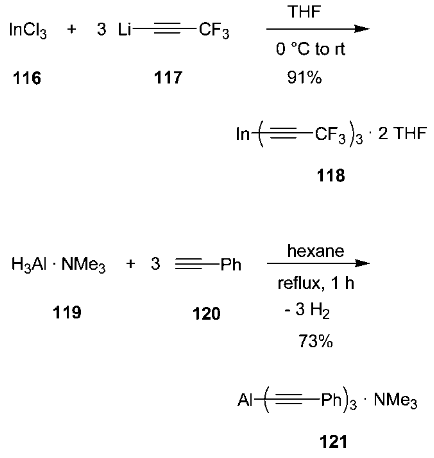
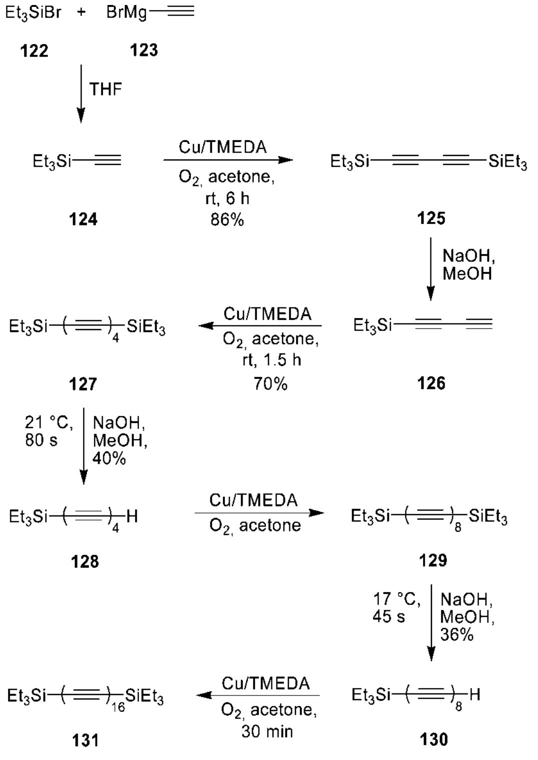


Figure 9. Various alkyne complexes **106**−**115** of the heavier group III elements Al, Ga, and In.

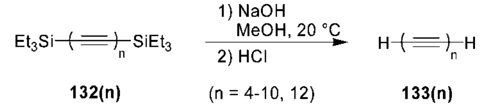
Scheme 18. Synthesis of 118 and 121



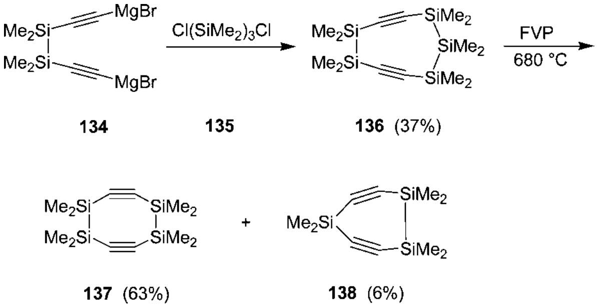
Scheme 19. Preparation of TES-Capped (Oligo)ynes 127, 129, and 131



Scheme 20. Deprotection of TES-Capped (Oligo)ynes 132(*n*) to Afford the Parent Systems 133(*n*)



Scheme 21. Synthesis of Highly Strained Cyclic Compounds 136, 137, and 138

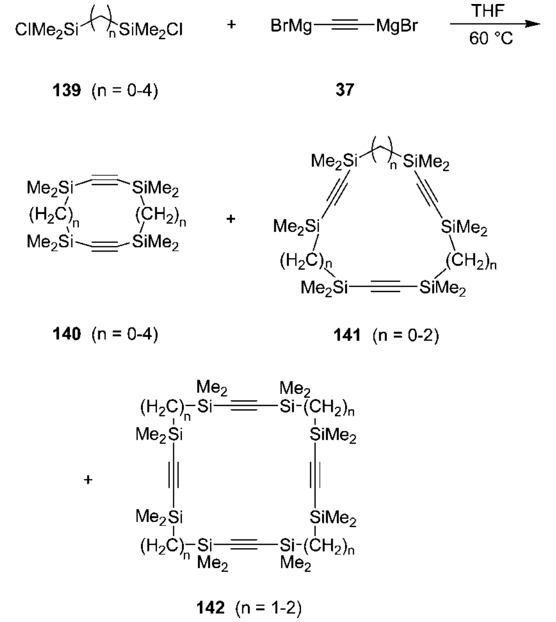


(Scheme 21). Flash vacuum pyrolysis (FVP) at 680 °C led to the extrusion of dimethylsilylene and yielded the octacycle **137** in 63%.[105] As side product the highly strained heptacyclic compound **138** was obtained in 6% yield. Later also a direct access to the eight-membered ring diacetylenes of type **137** was found.[106] Similar bicyclic systems were also prepared to study σ/π interactions.[107,108]

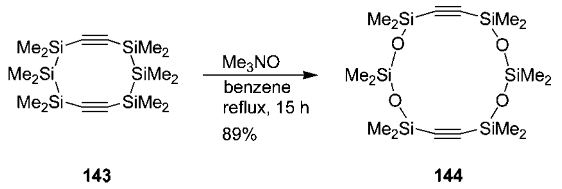
For the assembly of larger cycles, 1,2-dichlorodisilanes **139** with carbon tethers were reacted with bis(bromomagnesium)acetylide (**37**) to obtain a mixture of cyclic diynes, triynes and tetraynes and even higher oligomers in low yield (Scheme 22).[109,110] Many of them were also structurally characterized by means of X-ray diffraction analyses.[111,112] An unusual ring-enlargement reaction was observed when the cycle **143** was oxidized with trimethylamine *N*-oxide (Scheme 23). The trisila tethers were transformed into trisiloxa tethers as shown in **144**.[110,113]

A molecular square **146** as well as a molecular pentagon **147** with Si corners could be assembled by passing acetylene

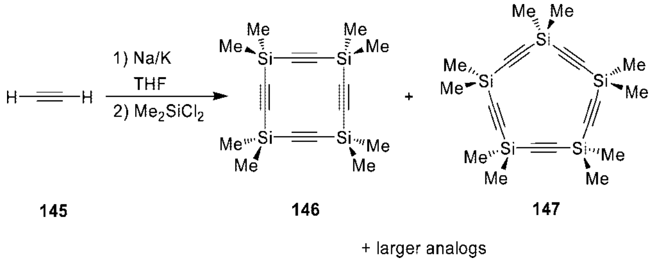
Scheme 22. Preparation of Silicon-Capped Cyclic Diynes 140, Triynes 141, and Tetraynes 142



Scheme 23. Ring-Enlargement of 143 by Me_3NO to Afford 144



Scheme 24. Generation of Cyclic Ethynylsilanes 146 and 147

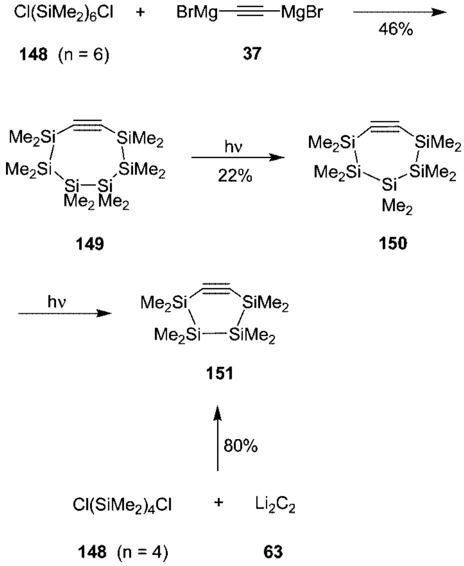


(**145**) into a suspension of alkali metal or a potassium/sodium alloy in THF and the simultaneous addition of dimethyldichlorosilane (Scheme 24).[114] In addition to these products, cyclic trimers and larger assemblies up to cyclic dodecamers were formed. The tetra- as well as the pentamer could be also structurally characterized by means of X-ray diffraction analyses.[115]

Strongly bent acetylene units were accessed by incorporating one acetylene unit into cycles of silicon atoms. The reaction of Li_2C_2 with 1,ω-dichlorosilanes such as **148** allows the preparation of rings as strained as cyclohexyne derivative **151**.[116] However, **151** could also be obtained by photofragmentation reactions starting with the corresponding cyclooctyne derivative **149** (Scheme 25).[117−121] Pure, neat compound **151** slowly decomposes at room temperature, but is completely stable when stored as a diluted solution in hexane at 0 °C. It shows the typical reactions of strained alkynes.[121−123]

By a similar procedure, compounds of type **152(*n*)** with bridging acetylene units connecting cyclic silane moieties were synthesized (Figure 10).[124]

Scheme 25. Preparation of Highly Strained Silicon-Capped Acetylene 151



Also disilylacetylenes with hydrogens attached to the capping Si atoms were prepared, such as $H_3Si-C\equiv C-SiH_3$,[125,126] aryl substituted examples, such as $PhH_2Si-C\equiv C-SiH_2Ph$[127−129] and $(i\text{-}Pr)_2HSiC\equiv CSiH(i\text{-}Pr)_2$,[130] by classical routes using nucleophilic acetylene and silyl chlorides (see Figure 11). Hydrogens could be substituted by their action with NBS to afford bromides such as **156**.[130] Acetylenes with all silyl-substituted silyl groups such as compound **157** were made accessible[131] and have been used as bridging units in silylmetal compounds such as **158** and **159** (Figure 11).[132]

Even Si-capped butadiyne units could be incorporated into cyclic entities.[133,134] Rings with an alternate arrangement of disilanylene and diyne units were created by the reaction of in situ generated lithium butadiynide **161** and disilane dichlorides **160** (Scheme 26). Size-exclusion chromatography yielded three different cycles **162** (11%), **163** (1.4%), and **164** (trace amount).[133] It is noteworthy that the course of

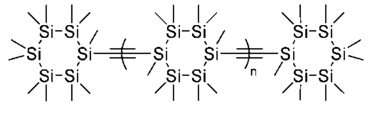

152(n) (n = 0, 1)

Figure 10. Cyclosilanylethynes **152(*n*)**.

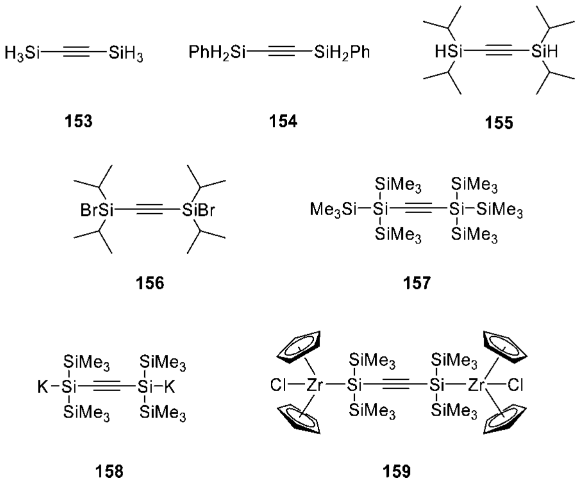
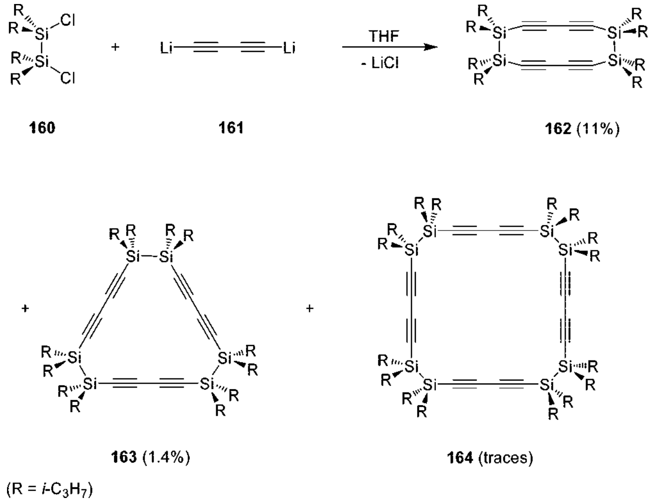
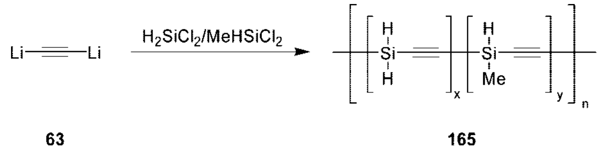


Figure 11. Variety of silicon-capped acetylenes **153**−**159**.

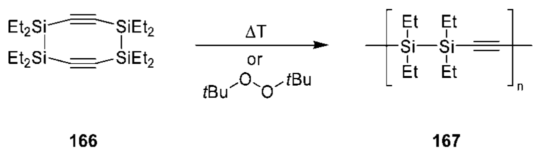
Scheme 26. Silicon-Capped Butadiyne Units Incorporated in Cycles



Scheme 27. Polymerization Reaction to Afford 165



Scheme 28. Ring-Opening Polymerization of 166 to Yield 167



the reaction strongly depended on the kind of substituent at the Si atoms. The formation of cyclic oligomers could not be achieved when Me groups were used; in this case, only polymeric material was obtained.

Silicon-capped alkyne units were also widely used in polymeric organosilicon systems.[135−143] A comprehensive report with respect to this class of compounds would go beyond the scope of this review. Therefore, we concentrate on several examples. In general two different approaches were envisioned, either a polymerization reaction with nucleophilic acetylene units such as Li_2C_2 and electrophilic silicon moieties such as silyl chlorides or silyl triflates or a ring-opening polymerization of strained tetrasilacyclooctatetraynes. A recent example for the polycondensation approach is shown in Scheme 27. Lithiated acetylene and dichlorosilanes were reacted yielding a silylene acetylene polymer.[144] This material was used as a new precursor for ceramics. Further polymeric architectures could be achieved by hydrosilylation reactions of poly[(silylene)diethynylenes].[145]

Treatment of tetrasilacyclooctadiynes such as **166** at high temperature (230 °C) in a degassed solution afforded thermal ring-opening polymerization products **167** (Scheme 28).[146,147] In the presence of a radical starter, such as di-*t*-butyl peroxide, the radical reaction could also be achieved at much lower temperature.

A large variety of different silylene acetylene, disilylene acetylene, siloxane diacetylene or even carborane siloxane acetylene polymers were created, especially by Uhlig[148−154] and Keller.[155−162] Three examples **168**−**170** are depicted in Figure 12.

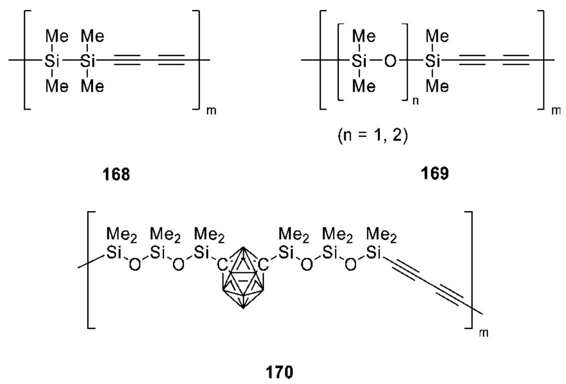
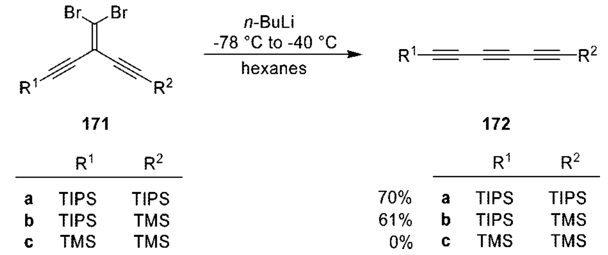


Figure 12. Various polymeric architectures with Si-capped alkyne units.

Scheme 29. Fritsch−Buttenberg−Wiechell (FBW) Rearrangement for the Synthesis of Silicon-Capped Triynes 172a−172c



	R^1	R^2
a	TIPS	TIPS
b	TIPS	TMS
c	TMS	TMS

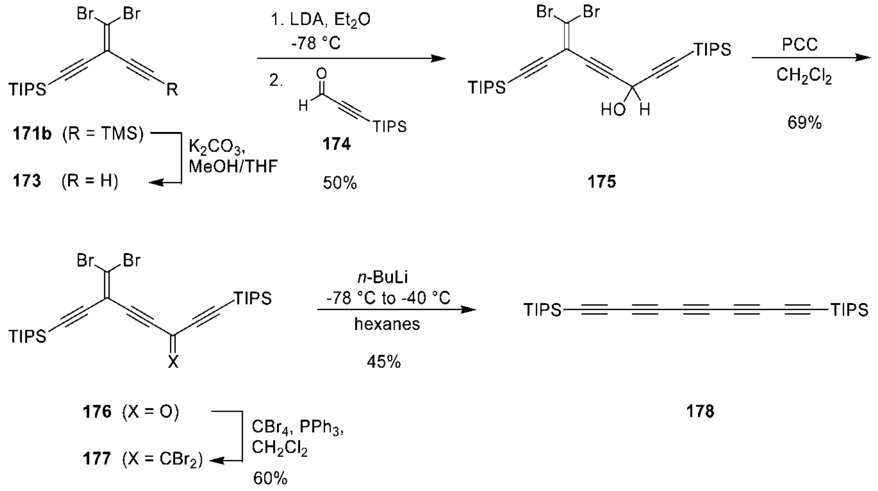
		R^1	R^2
70%	**a**	TIPS	TIPS
61%	**b**	TIPS	TMS
0%	**c**	TMS	TMS

Recently, the Fritsch−Buttenberg−Wiechell (FBW) rearrangement,[163,164] a well-established method for the synthesis of alkynes, has proven to be also a very powerful method for oligoyne synthesis.[165] Alkyne moieties readily undergo 1,2-shifts via intermediate alkylidene carbene/carbenoid species when 1,1-dibromo-2,2-diethynylethenes **171** are treated with *n*-BuLi at −78 °C. Lithium-halogen exchange takes place, followed by alkyne migration and the loss of LiBr. As a result, a further triple bond is incorporated into the sp-hybridized carbon system (Scheme 29).[164,166] The best results were achieved by using TIPS protection and apolar, noncoordinating solvents, such as hexane or cyclohexene. Benzene as a solvent could also be used, however, higher temperatures (−15 °C) are necessary.[165]

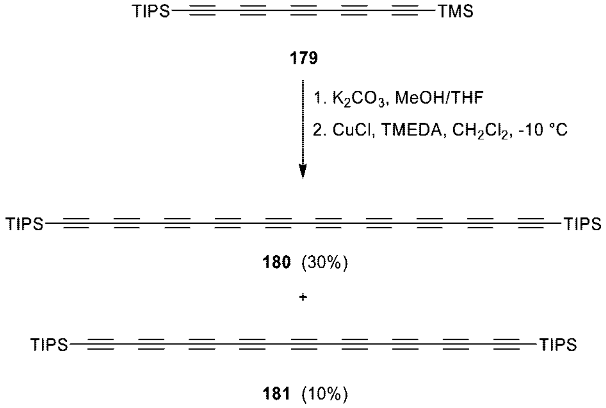
Tykwinski et al. utilized this method also for the construction of stable TIPS-protected oligoynes up to a decayne.[167,168] The synthesis of the pentayne is shown in Scheme 30. Starting from **171b** in a first step TMS was removed by using a weak base, the lithiation of the terminal triple bond is achieved by LDA which is not powerful enough for halogen-lithium exchange. The nucleophilic lithiated species was then reacted with aldehyde **174** to incorporate a third triple bond. PCC as oxidant transformed the alcohol **175** into the ketone **176** ready for Corey−Fuchs reaction using CBr_4 and PPh_3. A 2-fold FBW rearrangement generated the pentayne **178**.

By application of the FBW rearrangement to appropriate molecular architectures also TIPS-protected hexa- and octaynes could be generated. However, a quadruple FBW rearrangement yielding a decayne failed.[166] The synthesis of this TIPS-protected decayne was achieved by a more traditional approach (Scheme 31). The quite instable pentayne **179**, which was also accessible via FBW rearrangement was subjected to protiodesilylation and subsequent standard Hay

Scheme 30. Two-Fold Fritsch−Buttenberg−Wiechell (FBW) Rearrangement for the Synthesis of Silicon-Capped Pentayne 178



Scheme 31. Generation of TIPS-protected Decayne 180 and Nonayne 181



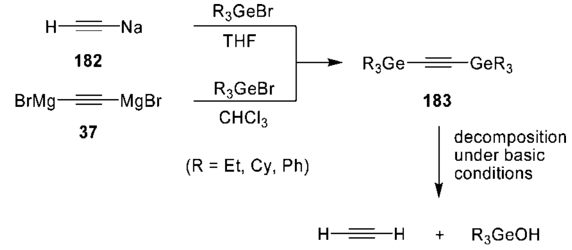
conditions using an excess of CuCl and TMEDA affording the homocoupled product **180**. Surprisingly, a byproduct was formed in about 10% yield, which proved to be the C_{18} moiety **181**. Obviously, a C_2 moiety of the carbon chain was lost during Hay coupling, a very rare observation. However, the formation of the nonayne **181** could be suppressed completely by lowering the temperature to −10 °C. Under these conditions, the bright orange decayne **180** was obtained in a yield of 30%. The compound shows limited stability when purified by column chromatography using silica gel or alumina. Day light and ambient temperatures for extended periods of time should be avoided. However, storage at −4 °C did not lead to any decomposition.

Attempts to use tris(biphenyl-4-yl)silyl (TBPS) protecting groups with a diameter of about 20 Å instead of TIPS groups (with a diameter of about 8 Å) to even more increase the stability of silicon-capped oligoynes proved to be difficult.[169] During the synthesis of the desired compounds a complete lack of chemoselectivity in the desilylation step (TMS vs TBPS) was observed. Only traces of the corresponding TBPS-capped hexayne could be isolated.

2.3.2. Alkynes Substituted by Germanium, Tin, and Lead

The synthetic methods to afford alkynes capped with the higher homologues of silicon are very similar to the procedures described above. Nucleophilic acetylenes, such as monosodium acetylide or acetylene dimagnesium bromide are able to react with trialkyl germanium bromides (Scheme 32).[170,171] If the monosodium salt of acetylene is used, the resulting terminal germanylacetylene disproportionates to acetylene and the bis-trialkylgermanium capped alkyne **183**. The latter compound is unstable under basic conditions.[169] Disproportionation reactions lead also to Ge-capped alkynes when tetraethynylgermane was synthesized.[172]

Scheme 32. Two Routes to Generate Bis-Germanium-Capped Acetylenes 183

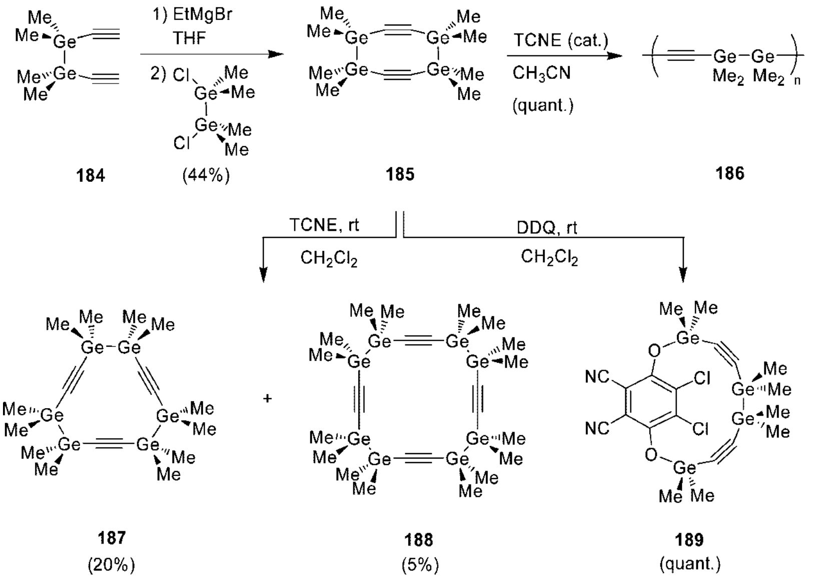


In analogy to the corresponding sila congeners, cycles of alternating acetylene and R_4Ge_2 moieties were constructed. A bis-Grignard reagent reacted with a dichlorodigermane furnishing the eight-membered ring **185** in 44% yield (Scheme 33).[173] Larger cycles **187** and **188** could be obtained by the reaction of **185** with tetracyanoethylene (TCNE) in dichloromethane; most of them were electronically and structurally characterized.[174] In the more polar solvent, acetonitrile, using only catalytic amounts of TCNE, a polymerization takes place.[175] This oligomerization/polymerization process can be rationalized in the following way: A Ge−Ge σ bond is more susceptible to electrophiles than a Si−Si σ bond. Thus TCNE is inserted in the Ge−Ge bond, mediating the oligomerization process. In contrast to TCNE the more powerful oxidizing agent DDQ leads to an irreversible adduct formation as shown for compound **189**.

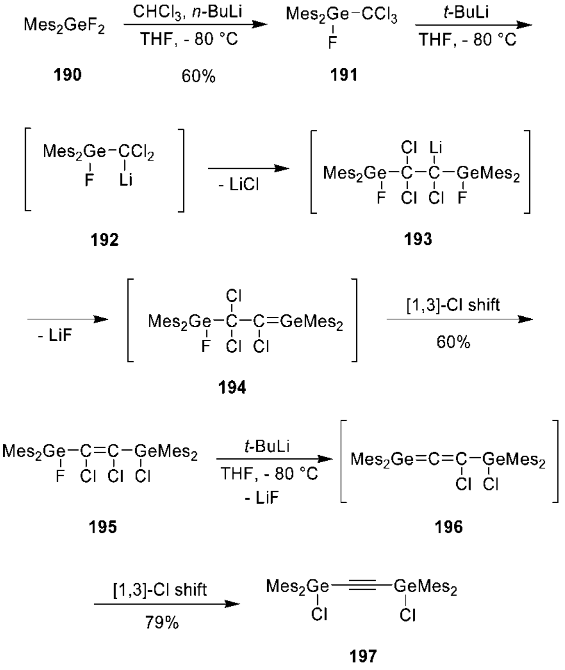
Recently, two new routes to digermylalkynes were investigated. The first one makes use of a germaallene/germylalkyne rearrangement.[176] The sequence starts with the reaction of lithiated chloroform and difluorodimesitylgermane (**190**) to afford adduct **191**. A further lithiation of **191** was achieved by *t*-BuLi, followed by dimerization under loss of LiCl and LiF. A 1,3-chlorine shift leads to alkene **195**. Further treatment with *t*-BuLi affords via an intermediate germylallene the bis-germanium capped acetylene **197** (Scheme 34).

The second route makes use of transition metal catalysts and was developed in 2007.[177] It utilizes monosubstituted alkynes **198** and terminal vinyl-substituted germanes **199**. A ruthenium

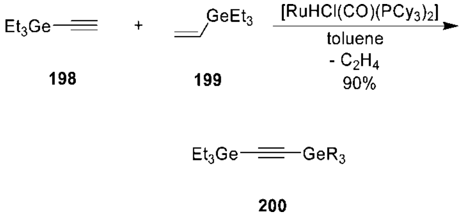
Scheme 33. Generation of Cyclic Germanium-Capped Oligoynes 187, 188, and 189



Scheme 34. Synthesis of 197 via a Germaallene/Germylalkyne Rearrangement



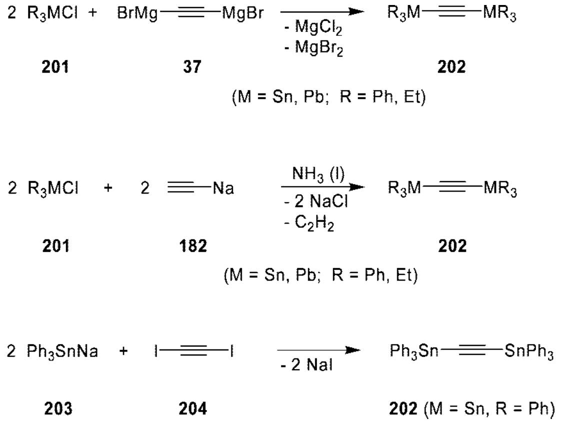
Scheme 35. Catalytic Transformation of Terminal Germaalkynes 198 with Vinylgermanes 199 to Afford Bis-Germanium-Capped Acetylenes 200



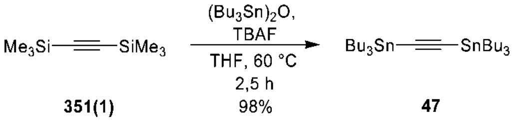
complex such as [RuHCl(CO)(PCy$_3$)$_2$] leads to the formation of the desired compounds with the evolution of ethylene (Scheme 35). The reaction is conducted in toluene at 110 °C.

Monoacetylene and diacetylene capped by the heavier homologues, tin and lead, were accessed via classical routes. In general trialkyl or triaryl substituted tin or lead chlorides were reacted with acetylene dimagnesium dibromide or monosodium acetylide (Scheme 36).[178−182] In the latter case a subsequent disproportionation takes place to afford the disubstituted alkyne. For the synthesis of bis-Ph$_3$Sn-capped acetylene also another pathway was reported making use of nucleophilic tin and electrophilic acetylene (Scheme 36).[177]

Scheme 36. Preparation of Alkynes 202 Capped by Tin and Lead



Scheme 37. Conversion of Silyl-Capped Alkynes into Stannyl-Capped Alkynes



A promising method for the conversion of silyl-substituted alkynes to stannyl-substituted alkynes was developed by Buchwald.[183] The reaction uses inexpensive bis(tributyltin) oxide and tetrabutylammonium fluoride (TBAF) as catalyst to afford the stannyl-capped alkyne in almost quantitative yield (Scheme 37). Removal of the volatile bis(trimethylsilyl) oxide is the only purification needed. The method can also be used for diyne units as well as benzyl and allyl systems.

Also a variety of butadiyne derivatives with capping units consisting of Ph$_3$M (M = Ge, Sn, Pb) showing an incredible stability (see Figure 13) were synthesized.[179] The corresponding tin-substituted congeners have been used in several reactions to introduce a C$_4$ moiety.[184,185]

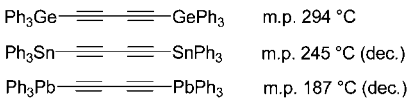


Figure 13. Ge-, Sn-, and Pb-capped butadiynes and their corresponding melting (decomposition) points.

3. Alkynes Substituted by Elements of Main Groups V−VIII

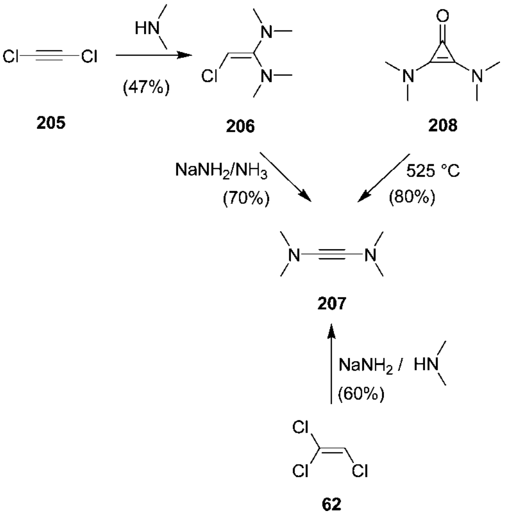
3.1. Alkynes Substituted by Pnictides

3.1.1. Alkynes Substituted by Nitrogen

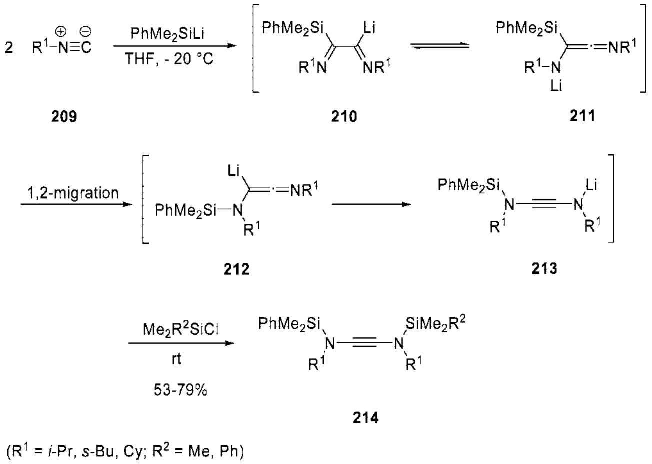
Alkynes substituted with elements of the fifth main group (pnictides) are commonly extremely electron-rich compounds, especially when substituted with amine residues. These yndiamines have been known for more than forty years;[186,187] a simple stable derivative such as **207** and some higher homologues were accessible from 2-fluoro-1,1-dichloroethylene or trichloroethylene (**62**) with or without isolation of the hazardous dichloroacetylene.[188] For the synthesis of **207**, the highly electrophilic dichloroacetylene (**205**) is attacked by dimethylamine to yield **206** that transformed via a three-membered ring intermediate to the desired compound.[189,190] Sodium amide in liquid ammonia acts as base (Scheme 38). Because of the hazards connected with dichloroacetylene a pyrolysis method was also developed for the preparation of **207**. Heating the electron-rich cyclopropenone derivative **208** to 525 °C leads to an CO extrusion to afford **207** (Scheme 38).[191] However, the best method available so far to synthesize **207** is the one-pot procedure starting with commercially available trichloroethene (**62**) in liquified dimethylamine.[192]

A variety of differently substituted acetylenediamines were synthesized by a similar approach.[193] Several derivatives with silyl groups attached to the nitrogen atoms are also known. They are available by the dimerization of alkyl isocyanides **209** as shown in Scheme 39.[194] This reaction is initiated by the attack of lithiated silane to the terminal carbon of the isocyanide. After tautomerization and 1,2-migration of the silyl substituent to the nitrogen the allenic species **212** rearranges to the triple bond system **213**. The sequence is terminated by trapping the intermediate with silyl chloride.

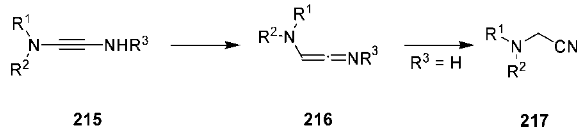
Scheme 38. Methods to Prepare Bis(dimethylamino)-Capped Acetylene 207



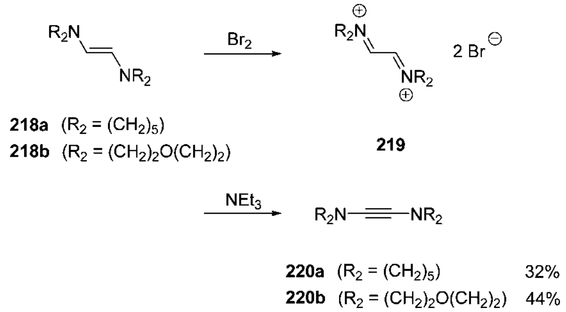
Scheme 39. Isocyanides 209 as Starting Materials for the Synthesis of Bis-Nitrogen-Capped Alkynes 214



Scheme 40. Tautomerization of Acetylenediamines 215 Into Ketenimines 216 and Nitriles 217



Scheme 41. Bis-Nitrogen-capped Acetylenes 220 Starting from Bis-Nitrogen-Substituted Olefins 218



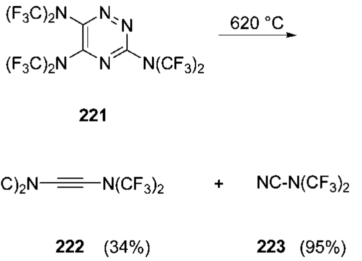
Acetylenediamines **215** bearing one or two hydrogen atoms at the nitrogen are unknown in the free state. They tautomerize instantaneously into ketenimines **216** or nitriles **217** (Scheme 40).[195] However, as ligands in molybdenum or tungsten complexes, they are well recognized.[196] In these cases both π orbitals of the electron-rich triple bond are involved into bonding, in total four electrons are donated to the metal center.

A few examples of other methods to construct nitrogen-substituted triple bonds are known. One of them commences with 1,2-di(piperidino)ethene **218a** or 1,2-di(morpholino)-ethene **218b**. Addition of bromine to the electron-rich double bond does not yield the bromide, but the ethane-1,2-diiminium salt **219** (Scheme 41).[197] The further reaction with triethylamine affords the nitrogen-capped acetylenic compounds **220a** and **220b**, respectively.

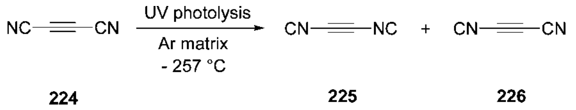
The 1,2,4-triazine core in **221** was destroyed by flash pyrolysis at 620 °C to yield the acetylene diamine **222** bearing four trifluoromethyl substituents along with cyanamide **223** (Scheme 42).[198] However, the species **222** can be obtained in much better yield by elimination of HBr from the corresponding bromoethylene-1,2-diamine.[199]

In contrast to acetylene between cyano groups, which have been synthesized and studied in great detail, diisocyanoacetylene (**225**) has only been isolated in an argon matrix at −257

Scheme 42. Flash Pyrolysis of Triazine 221 to Afford Bis-Nitrogen-Capped Alkyne 222



Scheme 43. Synthesis of Diisocyanoacetylene 225 Starting from Dicyanoacetylene 224



°C using dicyanoacetylene (**224**) as starting material (Scheme 43).[200] By UV laser photolysis, CN radicals are formed and combine with acetylene radicals resulting in the formation of compound **225** as the major and compound **226** as the minor isomer. Diisocyanoacetylene is the only example of bis(nitrogen-functionalized) acetylenes that is not an acetylenediamine. In contrast to 1,2-dicyanoacetylene, it has not been obtained as a pure compound but was only characterized by IR spectroscopy. The measured vibrational frequencies were in good agreement with computational results.[201,202]

Theoretical investigations have been performed for the hitherto unknown molecules dinitroacetylene (**227**) and dinitrosoacetylene (**228**) (Figure 14).[203,204] Both compounds are located as minima on the hyperpotential surface and reveal (as anticipated, see section 4.2.4) a nonplanar conformation. Only theoretical thermochemical investigations have been performed for 1,2-bisazidoethyne (**229**).[205]

Nitrogen-substituted diynes were first synthesized by Glaser coupling of terminal ynamines and by a dechlorination of a randomly obtained dichloroenynediamine.[206] However, only symmetrically substituted diynes could be obtained by such an approach. A more flexible method for the preparation of nitrogen-substituted diynes and even higher homologues was developed by Himbert in the 1980s.[207] This method uses perchlorobutenyne **230** as starting material (Scheme 44). In a first step, the terminal chlorine at the alkyne moiety was substituted by an amine or a lithiated amine to afford **231**. Two equivalents of *n*-butyllithium transform the olefinic moiety into a lithiated alkyne **232**. The lithium salt **232** was brominated with BrCN to afford the terminal bromide **233** which was transformed into the nitrogen-capped diacetylene **234**.[208] This procedure can be extended as shown in Scheme 45. When the lithium salt **232** is again reacted with perchlorobutenyne **230**, one obtains **235** that can be transformed in the same way as shown in Scheme 44 to the nitrogen-capped tetrayne **238** (see Scheme 45). Using this synthetic procedure nitrogen-substituted oligoynes with three and four triple bonds in a row have been prepared.[209] These compounds can be stored for several weeks at 0 °C without significant decomposition. Reactions with arylisocyanates and nitrile oxides have shown that these species possess a very high-lying HOMO with the largest coefficients at the triple bond capped by the nitrogen.[210,211]

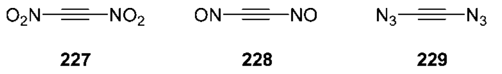
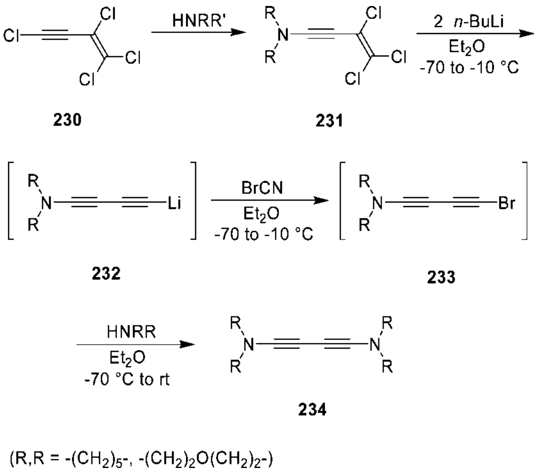
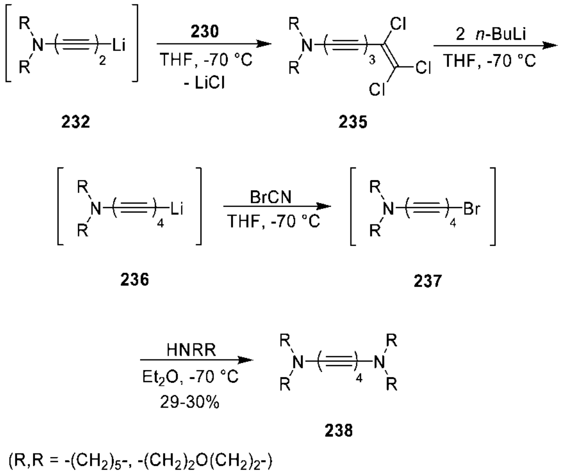


Figure 14. Dinitroacetylene (**227**), dinitrosoacetylene (**228**), and 1,2-bisazidoethyne (**229**).

Scheme 44. Synthesis of Nitrogen-Capped Diyne 234



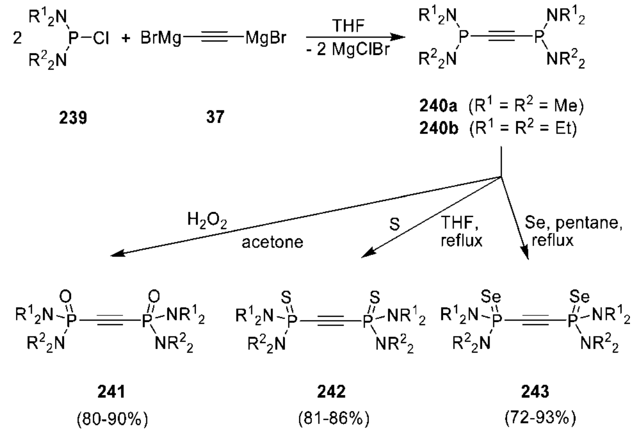
Scheme 45. Preparation of Bis-Nitrogen-Capped Tetraynes 238



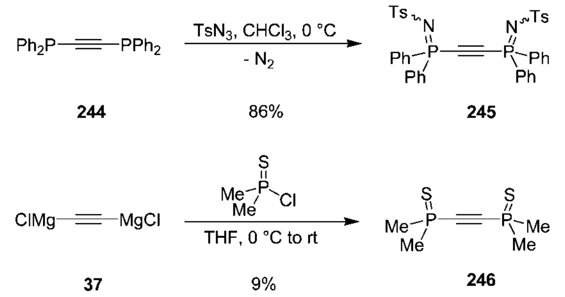
3.1.2. Alkynes Substituted by Phosphorus

When going to phosphorus, the higher homologue of nitrogen, as substituent at the alkyne moiety,[212] several properties have to be considered. First, an overlap between the lone pair and the π^* orbital of the alkyne is less effective than in the case of nitrogen. This leads to a decrease in electron density at the triple bond. Second, the difference between the electronegativities of phosphorus and carbon is small. The C−P bond is commonly (with the exception of strongly electron-withdrawing substituents at the phosphorus) not polar. These properties lead to more stable compounds. Third, for phosphorus-substituted alkynes there exists the possibility to go from trivalent to tetravalent or pentavalent phosphorus. In the latter cases, the lone pair is commonly capped by group VI elements, such as oxygen, sulfur, and selenium or used for a further bond. The first experiments using phosphorus as a substituent of an alkyne moiety are from the 1970s when Kuchen and co-workers investigated the reaction of bis(dialkylamino)chlorophosphines **239** with acetylene dimagnesium dibromide (**37**) to afford compounds of type **240** (Scheme 46).[213] Although the alkyne unit is relatively electron-rich, the compounds can be distilled without decomposition. In contrast to alkyl substituted phosphanes the acetylenic congeners are not prone to

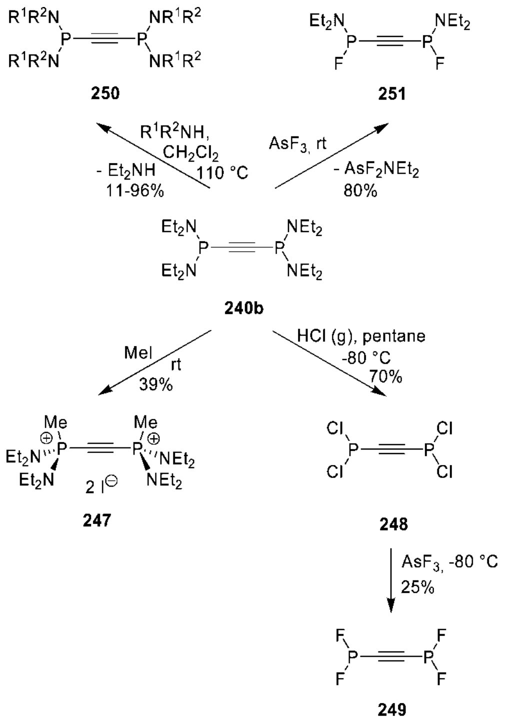
Scheme 46. Synthesis of Bis-Phosphorus-Capped Acetylenes 240−243



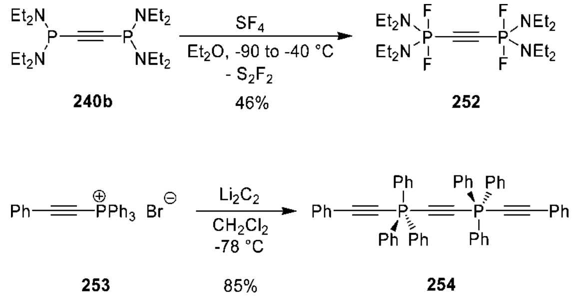
Scheme 47. Generation of Bis(phosphorimidoyl)acetylene (245) and Bis(dimethylthiophosphoryl)acetylene (246)



Scheme 48. Derivatization Reactions of 240b



Scheme 49. Generation of Phosphoranylacetylenes 252 and 254



spontaneous oxidation upon exposure to air. With electrophiles, such as hydrogen peroxide, a reaction takes place immediately to afford **241**, whereas the sulfurization as well as the selenization[214,215] needs elevated temperatures to yield **242** and **243**, respectively (see Scheme 46). It is worth to noting that these reactions lead to a pair of enantiomers and a meso compound when different groups of R^1 and R^2 were utilized. Today also compounds of this type with Ph substituents instead of the dialkylamino substituents are available.[216]

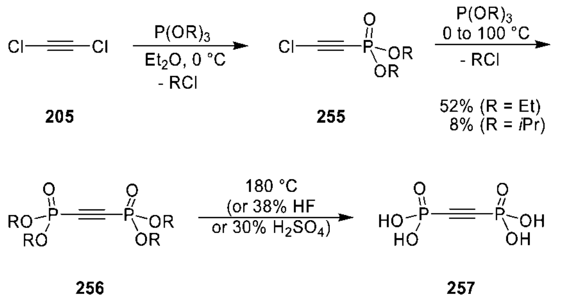
Bis(phosphorimidoyl)acetylenes are available in good yield via a Staudinger reaction between bis(diphenylphosphino)acetylene and tosyl azide,[217] whereas bis(dialkylthiophosphoryl)acetylenes are available by a direct substitution of nucleophilic acetylene with dialkylthiophosphonic chloride (Scheme 47).[218]

A quaternization of the phosphorus by MeI is also possible. Instead of transforming **240b** into the corresponding ammonium salt, a double phosphonium salt (and not the mixed ammonium phosphonium salt) is obtained. This result was unequivocally confirmed by the coupling pattern in ^{1}H NMR spectroscopy and a missing absorption (in the range of 2000−2100 cm^{-1}) in the IR spectrum of this species. Of course, because of the two positive charges situated next to the triple bond **247** is an example for an electron-poor alkyne substituted with a group V element. However, performing the same reaction with bis(diphenylphosphino)acetylene only the monophosphonium salt is obtained.[219] In contrast to the reaction with MeI that leads from **240b** to the rather stable salt **247**, the reaction with hydrogen chloride gives rise to the highly unstable tetrachloride **248** (Scheme 48). This compound is highly sensitive against hydrolysis and traces of oxygen; however under a nitrogen atmosphere at −80 °C it is stable for several days. The latter compound could be further transformed into the corresponding highly unstable bis(difluorophosphino)acetylene (**249**) by treatment with arsenic trifluoride at −80 °C. A direct treatment of **240b** with AsF_3 leads only to the exchange of two of the four amino groups yielding **251**.[220] The NEt_2 groups of **240b** could be exchanged with primary and secondary amines that are less volatile than diethylamine. A distillation removing $HNEt_2$ during the reaction shifts the equilibrium to the product **250** (Scheme 48).[219]

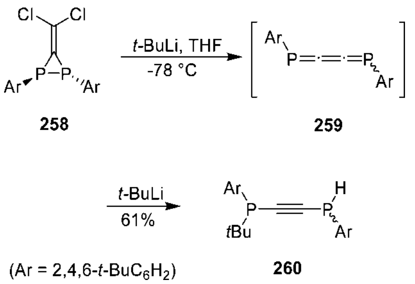
The very electron-rich phosphorus in **240b** was also utilized to create bis(phosphoranyl)acetylene, species with pentavalent phosphorus atoms next to the alkyne system. In a redox reaction two fluorine atoms are transferred from SF_4 to **240b** affording the corresponding (difluorophosphoranyl)acetylenes **252** as an air-stable crystalline compound (Scheme 49).[221,222] SF_4 is reduced to S_2F_2. As side product (thiophosphoryl)acetylenes are obtained. Another method for the preparation of phosphoranylacetylenes commences with the phosphonium salt **253** (Scheme 49). It is reacted at low temperature with dilithiated acetylene to afford compound **254**.[223] In contrast to **252** the latter phosphoranylacetylene is highly sensitive to moisture.

Ethyne-1,2-diylbis(phosphonate) **257** was prepared by a method related to the Arbuzov reaction. Starting materials were dichloroacetylene and trialkyl phosphates that were

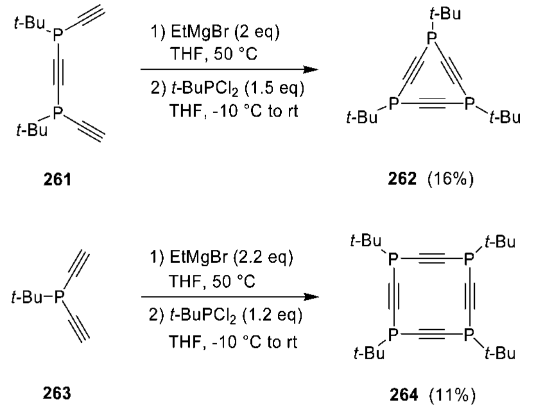
Scheme 50. Generation of Ethyne-1,2-diylphosphonates 257



Scheme 51. Synthesis of 260 via 1,4-Diphosphabutatriene 259



Scheme 52. Triangle 262 and Square 264 Consisting of Phosphorus-Capped Alkynes

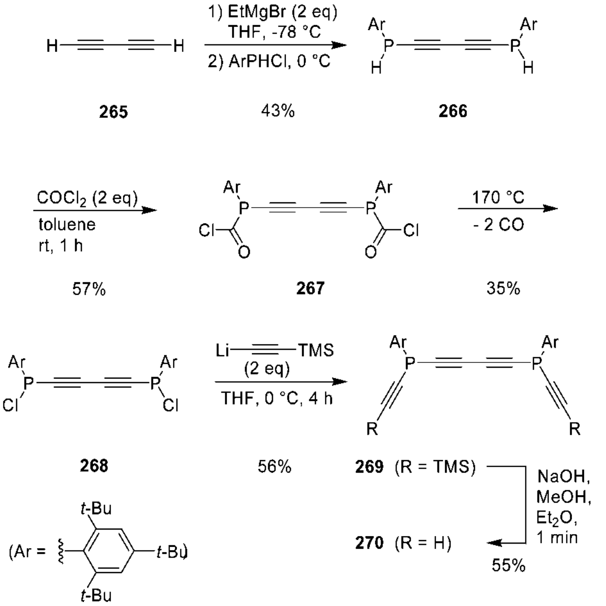


reacted at 0 °C to give the corresponding mixed chlorophosphonate **255**.[224−226] The further reaction afforded the desired bis-substituted compound **256** (Scheme 50). Alkyl groups could be removed either at 180 °C or by treatment with 38% hydrogen fluoride or 30% sulfuric acid to furnish **257**.[227] Such moieties have been used as mimetics of diphosphates such as in adenosine diphosphate ribose.[228]

From a mechanistic point of view, a method proceeding via a 1,4-diphosphabutatriene **259** is interesting. Starting material was the diphosphirane **258**[229] that rearranged under the influence of *t*-BuLi to the phosphorus-capped acetylene **260** (Scheme 51).[230]

Cyclic compounds with acetylene moieties capped by phosphorus atoms were prepared in 1990 when Scott initiated a program aiming to synthesize unknown phosphorus containing cage compounds as well as phosphocarbons C_nP_m.[231] Although these ambitious goals have not been achieved, it was the starting point for a series of highly interesting cyclic structures. The diphosphatriacetylene **261** and the phosphadiacetylene **263** that are accessible via acetylenic Grignard reagents and *t*-butylphosphorus dichloride were used as starting materials (Scheme 52). Their conversion into the corresponding organomagnesium species and the subsequent reaction with *t*-butylphosphorus dichloride afforded the 9-membered ring compound **262** in 16% and the 12-membered cycle **264** in 11% yield, respectively.

Scheme 53. Synthesis of Phosphorus-Capped Butadiyne Subunits 270 for the Preparation of Macrocycles 271−273

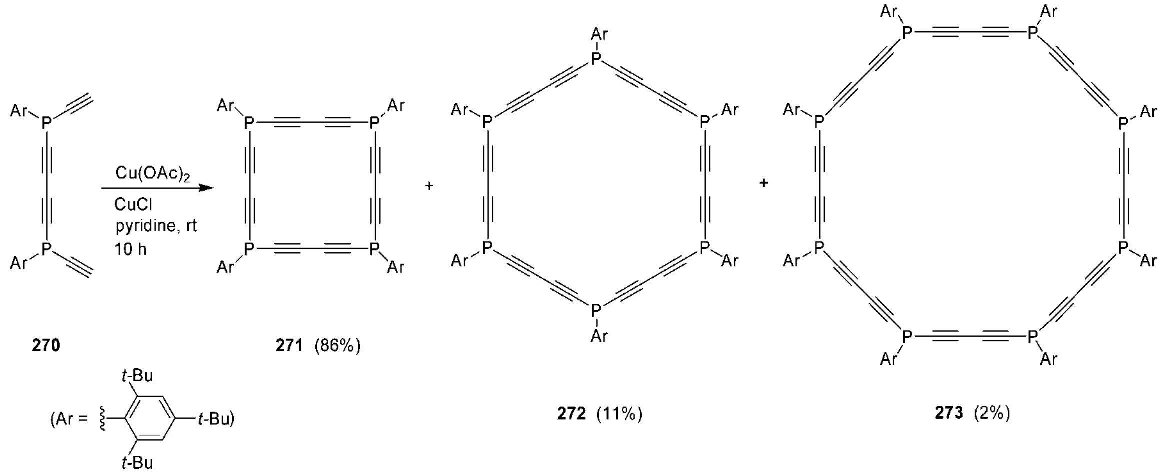


Similar reaction sequences were used for the creation of polyphospha[*m*]cyclo[*n*]carbons.[232] Butadiyne (**265**), easily obtained by a dehydrochlorination of 1,4-dichloro-2-butyne, was transformed into the bis-Grignard compound and treated at −78 °C with arylmonochlorophosphane leading in 33% yield to **266** (Scheme 53). An excess of phosgene afforded **267** and a subsequent decarbonylation at 160 °C gave butadiyne bis(phosphinous chloride) **268**. The latter species was substituted by lithiated trimethylsilylacetylene to afford **269** and desilylation with NaOH yielded the diphosphatetrayne **270**. This compound with the two terminal acetylene units is the key intermediate for the construction of the 20-, 30-, and 40-membered macrocycles **271**, **272**, and **273**. These species are the result of oxidative dimerization, trimerization, and tetramerization, respectively, and are obtained via Eglinton coupling in 86%, 11%, and 2% (Scheme 54).

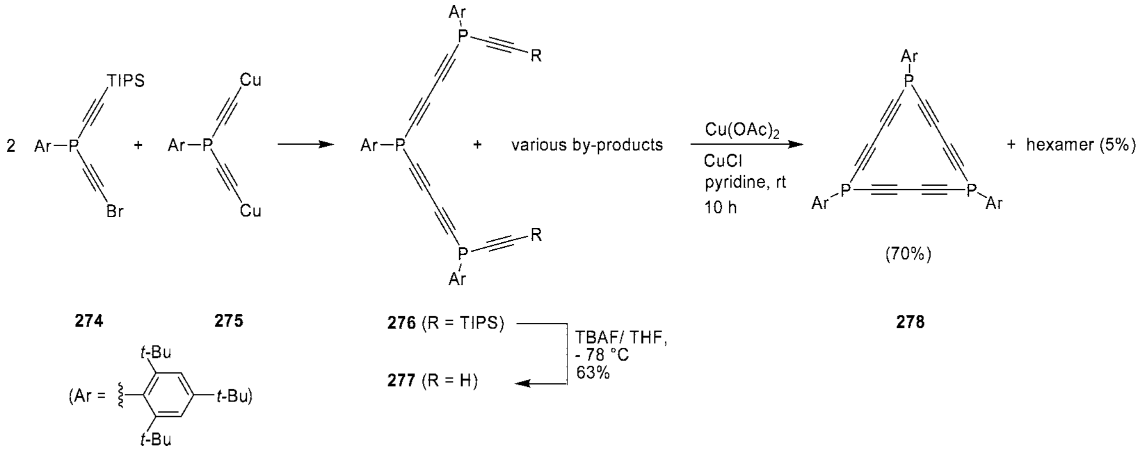
The corresponding triangle **278** could be obtained by an intramolecular Eglinton coupling in an excellent yield of 70%. The starting material **277** for this reaction was obtained by a double Cadiot-Chodkiewicz reaction of **274** and **275** (Scheme 55). Intensive NMR investigations have shown that inversion barriers (of about 65 kJ/mol) of the trivalent pyramidal phosphorus in the macrocycles **271**−**273** and **278** are one of the lowest ever measured for phosphorus. We ascribe this phenomenon to an effective overlap between the p orbital of the phosphorus and the π^* orbital of the triple bonds in the planar transition state.

Bis(diphenylphosphino)butadiyne (**279**) was utilized as a building block for metal-bridged metallacycles. Reaction of **279** with [Pt(CH_3)$_2$(COD)] led to a mixture of the platinum-bridged dimer **281** and the trimer **282** (Scheme 56). Because of a square-planar geometry at the platinum the alkyne−alkyne distance in **281** and **282** is relatively small (about 3.3 Å). When heated, these compounds undergo facile diyne coupling reactions leading to conjugated π systems.[233]

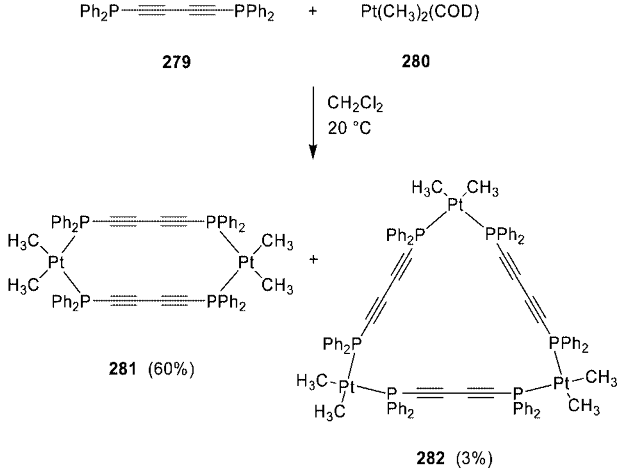
Scheme 54. Synthesis of Macrocycles 271−273 Consisting of Bis-Phosphorus-Capped Butadiyne Units by Glaser Coupling Reaction



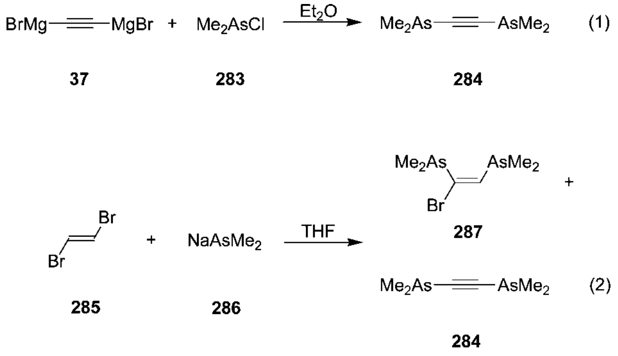
Scheme 55. Synthesis of a Triangular Macrocyle 278 Consisting of Bis-Phosphorus-Capped Butadiyne Units



Scheme 56. Preparation of Macrocycles 281 and 282 by Complex Formation of Bis-Phosphorus-Capped Butadiyne Units 279 and Pt Complex 280



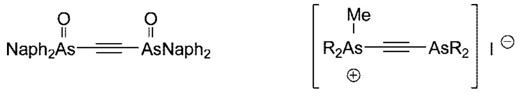
Scheme 57. Electrophilic and Nucleophilic Arsenic to Afford Arsenic-Capped Acetylene 284



3.1.3. Alkynes Substituted by Arsenic, Antimony, and Bismuth

As the cacodyl oxide ($((CH_3)_2As)_2O$ discovered by Bunsen can be viewed as the first organometallic compound, alkynes capped by arsenic are astonishingly one of the longest known representatives of the compound class described in this review. In 1921, de Mahler stated the existence of a binary carbon arsenic compound of the formula $As(C{\equiv}C)_3As$ where acetylenic units bridge arsenic centers.[234] Two years later, Wieland prepared the alkyne analog of cacodyl oxide $(H_3C)_2As(C{\equiv}C)As(CH_3)_2$) (**284**) by the reaction of nucleophilic acetylene and electrophilic arsenic (Scheme 57, eq 1).[235] Also several other analogs have been prepared by this method. This product can also be obtained by reversal of the polarity of the reaction partners. The reaction of $NaAs(CH_3)_2$ with 1,2-dibromoethene leads to **287** and to the desired compound **284** (Scheme 57, eq 2).[236]

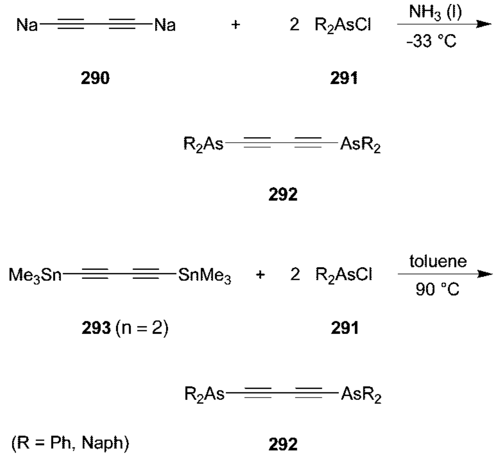
Another possibility is the reaction of the monosodium salt of acetylene with R_2AsCl. A subsequent disproportionation reaction leads to **284** and acetylene. A variety of different arsenic-capped acetylenes was prepared by this method.[237] Oxidation with perbenzoic acid in acetone leads to the



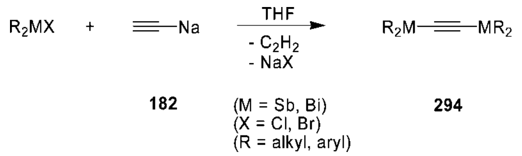
288 **289a** (R = Et) **289b** (R = Cy)

Figure 15. Oxidized and methylated arsenic-capped acetylenes **288** and **289**.

Scheme 58. Two Routes to Arsenic-Capped Diacetylenes 292



Scheme 59. Preparation of Antimony- and Bismuth-Capped Acetylenes



corresponding dioxide **288** in the case of naphthyl substituents.[236] With Et and Cy substituents also a monomethylation was possible affording compounds **289a** and **289b**, respectively (Figure 15). A dimethylation product could not be observed.

Arsenic-capped diacetylenes were available by using disodium diacetylide (**290**) in liquid ammonia as the nucleophile and dialkyl or diaryl arsenic chloride **291** as the electrophilic reagent (Scheme 58).[238,239] The dialkyne **292** with $As(Naph)_2$ substituents is an extremely stable solid compound that decomposes at 218 °C.[237]

The chemistry to afford the corresponding antimony- and bismuth-capped acetylenes is very similar to that of the arsenic-capped congeners. The best method to prepare such compounds is the reaction of monosodium acetylide with the corresponding diaryl or dialkyl pnictyl bromides or chlorides (Scheme 59).[240−244] Carried out in liquid ammonia the reaction leads under the evolution of acteylene to the bis-pnictide-capped acetylenes, whereas the use of THF as solvent affords mainly the terminal acetylenes. In the case of bismuth the use of acetylene dimagnesium bromide **37** as nucleophilic alternative to sodium acetylide did not lead to the bis-bismuth capped acetylenes.[243] Oxidation reactions leading to dioxides (as to the arsenic congener **288**) were not successful, neither for the Sb nor for the Bi containing compound.[243] An excess of MeI lead in both cases to bis-methylated dications.[241,242]

3.2. Alkynes Substituted by Chalcogens

Acetylenes capped by divalent chalcogens[245−247] possess electron-rich triple bonds similar to acetylenes capped by trivalent pnictides. This property is associated with an unique reactivity toward electrophiles[248] and demonstrated by a variety of cyclopropanation[249−251] and complexation reactions.[252−256]

3.2.1. Acetylenes Between Oxygen

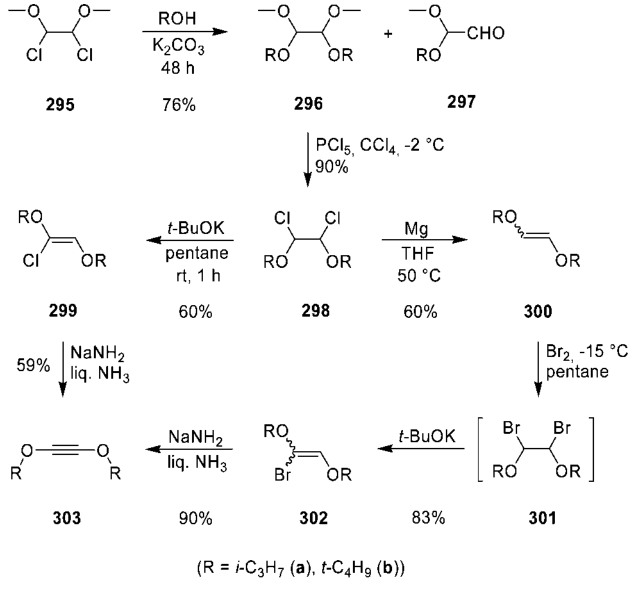
Acetylene diethers were known to be highly unstable at room temperature. In 1973 Serratosa et al.[257] reported the generation of dimethoxyethyne at very low temperature. Finally, in 1977, the synthesis of bis(*t*-butoxy)ethyne was described,[258] the only bis(alkoxy)alkyne reported which is stable at room temperature. The key compounds in the Serratosa protocol are bis-chloroacetals, which are injurious to health, and this might be one of the reasons why this chemistry was not used any further.

For the first synthesis of bis(*iso*-propoxy)- and bis(*t*-butoxy)ethyne **303** a mixture of *meso*- and *d,l*-1,2-dichloro-1,2-dimethoxyethane (**295**) was treated with either isopropanol or *t*-butanol and dry potassium carbonate to yield *meso*- and *d,l*-bis(alkoxy-1,2-dimethoxyethane (**296**) (R = *i*-propyl, *t*-butyl, Scheme 60).[259]

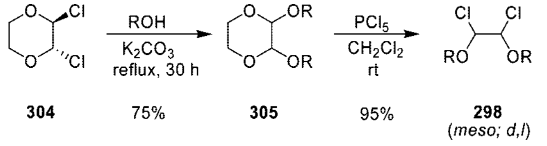
As a side product the monoaldehyde **297** can also be formed. Treatment of **296** with PCl_5 affords a mixture of *meso*- and *d,l*-bis-chloroacetal **298**, the key intermediate. From **298** there are two routes to the final product **303** (Scheme 60). The shorter path (**298** → **299** → **303**) involves two elimination steps. The disadvantage of this route is that the final product was contaminated with (*E*)-**299** which could not be separated from the alkyne by distillation. The second path involves a dechlorination, bromination and two elimination processes (**298** → **300** → **301** → **302** → **303**). It turned out that bis(isopropoxy)ethyne (**303a**) is only moderately stable, whereas the bis(*t*-butoxy)ethyne (**303b**) can be handled at room temperature.

The *meso*- and *d,l*-mixture of **298** is also available from 2,3-dichloro-1,4-dioxane (**304**) (Scheme 61).[260] This compound reacts with isopropanol and *t*-butanol in the presence of K_2CO_3 to give a mixture of *cis*- and *trans*-2,3-dialkoxy-

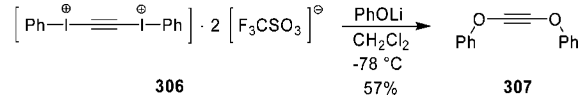
Scheme 60. Two Routes for the Synthesis of the Bis-Oxygen-Capped Alkyne 303



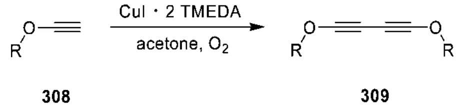
Scheme 61. Alternative Route for the Synthesis of Precursor 298



Scheme 62. Synthesis of 307 Starting From the Bis-Iodonium Salt 306

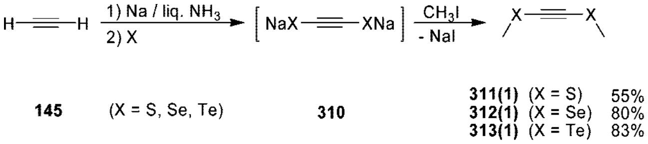


Scheme 63. Glaser Coupling for the Synthesis of Oxygen-Capped Diacetylene 309



(R = *t*-Bu (77%), adamantyl (85%), cyclohexyl (95%))

Scheme 64. Synthesis of Chalcogen-Capped Acetylenes 311(1)−313(1) Using Elemental Chalcogens



1,4-dioxane (**305**). Treatment of the latter substance with PCl_5 yields **298** (Scheme 60).

Easier access to bis(phenoxy)acetylene (**307**) was achieved by the reaction of bis(iodonium)acetylene triflate **306** (see chapter 3.3) with lithium phenolate (Scheme 62).[261]

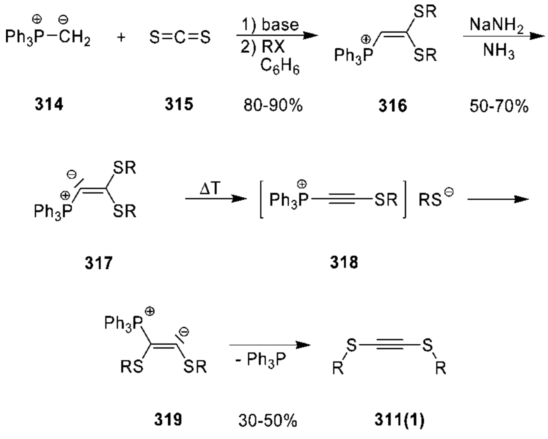
1,4-Bis(alkoxy)-1,3-butadiynes (**309**) were generated by a Glaser-type coupling of the corresponding alkoxyacetylenes **308** as summarized in Scheme 63. The most stable 1,4-bis(alkoxy)-1,3-butadiynes were those with the bulky adamantyl- and *t*-butoxy substituents.[262] The latter was also crystallographically characterized.[263]

3.2.2. Acetylenes Between Sulfur, Selenium, and Tellurium: Acyclic Systems

The kinetic instability of bis(alkoxy)acetylenes severly limits their preparation. So far, only the elimination of two equivalents of HCl from **298** or HBr from **301** (c.f., Scheme 60) has led to the desired products. In contrast to these limitations, there are many more reports on procedures to generate alkynes capped by organosulfur, -selenium, and -tellurium fragments.

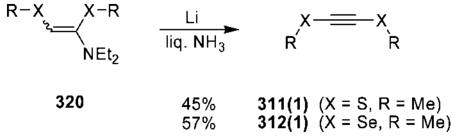
A very simple method to produce dithioethers of acetylene applies the Wurtz procedure. The disodium salt of acetylene was generated in liquid ammonia from acetylene and sodium. By adding sulfur, the sodium salt of acetylenedithiolate (**310**) is generated as the intermediate, which was then quenched with alkyl halides to afford the corresponding dithioether **311(1)** (Scheme 64). This protocol can also be extended to the corresponding selena and tellura ethers **312(1)** and **313(1)**.[264,265]

Scheme 65. Another Way to Synthesize Sulfur-Capped Acetylenes 311(1)

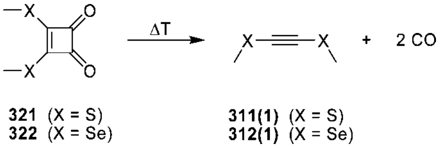


(R = CH_3, C_2H_5, *n*-C_3H_7, *n*-C_4H_9)

Scheme 66. Amine Elimination Used for the Synthesis of 311(1) and 312(1)



Scheme 67. Thermolysis of Squaric Acid Derivatives to Form 311(1) and 312(1)



A further procedure for the preparation of bis(alkylthio)acetylenes was available via bis(alkylthio)vinylidene triphenylphosphoranes **317**,[266] which can be generated from ylid **314**, carbon disulfide (**315**) and base. By heating **317** it is assumed that **318** is formed, which rearranges via **319** to **311(1)** (Scheme 65).[265]

The formation of bis(methylthio)ethyne (**311(1)**) and bis(methylseleno)ethyne (**312(1)**) was reported by treatment of the enamine **320** (Scheme 66) with two equivalents of lithium in liquid ammonia.[267]

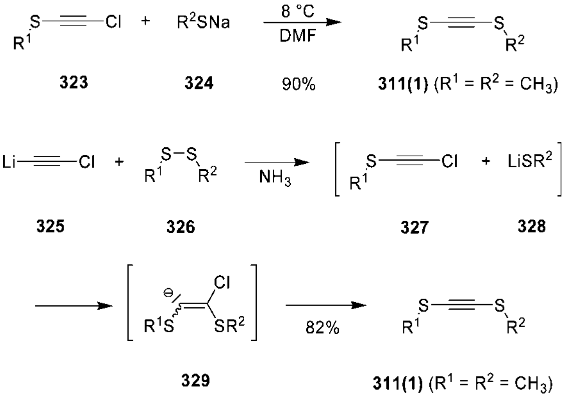
The thermolysis of 3,4-bis(alkylthio)- and 3,4-bis(alkylseleno)cyclobutene-1,2-dione (**321** and **322**), respectively, in the gas phase afforded the corresponding alkynes **311(1)** and **312(1)** (X = S, Se) (Scheme 67).[268] The alkynes **311(1)** and **312(1)** were not isolated but were identified by their PE spectra together with CO.

The substitution of organylthiochloroacetylene **323** with sodium organothiolates **324**,[269] and the reaction of lithium chloroacetylene (**325**) with dialkyldisulfides **326** afforded acetylenedithioether **311(1)** in good yields (Scheme 68).[270] The reaction of β,β-dichlorovinyl organyl sulfides with thiols in the presence of potassium hydroxide (1:1:2.5) in DMF at 100 °C afforded also **311(1)**.[271]

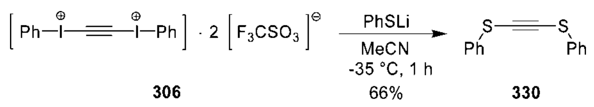
Further difunctional acetylenes which can be attacked at the sp centers by nucleophiles are the acetylene diiodonium salts **306** (Scheme 69).[260] Reaction of **306** with lithium thiophenolate leads to bis(phenylthio)acetylene (**330**), analogous to the sequence shown in Scheme 62.

As pointed out on several occasions many of the reaction schemes shown for alkyne thioethers can also be applied for the corresponding selenaethers (see Schemes 64, 66 and 67). The disproportionation of ethynyl selenides (e.g., **331**) in the presence of bases (Scheme 70) is also worth mentioning.[263]

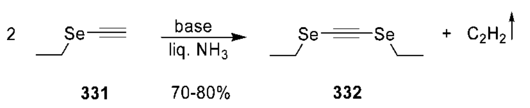
Scheme 68. Another Procedure to Prepare Sulfur-Capped Acetylenes 311(1)



Scheme 69. Bis-iodonium Salt 306 for the Generation of the Sulfur-Capped Acetylene 331



Scheme 70. Disproportionation Reaction of Terminal Selenaalkyne 331 to Form 332



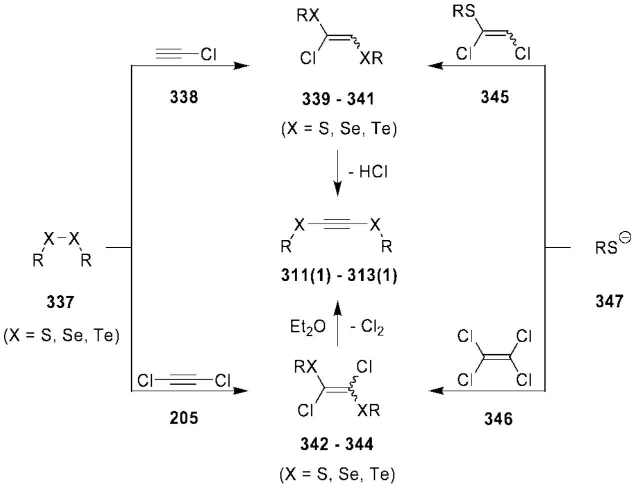
This disproportionation does not seem to take place in ethylthioacetylene.[263]

Phenylchalcogenyl halides were used to synthesize phenylchalcogen acetylenes **336** by a copper(I) iodide assisted reaction of terminal alkynes **333** with phenylchalcogenyl bromide or chloride as summarized in Scheme 71.[272] The yields of these reactions are given for some substituents as examples.

A related procedure to that just described is the reaction of terminal alkynes **333** with diphenyldiselenide (**334**) and phenyliodide diacetate (**335**).[273] With trimethylsilylacetylene the main product was bis(phenylseleno)acetylene **336** (X = Se).[272] Instead of phenyliodide diacetate as oxidizing agent the reaction can also be performed in DMSO acting as oxidant in the presence of catalytic amounts of copper iodide.[274] Alkynyl selenides were also prepared by using terminal alkynyl bromides and diaryl diselenides as starting materials,[275] as well as by selenodecarboxylation of acetylene carboxylic acids.[276]

Martynov et al.[277] used a combination of addition and elimination reactions to prepare symmetrical bis(organylchalcogeno)acetylenes **311(1)**−**313(1)**. This sequence is summarized in Scheme 72. By adding diorganyldichalcogenides **337** to monochloro- (**338**) and dichloroacetylene (**205**), the 1,2-bis[organochalcogeno]chloroethylenes (**339**−**341**) and 1,2-bis[organylchalcogeno]-1,2-dichloroethylenes (**342**–**344**) were available in good yields.[276,278,279]

Scheme 72. Various Methods to Synthesize Chalcogen-Capped Acetylenes 311(1)−313(1)

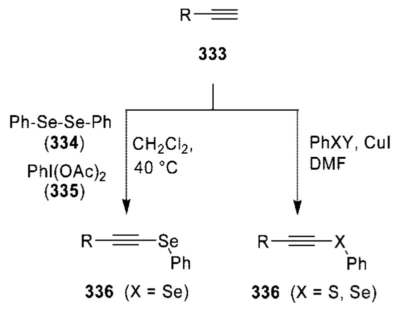


Analogously 1,2-bis(organylthio)chloroethylenes **339** are obtained by the substitution of one chlorine in 1,2-dichlorovinylsulfides (**345**).[280−282] (*E*)-1,2-Bis(organylthio)-1,2-dichloroethylenes (**339**) are generated when organothiolates **347** (R = Ph, alkyl) are treated with tetrachloroethylene (**346**). For the dehydrochlorination of the three chloroethylenes **339**−**341** (X = S, Se, Te) strong bases such as *t*-BuOK/*t*-BuOH (at 50 °C) and KOH/DMSO (at rt) were used to prepare **311(1)**−**313(1)** in good yields (65−95%).[276] The dehalogenation turned out to be more complex. With 1,2-bis(organylthio)-1,2-dichloroethylenes (R = *n*-C_3H_7, tolyl) the ratio **342**/butyllithium = 1:2 (at −55 to 20 °C) was used successfully for R = tolyl (98%). For R = *n*-propyl, the yield was only 48%. The dehalogenation of **343** was not successful with *n*-butyllithium and the dehalogenation of **344** gave only low yields.

Most procedures described so far show disadvantages. Mono- and dihaloacetylenes are highly toxic and carcinogenic, and the latter is even explosive. The chlorine chemistry shown in Scheme 72 is also not favorable under ecological considerations. Moreover, many reagents are very malodorous, and in most cases considerable experimental skills are required to carry out the reactions.

Brandsma published a very simple procedure which avoids the above-mentioned problems and imponderables, it is shown in Scheme 73. The Brandsma protocol can be used to generate bis(alkylthio)- and bis(alkylseleno)acetylenes.[283,284] It is a one-pot reaction which uses the sodium or lithium salt of acetylene (**182**) and the alkyl thiocyanates **348** or selenocyanates. The yields are remarkably good.

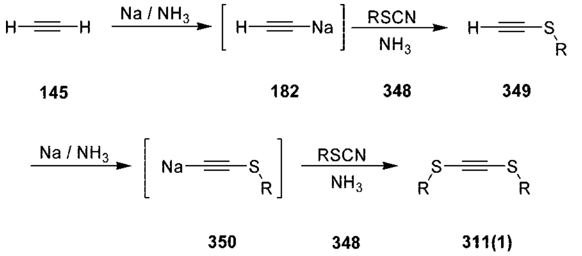
Scheme 71. Preparation of 336



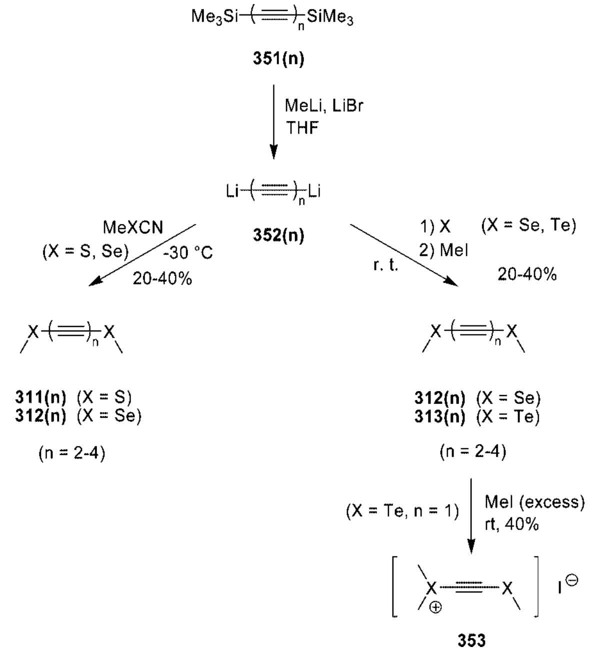
R	Yield
Ph	81%
C_4H_9	57%
C_6H_{13}	59%
CO_2Me	30%

R	X	Y	Yield
C_5H_{11}	S	Cl	48%
C_5H_{11}	Se	Cl	79%
C_5H_{11}	Se	Br	82%
C_5H_{11}	Te	Br	28%

Scheme 73. Preparation of Sulfur-Capped Acetylenes 311(1) Using Thiocyanates 348

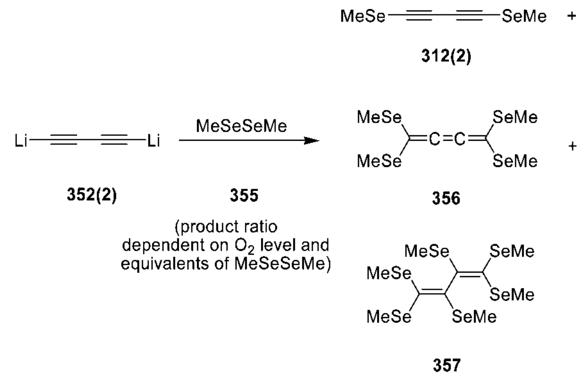


Scheme 74. Direct Synthesis of Chalcogen-Capped Oligoynes 311(*n*)−313(*n*) from Silicon-Capped Oligoynes 351(*n*)

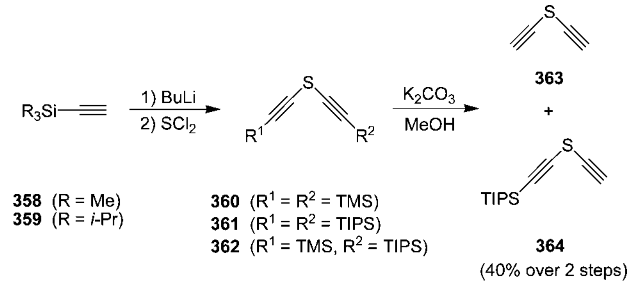


This method can also be applied for more than one triple bond.[367,368] Bis(trimethylsilyl)substituted alkynes **351(*n*)**, which have been described in the literature[285,286] were reacted with methyllithium in the presence of lithium bromide to achieve a deprotection−lithiation sequence in a one-pot reaction (Scheme 74). The resulting lithiated oligoacetylide anions **352(*n*)** react easily as nucleophiles with thio- or selenocyanates affording sulfur- and selenium-capped carbon rods **311(*n*)** and **312(*n*)**. In the case of selenium and tellurium, respectively, an insertion of the pure element in the carbon−lithium bond is also possible. In a further step the reaction is finished by an electrophilic capture of methyl iodide to afford the compounds **312(*n*)** and **313(*n*)**, respectively.[367,368] For the methyl tellurium-capped acetylene also a further methylation of one of the two capping tellurium atoms was possible to afford the alkynyltelluronium iodide **353** whose solid-state architecture is strongly determined by p → σ^* interactions.[287]

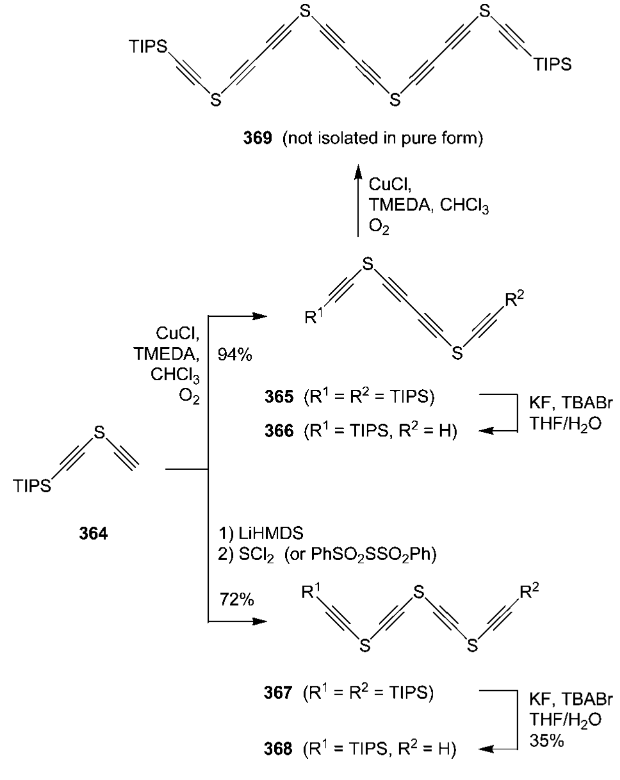
Scheme 75. Another Method for the Preparation of 312(2) and Side Products



Scheme 76. Preparation of the Precursor 364 for Acyclic Alkyne Oligosulfides 365−371



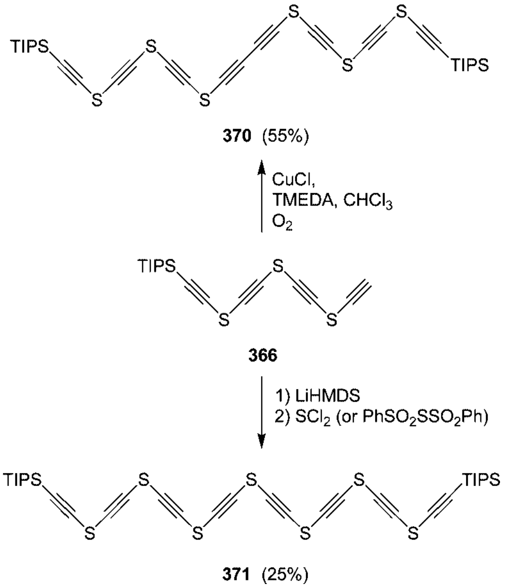
Scheme 77. Preparation of Oligoacetylenic Sulfides 365−369



For bis-selenium-capped butadiynes also the preparation via dilithium butadiynide **352(2)** and dimethyl diselenide (**355**) was reported (Scheme 75).[288] However, depending on the choice of the group attached to the selenium, the desired compound is further attacked by Se nucleophiles leading either to perselenated 1,3-butadiynes such as **357** or perselenated [3]cumulenes such as **356**. The nature of the products can further be controlled by regulating the O_2 level of the reaction atmosphere; a higher O_2 level destroys the in situ generated MeSeLi, as a result the butadiyne **312(2)** is observed as the major product. Experiments to extend this reaction to triynes and MeTeTeMe proved to be unsuccessful.

Recently, a series of acyclic oligosulfides were synthesized and proved to be stable compounds.[289,290] The key reactions in this synthesis were sulfurization using SCl_2 or $PhSO_2SSO_2Ph$ and oxidative coupling via Hay and Glaser-type methods. As crucial starting material a monoprotected

Scheme 78. Generation of Oligoacetylenic Sulfides 370 and 371



bis-acetylene sulfide **364** was first prepared using a mixture of TMS- and TIPS-protected acetylene **358** and **359** (Scheme 76).

Chain elongation of acetylenic sulfide **364** was achieved by oxidative coupling and sulfurization reactions (Scheme 77). Monodeprotection of the products could be achieved by a carefully controlled desilylation procedure using KF in THF/water in the presence of catalytic amounts of TBABr. A repetition of the above-mentioned reactions afforded the oligoacetylenic sulfides **370** and **371** (Scheme 78).[288]

We assume that because of the new methods established in the past few years also cyclic congeners of **365**−**371** are within the reach of synthesis.[291] Quantum chemical calculations by means of density functional theory (B3LYP/6-311G*) demonstrate that these so-called [*N*]chalcogena[*N*]pericyclynes are local minima on their potential energy surface possessing a singlet ground state.[292] Most of their molecular structures are determined by interactions between the chalcogens' lone pairs. Because of a minimum of repulsion, an almost perpendicular arrangement of their p orbitals is, whenever possible, favorable (see section 4.2.4). Many of their molecular structures resemble, in shape, cycloalkanes or elemental chalcogens like S_8.[291] In Figure 16, we show the calculated minimum structure of [8]selena[8]pericyclyne (**372**).

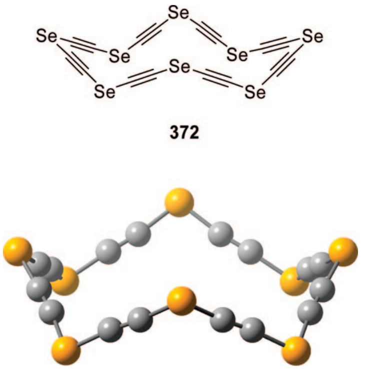
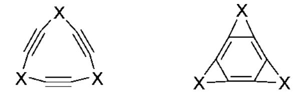


Figure 16. Structural formula (top) and calculated minimum structure (bottom) of [8]selena[8]pericyclyne (**372**).[291] The selenium centers are depicted in orange and the carbon centers in gray.

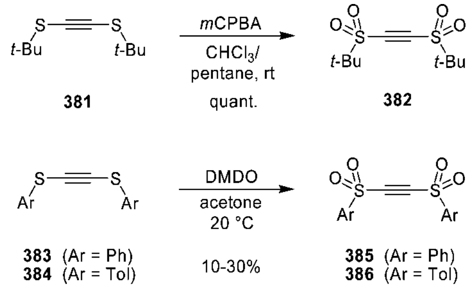


373 (X = O)
374 (X = S)
375 (X = Se)
376 (X = Te)

377 (X = O)
378 (X = S)
379 (X = Se)
380 (X = Te)

Figure 17. [3]Chalcogena[3]pericyclynes **373**−**376** and the corresponding benzene-like valence tautomers **377**−**380**.

Scheme 79. Formation of Bis(sulfonyl)acetylenes 382, 385, and 386



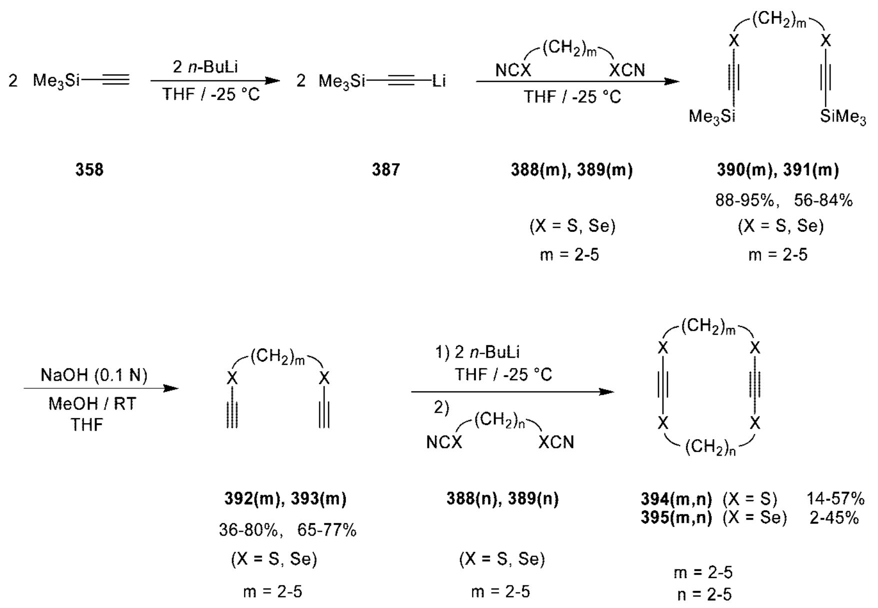
In the case of [3]chalcogena[3]pericyclynes **373**−**376** (Figure 17), valence tautomers with a benzene-like structure saturated by three bridging chalcogen moieties also seem to be reasonable (**377**−**380**). For the heavier chalcogens (Se, Te) these benzene-like structures **379** and **380**, respectively, are calculated to be more stable than the acetylenic ones **375** and **376**.

So far, we have reported in this chapter only alkynes capped by divalent chalcogen atoms. Whereas divalent chalcogens possess two lone pairs to interact with the π orbital of the triple bond rendering this bond electron-rich, further substituents at the chalcogen need the lone pairs for bonding. Only a few examples of alkynes capped by chalcogens with an extended valence shell exist. The most prominent example is the oxidation of sulfur atoms leading to sulfone moieties. In general, the bis-sulfonyl-capped acetylenes are highly reactive alkynes. Both important frontier orbitals, HOMO and LUMO, are significantly lowered in energy (see section 4.1). Only the bis(*t*-butylsulfonyl)acetylene proved to be an isolable compound.[293] Pericàs and co-workers found a procedure yielding quantitatively the desired product **382** by oxidizing bis(*t*-butylthio)acetylene (**381**) with *m*CPBA in chloroform (Scheme 79).[294] Bis(*t*-butylsulfonyl)acetylene, the structural properties of which could even be elucidated by X-ray analysis,[295] was widely used as a highly reactive dienophile in Diels−Alder reactions[293,296−299] and as alkyne component in highly electrophilic CpCo(monoalkyne) complexes.[300−302] Also bis(arylsulfonyl)acetylenes **385** and **386** were synthesized;[303] however, a neutral oxidizing agent, such as dimethyldioxirane (DMDO), was necessary to achieve high yields (Scheme 79); the corresponding products **385** and **386** could not be isolated without decomposition.[302]

3.2.3. Macrocycles with Thia- and Selena-Substituted Acetylene Units

The Brandsma protocol (Scheme 73) for the syntheses of alkylthia- and alkylselenaacetylenes also proved to be the method of choice to prepare cyclic congeners. In a one pot-procedure starting with dilithium acetylide and thio- or selenocyanates, respectively, highly symmetrical cyclic diynes and triynes could be obtained.[304,305] Following a

Scheme 80. Synthesis of Cyclic Tetrachalcogenadiynes 394(*m*,*n*) and 395(*m*,*n*)



stepwise approach (Scheme 80), cyclic tetrathia- and tetraselenadiynes **394(*m*,*n*)** and **395(*m*,*n*)** with different alkyl chains were also within the reach of synthesis.[303,306] As side products also octathiacyclotetraynes were observed.[307]

Ortho-, *meta*-, and *para*-cyclophanes with bridging SeC≡CSe units (Figure 18) were assembled by a similar route starting with diselenocyanates having benzene moieties in the tethers.[308]

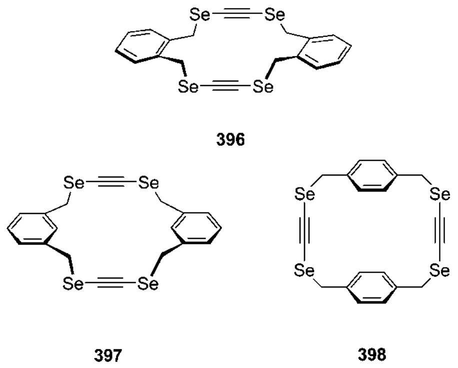
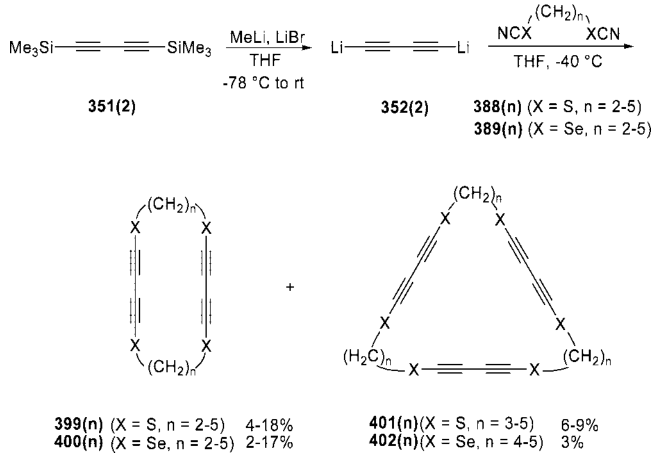


Figure 18. *Ortho*-, *meta*-, and *para*-cyclophanes **396**−**398** with SeC≡CSe units as tethers.

Scheme 81. Synthesis of Cyclic Tetrachalcogenatetraynes 399(*n*) and 400(*n*), as well as Hexachalcogenahexaynes 401(*n*) and 402(*n*)



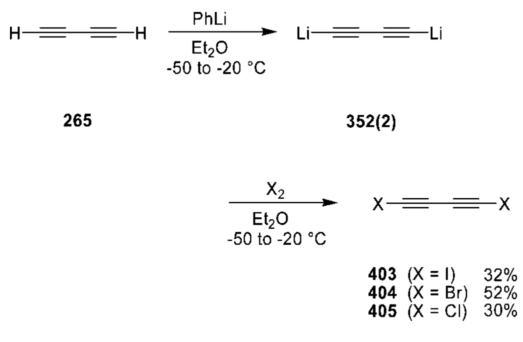
The one-pot multicomponent reactions also proved to be successful when starting with dilithium butadiynide **352(2)** which is generated *in situ* from **351(2)** and the corresponding thio- and selenocyanates **388(*n*)** and **389(*n*)**, respectively, to get macrocycles **399(*n*)**−**402(*n*)** with four or even six acetylene units (Scheme 81).[304,309]

3.3. Alkynes Substituted by Halogens

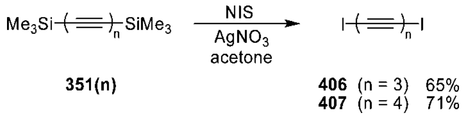
Acetylenes capped by halogens (considered in IUPAC nomenclature as group VIIA) have captured the chemists' interest for more than 120 years.[310] These binaric compounds consisting only of carbon and halogen were targets from a synthetic,[311] as well as from a theoretical point of view. They were used as intermediates (see section 3.2.2) and proved also to be key compounds for experimental and theoretical studies of the carbon−carbon triple bond (see section 4.2.1). In recent years, they received attraction from the field of material science, too. In contrast to the other chapters, where we started with the lightest element, we would like to begin here, for historical reasons, with the heaviest element of this group, iodine.

In 1885, Baeyer first reported the syntheses of diiodoacetylene **204** and diiodobutadiyne **403**.[309] In pure form **403** was isolated in the 1970s.[363,312,313] Diacetylene **265** was reacted with two equivalents of phenyllithium in ether yielding the dilithiated species. After addition of elemental iodine the diiodobutadiyne **403** was obtained. This procedure (Scheme 82) was also successful for other dihalodiacetylenes (X = Cl, Br).

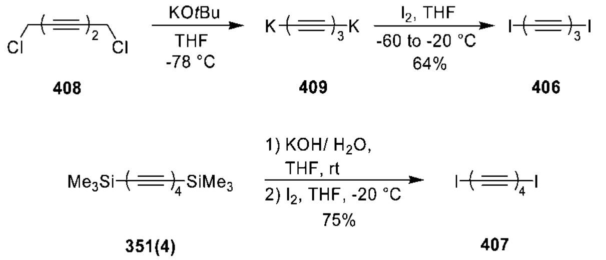
Scheme 82. Synthesis of Diacetylenes 403−405 Capped with Iodine, Bromine, and Chlorine



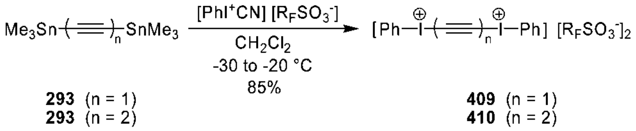
Scheme 83. Direct Synthesis of Bis-iodo-Capped Oligoynes 406 and 407 from Silicon-Capped Precursors 351(*n*)



Scheme 84. Safer Methods to Afford Bis-iodo-Capped Hexatriyne 406 and Octatetrayne 407



Scheme 85. Preparation of Bis-iodonium Salts 409 and 410 from Stannyl-Capped Acetylenes 293



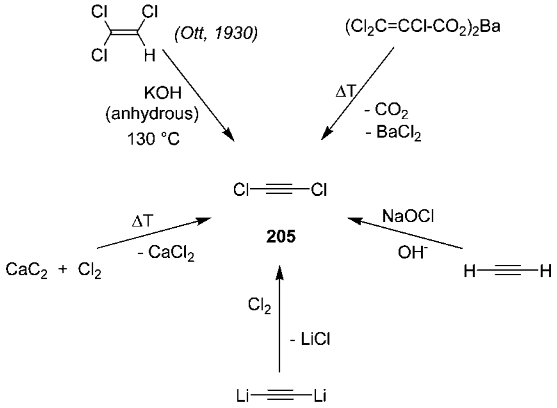
Recently, two other members of this family have been reported: C_6I_2 (**406**) and C_8I_2 (**407**).[314] Silyl-protected carbon-rods **351(*n*)** (see section 2.3.1) provided rationale routes for the syntheses of these compounds by avoiding free tri- and tetraacetylene, respectively, which are volatile and rather unstable explosive intermediates.

Compounds **406** and **407** were prepared in rather good yields from $SiMe_3$-protected oligoynes by reaction with *N*-iodosuccinimide (NIS) in the presence of silver nitrate (Scheme 83).[313] Nevertheless, because of the intermediate formation of explosive silver alkynides this method is problematic for larger-scale syntheses. In 2002, a safer method (with similar yields) of direct iodination of potassium-capped hexatriyne **409** and the corresponding octatetrayne was reported (Scheme 84).[315]

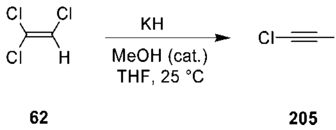
The two recently prepared iodine-capped carbon-rods **406** and **407** proved to be explosive compounds on heating with high tendency for polymerization. Diiodobutadiyne and diiodohexatriyne were cocrystallized with bis(pyridyl)-oxalamides and ureas.[316] Because of nitrogen−halogen noncovalent interactions formed in the solid state the compounds could be aligned in an optimal fashion for topochemical polymerization. By this way, Goroff et al. could afford poly(diiododiacetylene), an ordered conjugated polymer that consists only of carbon and iodine.[317] Depending on the type of the host the crystals either undergo spontaneous polymerization or can be forced to polymerize upon exposure to high pressure.[318−320]

In contrast to other halogens capping the acetylene unit, iodine proved not to be an ideal leaving group for substitution reactions at the sp carbon center. The polarization of the C−I bond is rather weak as a result of their similar electronegativity. To increase the electron-withdrawing effect of this halogen, bisiodonium salts **409** and **410** were synthesized.[321] Starting materials were the Me_3Sn-capped acetylene **408** and butadiyne **293**, which were reacted with phenyliodonium fluorosulfonates (Scheme 85). Whereas the monoacetylenic compound **409** was stable, the diacetylenic one (**410**) decomposes above −10 °C. It was shown that these adducts readily react with nucleophiles resulting in C_2 and C_4 group transfer yielding difunctional acetylenes and butadiynes.[321]

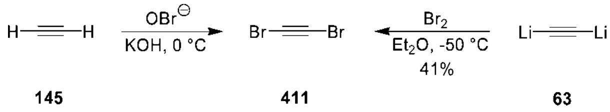
Scheme 86. Various Previous Methods to Synthesize Dichloroacetylene (205)



Scheme 87. Most Convenient Method to Prepare Dichloroacetylene (205)



Scheme 88. Two Routes for the Preparation of Dibromoacetylene (411)



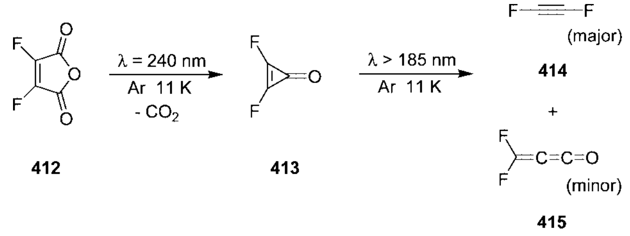
The synthesis, as well as the study, of the properties of dichloroacetylene and dibromoacetylene were challenging goals for generations of chemists to face. First attempts to synthesize the simple molecule C_2Cl_2 (**205**) were reported in 1898. In 1908, it was shown that by reacting trichloroethylene with an alcoholic solution of KOH monochloroacetylene (**338**) was formed instead of the desired dichloroacetylene. It was assumed that the alcoholic solution was acting not only as a base but also as a kind of reducing agent. The first general and reliable report about dichloroacetylene was published in 1930 by Ott.[322] A trichloroethylene vapor at 130 °C was used to react with absolutely anhydrous KOH (Scheme 86). Other procedures used hypochlorite and gaseous acetylene,[323,324] a thermal decomposition of trichloroacrylic acid[322,325] or the reaction of CaC_2[326,327] and Li_2C_2, respectively, with elemental chlorine[328] (Scheme 85). Nevertheless, some of them described in the early decades of this chemistry have remained mysterious and have never been used again.

Therefore, for more than 50 years the Ott procedure described in Scheme 86 proved to be the method of choice until a highly convenient preparation was published.[329] The reaction of trichloroethylene (**62**) in THF with KH and catalytic amounts of methanol yielded dichloroacetylene (**205**) (Scheme 87).

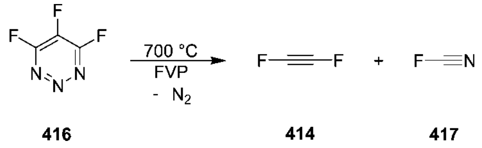
Pure dichloroacetylene is a colorless liquid with a nauseating smell. Furthermore, the endothermic compound is highly explosive and cancerogenic. In any case, the concentration of C_2Cl_2 solutions should be avoided.

For dibromoacetylene (**411**) two different kinds of preparations are known (Scheme 88). The older one, invented in the 1930s, commences with acetylene gas, which was

Scheme 89. Synthesis of Difluoroacetylene (414) Using CO Extrusion of a Cyclopropenone Derivative 413



Scheme 90. Preparation of Difluoroacetylene (414) Using a Perfluorinated 1,2,3-Triazine 416 as Precursor



oxidized by hypobromite in the presence of KOH. The other method, extensively studied by Kloster-Jensen,[327] proved to be already successful in the syntheses of the chlorinated homologue and butadiyne derivatives (cf., Schemes 86 and 82).

Hitherto, nothing is known about a dibromohexatriyne. However, Gladysz et al. reported and characterized the corresponding dibromotetrayne (C_8Br_2) by usual analytical techniques. Because of the violent detonations that were often observed during its synthesis, the authors abstained from reporting that extremely hazardous procedure in the open literature.[22a]

An extension of this acetylene chemistry to fluorine, the most electronegative element of the periodic table, has proved to be a rather difficult endeavor. Nevertheless there are a few reports dealing with the preparation of difluoroacetylene. Flash vacuum pyrolysis (FVP) of difluoromaleic anhydride **412** is reported to yield small amounts of difluoroacetylene **414**.[330] A better method[331] is irradiating the former compound **412** in an Ar matrix at 11 K with light of the wavelength 240 nm yielding in a first step difluorocyclopropenone (**413**). By prolonged irradiation with smaller wavelength, this compound decomposes and C_2F_2 (**414**) is formed as the major product as identified by its IR vibrations (Scheme 89).

A possible vinylidene structure as $F_2C{=}C$ (C_{2v} symmetry) could be ruled out.[330] Another method started with perfluoro-1,2,3-triazine (**416**) which decomposed cleanly at 700 °C and a pressure of 0.02−0.1 mbar according to Scheme 90.[332] C_2F_2 slowly decomposes even at −196 °C yielding a polymer and CF_2, the latter either oligomerizing or reacting with difluoroacetylene to form three different C_3F_4 isomers. At room temperature (300 K) its half-lifetime (at 2.5 mbar) was determined to be ∼15 min.

The higher homologue C_4F_2 was studied by theoretical means and obtained by a plasma reaction of either **418**, **419**, or **420** (Figure 19).[333] Passing these compounds through a discharge (*Tesla* frequency), difluorobutadiyne could be isolated. The authors claim difluorobutadiyne being even more stable than the monoacetylenic homologue **414**.

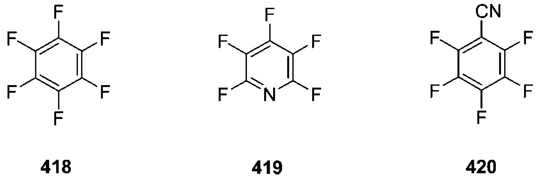
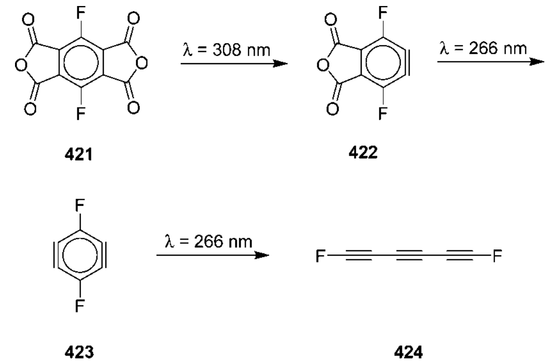
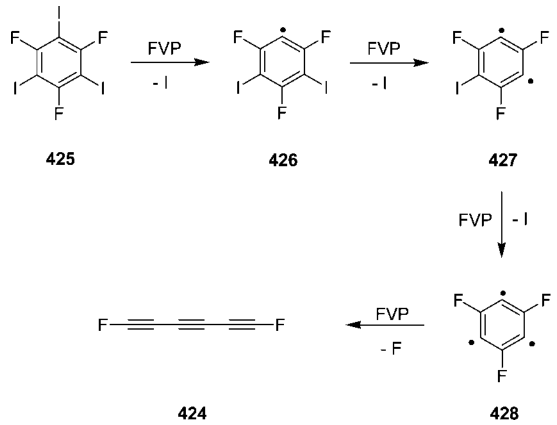


Figure 19. Starting materials **418**, **419**, and **420** for the generation of difluorobutadiyne.

Scheme 91. Preparation of Difluorohexatriyne (424)



Scheme 92. Generation of Difluorohexatriyne (424) via the Triradical 428



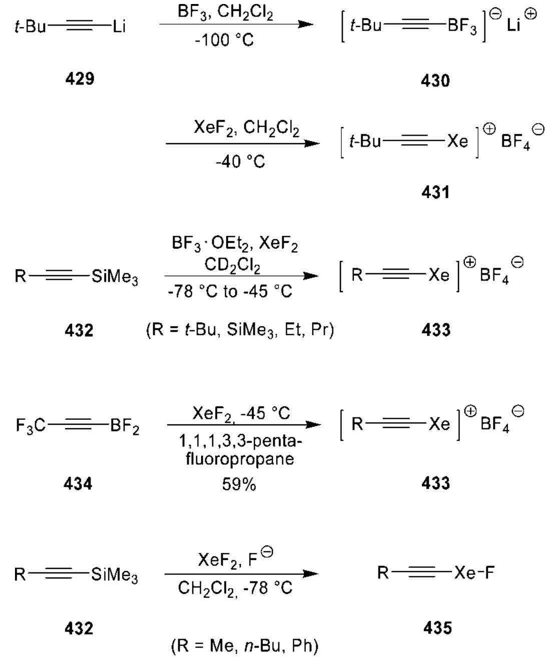
However, further progress toward longer fluorine-capped carbon rods is done in view of the recent photolysis of *p*-difluorobenzenetetracarboxylic dianhydride **421**.[334] In a nitrogen matrix at 13 K, the dianhydride was converted into benzynedicarboxylic anhydride **422** with loss of CO and CO_2 upon irradiation at 308 nm. In a second step, the benzyne intermediate **422** was photolyzed at 266 nm yielding a highly unstable benzdiyne **423**, which was converted into the more stable difluorohexatriyne **424** upon further irradiation at 266 nm (Scheme 91). The product was detected by the corresponding IR bands which were assigned by quantum chemical calculations.[333]

Another method to access difluorohexatriyne (**424**) was recently developed by Sander who used 1,3,5-triiodo-2,4,6-trifluorobenzene (**425**).[335] This compound was subjected to flash vacuum pyrolysis (FVP). The weak C−I bonds were cleaved homolytically and the finally resulting triradical (trifluoro-1,3,5-tridehydrobenzene) **428** rearranged to triyne **424** (Scheme 92). In contrast to difluorotriacetylene **424** the difluorotetraacetylene still remains unknown.

3.4. Alkynes Substituted by Noble Gas Elements

In this section, we will again deviate from our original intension to treat only symmetrically substituted alkyne systems. Commonly, noble gases are seen as rather inert elements. However, with electron-poor elements various derivatives of the heavier noble gases are known. In the field of organic noble gas derivatives, alkynyl noble gas compounds, the alkynyl moiety has a higher electronegativity than an alkyl unit, were in the focus. The stability of these compounds was first predicted by theoretical calculations, not only for Xe but also for the lighter elements Ne and Ar.[336] In contrast, alkynyl He species decompose via loss of

Scheme 93. Synthesis of Various Xenon-Substituted Alkynes 431, 433, and 435



He and an alkynyl cation.[337] The most experiments have been carried out with xenon, the heaviest and most easily polarizable element, of this group. Xe(II) species are isoelectronic with I(III) species; therefore similar compounds should be accessible. Indeed, alkynyl xenonium salts, isoelectronic with alkynyl iodonium salts, were synthesized by different methods[338,339] (Scheme 93). Common to all of them is the formation of a highly stable BF_4^- counterion and formation of a highly stable Si−F bond as driving force of the reaction. Precursors for the xenonium salts **431** and **433** were either lithiated alkynes **429**, trimethylsilyl-substituted alkynes **432** or alkynyldifluoroboranes **434**.[340]

If a trimethylsilyl-substituted alkyne **432** is treated with XeF_2 in the absence of BF_3, alkynyl xenonium ions cannot be formed. In these cases, alkynylxenon(II) fluorides **435** result.[341] However, recent investigations have shown that fluorine is not crucial to access xenon-capped acetylenes. Photolysis of an acetylene/xenon matrix (∼1/1000) at 8 K by 193 and 250 nm light pulses afforded species that were assigned by IR absorption spectra to HXeC≡CH, HXeC≡C, and HXeC≡CXeH.[342,343] A similar experiment using a diacetylene matrix and krypton and xenon, respectively, as the other component yielded the $HKrC_4H$ and $HXeC_4H$ molecules, respectively.[344] Experimental and theoretical investigations suggest a higher stability of these molecules compared with their smaller counterparts consisting of only one acetylene moiety. Next to these experimental reports several theoretical papers have appeared that describe energetics and structures of rare gas elements with two or more adjacent alkyne moieties.[345,346] Computations (DFT) have also predicted the existence of a linear periodic polymer, made of the repeat unit −(XeC≡C)−, having a strong partly ionic nature with the positive charge on the Xe atoms and the negative one on the C≡C groups.[347] High-energy barriers were calculated for the removal of a Xe atom from the chain.

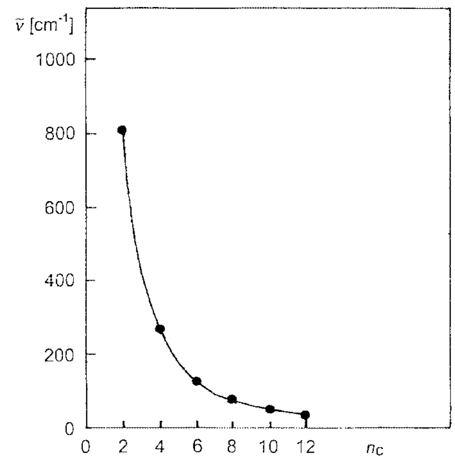


Figure 20. Calculated dependence of the wavenumber of the lowest energy harmonic deformation mode on the number of C atoms of oligoacetylenes at the HF/cc-pVTZ level of theory.[349] Reprinted with permission from ref 350. Copyright 2000 Wiley-VCH.

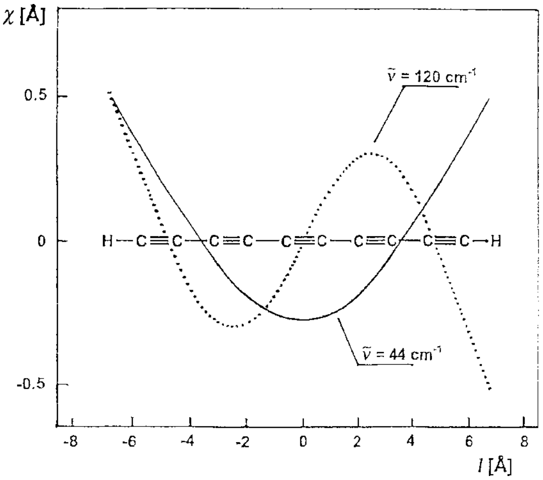


Figure 21. Graphical representation of the vibrational wave function for the two lowest energy deformation modes for pentaacetylene at the HF/cc-pVTz level of theory.[349] Reprinted with permission from ref 350. Copyright 2000 Wiley-VCH.

4. Quantum Chemical Calculations and Spectroscopic Investigations on (Oligo)alkynes

4.1. Ground State Properties

An all valence electron treatment of (oligo)alkynes was published in 1966 by R. Hoffmann.[348] He computed bond lengths and electron densities by applying the extended Hückel (EH) method on $H-(C\equiv C)_n-H$ ($n = 2-16$). Using an iterative method, which relates bond distances to Mulliken overlap populations, he found that bond length alternations persist for (oligo)alkynes. The terminal C atoms of the oligoacetylene chain bear the highest negative net charge according to the EH method.

In recent years, more sophisticated methods were available to derive the ground state and excited state properties of oligoacetylenes. Application of the restricted Hartree−Fock (RHF) self-consistent field (SCF) procedure to (oligo)alkynes $H-(C\equiv C)_n-H$ ($n = 3-5$) allowed the strongly alternating carbon−carbon bond lengths for the singlet ground state to be computed.[349]

A very detailed investigation by Zahradnik and Šroubkova[350] used the Gaussian98 program package to investigate

Table 1. Gas Phase Dissociation Energy [kcal/mol] of Acetylene and 1,3,5-Hexatriyne (HF/cc-pVTZ)

$$\mathrm{H{-}(C{\equiv}C)_m{-}H \rightleftharpoons H{-}(C{\equiv}C)_m|^{\ominus} + H^+} \qquad \Delta E_1$$

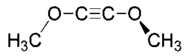
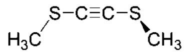
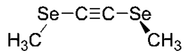
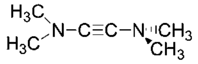
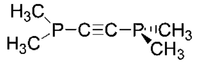
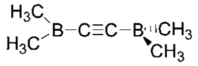
$$\mathrm{H{-}(C{\equiv}C)_m|^{\ominus} \rightleftharpoons |(C{\equiv}C)_m|^{2\ominus} + H^+} \qquad \Delta E_2$$

m	ΔE_1	ΔE_2
1	392	547
3	362	450

(oligo)alkynes. For smaller species, the Møller−Plesset perturbation treatment (MP2, MPL) and coupled cluster with singly and doubly excitations (CCSD) models were used. The HF and density functional theory (DFT) using the hybrid functionals B3P86 and B3LYP were applied for longer alkynes, and several correlation consistent Gaussian basis sets of atomic orbitals were used. They ranged from correlation consistent polarized valence double-ζ (cc-pV2Z) to valence quintuple-ζ (cc-pV5Z). In the cases of the alkynes with a smaller number of carbon atoms also augmented basis sets were used (aug-cc-pVnZ). Good estimates for the total energies were obtained by plotting the calculated total energies against the reciprocal values of the total number of atomic functions, $1/m$. Also heats of formation, ΔH_f, ionization energies, and electron affinities of the (oligo)alkynes were calculated and compared with experimental data. It was concluded[349] that in the case of heats of formation the MP2 and CCSD(T) values agree well with experiment. Vertical ionization energies and electron affinities were obtained by combining Koopmans' theorem with HF orbital energies for the highest occupied and lowest virtual orbitals.

The geometrical parameters can be obtained by applying B3P86/cc-pVTZ and MP2/cc-pVTZ procedures. When plotting the calculated (HF/cc-pVTZ) terminal bond lengths in

Table 2. Frontier Orbital Energies of Symmetrically Bis-Hetero-Substituted Alkynes and Their Respective Character According to HF/6-311G(d) Calculations Based on B3LYP/6-311G(d) Optimized Geometries

	Point Group	HOMO [eV] (Character)	LUMO [eV] (Character)
$\mathrm{H_3C{-}C{\equiv}C{-}CH_3}$	D_{3d}	-9.85 (π)	+4.36 (σ*)
	C_2	-9.46 (π, n)	+4.21 σ*(CH)
	C_2	-8.91 (π, n)	+3.45 (π*, n)
	C_2	-8.64 (π, n)	+3.18 (π*, n)
	C_1	-8.26 (π, n)	+4.14 (σ*)
	C_1	-8.92 (π, n)	+3.22 (π*)
F−C≡C−F	$D_{\infty h}$	-11.66 (π, n)	+5.94 (σ*)
Cl−C≡C−Cl	$D_{\infty h}$	-10.55 (π, n)	+4.17 (σ*)
Br−C≡C−Br	$D_{\infty h}$	-10.15 (n)	+3.18 (π*)
	D_{2d}	-10.49 (π)	+2.45 (π*, n)
$\mathrm{Me_3Si{-}C{\equiv}C{-}SiMe_3}$	C_1	-10.15 (π)	+3.68 (π*)
$\mathrm{H_3CCO{-}C{\equiv}C{-}COCH_3}$	C_2	-11.64 (π)	+2.03 ($\pi^*_{C\equiv C}$, π^*_{CO})
NC−C≡C−CN	$D_{\infty h}$	-11.99 (π, π_{CN})	+0.50 (π*)
$\mathrm{F_3C{-}C{\equiv}C{-}CF_3}$	D_3	-13.24 (π)	+2.87 (π*)
$\mathrm{H_3CSO{-}C{\equiv}C{-}SOCH_3}$	C_1	-10.25 (π, n)	+2.19 (π*)
$\mathrm{H_3CSO_2{-}C{\equiv}C{-}SO_2CH_3}$	C_{2h}	-12.47 (π)	+1.65 (π*)
$\mathrm{O_2N{-}C{\equiv}C{-}NO_2}$	D_{2d}	-13.63 (n_O)	-0.07 (π*)

As anticipated, substituents with donor character raise the energy of the HOMO, whereas typical acceptor groups lower the HOMO. For the calculated LUMO energies, such a clear-cut behavior is not observed.

alkynes against the reciprocal number of C atoms one finds a linear dependence leading to 1.190 Å for the triple bond and 1.366 Å for the single bond. All the calculations predict a linear structure. The authors[349] also comment the recent findings that long alkynes capped by organometallic fragments are not linear. Instead of invoking intermolecular interactions of the C−H•••π type, they point out that the lowest energy deformation vibration decreases dramatically when going from acetylenes to (oligo)alkynes. This result shows that longer systems are much softer than shorter ones. In Figure 20, the dependence of the wavenumber of the lowest energy harmonic deformation mode is given as a function of the number of C atoms (n_C). The shape of the two lowest eigenfunctions of the deformation vibration are shown in Figure 21. The small value (44 cm^{-1}, 526 J mol^{-1}) of the lowest deformation mode for pentaacetylene may rationalize the observation that various (oligo)alkynes capped by voluminous groups show nonlinearity in the solid state and in solution.

Also the more sophisticated calculations predict a surplus of electron density at the terminal C atoms (~0.3−0.5 e) and a small deficiency of electron density at the remaining carbon and hydrogen atoms. These numbers explain the high acidity of alkynes. In Table 1, the gas phase energies of the two step deprotonation of acetylene and 1,3,5-hexatriyne are shown. The results show that the acidity of alkynes increases with the chain length m what was also proven by kinetic experiments and seems to reach limiting values at m = 8−10.[102] The proton affinity of 1,3-butadiyne was calculated to be 177.0 kcal/mol.[351]

A question of considerable interest in connection with oligoenes and oligoynes is their stabilization by conjugation. Using the G3 (MP2) level of computation, it was found that 1,3-butadiyne is stabilized by 9.8 kcal/mol.[352] This is 1.3 kcal/mol more than that obtained for 1,3-butadiene.[351] By using an energy decomposition analysis, it was shown that the conjugative stabilization in 1,3-butadiyne is more than twice of that calculated for 1,3-butadiene.[353]

To estimate the reactivity of alkynes their frontier orbital energies can be used as a guide. In Table 2, we list the energies of the highest-occupied (HOMO) and the lowest-unoccupied (LUMO) molecular orbitals of 16 symmetrically hetero-bis-substituted alkynes, together with 2-butyne as a reference compound.[354] The energies are based on structures whose geometry was optimized by density functional theory (B3LYP/6-311G(d)). The orbital energies were derived with the HF method using the same basis set.

4.2. Spectroscopic Properties

4.2.1. Photoelectron Spectra of (Oligo)alkynes

Photoelectron (PE) spectroscopy using a He(I) or He(II) light source has been used to elucidate the electronic structure of molecules.[355] By using a light source of defined energy, electrons are ejected from molecules. By measuring the kinetic energy E_{kin}(e) of the ejected electrons one can determine the ionization energies (IE_n) of a molecule (M).

$$E(\text{M}^{+}_{\bullet}) - E(\text{M}) = \text{IE} = h\nu - E_{\text{kin}}(\text{e}) \qquad (1)$$

According to eq 1, it is necessary to calculate the total energy of the ground and various ionic states of a molecule to derive the ionization energy. However, experience has shown that it is sufficient to calculate the electronic structure of the ground state of the molecule within the self-consistent field (SCF) method. According to Koopmans' theorem,[356] the canonical orbital energy ε_j is equal to the negative vertical ionization energy $I_{\text{v},j}$, resulting from the ionization event. This implies that a single SCF calculation is sufficient to relate the measured ionization energies of a molecule with the calculated orbital energies.

$$I_{\text{v},j} = -\varepsilon_j \qquad (2)$$

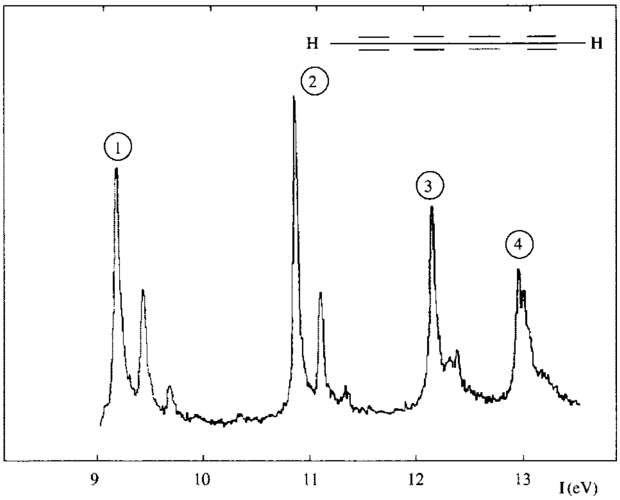


Figure 22. Photoelectron spectrum of 1,3,5,7-octatetrayne.[357] Reprinted with permission from ref 357. Copyright 1976 Elsevier.

The PE spectra of acetylene and of the unsubstituted oligoacetylenes have been reported in the literature.[354,357] The photoelectron spectra of acetylene, 1,3-butadiyne, 1,3,5-hexatriyne, and 1,3,5,7-octatetrayne consist of well separated π bands in the region of 9−13 eV with well resolved vibrational fine structure. In Figure 22, the PE spectrum of tetraacetylene is depicted.[358]

In Figure 23, we show a diagram which correlates the π bands of acetylene and di-, tri-, and tetraacetylene. By implying Koopmans' theorem (eq 2), we give the ionization energies in terms of orbital energies at the left of Figure 22. At the right side we show a schematic drawing of the four highest occupied π molecular orbitals of tetraacetylene ($1e_u$, $1e_g$, $2e_u$, $2e_g$). The filled circles refer to the mean of the π orbital energies. In the case of the dimethyl-substituted alkynes the PE spectra of dimethyl acetylene and dimethyldiacetylene were reported.[359]

A very detailed study on 11 monosubstituted and 25 disubstituted alkyl acetylenes,[360] as well as dialkyl substituted diacetylenes,[361] reveals shifts of the first bands by 1.04 (CH_3), 1.23 (C_2H_5), 1.31 (n-C_3H_7), and 1.23 eV (n-butyl). The bulkier t-butyl substituents stabilize the alkyne units considerably; thus, the π energies of the bis-t-butyl(oligo)acetylenes with two to five conjugated triple bonds have been determined by He(I) PE spectroscopy.[362] A comparison between the PE bands of the bis-t-butyl alkynes and those of the parent systems shows that the shift does not always increase with increasing energy of the band.[363] In Table 3, we list the energy difference between the first and second (third) band in the spectra of di-R-diacetylenes (di-R-triacetylenes).[361] It is found that these differences do not depend significantly on R.

Several studies are known about PE spectra of symmetrical dihaloacetylenes and dihalodiacetylenes (X−C≡C−X, X =

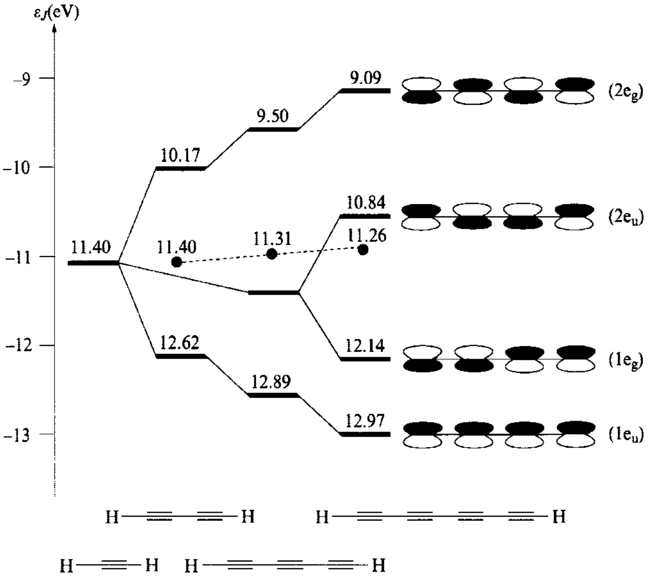


Figure 23. Correlation between the π orbital energies of mono-, di-, tri- and tetraacetylene (left). Schematic drawing of the highest π MOs of tetraacetylene (right).[357a] Reprinted with permission from ref 357a. Copyright 1977 Royal Swedish Academy of Sciences.

Table 3. Energy Difference [eV] Between the First and Second (Third) Band in the PE Spectra of bis-R-Substituted Diacetylenes and Triacetylenes[361]

R	$R(C\equiv C)_2R$	$R(C\equiv C)_3R$
H	2.5	3.4
Me	2.6	3.5
Et	2.5	-
t-Bu	2.5	3.7

F, Cl, Br, I,[364,364] and $X{-}(C{\equiv}C)_2{-}X$, X = F, Cl, Br, I[365,366]). Those compounds with the heavier elements (Br, I) were also attractive for spectroscopists because of the splitting of the bands caused by spin−orbit coupling. This effect facilitated the assignment of the bands to various ionization events. In Figure 24, we show the photoelectron spectrum of triiodotriacetylene.[349] It is seen that the spin−orbit coupling is especially large (0.4 eV) in the cases of bands 2 and 3.

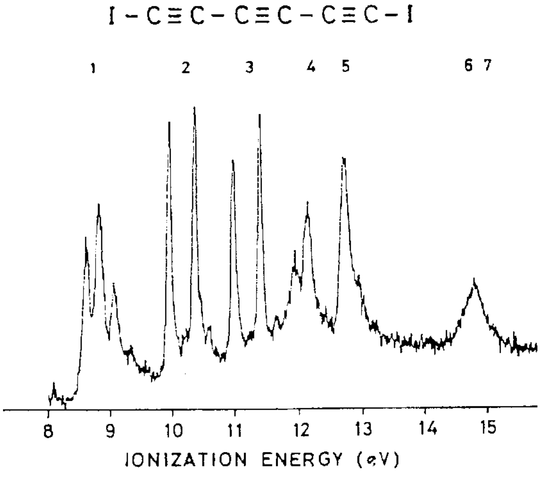


Figure 24. Photoelectron spectrum of diiodotriacetylene.[357a] Reprinted with permission from ref 357a. Copyright 1977 Royal Swedish Academy of Sciences.

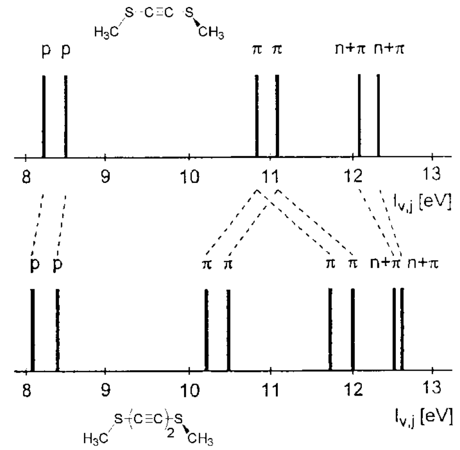


Figure 25. Correlation between the first PE bands of $CH_3{-}S{-}[C{\equiv}C]_n{-}S{-}CH_3$ for $n = 1$ and 2.[369] Reprinted with permission from ref 369. Copyright 2003 American Chemical Society.

The photoelectron spectra of acetylenes capped by CH_3X (X = S, Se, Te) groups were also reported.[367−369] The PE spectra of the CH_3X-capped monoalkynes[366,367] show three pairs of peaks between 7 and 12 eV which are assigned to the ejection of electrons from the n_p-type at the chalcogen centers and the π orbitals of the triple bond. In Figure 25, we show a correlation of the first bands of $CH_3{-}S{-}[C{\equiv}C]_n{-}S{-}CH_3$ for $n = 1, 2$.[368] The assignments of the bands agree with the assumption of a C_2 symmetry of the measured species.

The photoelectron spectrum of bis(dimethylamino)acetylene shows an analogous band sequence as the bis(methylchalcogeno)acetylenes: two close lying bands arising from the nitrogen lone pairs, followed by two π-bands.[370]

A comparison between the PE spectra of dimethyl- and disilylacetylene[371] reveals a higher (10.46 eV) ionization energy for the silyl substituted compound than for dimethylacetylene (9.61 eV) as expected for the less electron donor properties of the SiH_3 group compared with the CH_3 group. The photoelectron spectra of bis(trimethylsilyl)di- and triacetylene[372] show a shift of the π-bands toward lower energy when compared to the *t*-butyl substituted congeners.[362] The results when acetylene and 1,3-butadiyne were substituted with $(H_3C)_3Ge$[175,357b] and $(H_3C)_3Sn$[373] were similar.

The emission spectra of radical cations of di-, tri- and tetraacetylene excited in the gas phase by electron impact were reported.[358] The band systems have been established to be the $\tilde{A}^2\pi_u \rightarrow \tilde{X}^2\pi_g$ transition for all three species. Also the lifetime (τ) of the excited $\tilde{A}^2\pi$ states of the radical cationic states of di-, tri-, and tetraacetylene were obtained. In Table 4, the measured energies of the band maxima are compared with the ΔE values from the adiabatic ionization energies for IE_1 ($\tilde{X}$) and IE_2 ($\tilde{A}$).[358] It is seen that the ionization energy difference between the dominant 0.0 vibrational peak (ΔI) of the first two bands in the PE spectra corresponds to the value of the most intensive peak of the emission spectrum (Table 4).

4.2.2. Electronic Absorption Spectra of (Oligo)alkynes

The instability of the higher members of the parent (oligo)alkynes has hampered their detailed spectroscopic

Table 4. Comparison Between the Wave Numbers of the $\tilde{\nu}_{00}$ Band Maxima of the $\tilde{A}^2\pi_n \rightarrow \tilde{X}^2\pi_g$ Transition from the Emission Spectra of $[H-(C{\equiv}C)_n-H]^+$ (n = 2, 3, 4) and the Photoelectron Spectroscopic Ionization Energies IE_n to the $^2\pi$ States. Also Listed are the Lifetimes (τ) of the $\tilde{\nu}_{00}$ Level, $\tilde{\iota}$[358]

	$\tilde{\nu}_{00}$ [cm^{-1}]	τ [ns]	IE_1 ($\tilde{X}$) [eV]	IE_2 ($\tilde{A}$) [eV]	ΔI [cm^{-1}]
$[H-(C{\equiv}C)_2-H]^+$	19724	71	10.17 ($^2\pi_g$)	12.62 ($_2\pi_n$)	19762
$[H-(C{\equiv}C)_3-H]^+$	16670	17	9.50 ($^2\pi_g$)	11.55 ($_2\pi_n$)	16535
$[H-(C{\equiv}C)_4-H]^+$	14160	≤6	9.09 ($^2\pi_g$)	10.84 ($_2\pi_n$)	14115

studies. Therefore in the beginning of this chemistry only the UV/vis spectra of the end-protected species were studied systematically.[374−376] The recent availability of end-protected species with longer chains[23,24] augmented these studies. Finally, in the 1970s, the electronic absorption spectra of the parent systems were explored.[377,378] The electronic absorption spectra of mono- to pentaacetylene in the gas phase and in solution revealed in the visible and near UV regions[377] three bands (**A**, **B**, **C**) in the gas phase and two (**A**, **B**) in solution. The longest wavelength band **A** was assigned to the vibrational progressions of two forbidden electronic transitions $^1\Sigma_u^- \leftarrow {}^1\Sigma_g^+$ and $1\Delta_u \leftarrow {}^1\Sigma_g^+$, which overlap each other. The next, about 10^3 times more intense band, **B**, is attributed to the allowed $^1\Sigma_u^+ \leftarrow {}^1\Sigma_g^+$ transition.[379] In the case of diacetylene, the third band **C**, of similar oscillator strength as **B,** was associated with the first $^1\Pi_u \leftarrow {}^1\Sigma_g^+$ transition.[379,380] This band is situated between **A** and **B** in the case of acetylene. In Figure 26, the transition energies of the **A**, **B**, and **C** band maxima of mono-, di-, tri-, tetra-, and pentaacetylene, measured in the gas phase are plotted against the number of the triple bonds. One finds a decrease of the transition energies with the extension of the π system. It parallels approximately the decrease of the ionization potential (IP) as a function of n (Figure 26).

In Figure 27, we show the **A** and **B** bands of tetraacetylene in n-pentane solution. It is found that the **A** band has a low intensity and a Gaussian shape when one considers the envelope of the fine structure. Band **B** is 10^3 more intense and shows a pronounced vibrational fine structure with the $0 \leftarrow 0$ vibrational component as the most intense one of the progression. The difference between the vibrational bands of band **B** amounts to ~2000 cm^{-1}. The low intensity of band **A** might be the reason that it is rarely seen when electronic absorption spectra are reported in the literature. The slightly yellow color reported for the longer (oligo)alkynes might be due to band **A**.

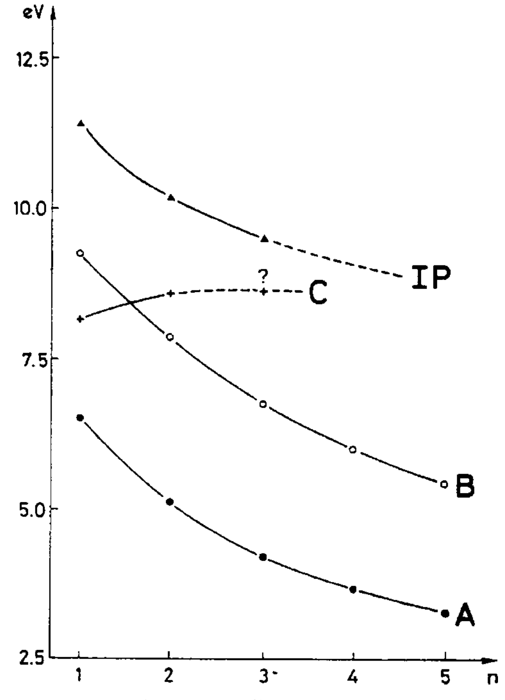


Figure 26. Plot of **A**, **B**, and **C** band maxima as a function of the number of triple bonds (n) for $H-(C{\equiv}C)_n-H$. Also shown is a plot of the ionization potential (IP) for $n = 1$ to $n = 4$.[378] Reprinted with permission from ref 378. Copyright 1974 Wiley-VCH.

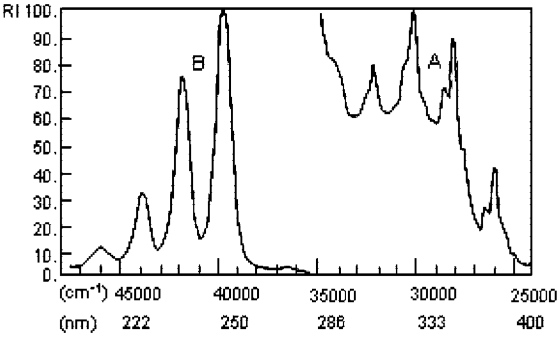


Figure 27. Relative intensities (RI) of the electronic absorption spectrum (**A** and **B** bands) of pentaacetylene in n-pentane[377] as a function of the wavenumbers [cm^{-1}] and wavelengths [nm]. Band **B** is about 10^3 more intense than band **A**. Reprinted with permission from ref 378. Copyright 1974 Wiley-VCH.

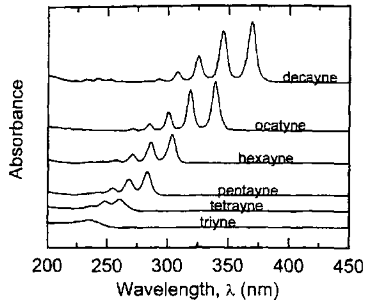


Figure 28. Most intensive band of the electronic absorption spectra of $(i\text{-Pr})_3Si-(C{\equiv}C)_n-Si(i\text{-Pr})_3$ measured in n-hexane as solvent. For the sake of clarity the spectra have been shifted vertically.[167] Reprinted with permission from ref 167. Copyright 2005 American Chemical Society.

In Figure 28, we show the most intensive band of the electronic absorption spectra of $(i\text{-Pr})_3Si-(C{\equiv}C)_n-Si(i\text{-Pr})_3$ in n-hexane as solvent.[166] This comparison demonstrates again the red shift of band **B** (see also Figure 26) with increasing length of the π system.

A plot of the squares of the wavelength λ of the most intense peaks of bands **A** and **B** against the number n of alkyne units (Lewis−Calvin plot)[381] of various alkynes[167] yields straight lines. These results resemble those found for linear (oligo)alkenes. If one associates the red shift of λ_{max} of band **B** with a decrease of the HOMO−LUMO gap E_g as the number of n increases, an empirical relationship of $E_g \approx n^{-0.379\pm0.002}$ was reported. An extrapolation toward the electron absorption properties of an (oligo)alkyne with infinite chain length, named carbyne, yields values of 565−570 nm.[24,101] The third-order nonlinear optical (NLO) properties of triisopropylsilyl-capped oligoynes containing 2−10 alkyne units have also been examined. The nonreso-

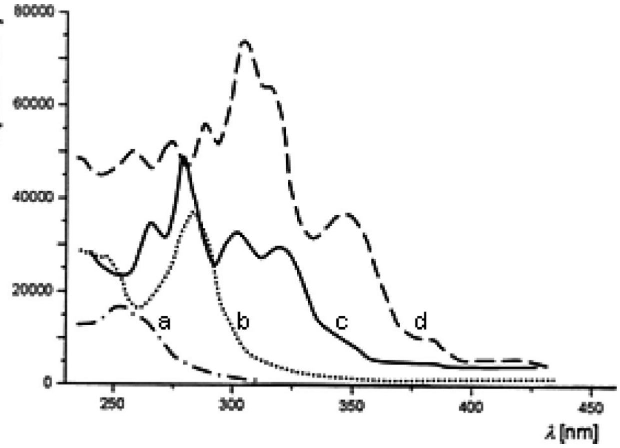


Figure 29. Comparison of the low-energy bands in the electronic absorption spectra of the bis-methyltellurium-capped mono-, di-, tri, and tetrayne **313(1)**−**313(4)** (from **a** to **d**).[368] Reprinted with permission from ref 368. Copyright 2002 American Chemical Society.

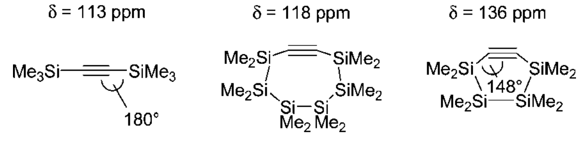
nant molecular second hyperpolarizabilities (γ) tremendously increase as a function of alkyne units (n) according to $\gamma \approx n^{4.28\pm0.13}$.

A comparison between the electronic absorption spectra of the parent (oligo)alkynes (Figures 27 and 28) with those of the α,ω-disubstituted congeners with nonconjugated groups (e.g., SiR_3, CR_3) reveals only a shift of the bands toward lower energy. However, when the alkynes are substituted by those main group elements which provide lone pairs a strong change is observed. As one example we show in Figure 29 the electronic absorption spectra of bis-tellurium-capped acetylene, diyne, triyne, and tetrayne **313(1)**−**313(4)**.[368]

Table 5. Overview of Common Ranges for ^{13}C NMR Shifts [ppm] of α,α′-Bis-homosubstituted Alkynes with Corresponding Heteroelements[a]

alkyne	δ (^{13}C) [ppm]	alkyne	δ (^{13}C) [ppm]
HC≡CH	72	PC≡CP	103
BC≡CB	86−108[b]	OC≡CO	117
CC≡CC	70−90	SC≡CS	85−88
SiC≡CSi	113	SeC≡CSe	79−82
GeC≡CGe	114	TeC≡CTe	66−68
SnC≡CSn	115	BrC≡CBr	43[c]
PbC≡CPb	119	IC≡CI[384,385]	1[e]
NC≡CN[386]	75[d]	RC≡CXe$^+$	−20

[a] Commonly, alkyl groups as further substituents are considered. If not otherwise stated, values are given in $CDCl_3$ as solvent. [b] Strongly dependent on the type of boron (trivalent or boron cluster) involved; the signal is rather difficult to observe (broadening because of the large quadrupolar moment of ^{11}B ($I = 3/2$)). [c] This value is the chemical shift of the terminal ^{13}C atoms in $Br(C{\equiv}C)_4Br$. A value for the corresponding monoalkyne is not reported. [d] C_6D_6 was used as solvent. [e] Strongly dependent on solvent basicity because of complexation.



352(1) **149** **151**

Figure 30. Comparison of ^{13}C NMR shifts depending on the bending of the alkyne moiety.

Table 6. Overview of ^{13}C−^{13}C Nuclear Spin−Spin Coupling Constants ($^1J(^{13}C^{13}C)$) [Hz] for Bis-Homosubstituted Derivatives of Acetylene

alkyne	$^1J(^{13}C^{13}C)$ [Hz]	alkyne	$^1J(^{13}C^{13}C)$ [Hz]
LiC≡CLi	31.8[b]	HC≡CH[a]	171.5
HBeC≡CBeH	72.0[b]	MeC≡CMe[a]	184.3
$Me_3SnC{\equiv}CSnMe_3$	81.0[a]	$H_2NC{\equiv}CNH_2$[b]	219.5
$H_2BC{\equiv}CBH_2$	110.4[b]	HOC≡COH[b]	269.3
$Me_3SiC{\equiv}CSiMe_3$	101.4[a]	FC≡CF[b]	356.0

[a] Measured value.[387−389] [b] Calculated (extrapolated) value.

4.2.3. NMR Spectroscopy on (Oligo)alkynes

Commonly the carbons of a triple bond resonate in the range of 70−90 ppm with the native acetylene at 71.9 ppm. However, heterosubstituents are able to influence the chemical shift of the triple bond dramatically. An understanding whether the heteroelement shields or deshields the carbon atoms of the triple bond is not easy.[382] Nevertheless, some trends are observed. With exception of heteroelements of the fourth main group,[383] heavier elements shield the triple bond tremendously. If chalcogen substituents are considered, the triple bond of the oxygen-substituted congener is deshielded in comparison to a native carbon-substituted alkyne whereas the heavier chalcogens such as selenium and tellurium shield the triple bond carbons compared with the oxygen-substituted one. This trend is even better illustrated when iodine is used as heterosubstituent (IC≡CI), where a chemical shift of only 1 ppm of the alkyne carbon atoms is observed. Xenonium salts (even the heteroelement is positively charged) shift this value to the negative region. Unfortunately, for several alkynes capped by main group elements no ^{13}C NMR data are available in the literature. This is specially true for molecular entities such as aluminum and arsenic-substituted congeners accessed several decades ago when ^{13}C NMR experiments were far from routine measurements. Therefore, Table 5 providing an overview of the ^{13}C NMR chemical shifts of α,α′-disubstituted alkynes remains imperfect. If not otherwise stated, molecules with alkyl substituents attached to the heteroelement were used for the values in Table 5. In general, aromatic moieties shift these values to slightly lower field. Also the bending of alkyne units in strained ring systems has a major impact on their chemical shifts and leads to shifts which are known from the olefinic region.[116] A representative example is given in Figure 30.

Extensive ^{13}C−^{13}C spin−spin coupling studies on a large and representative group of acetylenes with different capping units revealed significant differences of the $^1J(C{\equiv}C)$ coupling constant across the alkyne moiety.[387] These investigations showed that a high electronegativity of the capping substituents leads to large $^1J(C{\equiv}C)$ coupling constants, whereas rather electropositive elements decrease the $^1J(C{\equiv}C)$ values in comparison with the native HC≡CH.[388] For acetylene, the $^1J(C{\equiv}C)$ coupling constant has been found to be 171.5 Hz.[389] An overview of different α,α′-disubstituted alkynes is given in Table 6.

These values clearly illustrate the rule of Walsh[390] and Bent[391] which states that the atomic s character is concentrated in orbitals directed toward electropositive substituents. By using the Frei−Bernstein eq 3,[392] it is possible to calculate the *s* characters of the corresponding carbon hybrid orbitals forming the carbon−carbon bond in disubstituted acetylenes

$$^1J(C{\equiv}C) = 575s(i)s(j) - 3.4 \tag{3}$$

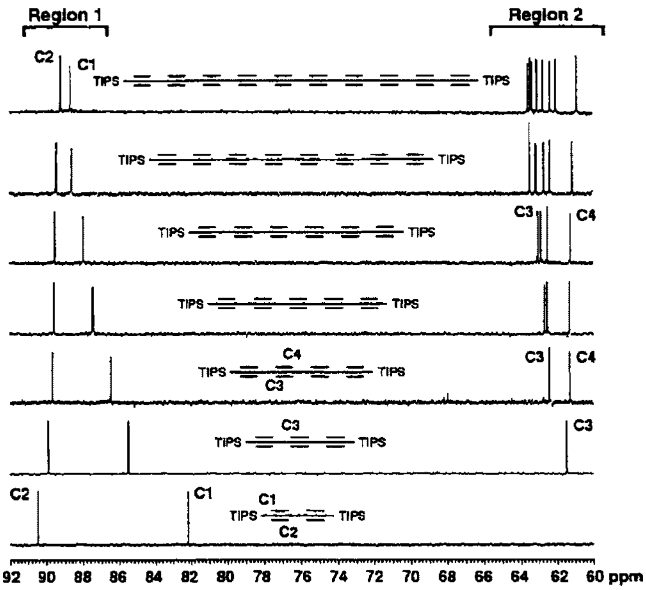


Figure 31. ^{13}C NMR chemical shifts (sp region) for TIPS-protected oligoynes.[167] Reprinted with permission from ref 167. Copyright 2005 American Chemical Society.

with $s(i)$ and $s(j)$ being the s character of the corresponding carbon hybrid orbitals.

The s values obtained in this way range between 0.25 in LiC≡CLi and 0.8 in FC≡CF. This wide region covered by the values of the $^1J(C{\equiv}C)$ coupling constant across the triple bond clearly demonstrates the flexibility of the electronic system in an alkyne. The coupling constant can be considered as a highly characteristic parameter for the electronic properties of a heteroelement-capped carbon−carbon triple bond.

Very important for the structural characterization of (oligo)alkynes are their ^{13}C NMR spectra. In Figure 31, we show the acetylenic region of triisopropylsilyl (TIPS) capped[167] oligoynes. The values compare very well with those reported for bis(t-butyl)oligoynes.[26,393]

One finds two regions in which the signals are grouped. The signals at lower field resonance stem from the carbons for the acetylene unit closest to the substituents, C1 and C2. Region 2 contains resonances for all the internal sp centers. Very similar results were reported for the ^{13}C NMR spectra of dicyano(oligo)ynes with 3 to 8 alkyne units.[27]

4.2.4. Structural Investigations on (Oligo)alkynes

Among the various structural investigations of main group-capped (oligo)alkynes we would like to focus on two major aspects: first, the influence of the heteroatom next to the C≡C triple bond. Geometrical properties and preferred conformations of single molecules are elucidated and discussed. Second, the solid state structures of a variety of different (oligo)alkynes substituted by main group elements have attracted considerable attention because of their supramolecular organization or the nonlinearity of long (oligo)alkyne carbon chains.

For a detailed understanding of the molecular structures an overview about the respective bond lengths between the terminal alkyne carbon atom and a main group atom located in the α position is useful. In Table 7, we provide such a compilation. Most values are either obtained by means of X-ray crystallography and a few by quantum chemical calculations (B3LYP/6-311G(d)),[394] if no experimental data were obtainable. As anticipated, the shortest X-C(sp) bond is the one between carbon and hydrogen (1.07 Å), whereas the longest one listed in this table is the one between bismuth and carbon (up to 2.29 Å) or considering bonds with a strong polar component the one between barium and carbon (2.85 Å). Two obvious trends should be mentioned: Within a period the bond length decreases (e.g., for Li−C(sp) 1.86 Å and for F−C(sp) 1.27 Å), whereas in a main group the respective bond length increases with increasing atomic mass (e.g., O−C(sp) 1.30 Å and Te−C(sp) 2.04 Å). The bond length of the C≡C triple bond itself does not change considerably and ranges in most cases between 1.19 and 1.21 Å. Calculations have shown that in molecules such as acetylene capped by alkali metals (Li, Na, K) the C≡C bond length increases up to 1.25 Å because of the highly dianionic character of the acetylene fragment. A similar effect leading to augmented triple bond lengths was observed when elements of the third main group such as aluminum and gallium were attached. The empty p orbital of these electron-deficient atoms leads to an effective overlap with the occupied π orbitals of the C≡C triple bond resulting in a decrease of electron density in the triple bond and, thus, longer C≡C bond lengths.[394]

Table 7. Bond Lengths [Å] of X−C(sp) Bonds[395]

bond type	bond length [Å]	bond type	bond length [Å]
H−C(sp)	1.07^a	Sn−C(sp)	$2.03-2.15^a$
Li−C(sp)	1.86^b	Pb−C(sp)	2.20^a
Na−C(sp)	2.17^b	N−C(sp)	1.32^b
K−C(sp)	2.46^b	P−C(sp)	1.75^b
Be−C(sp)	$1.49-1.67^{b,c}$	As−C(sp)	$1.78-1.98^a$
Mg−C(sp)	$2.18-2.24^a$	Sb−C(sp)	$2.06-2.23^a$
Ca−C(sp)	$2.52-2.56^a$	Bi−C(sp)	$2.15-2.29^a$
Sr−C(sp)	$2.69-2.72^a$	O−C(sp)	1.30^a
Ba−C(sp)	2.85^a	S−C(sp)	$1.67-1.68^a$
B−C(sp)	$1.53-1.56^a$	Se−C(sp)	$1.81-1.83^a$
Al−C(sp)	$1.89-1.97^a$	Te−C(sp)	$2.03-2.04^a$
Ga−C(sp)	$1.91-2.01^a$	F−C(sp)	1.27^b
In−C(sp)	$2.10-2.19^a$	Cl−C(sp)	1.62^b
$C(sp^3)$-C(sp)	$1.43-1.45^a$	Br−C(sp)	1.77^b
Si−C(sp)	$1.84-1.85^a$	I−C(sp)	2.02^a
Ge−C(sp)	$1.86-2.00^a$		

[a] Measured value(s). [b] Calculated values. If not otherwise stated, B3LYP/6-311G(d) optimization. [c] Strongly dependent on electronic state (of BeC≡CBe), as well as method and basis set used.[71]

An elucidation of the molecular structures by means of photoelectron spectroscopy, X-ray crystallography and quantum chemical calculations revealed interesting geometrical features. A substitution with electron-deficient atoms such as boron, aluminum and gallium leads to a D_{2d} arrangement of the carbon−aluminum skeleton as the preferred conformation. As already mentioned each of the two perpendicular π orbitals of the C≡C triple bond interacts with the empty p orbital at the boron, aluminum and gallium, respectively. As a result a conformation as depicted in Figure 32 results. Regarding alkynes substituted by heteroelements with a lone pair similar geometrical properties result (see Figure 16 and 32).[393,396] However, in the latter cases the important interaction leading to the perpendicular $C(sp^3)$-X$\cdots$X-$C(sp^3)$ torsional angle is the overlap of the n_p orbital of the heteroelement (lone pair) with the unoccupied π^* orbital of the triple bond. Each of the two orthogonal π^* orbitals interacts with one lone pair; a torsional angle of about 90° results.[304,306]

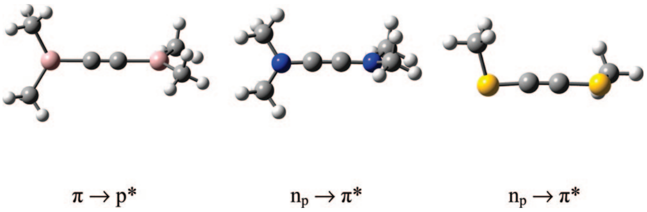


Figure 32. Preferred conformations of bis(dimethylaluminium)-, bis(dimethylamino)- (**207**), and bis(methylthio)-substituted acetylene (**311(1)**) (from left to right) and major interaction responsible for the preferred arrangement obtained by B3LYP/6-311G(d) optimizations and NBO analyses.

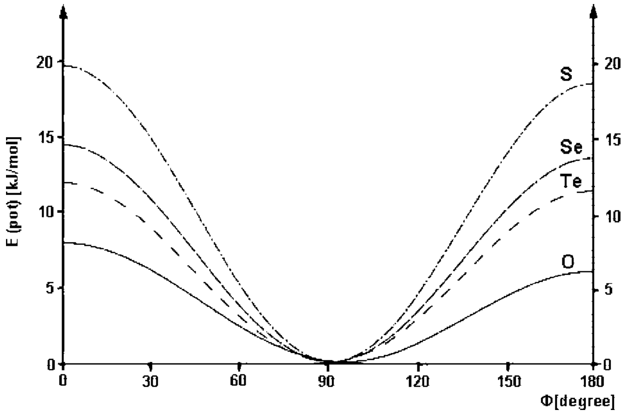


Figure 33. Comparison of the potential energies of the bis(methylchalcogen)-substituted acetylenes as a function of the torsional angle ϕ.[306] Reprinted with permission from ref 306. Copyright 2002 American Chemical Society.

For $CH_3X-(C{\equiv}C)_n-XCH_3$ (X = S, Se and n = 1, 2) photoelectron spectroscopic investigations (see section 4.2.1) have proven this rationalization: The spectrum showed for the first peaks two close transitions (see Figure 25).[367,368,266] A comparison with quantum chemical calculations suggests that the preferred conformation in the gas phase is a perpendicular arrangement of the Me substituents.[266,367,368] Calculations have shown that the sulfur-containing compound **311(1)** reveals the highest rotational barrier, followed by the selenium- (**312(1)**), tellurium- (**313(1)**), and oxygen-containing one.[305] In comparison with hydrocarbon derivatives, the calculated barriers are remarkably high. A graphical representation of the potential energy as a function of the torsional angle ϕ is given for the chalcogen-substituted compounds in Figure 33.

A natural bond orbital (NBO) analysis reveals that the magnitude of these barriers results essentially as a compromise of two effects: the overlap of the lone pairs at the chalcogen atoms with the π^* orbitals and the energy difference between these orbitals. The overlap decreases from oxygen to tellurium. The same holds for the energy difference being largest for oxygen and smallest for tellurium. As a result the highest barrier for **311(1)** emerges. This rationalization is also valid for an increasing number of acetylene units[368,369] as quantum chemical calculations (B3LYP/6-311G(d)) have shown (Table 8).

Table 8. Rotational Barriers [kJ/mol] for Bis(methylchalcogen)-Substituted Oligoynes ($n = 1-4$) According to B3LYP/6-311G(d). Reprinted with permission from ref 306. Copyright 2002 American Chemical Society

compound	$n = 1$	$n = 2$	$n = 3$	$n = 4$
O	7.8	3.3	1.9	1.2
S	19.7	10.6	6.6	4.2
Se	14.4	8.0	5.0	3.2
Te	11.5	6.9	4.3	2.8

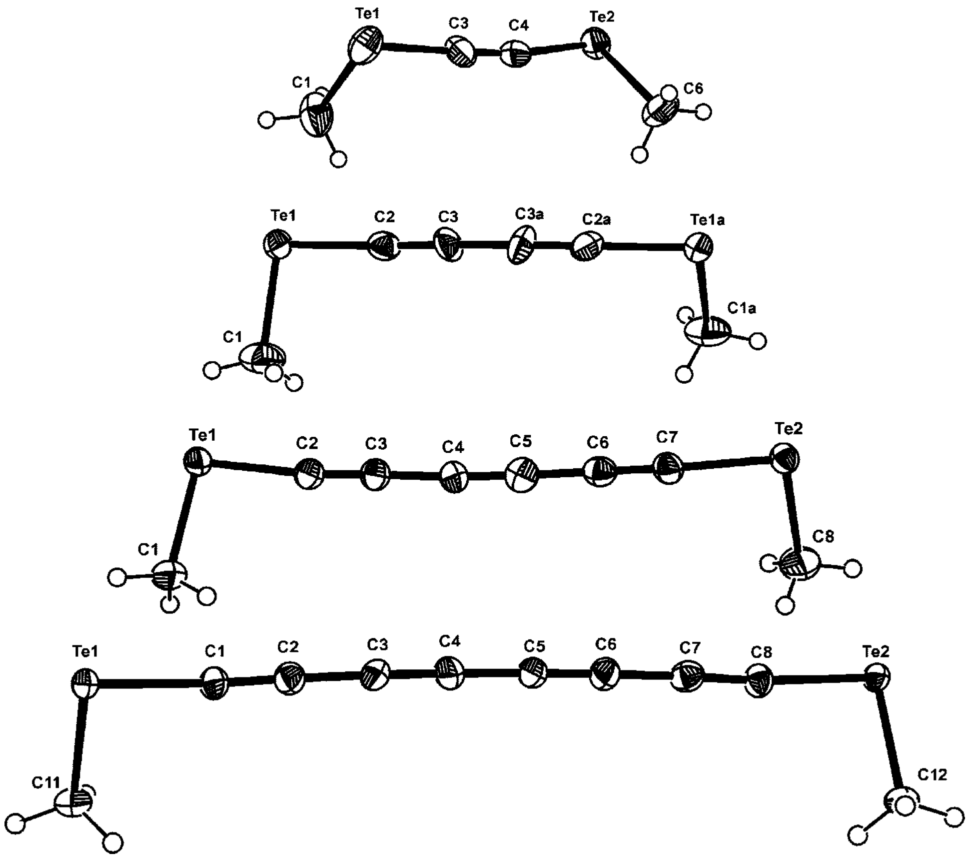


Figure 34. ORTEP plots (50% ellipsoid probability) of the molecular structure of tellurium-substituted oligoynes **313(1)**−**313(4)** (from top to bottom).[368] Reprinted with permission from ref 368. Copyright 2002 American Chemical Society.

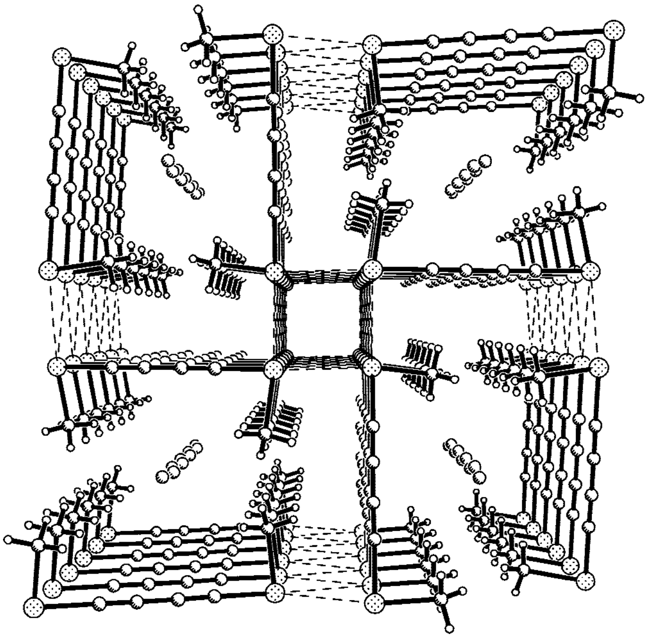


Figure 35. Solid-state structure of **313(2)** forming a square cavity with disordered guest molecules inside. Close tellurium–tellurium contacts are indicated by dotted lines.[305,368] Reprinted with permission from ref 368. Copyright 2002 American Chemical Society.

Nevertheless, for the tellurium-substituted acetylenes an X-ray elucidation was also possible.[367] A large variation of the torsional angles between the Te-Me bonds was found: the longer the rod, the smaller the angle. This result mirrors the decreasing rotational barrier with increasing chain length. As anticipated, the bond lengths between the sp centers alternate strongly. In Figure 34 we show the molecular structures of **313(1)**−**313(4)**.[368]

In their solid-state structures in almost all cases, close tellurium−tellurium interactions between different molecules were reported. In many cases the molecules with the chalcogen-capped alkyne moieties were stacked on top of each other to build columnar or even tubular motives.[397,398] In the case of **313(2)**, a helical arrangement of the tellurium-substituted carbon rods forms an almost square cavity being able to host guest molecules (Figure 35).

Because of the medium ring size of cyclic diynes **394(*m*,*n*)** and **395(*m*,*n*)**, no inclusion of guests was possible inside the cavities. But by utilizing the enlarged cyclic systems **399(*n*)**−**402(*n*)**, solvent molecules as guests were incorporated into the tubes. If an aliphatic solvent, for example, *n*-hexane, was used, only disordered electron density could be detected. In contrast, by recrystallization from aromatic solvents, the tubes of **402(5)** contain one guest molecule per cycle in an ordered fashion. Systematic studies to determine the solid-state behavior dependent on the kind of guest molecule have shown that not only a large variety of different guests (electron-rich and electron-poor) can be included but also that the diameter of the tubes depends on the size of the guest.[308,397,399] The larger the guest, the more the tubes are stretched (Figure 36). To differentiate this special behavior from that of shape-persistent macrocycles the term "elastic cycle" was introduced.[309,398]

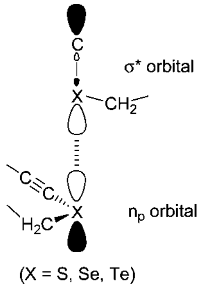


Figure 37. Most important chalcogen−chalcogen interaction between an occupied n_p orbital and an unoccupied σ^* orbital.[402]

A deeper understanding of these structure-determining chalcogen−chalcogen interactions[400,401] was possible by quantum chemical analyses.[402,403] In terms of frontier orbital theory the most important interaction can be described as an interplay between the occupied n_p-type orbital of one chalcogen center with the unoccupied X−C σ^*-orbital of the other as shown in Figure 37. Furthermore correlation effects contribute significantly. MP2 calculations show for sulfur-, selenium-, and tellurium-containing systems values in the range of 13−19 kJ/mol.[401] These values (for systems with acetylene units adjacent to the chalcogen) are considerably larger than for systems without acetylene units. This behavior can easily be understood by considering their different acceptor capability and their influence to the energetic level of the σ^* orbital. Therefore, the use of acetylenes to construct tubular structures is also an energetic reason, beyond their relative rigidity.

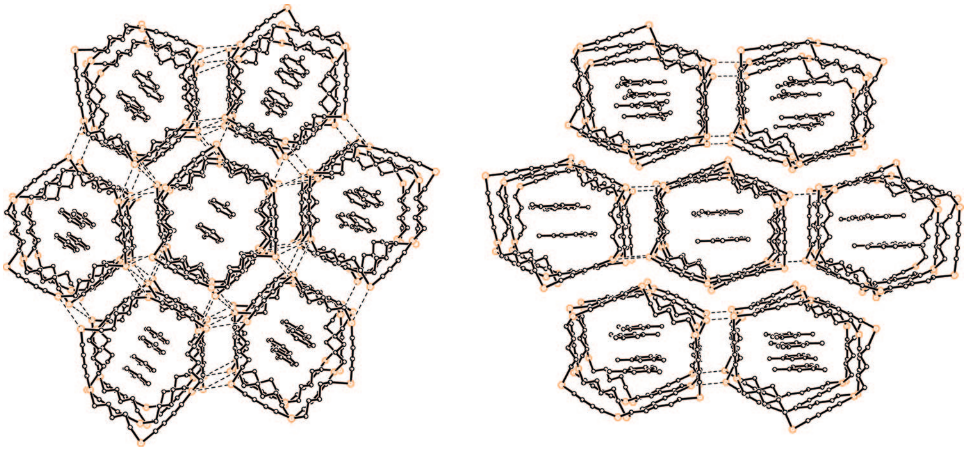


Figure 36. Comparison between the solid-state structures of the hexaselenacyclohexayne **402(5)** with toluene as guest (left) and the larger mesitylene as guest (right).[309] Selenium centers are shown in orange. Reprinted with permission from ref 309. Copyright 2004 American Chemical Society.

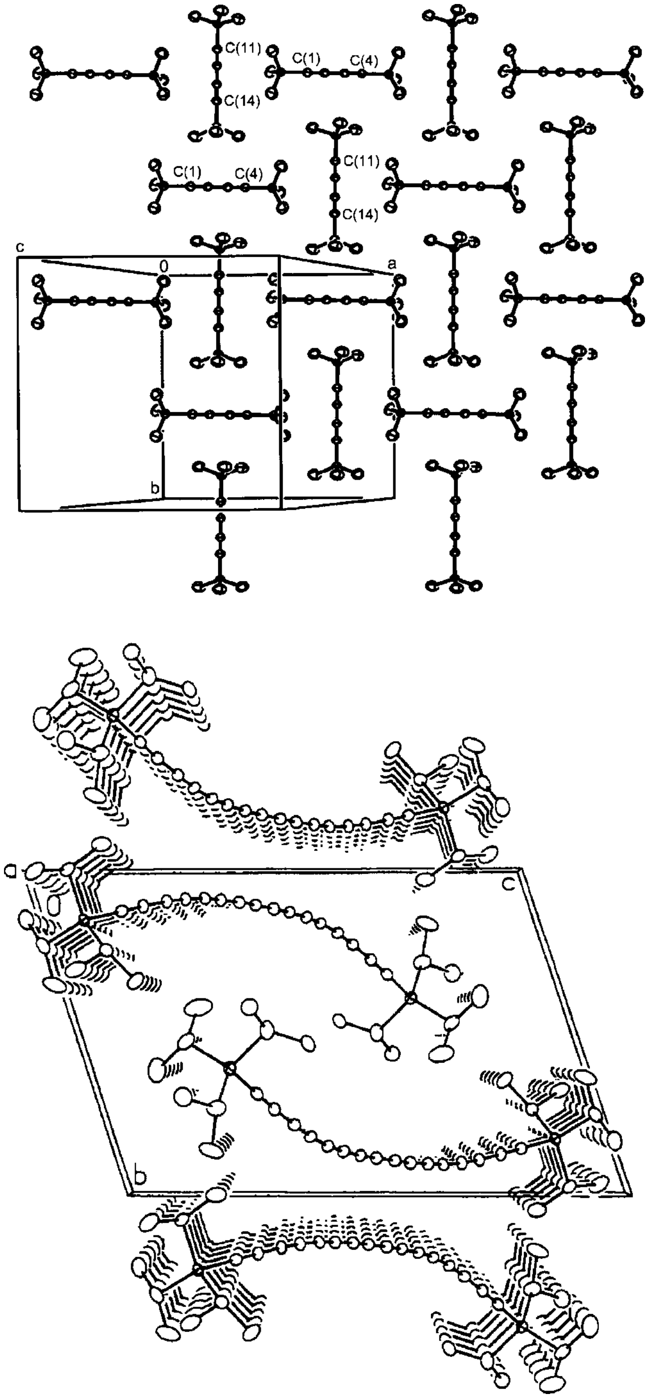


Figure 38. Comparison of solid state structures of bis-trimethylsilyl capped butadiyne (top)[185] with TIPS-protected hexadecaoctayne (bottom) showing the bent (olig)oalkyne chain in the latter structure.[167] The unit cells are also depicted. Reprinted with permission from refs 185 and 167. Copyright 2003 amd 2005 American Chemical Society.

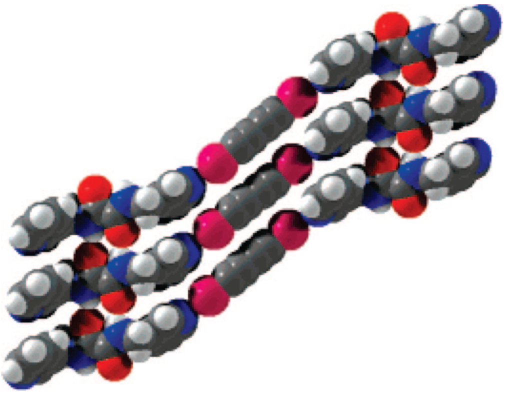


Figure 39. Solid-state structure of aligned 1,4-diiodobutadiyne molecules with bis(*m*-pyridyl)oxalamide. A weak N−I interation is responsible for the alignment. Iodine atoms are shown in pink.[318] Reprinted with permission from ref 318. Copyright 2008 American Chemical Society.

X-ray investigations of long alkyne chains have revealed astonishing shapes. In general, each individual acetylene unit bears only a slight deviation from linearity. However, overall, as a kind of cumulative effect dramatic curvatures leading to bow shape conformations can result. Figure 38 compares the solid-state structure of a small stiff diyne unit[185] with a long alkyne chain revealing a bow-like conformation.[167] As already mentioned in section 4.1, the lowest energy harmonic deformation mode is a function of the number of C atoms in the (oligo)alkyne chain.[350] The energy associated with this deformation decreases with increasing chain length. Therefore, such "unusual" bow- or S-like shapes may be seen as frozen low-energy eigenfunctions of the deformation vibration that may further be favored by C−H···π interactions.

Cocrystallization experiments using diiodobutadiyne as well as diiodohexatriyne with pyridyl-substituted ureas and oxalamides, respectively, afforded aligned iodine-capped carbon rods as shown in Figure 39. Weak intermolecular N−I interactions between the rod and the pyridyl moiety play a crucial role in the solid-state architecture. This arrangement is ideally suited for a polymerization of diiodobutadiyne under high pressure (see Chapter 3.3).[317−319]

5. Conclusion

Mono- and (oligo)alkyne units between main group elements comprise the vast majority of the hitherto known alkynes. The various preparation procedures of these species presents a compendium of the most known methods to prepare C≡C triple bonds. The methods of preparation are augmented by information about the stability at room temperature and the molecular structures in the solid state and solution. The rigidity of the triple bonds allows the built-up of structural units, which vary from dumbbells via rods to squares and tubes. The spectroscopic properties together with quantum chemical calculations add further insight to the properties of the most simple group existing in organic chemistry, the alkyne unit.

6. Abbreviations

Ar	aryl
B3LYP	Becke 3-parameter functional according to Lee, Yang and Parr
cc-pV2Z	correlation consistent polarized valence double-ζ
cc-pVTZ	correlation consistent polarized valence triple-ζ
cc-pV5Z	correlation consistent polarized valence quintuble zeta
CCSD(T)	coupled cluster with singly and doubly (triple) excitations
COD	1,5-cyclooctadiene
Cy	cyclohexyl
δ	chemical shift
DDQ	2,3-dichloro-5,6-dicyano-1,4-benzoquinone
DFT	density functional theory
DMDO	dimethyldioxirane
ΔI	ionization energy difference

EH	extended Hückel
ε_{j}	orbital energy
E_{kin}	kinetic energy
E_{pot}	potential energy
eV	electronVolt
FBW	Fritsch−Buttenberg−Wiechell rearrangement
FVP	flash vacuum pyrolysis
h	Planck constant
Hal	halogen
IE	ionization energy
IP	ionization potential
IR	infrared
HOMO	highest occupied molecular orbital
λ	wavelength
LDA	lithium diisopropylamide
LiHMDS	lithium hexamethyldisilazide
LUMO	lowest unoccupied molecular orbital
*m*CPBA	*m*-chloroperoxybenzoic acid
Mes	mesityl
MO	molecular orbital
MP	Møller−Plesset
$\tilde{\nu}$	wavenumber
Naph	naphthyl
NBO	natural bond orbital
NBS	*N*-bromosuccinimide
NIS	*N*-iodosuccinimide
NMR	nuclear magnetic resonance
PE	photoelectron
PCC	pyridinium chlorochromate
RHF	restricted Hartree−Fock
RI	relative intensity
SCF	self-consistent field
TBABr	tetra-*n*-butyl ammonium bromide
TBAF	tetra-*n*-butyl ammonium fluoride
TBPS	tris(biphenyl-4-yl)silyl
TCNE	tetracyanoethylene
TES	triethylsilyl
THF	tetrahydrofuran
TIPS	triisopropylsilyl
TMS	trimethylsilyl
TMEDA	*N*,*N*′-tetramethylethylenediamine
tmhda	*N*,*N*,*N*′,*N*′-tetramethyl-1,6-hexanediamine
tmpda	*N*,*N*,*N*′,*N*′-tetramethyl-1,3-propanediamine
Tol	toluyl
Ts	tosyl

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