Carbo-mers: from skeleton to function

Valérie Maraval* and Remi Chauvin*

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Since it has been proposed in 1995, the *carbo*-mer definition has been mainly applied to saturated and unsaturated rings of molecular skeletons, in view of studying their (homo)-aromatic character as compared to the electronic (de)localisation prevailing in the parent molecules. More generally, even acyclic or partial ethynylogues of common molecules exert fascination because the rigid expansion (preserving local symmetry) brought by the inserted acetylenic units gave them the status of ''first-level nano-objects''. When the C_2 insertion applies to the first shell of bonds at a given carbon or hetero-atom, the ''exploded'' unit can be considered a local *carbo*-mer of the corresponding function. The chemistry of molecules featuring a per-alkynylated atom is herein surveyed and perspectives are proposed. Some of them are ''mysteriously'' stable, while other remain ''surprisingly'' unknown in spite of their structural simplicity.

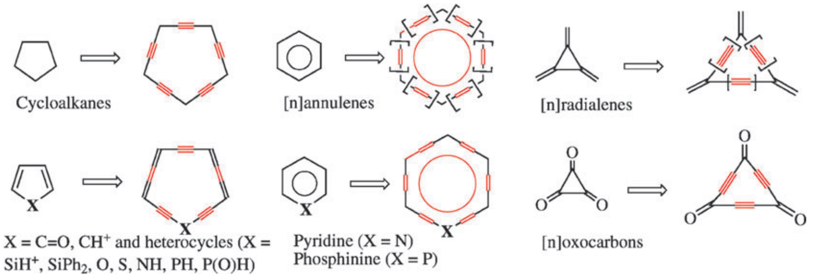
Introduction

The *carbo*-mer concept has been devised from the concern of separating size from other features of molecular structures (connectivity, symmetry, shape, π-resonance,...). A ''total'' *carbo*-mer is thus built by the insertion of $(C_{sp})_2$ dicarbon units into *all* the bonds of a parent Lewis structure.[1] Partial *carbo*-mers, are also worth to be considered, and in particular ring *carbo*-mers have attracted a peculiar attention.[2] Ring *carbo*-mers were first illustrated in 1983 by Scott's pericyclynes[3] which were then extensively studied.[4] Functional [*n*]pericyclynes (*carbo*-[*n*]cyclitol derivatives) have also been exemplified for $n = 5$,[5] and $n = 6$, the latter being devised as precursors of substituted benzene ring *carbo*-mers

Laboratoire de Chimie de Coordination du CNRS, UPR 8241, 205 Route de Narbonne, 31077 Toulouse Cedex 4, France. E-mail: chauvin@lcc-toulouse.fr. E-mail: valerie.maraval@lcc-toulouse.fr; Tel: 33 (0)5 61 33 31 13

Remi Chauvin received his PhD in 1988 under the supervision of Henri Kagan (Orsay, France). He pursued as a post-doctoral fellow with K. B. Sharpless at MIT (MA, USA), and then with Andrea Vasella in Zürich (Switzerland). From 1990 to 1993, he worked at the Roussel Uclaf Company in Romainville (France). He finally came back to the academic research at the CNRS Laboratory of Coordination Chemistry in Toulouse (LCC), and in September 1998, he was appointed as a Professor at the Paul Sabatier University. Today he manages two research groups in Toulouse: one at the LCCC, and the other (since 2007) at the Laboratory of Molecules of Biological Interest. His research activities focus on four main aspects of molecular chemistry: (i) theoretical chemistry (analysis of the electron delocalization, aromaticity and related properties); (ii) acetylenic chemistry (synthesis of aromatic carbo-mers, OPEs, complexes of functional alkyne ligands, asymmetric synthesis of alkynyl carbinols, alkyne metathesis,...); (iii) phosphorus and coordination chemistry for catalysis (chiral phosphoniums, X,C-chelating ylide ligands with X = phosphines, diaminocarbenes,...); (iv) synthesis of biologically active natural products and analogues (oligoacetylenes and polyalkyne–polyols).

Valérie Maraval graduated from the University Paul Sabatier (Toulouse, France) in 1997. She then prepared a thesis in the field of dendrimer chemistry under the supervision of Jean-Pierre Majoral, and she received her PhD in 2000. In 2001, she worked as a post-doctoral fellow with Bernard Meunier in collaboration with the Aventis company. She then came back to Jean-Pierre Majoral's team as a CNRS Engineer for two years. In 2005, she joined the group of Remi Chauvin at the Laboratoire de Chimie de Coordination (LCC) in Toulouse. Her research activity focusses on the chemistry of carbo-meric molecules, and particularly on the development of novel approaches to carbo-meric compounds based on organometallic catalysis (alkyne metathesis).



Scheme 1 Examples of ring *carbo*-mers. The symbols [=] and [≡] denote C_2 or C_4 units.

(“*carbo*-benzenes”).[6] Theoretical studies also focussed on ring *carbo*-mers of various saturated and unsaturated cyclic molecules,[7] and in particular on their (homo)aromatic character (Scheme 2):[8] benzene and other [*n*]annulenic species,[9] heterocycles,[10] radialenes,[11] oxocarbons,[12]... Calculations of specific molecular properties were also performed: hapticity,[7] hyperpolarizability,[13] redox potential,[11] conducting properties[14]... The second ring *carbo*-mers of [3]radialene and benzene derivatives (devised by insertion of C_4 instead of C_2 units into the ring bonds) were also studied at both theoretical and experimental levels.[7,8,11]

By generalization, partial *carbo*-merization may apply to topologically relevant parts of a parent Lewis structure other than rings (Scheme 1), *e.g.* to the sets of exocyclic or terminal bonds. Beyond topological information however, Lewis–Cram structures also contain topographical and geometrical informations (Scheme 2).

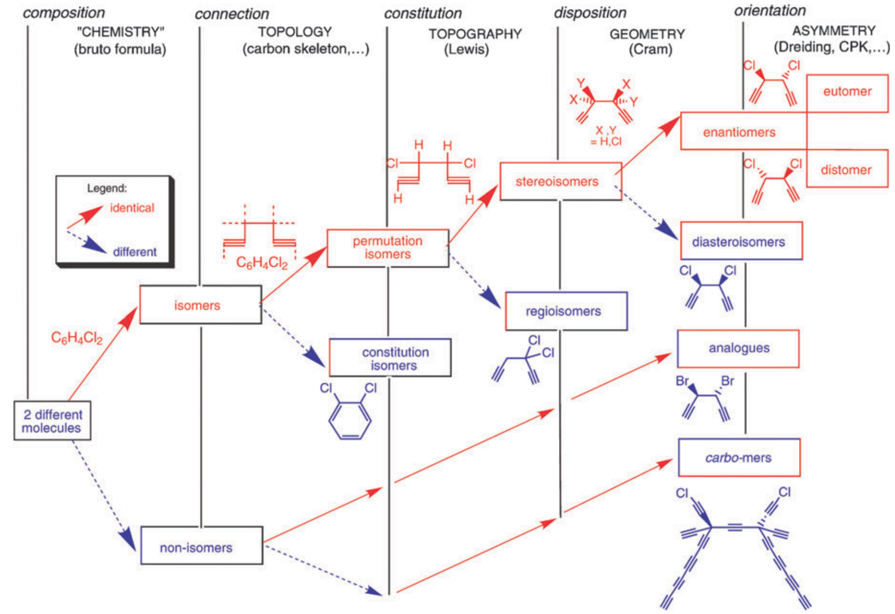
According to Scheme 2, topographical information is thus completed by assigning functional groups onto carbon skeletons. A natural perspective of the partial *carbo*-mer concept is thus its generalization from skeleton to functions. This is the topic of the present report, which focusses on the local *carbo*-merization of chemical functions. Although the concept of “chemical function” comes under a rather empirical appraisal, “atom-centered” and “bond-centered” functions can be formally distinguished (Scheme 3). The “extent” of a given bond-centered function is quite arbitrary (*e.g.* ketone, ester and aldehyde functions are distinguished), but an atom-centered function is simply a substituted atom and its *carbo*-mer is non-equivocally the corresponding per-alkynylated atom. The state of the art in the local *carbo*-mers of both kinds of functions is hereafter reviewed. Applications of such fascinating molecules will be illustrated.

1 *Carbo*-mers of homodiatomic molecules Z_2

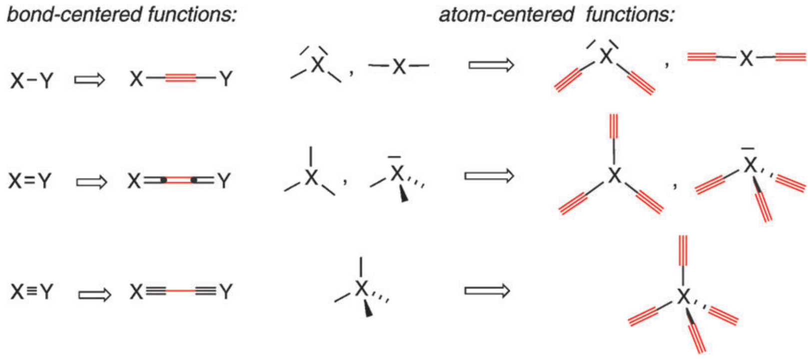
The paradigm of the *carbo*-meric relationship is given by hydrogen and acetylene (Z = H) or by nitrogen and cyanogen (Z = N). More generally, Z_2 diatomic molecules are degenerate cases of bond-centered and atom-centered functions often considered as “reagents” in chemical synthesis. Their *carbo*-mers are hereafter illustrated by less common molecules.

1.1 *Carbo*-mers of dihalogens (Z = F, Cl, Br, I)

In 1885, Baeyer reported the first synthesis of C_2I_2 and C_4I_2.[15] In 1974, Heilbronner *et al.* described the preparation of pure C_4Z_2 with Z = Cl, Br, I from the dilithium salt of diacetylene and Cl_2, Br_2, I_2,[16] and in 2000 Gao and Goroff reported the synthesis of two new members of the $C_{2n}I_2$ family (**1**: n = 3, **2**: n = 4) by reaction of *N*-iodosuccinimide and silver nitrate

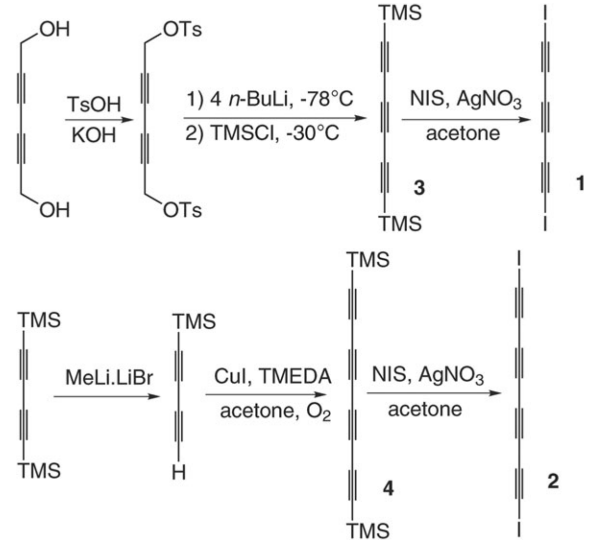


Scheme 2 Stepwise assignment of structural informations in the analysis of relationships between two different molecules.



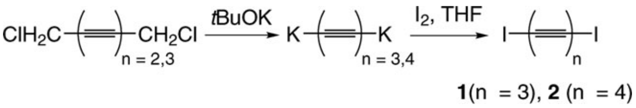
Scheme 3 Typology of chemical functions and local *carbo*-merization thereof.

with silyl-protected polyynes **3** and **4**, respectively (Scheme 4).[17] C_6I_2 and C_8I_2 (the *carbo*-mer of C_2I_2) are sensitive species exploding at 100 and 85 °C, respectively, and decomposing in a few days at room temperature. C_6I_2 can however be kept at −10 °C for several months.



Scheme 4 Goroff's synthesis of diiodohexatriyne and diiodooctatetrayne.[17]

Two years later, Hlavaty *et al.* prepared **1** and **2** by circumventing the formation of explosive silver alkynyde intermediates:[18] the method consists in the dehydrochlorination of bispropargylic dichloro derivatives (Scheme 5).



Scheme 5 Hlavaty's procedure for the preparation of IC_6I and IC_8I, the *carbo*-mer of the *carbo*-mer of I_2.[18]

Iodination of C_4I_2 **5** in concentrated hexane solution lead to tetraiodobutatriene. Without a careful handling, butatriene **6** decomposes to hexaiodobutadiene **7** *via* a disproportionation mechanism (Scheme 6).[19] Rather surprisingly, the cumulene **6** is easily isolated, and is stable in the solid state.

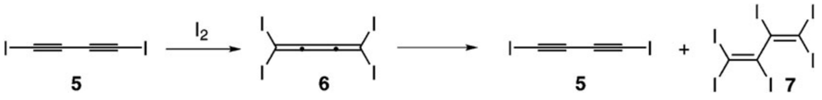
The weakness of the C–I bonds makes this compound a promising candidate as a precursor to carbon-rich molecules. Very recently, diiodobutadiyne **5** was found to form co-crystals with bis(nitrile)oxalamides, and this assembly spontaneously polymerizes to form poly(diiododiacetylene) **8** (PIDA).[20] This linear conjugated polymer is a promising precursor to fully ordered carbyne **9** (Scheme 7).

Goroff also reported an unusual solvent effect in the ^{13}C NMR spectra of iodoalkynes. The chemical shift of the carbon atom bound to iodine was described to change by as much as 15 ppm, depending on the solvent.[21] Specific intermolecular interactions between the Lewis-acidic iodoalkyne and basic solvents can explain this phenomenon. The Lewis acidity of iodoalkynes has indeed been studied by Laurence *et al.* who invoked donation of a iodine lone pair into the C–I antibonding orbital.[22] A mesomeric illustration of a possible hyperconjugative stabilization of the hypervalent iodine atom is suggested in Scheme 8.

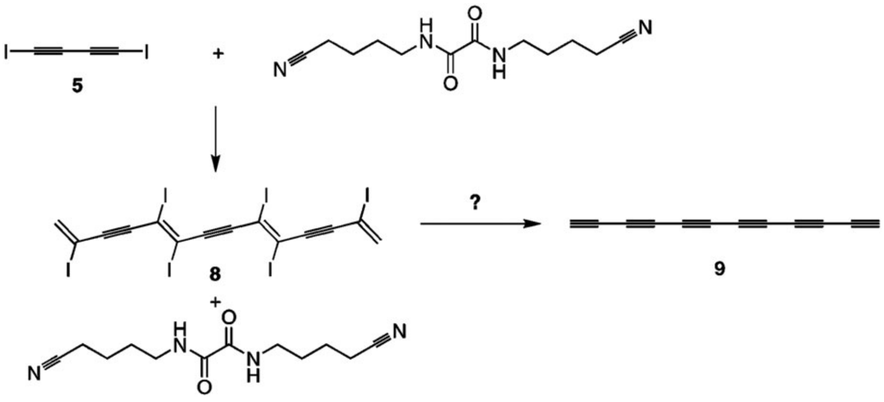
For C_2I_2 (and IC_6H as well), correlations with various empirical measures of solvent basicity confirmed this interpretation. More recently, theoretical DFT studies focussed on the NMR spectrum of C_2I_2 and its complexes with one or two ammonia molecules.[23]

Dichloro-, dibromo- and diiodo-representatives of the ZC_4Z family have been known since 1974,[16] in particular from their vibrational spectra.[24] An alternative preparation method of dichlorodiacetylene from hexachlorobutadiene at high temperature was later disclosed.[25]

The formation of the *carbo*-mer of F_2, FC_2F **10**, was first mentioned in 1958 in a patent,[26] but it was definitely identified in 1989 by its infrared (IR) absorption (1341 cm^{-1}) among the thermolysis products of difluoromaleic anhydride in an argon matrix.[27] However, difluorodiacetylene C_4F_2 **11** was obtained by fragmentation of hexafluorobenzene in an electrodeless



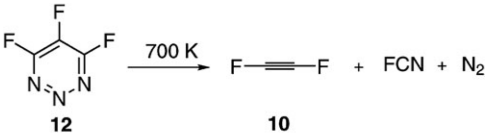
Scheme 6 Iodination of 1,4-diiodobutadiyne **5**.[19]



Scheme 7 Preparation of PIDA **8** from diiodobutadiyne **5**.[20]

Scheme 8 Interaction of a Lewis base B with iodoalkynes.

discharge in 1977.[28] The photoelectron spectra of C_2F_2 **10** and C_4F_2 **11** were compared. These compounds are extremely instable and explosive. In 1991, the first efficient synthesis of C_2F_2 **10** (in the pure state and in mmol quantities) was achieved by thermolysis of perfluoro-1,2,3-triazine **12** at 700 K (Scheme 9).[29] Although **10** slowly decomposes in the condensed phase even at −196 °C, its IR spectrum could be recorded. More recently, C_6F_2 has also been obtained by photolysis of benzenetetracarboxylic dianhydrides.[30]



Scheme 9 Bürger's synthesis of difluoroacetylene **10**.[29]

Several theoretical studies on dihalogeno-oligoacetylenes should also be mentioned, as they focussed not only on their structural parameters,[31] quadrupole moments,[32] and ^{19}F NMR spectra,[33] but also on their NLO properties.[34]

1.2 *Carbo*-mers of dialkali (Z = Li, Na, K)

Covalent dialkali, Li_2, Na_2, K_2 are stable in the gas phase only, but have been thoroughly studied at the theoretical level.[35] Their *carbo*-mers are strongly ionic diacetylides, which can be generated from acetylene in solution and used for synthetic purposes.[36] Their isolation in the pure state is however more problematic.

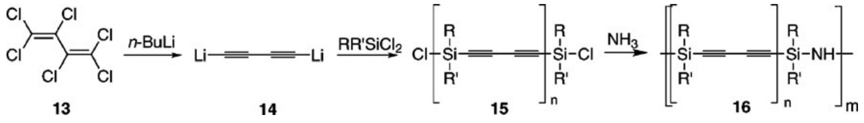
In 1896, Moissan reported on the existence of the *carbo*-mer of Li_2, LiC_2Li.[37] This compound was later quantitatively obtained by reaction of lithium vapor over amorphous coal or graphite at 800–900 °C.[38] A simpler patented preparation of the potassium analogue, K_2C_2, is based on the reaction of KOH with acetylene.[39] In 1999, Ruschewitz and Pöttgen reported an alternative synthesis from lithium and graphite by arc-melting.[40] They also described powder X-ray investigations of C_2Li_2 between −263 and 550 °C showing a reversible phase transition at 500 °C. A similar phase transition was also observed for Na_2C_2 and K_2C_2 (prepared by heating acetylene and the alkali metal in liquid ammonia).[41] The reported transition temperatures are 150, 320 and 500 °C for K_2C_2, Na_2C_2 and Li_2C_2, respectively. The phase transition of K_2C_2 has also been investigated by synchrotron powder X-ray diffraction and solid-state ^{13}C NMR spectroscopy.[42] At 150 °C, the tetragonal symmetry of K_2C_2 thus changes to a cubic symmetry with disordered C_2 dumbbells.

In 1990, dilithiobutadiyne was used for the preparation of silylene-diacetylene polymers (Scheme 10).[43] Hexachlorobutadiene **13** could be cleanly converted to dilithiobutadiyne **14** by reaction with four equivalents of butyllithium. Subsequent quenching with dichlorosilanes afforded polymers **15** in high yield.

A similar strategy was reported in 1998 for the preparation of the same kind of polymers containing siloxane and acetylene units.[44] The insertion of organometallic moieties such as ferrocenyl units in these siloxane-acetylene polymers, giving ceramics with peculiar thermal and magnetic properties was reported in a patent.[45] Very recently, linear conjugated poly-[(silylene)diacetylene silazanes] **16** were synthesized by ammonolysis of type **15** oligomers (Scheme 10).[46]

Zirconium-containing polymers were prepared by quenching dilithioacetylene or dilithiobutadiyne with $Cp_2{}^*ZrCl_2$.[47] In spite of their poor solubility, they could be characterized by elemental and thermogravimetric analyses, and by gel permeation chromatography. In 1994, a successful route to poly-(carborane-siloxane-acetylene)s using dilithiobutadiyne as precursor has been described.[48]

In 2002, Hlavaty *et al.* reported the synthesis of carbon nanotubes (CNTs) by spontaneous polymerization/



Scheme 10 Preparation of polymers from dilithiobutadiyne.[43,46]

carbonization of dilithium and dipotassium α,ω-hexatriynides ZC_6Z.[49] C_6Li_2 and C_6K_2 were polymerized and hydro- or methano-lyzed, and CNTs were thus produced. The synthesis of CNTs was also recently described by solid-state exchange reactions (metathesis) between hexachloroethane C_2Cl_6 and Li_2C_2 using FeS as initiator.[50]

A wide variety of molecules of general formula $ZC_{2n}Z$ has been reported, were Z is now a monovalent capping group such as SR_2,[51] SiR_3,[52] CN,[53] OR,[54] or an organometallic moiety. Many studies focussed on structural characteristics of the latter polyynes, such as bond lengths, linearity or distorsion of the chain.[55]

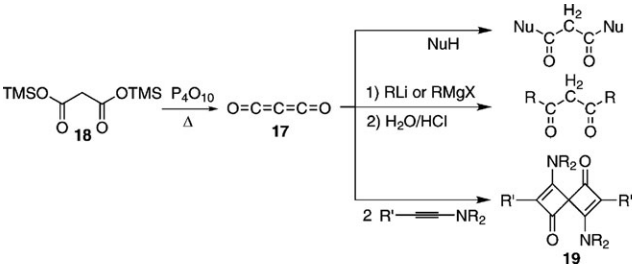
1.3 *Carbo*-mers of dichalcogens (Z = O, S)

While the odd-*n* members of the $O{=}C_n{=}O$ family have long been known, the even-*n* members remain either putative or elusive. In 1913, Staudinger and Anthes reported a first unsuccessful attempt to prepare C_2O_2, and all subsequent attempts failed hitherto.[56] This target is the *carbo*-mer of dioxygen, but it is often regarded as the long sought dimer of carbon monoxide, a degenerate singlet carbene.[57] Many theoretical investigations concluded to the existence of C_2O_2 as a covalently bound minimum on the potential energy surface,[58] but C_2O_2 has been claimed to be an intrinsically short-lived species.[57b]

Just as C_2O_2, C_2S_2 has also been theoretically predicted to be an absolute minimum on the potential energy surface.[58a,59] By contrast to C_2O_2 however, the CS dimer was incidentally evidenced by Sülzle and Schwarz in 1988 using neutralization–reionization mass-spectrometry.[60] Since then, several alternative routes to C_2S_2 have been reported. It was thus obtained by flash vacuum pyrolysis (FVP) of isoxazolones[61] and characterized by mass spectrometry, UV and IR spectroscopies.[62] Electrical discharge in an Ar–CS_2 gas stream allowed for the production of C_2S_2 from a simpler precursor.[63] Ethylenedithione has been described to be stable over extended periods of time at low pressure, even at high temperatures.

For a comparison purpose, molecules of general formula ZC_nZ (Z = O, S) with odd-*n* are worth mentioning. Carbon suboxide OC_3O, which cannot be considered as a *carbo*-meric molecule, was first prepared more than a century ago by Staudinger.[64] As discovered by Diels in 1906, OC_3O is a metastable gas at room temperature which readily polymerizes to a brown–red amorphous solid $(C_3O_2)_x$.[65] The crystal structure of the monomer has been solved recently, showing slight deviations from linearity.[66] Several methods for the preparation of C_3O_2 **17** have been described and the highest yields are provided *via* thermolysis of malonic acid bis-trimethylsilyl ester **18** over P_4O_{10} at 160 °C (Scheme 11).[67]

In atmospheric and combustion chemistry, C_3O_2 serves as a fuel. It is also used as a source of triplet carbon monoxide.[68] Furthermore, some applications of carbon suboxide as reagent for organic synthesis have been described. For example, in the presence of an excess of nucleophiles such as amines, alcohols, phenols or thiols, C_3O_2 forms malonamides, esters or thioesters (Scheme 11). Similarly, it furnishes diketones by reaction with organolithium or magnesium compounds followed by hydrolysis.[69] C_3O_2 can also be used for the synthesis of cyclic or heterocyclic compounds. For example, a twofold [2 + 2] cycloaddition of C_3O_2 with ynamines[70] has been reported to give 1,1′-spirocyclobutenones **19** (Scheme 11).[71]



Scheme 11 Preparation and examples of reactivity of carbon suboxide **17**.[67,69,71]

The case of C_5O_2, the *carbo*-mer of CO_2, is discussed in Section 4.5.

Many theoretical studies of ZC_nZ molecules dealt with both their structure[72] and their reactivity.[73] Either linear and bent structures were proposed for C_nO_2 derivatives.[74] While the early literature seemed to favor a nonlinear form,[75] IR and Raman spectra validated the linear structure.[76] DFT and *ab initio* calculations confirmed that these compounds are linear in their ground state. The ZC_nZ molecules exhibit a drastic odd/even alternation in stability and bond lengths, the odd-*n* being generally more stable than the even-*n*.[72]

2 *Carbo*-mers of diatomic hydrides ZH

From a general viewpoint, the *carbo*-mer concept might be analyzed by the thermochemistry of C_2 insertion, and in particular into Z–H bonds. For any atom Z of valence v, we might thus define the average standard enthalpy of 2C insertion as: $\Delta H^\circ_{2Cins}(Z) = \Delta H^\circ_f((HC{\equiv}C)_{n+1}ZH_{v-n-1}) - \Delta H^\circ_f((HC{\equiv}C)_nZH_{v-n})$. Inspection of experimental and calculated data indeed shows that the value is nearly constant (±1 kcal mol^{-1}) *versus n*, and that $\Delta H^\circ_{2Cins}(Z)$ varies in the range 50–70 kcal mol^{-1} (Table 1).[77] For non-metal atoms Z = H, F, Cl, Br, I, and atoms of higher valence (C, N, O, P, S), $\Delta H^\circ_{2Cins}(Z)$ turns out to vary as the electronegativity and, to a lesser extent, as the softness of Z.[78] Let us here notice that since the standard enthalpy of formation of the C_2 diradical has been estimated as $\Delta H^\circ_f({}^\bullet C{\equiv}C^\bullet)$ = 194.7 kcal mol^{-1},[79] the standard enthalpy of C_2 insertion (*carbo*-merization) into a Z–H bond is equal to $\Delta H^\circ_{C2ins}(Z) = \Delta H^\circ_{2Cins}(Z)$ –194.7 kcal mol^{-1}.

Carbo-mers of the halogen acids ZH are all much more unstable than their dihalogeno counterparts. In spite of this, monofluoro-oligoacetylenes of general formula $F(C{\equiv}C)_nH$ (n = 1–4) can be produced by electrical discharge and their rotational spectra have been recorded.[80] Monoiodo-oligoacetylenes $I(C{\equiv}C)_nH$ are also known for n = 1,[81] 2[82] and 3.[83] For example, the synthesis of iodohexatriyne HC_6I **20** was reported recently by Hlavaty from hexatriyne (Scheme 12). First, C_6H_2 was monolithiated by a stoichiometric amount of methyllithium at low temperature, then Li was subsequently substituted with iodine to give **20**.[83]

Table 1 Thermochemistry of C_2 insertion into Z–H bonds (data from ref. 77)

	ΔH°_f(298 K)	ΔH°_{2Cins}(Z)
H_2	0	
HC≡C–H	54.2	54.2
HF	−64.4	
HC≡C–F	6.0	70.4
HCl	−22.1	
HC≡C–Cl	45.5	67.6
HBr	−8.7	
HC≡C–Br	58	66.7
HI	+6.2	
HC≡C–I	71	64.8
PH_3	+2.21	
HC≡C–PH_2	59.5	57.3
SiH_4	−14.8	
HC≡C–SiH_3	51.5	66.3
CH_4	−17.9	
HC≡C–CH_3	(44.2)	62.1
(HC≡C)$_2$CH$_2$	104.5	60.3
(HC≡C)$_3$CH	163.0	58.5
(HC≡C)$_4$C	225.0	62.0
NH_3	−11.0	
HC≡C–NH_2	54	65
(HC≡C)$_2$NH	117	63
H_2O	−57.9	
HC≡C–OH	10	67.9
(HC≡C)$_2$O	78	68.0
H_2S	−4.8	
HC≡C–SH	60.0	64.8

Monoalkali-oligoacetylenes are of course also known and used as intermediates in the synthesis of substituted oligoacetylenic molecules. An example is reported above in the Scheme 12 for the preparation of the iodohexatriyne **20**. Several theoretical studies have also been performed on these mono-[84] or poly-yne carbon chains substituted on one side with an hydrogen atom and on the other side with an halogen or an alkali.[85]

3 *Carbo*-mers of other heterodiatomic molecules ZY (Y ≠ H, Z)

Beyond metallic salts (NaCl, CuI, *etc*..., which are highly ionic), heterodiatomic molecules can be exemplified by heterodihalogens (FCl, BrCl, ClI, BrI,...), by carbon and nitrogen monoxides (CO, NO), or by the cyanide ion (CN^-). The *carbo*-mer of these ZY molecules is just an "hybrid" of the *carbo*-mers of Z_2 and Y_2. The case of carbon monoxide: C═O deserves a particular mention: its *carbo*-mer: C═C═C═O has been trapped at low temperature. The structural and metal-coordinating properties of CO and C_3O have also been studied at the theoretical level.[7,12*b*]

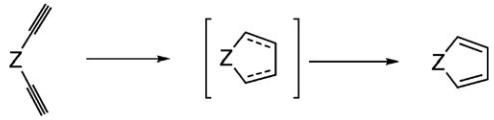
4 *Carbo*-mers of triatomic molecules ZX_2 (Z = C, O, S)

Diethynyl-Z (Z = O, S) are attractive species for various reasons. For example, in astrochemistry, such compounds exist in the interstellar medium; and from a synthetic viewpoint, they can be considered as potential precursors to aromatic thiophene or furan derivatives.

4.1 Diethynyl ether or "*carbo*-water"

The first synthesis of the trimethylsilyl-protected *carbo*-mer of H_2O was reported in 1989 by Ooi and Smithers,[86] while the dimethyl disubstituted derivative was described in 1962.[87] The synthesis proceeded in three steps (Scheme 13) and the resulting product appeared to be reasonably stable. However, a neat sample of bis(trimethylsilylethynyl) ether **21** decomposes over one night at room temperature and can only be stored in solution in a freezer.

To the best of our knowledge, the unprotected diethynyl ether which can be viewed as the free "*carbo*-water" has not been reported hitherto, but it has however been considered at the theoretical level. For example, it appears in a study by Schreiner concerning the ability of 1,4-diynes of general formula Z(C≡C–H)$_2$ to cycloaromatize in a Bergman-like process[88] (Scheme 14). This study indicates that the ideal Z should be σ-withdrawing and π-donating and finally concludes that diethynyl ether, in the presence of a Lewis acid, should be the most prone candidate to perform the Bergman-like cyclization.



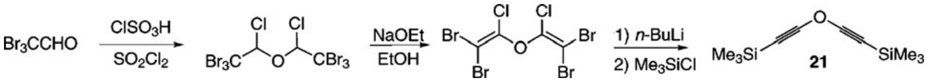
Scheme 14 The Bergman-like cyclization of hetero-diynes.[88]

4.2 Diethynyl sulfide or *carbo*-H_2S

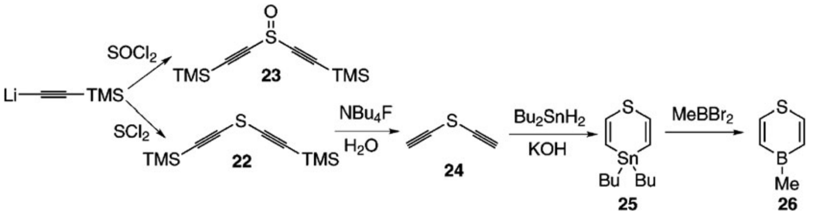
The first report on *carbo*-H_2S, was Brandsma's synthesis of the bis-trimethylsilyl-protected version **22** in 1978.[89] The latter was prepared by reaction of lithium trimethylsilylacetylide with SCl_2 at low temperature. This procedure was also used to synthesize the previously unknown dialkynyl sulfoxide **23** by reaction of a lithium alkynylide with $SOCl_2$ (Scheme 15).

In 1995, diethynyl sulfide **24** was used as starting material for the preparation of thiaborins.[90] It was obtained by desilylation of the bis-trimethylsilyl derivative **22** with tetra-*n*-butylammonium fluoride (TBAF), but it has not been isolated

Scheme 12 Monoiodohexatriyne synthesis.[83]



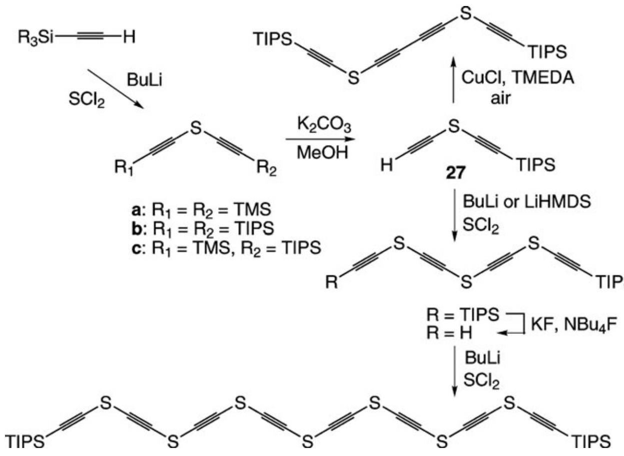
Scheme 13 Synthesis of the bis(trimethylsilylethynyl) ether **21**.



Scheme 15 Syntheses of protected and unprotected diethynyl sulfide and sulfoxide derivatives.[89,90]

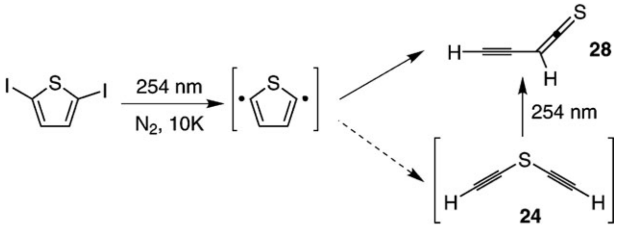
and was directly subjected to base-catalyzed dihydrostannylation (Scheme 15). The resulting thiastannin **25** was then transformed into thiaborin **26** by reaction with $MeBBr_2$. The low-field ^1H NMR chemical shifts of thiaborin **26** are indicative of a diatropic ring current and thus of the aromatic character of this molecule.

In 2000, the synthesis of oligoacetylenic sulfides with alternating sulfur atoms and acetylene or diacetylene units, has been reported using monoprotected diethynyl sulfide **28** as starting material.[91] This key monomer was first prepared using Brandsma's procedure[89] giving a mixture of three compounds (Scheme 16). The trimethylsilyl group was then removed under mild conditions, and the key monosilylated dialkynyl sulfide **27** was isolated after chromatography. Oxidative coupling under Hay conditions on one hand, and sulfurization with SCl_2 on the other hand, were used to elongate the chain of the oligoacetylenic sulfides. Monodeprotection of the resulting disilylated compounds using KF and a catalytic amount of TBAF, followed by another oxidative coupling or sulfurization reactions sequence, afforded higher oligoacetylenic sulfides.



Scheme 16 Synthesis of oligoacetylenic sulfides.[91]

The structure of diethynyl sulfide **24** as determined by microwave spectroscopy has been compared to the X-ray crystal structure of the diphenyl-substituted homologue,[92] showing that S–C≡C linkages are non-linear, as if the two C atoms bound to sulfur were repelling each other. The C–S bonds are intermediate between single and double bonds. Electronic structures and rearrangement pathways of several C_4H_2S isomers of **24** have been recently considered.[93] Matrix-isolated diethynyl sulfide **24** undergoes a photochemical rearrangement to its low-energy isomer, ethynyl thioketene **28**. The latter can also be obtained by photolysis of 2,5-diiodothiophene by a retro-Bergman cyclization *via* the diethynyl sulfide intermediate (Scheme 17).[94]

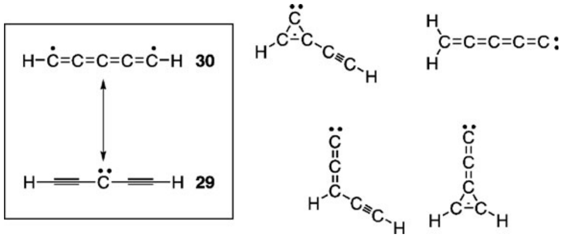


Scheme 17 C_4H_2S isomers obtained by irradiation of 2,5-diiodothiophene.[94]

Dialkynyl sulfides have also been involved in the synthesis of ruthenium and iron clusters. Indeed, oxidative addition of one S–C bond in the presence of ruthenium or iron carbonyls lead to clusters containing SC≡CR and C≡CR ligands.[95]

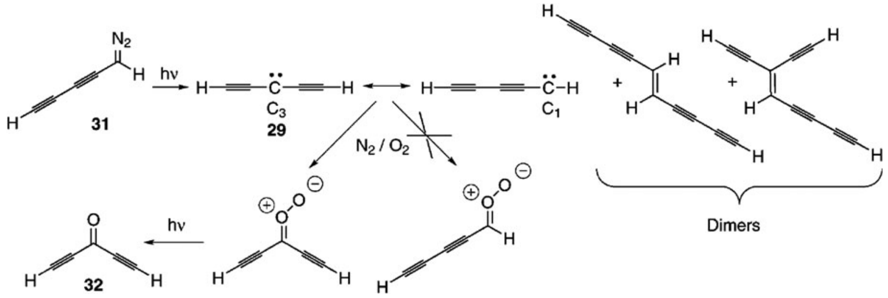
4.3 Diethynylcarbene or *carbo*-H_2C:

Triplet pentadiynylidene was generated in a neon matrix by reduction of HC_5H^+ and its electronic spectrum was recorded.[96] Theoretical studies of the singlet and triplet states of C_5H_2 focussed on their geometries and frontier orbitals. The computed structure of pentadiynylidene revealed a shorter distance between the central carbon atom and its neighbours than in a classical single bond between two C_{sp} atoms. Furthermore, the triple bonds were found to be longer than typical ones. These features can be rationalized by the existence of two resonance structures: the diethynylcarbene **29** and the 1,5-cumulenic diradical **30** (Scheme 18).[97]



Scheme 18 The diethynylcarbene **29** and its isomers.

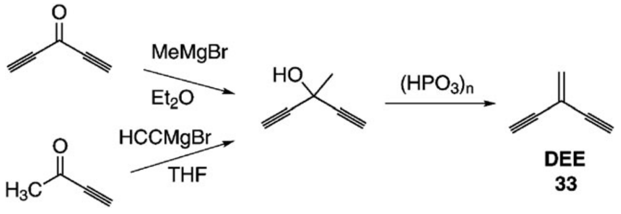
Five isomers of C_5H_2 were investigated theoretically, the HC_5H linear carbene **29** being the apparent global energy minimum. Three of the corresponding radical anions were also generated in the gas phase.[98] Very recently, a synthetic strategy for preparing diacetylenic carbene from diazo precursors **31** was described.[99]



Scheme 19 Synthesis of the diethynylcarbene **29** from diazo precursors and oxygen trapping experiments.[99]

Long-wavelength photolysis of matrix-isolated **31** afforded the expected diethynylcarbene **29**, which was evidenced by IR spectroscopy. UV-visible spectrum of the photolysis mixture revealed also the formation of the dimers of the carbene. Oxygen-trapping experiments by irradiation of **31** in an N_2 matrix doped with O_2 revealed that the trapping occurred regioselectively at the C_3 position of the carbene (and not at the C_1) thus giving the β-diynone **32**, as theoretically anticipated (Scheme 19).

While diynone **32** is the oxygen-trapped diethynylcarbene, diethynylethene (DEE) **33** is the methylene-trapped counterpart. The first synthesis of **33** was described by Böhm-Gössl *et al.* in 1963 (Scheme 20).[100]



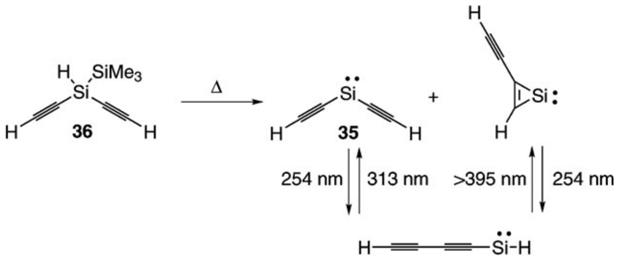
Scheme 20 Böhm's first synthesis of *gem*-diethynylethene **33**.[100]

Using the same nucleophilic addition/elimination procedure, substituted *gem*-DEEs have been prepared. Similarly, tetraethynylethenes (TEEs) are the dimers of the corresponding diethynylcarbenes. The tetraphenyl derivative **34** has been the first member of this family to be reported by Hori *et al.* in 1969.[101] A mixture of three compounds was obtained upon treatment of 3-bromo-1,5-diphenylpenta-1,4-diyne with potassium *tert*-butoxide (Scheme 21). Since then, several other routes to TEEs, with four identical substituents or with two different ones (in *cis* or *trans* positions) have been proposed.

The syntheses, properties and reactivities of DEEs and TEEs are well described in a recent review by Nielsen and Diederich and will not be developed here.[102]

4.4 Diethynylsilylene

Diethynylsilylene **35** has been described by Maier *et al.* in 1998.[103] It was identified among the mixture of compounds generated by pyrolysis of 1,1-diethynyl-2,2,2-trimethyldisilane **36** and subsequent matrix photolysis of the thermolysis products (Scheme 22).

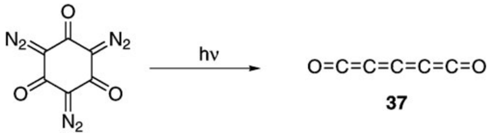


Scheme 22 Maier's synthesis of the diethynylsilylene **35**.[103]

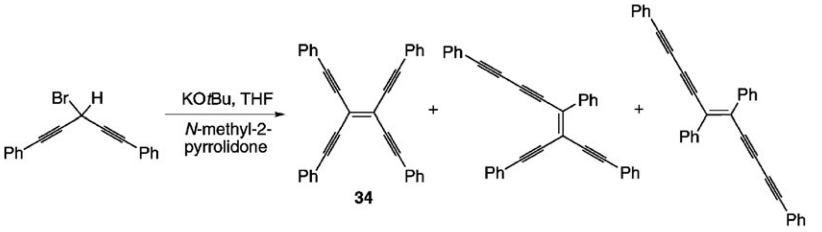
The three compounds obtained by irradiation of the thermolysis mixture are three isomers of general formula SiC_4H_2 which were identified by comparing their IR spectra with the calculated ones.

4.5 C_5O_2 or *carbo*-CO_2

The "*carbo*-carbon dioxide" C_5O_2 **37** has been first synthesized in 1988 by photolysis of a tris-diazoketone, and was reported to be stable in solution in organic solvents at room temperature although very reactive (Scheme 23).[104]



Scheme 23 Photolytic preparation of C_5O_2 **37** from a tris-diazoketone.



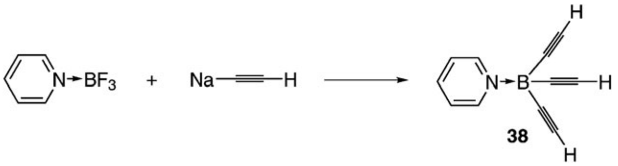
Scheme 21 First synthesis of a tetraethynylethene (TEE) derivative.[101] (For exhaustive discussion of TEE chemistry see ref. 102).

The same year, most of the bands of its Raman and IR spectra were described.[105] In 2002, the development of a novel multipass optical system for FTIR jet spectroscopy allowed for obtaining the total IR spectrum of C_5O_2.[106]

5 *Carbo*-mers of ZH_3 molecules (Z = group 13 or 15 element)

5.1 Triethynylborane or *carbo*-BH_3

While the preparation of sodium tetraalkynylborate[107] and ammonium tetraalkynylborate[108] were already known, the first synthesis of trialkynylboranes was described in 1964.[109] All attempts to prepare triethynylborane either from BF_3, BCl_3 or $B(OMe)_3$ and sodium acetylide resulted in the formation of polymeric compounds. Amine complexes were however successfully obtained by reaction of sodium acetylide with the corresponding amine–boron halide adducts (Scheme 24).



Scheme 24 Synthesis of pyridine-protected triethynylborane **38**.[109]

Various triethynyl borane-amines were also prepared by transamination of the triethynylborane–pyridine adduct **38**. Later, the synthesis and properties of triethynylboranes stabilized as tetrahydrothiophene, tetrahydrofuran or diethyl ether adducts were also reported.[110] But all attempts to prepare donor-free trialkynylboranes have failed hitherto.

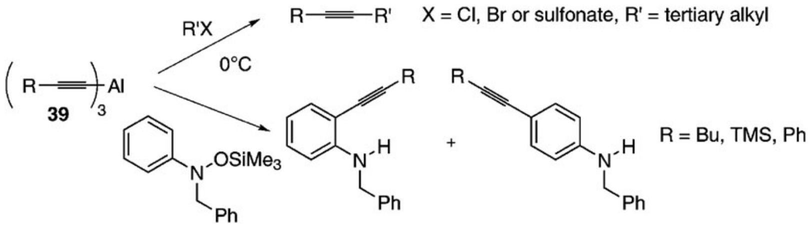
5.2 Triethynylaluminium or *carbo*-AlH_3

Trialkynylaluminium derivatives **39** were first prepared in 1962 from $AlCl_3$ and sodium alkynydes,[111] and Negishi and Baba described the alternative use of lithium acetylides in 1975.[112] Their reactivity towards tertiary alkyl halides has also been considered, leading to cross-coupling products in high yield (Scheme 25). In 1983, Yamamoto and co-workers used $AlBr_3$ instead of $AlCl_3$ for a more reproducible preparation of trialkynylaluminium reagents. Friedel–Crafts transfer of an alkynyl group to the aromatic nuclei of arylhydroxylamine afforded alkynylanilines which were further used as building blocks for the elaboration of polyaromatic compounds and fused heterocycles (Scheme 25).[113]

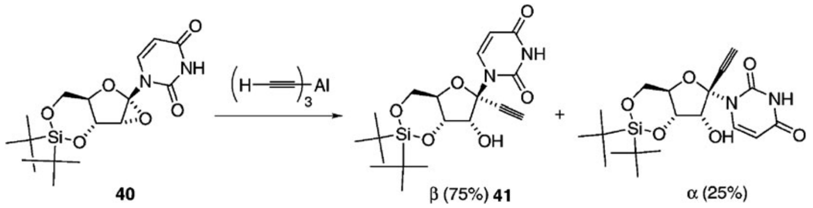
More generally, trialkynylaluminium derivatives are useful reagents in stereoselective organic synthesis. For example, Haraguchi recently proposed their application for a novel synthesis of 1′-branched ribofuranosyl nucleosides.[114] Triethynylaluminium thus reacted with 1′,2′-α-epoxide **40** in a preferential *syn*-ring opening manner, yielding preferentially the β-anomer **41** of the 1′-ethynyl uridine derivative (Scheme 26).

Trialkynylaluminium reagents were also used by Padmanabhan and Nicholas in $Co_2(CO)_6$-activated attack of propargylic carbocations generated in the absence of auxiliary Lewis acid (Scheme 27).[115]

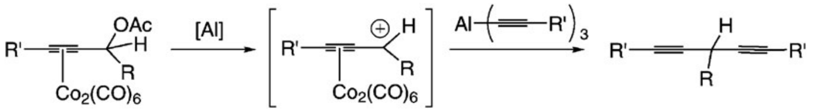
Sodium tetraalkynylaluminates **42** can be obtained in high yield by reaction of $NaAlH_4$ with terminal alkynes. They react with aryl bromides in the presence of Pd(0) or Pd(II) catalysts without formation of homocoupling or dehydrohalogenation product from the bromoarene substrate (Scheme 28).[116] This process is applied to the selective conversion of polybromo compounds into polyalkynes, while chloro, cyano, triflate or acyloxy substituents are not affected.



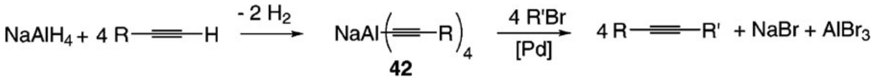
Scheme 25 Reactivity of trialkynylaluminium derivatives **39**.[112,113]



Scheme 26 Synthesis of 1′-ethynyl uridine derivatives using triethynylaluminium.[114]



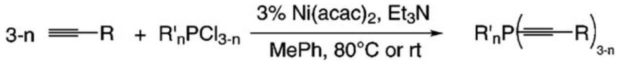
Scheme 27 Attack of a Nicholas' carbocation by a trialkynylaluminium reagent.[115]



Scheme 28 Synthesis and reactivity of sodium tetraalkynylaluminates **42**.[116]

5.3 Triethynylphosphine or *carbo*-PH_3

Triethynylphosphine (TEP) was first obtained in 1964 by addition of three equivalents of ethynylmagnesium bromide to PCl_3.[117] Its crystal structure was determined few years later, thus evidencing a non-linearity of the P–C≡C bonds.[118] This compound is reported to be explosive, while its *tert*-butyl substituted analogue is more stable.[119] Tris(trimethylsilylethynyl)phosphine has also been described in 1969.[120] All syntheses of alkynylphosphines are usually accomplished by treating P(III)-halides with sodium, lithium or magnesium acetylides. These methods are thus more efficient for the preparation of tris-alkynylphosphines. In 2003, Beletskaya *et al.* reported a route to all kinds of alkynylphosphanes by transition-metal catalyzed cross-coupling reaction (Scheme 29).[121]



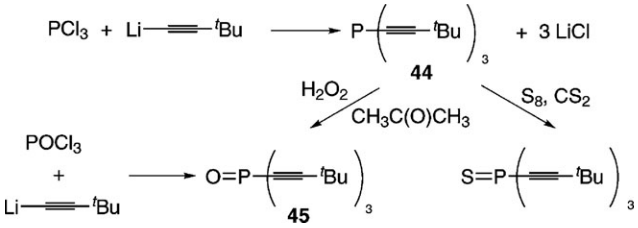
Scheme 29 Beletskaya's route to alkynylphosphanes.[121]

Several Pd and Ni catalysts have been tested. $Ni(acac)_2$ or $Ni(cod)_2$ allowed for high yield production of mono-, bis- or tris-alkynylphosphanes, while palladium complexes proved to be less active.

In 2005, the first example of organometallic complex with a TEP ligand [*fac*-Re(bpy)$(CO)_3$(TEP)$]^+$ was prepared from Re(bpy)$(CO)_3$(OTf).[122] Its photochemical properties proved to be very different from those of the PPh_3 complex analogue. To our knowledge, the sole application of TEP ligands in catalysis was reported in 2006 by Sawamura and co-workers.[123] Indeed, TEPs bearing bulky substituents were applied to the gold catalyzed alkyne cyclization (Scheme 30). It was then found that the holey catalytic environment created by bulky end groups at the alkyne termini of the TEP ligand is crucial to promote the cyclization reaction.

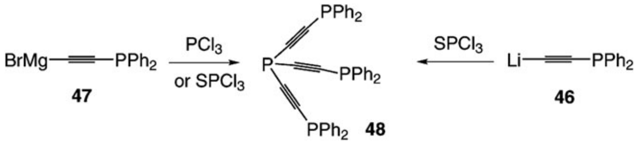
The bonding in $P(C{\equiv}CH)_3$ has been systematically studied at the theoretical level, and compared with those of $O{=}P(C{\equiv}CH)_3$ and $S{=}P(C{\equiv}CH)_3$ derivatives.[124] One striking feature is the high zwitterionic character of the oxide, with a dipole moment of 5.3 D resulting from the π-donation of ethynyl substituents into the antibonding orbitals of the P=O bond.

In 1969, Reiff and Pant described the synthesis of trialkynyl-P(V) derivatives by oxidation or treatment with sulfur of the corresponding trialkynyl-P(III) precursor **44** (Scheme 31),[119] but trialkynylphosphine oxide **45** were also prepared by addition of three equivalents of lithium alkynydes to $P(O)Cl_3$.



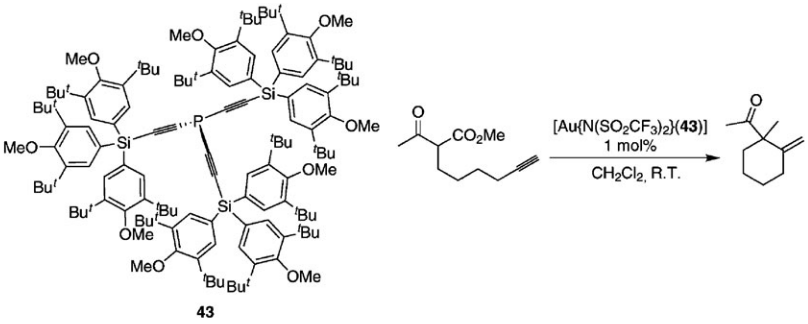
Scheme 31 Routes to trialkynylphosphine oxides and trialkynylthiophosphines.[119]

In their attempts to synthesize new phosphorus-containing dendrimers, Majoral and co-workers reported the preparation of a trialkynylphosphine derivative bearing one phosphino group on each alkynyl moiety (Scheme 32).[125] Reaction of the magnesium or lithium alkynyde (**46** or **47**) with $SPCl_3$ afforded the tetraphosphine **48**, albeit in low yield. This result is quite surprising since it implies a desulfuration step which is quite uncommon with organolithium derivatives. This tetraphosphine **48** can also be obtained in better yield using directly PCl_3 with the Grignard reagent (Scheme 32).



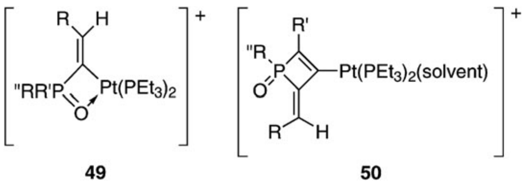
Scheme 32 Majoral's synthesis of a trialkynyltetraphosphine **48**.[125]

Lukehart studied the coordination chemistry of mono-, di- and tri-alkynylphosphine oxides with a cationic platinum–hydride moiety.[126] The Pt–H bond of [*trans*-PtH$(PEt_3)_2$(solvent)$]^+$ adds regioselectively to one alkynyl substituent of alkynylphosphine oxides, giving Pt,P-μ-alkenylidene complexes **49**. However, with *tert*-butylethynyl substituents, addition of a second



Scheme 30 Application of a TEP ligand in catalysis.[123]

alkynyl group lead to complexes **50** with a 2-alkylidene-1,2-dihydro-3-phosphete P-oxide ligand (Scheme 33).

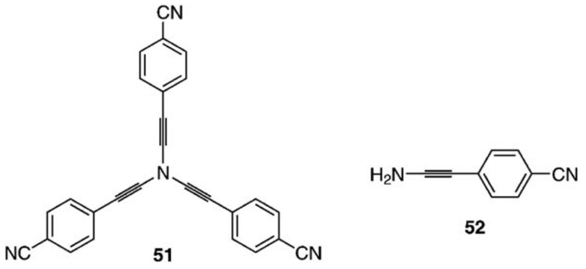


Scheme 33 Platinum complexes formed with mono-, di- or tri-alkynylphosphine oxide ligands.[126]

5.4 Triethynylamine or *carbo*-NH_3

Rather surprisingly, while trisalkynylphosphines and oxide thereof are widely exemplified, a close inspection of the literature suggests that no trialkynyl amine has ever been described. Although monoalkynylamines (ynamines) are well known,[70] dialkynylamines are also not known, or at best poorly described.[127] Schreiner showed theoretically (at the DFT level) that among a wide family of α-dialkynyl derivatives $(HC{\equiv}C)_2Z$ (Scheme 14) their kinetic and thermodynamic propensity to cyclize as "singlet" diradicals is significant and maximum for $Z = OH^+$, and just below for $Z = NH_2^+$.[88] Owing to the basicity of dialkynylamines, it is plausible that traces of proton might be sufficient to induce the formation of the Schreiner ammonium biradical, which could irreversibly decompose or polymerize. This scenario might explain why the less basic dialkynyl ethers are known while dialkynylamines are not.

Due to their octupolar character, putative trialkynylamines have however attracted some interest in theoretical nonlinear optics, in particular for their two-photon absorption (TPA) properties (Scheme 34).[128] The nitrogen atom of **51** was indeed devised to allow delocalization of excited-state wavefunctions through strong interactions between three (*p*-cyanophenyl)-ethynyl substituents exhibiting optimal ground-state polarization.



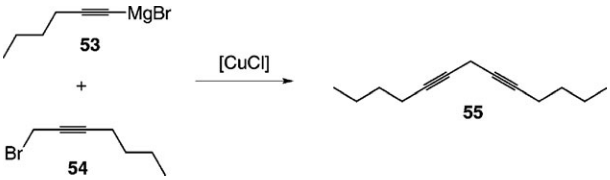
Scheme 34 Alkynylamines theoretically studied for their promising TPA properties.[128]

Comparison of the transition dipole moments in the octupolar trialkynylamine **51** calculated at the INDO/MRD-CI level with those predicted by the exciton theory from the dipolar chromophore p-$(CN)C_6H_4$–$C{\equiv}C$–NH_2 **52** shows that charge transfer per push–pull alkynyl substituent in **51** is twice that occuring in **52**. Since the two lowest excited states of **51** are also non-degenerate (by 0.5 eV) and since the corresponding $g \rightarrow e/g \rightarrow e'$ transition energies are different from the first transition energy of **52**, the TPA spectrum of **51** displays two separate bands: the maximum values of the TPA cross-section is much higher than those predicted from the exciton theory which assumes that the substituents are independent. The intense cross-talk between the arms thus accounts for the modulation of TPA from **52** to **51**.

6 *Carbo*-mers of ZH_4 molecules (Z = group 14 element)

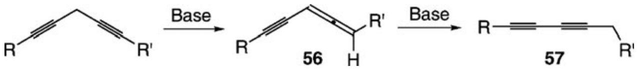
6.1 Tetraethynylmethane or "*carbo*-methane"

As an introduction to tetraethynylmethane, the *carbo*-mer of CH_4, we will focus briefly on partially alkynylated derivatives and first on 1,4-diynes, also called "skipped" diynes. The most natural route to 1,4-diynes commonly proceeds through alkynyl—propargyl couplings. The methods for their preparation have been reviewed in 2003.[129] After several unsatisfactory attempts by Lai,[130] Bell[131] and Taylor,[132] their first efficient synthesis was reported in 1955.[133] CuCl was found to be the most efficient catalyst to perform the reaction of hexynylmagnesium bromide **53** with 1-bromohept-2-yne **54**, giving the expected diyne **55** in 50–80% yield (Scheme 35).



Scheme 35 Gensler's synthesis of "skipped" diynes.[133]

Other metals than Mg have also been tested in this reaction, confirming that the use of Grignard acetylides and CuCl as catalyst is the method of choice.[134] The method was applied to the synthesis of several "skipped" diynes.[135] Their stability has also been discussed,[136] and in particular with respect to possible rearrangements. A base-catalyzed isomerization thus proceeds *via* the allene–acetylene **56**, the conjugated 1,3-diyne **57** being the final product (Scheme 36).[137]



Scheme 36 Base-catalyzed isomerization of "skipped" diynes.[137]

Copper(I) alkynydes can also be generated from terminal alkynes by action of a weak base. Indeed, propargylic halides can be treated with 1-alkynes in the presence of CuI, Na_2CO_3 and tetra-*n*-butylammonium chloride,[138] or by a mixture of K_2CO_3, CuI and NaI.[139] Recently, Caruso and Spinella reported that changing the alkali metal cation of the carbonate from potassium to caesium improved the reaction selectivity, thus limiting isomerization or polymerization.[140]

The coupling of "skipped" diynes into tetraynes was early applied to the synthesis of arachidonic acid.[141] More recently, they appeared as intermediates in the preparation of many natural products such as pheromones,[142] ichthyotoxic macrolides[143] or Crocacin which are potent antifungal and cytotoxic agents.[144]

Trialkynylmethanes were first synthesized in 1928 by Salzberg and Marvel who prepared tri-*tert*-butylethynyl carbinol **58** and the corresponding bromide **59**, as a synthon of the hexayne dimer **60** (Scheme 37).[145]

Other trialkynyl carbinols were reported shortly after.[146] The non-substituted triethynyl carbinol **62** was first described by Dillard and Pavey in 1971, albeit in poor yield (1–8%), by reaction of sodium acetylide with diethyl carbonate.[147] A much more efficient procedure involving the intermediate preparation of the protected tris(trimethylsilylethynyl) carbinol **61** was described by Alberts and Wynberg in 1988 (Scheme 38).[148] Deprotection of the acetylenic moieties finally led to the expected triethynyl carbinol **62** in good yield.

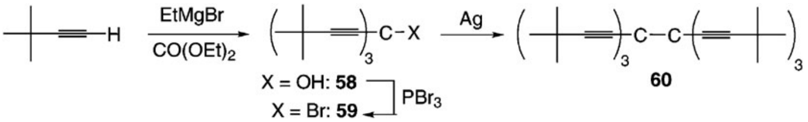
Using the same methodology, Diederich and co-workers recently prepared a chiral triethynyl carbinol **63** bearing three different silylated substituents in its racemic form.[149] This molecule was subsequently used for the synthesis of the expanded cubane **64** through a sequence of selective deprotections and C_{sp}–C_{sp} coupling reactions of the free terminal acetylene units (Scheme 39).

More recently, Pale and co-workers reported a direct synthesis of racemic trialkynyl carbinols possessing one terminal alkyne moiety and two differently protected ones.[150]

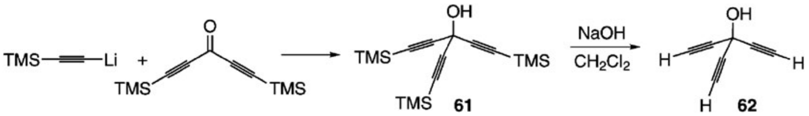
The first asymmetric synthesis was described recently by Diederich and co-workers.[151] Starting from enantiomerically pure ethyl (–)-(*S*)-lactate, the optically pure tris-propargylic alcohol derivative was obtained by a 11-step procedure involving preparative HPLC separation. The key step is a diastereoselective addition of a lithium acetylide to an optically active alkynyl ketone.

The preparation of a tetraalkynylmethane was early claimed by Cadiot and co-workers *via* the condensation of propynylmagnesium bromide on carbon tetrabromide,[152] but subsequent attempts to reproduce this synthesis failed.[153] Tetraethynylmethane itself (TEM) **65** was first prepared by Feldman *et al.* in 1993 from a dialkynyl ketone in a 10-step procedure (Scheme 40).[153] The same authors also reported preliminary results concerning the reactivity of the tris-trimethylsilylated TEM **66** in C_{sp}–C_{sp} coupling reactions.[154]

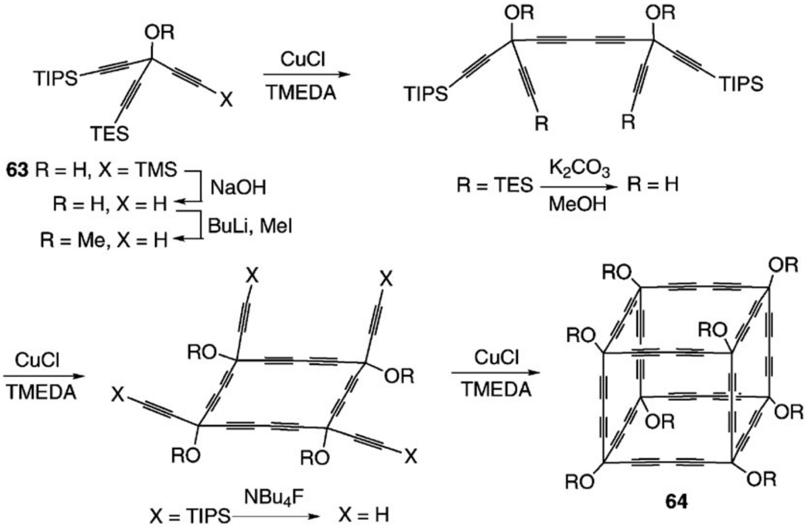
Solid TEM rapidly decomposes at room temperature even in the absence of oxygen, but it can be kept in solution at 0 °C for several weeks without any deterioration. Tris-trimethylsilylated TEM **66** is much more robust and its X-ray crystallographic analysis has been performed, revealing a significant geometric distortion due to the attachment of four alkyne units around a single sp^3 carbon atom.[153] The molecular structures and vibrational frequencies of six TEM derivatives were theoretically studied by Schaefer III in order to explain the 0.04 Å contraction observed for the C≡C bonds in the crystal structure of **66**.[155] None of the theoretically considered TEM derivatives showed a similar contraction of the triple



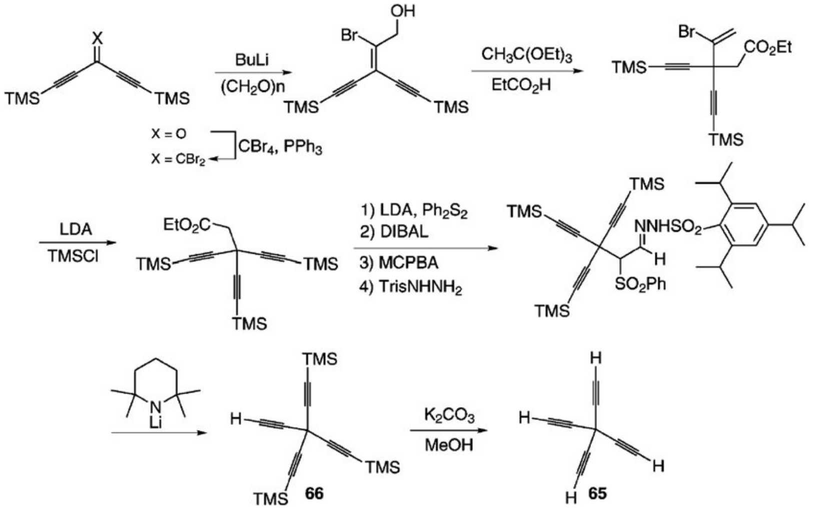
Scheme 37 First preparation of trialkynylmethane derivatives and application to the synthesis of a hexaalkynylethane.[145]



Scheme 38 Alberts' route to the unprotected triethynyl carbinol **62**.[148]



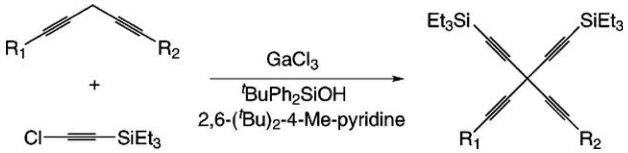
Scheme 39 Diederich's synthesis of expanded cubane.



Scheme 40 Synthesis of tetraethynylmethane **65**.[153]

bonds. Experimental XRD results were thus explained by a π-electrons compression in **66** due to the close vicinity of the four triple bonds and the authors suggest that neutron diffraction experiments should confirm this hypothesis.

Very recently, Yamaguchi and co-workers described a novel straightforward synthesis of TEM derivatives *via* the C–H activation of 1,4-diynes with gallium trichloride and ethynylation with a chloroacetylene derivative (Scheme 41).[156]



Scheme 41 Yamaguchi's straightforward synthesis of TEM derivatives.[156]

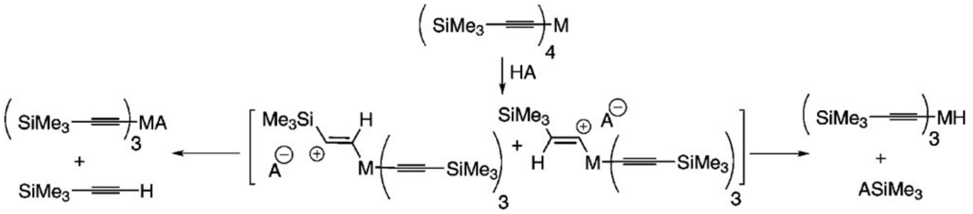
The development of carbon-rich precursors for the construction of novel nanostructures have attracted much attention in the recent years. Within this prospect, TEM is an interesting monomer whose polymerization could lead to a three-dimensional carbon network. In 1996, Feldman *et al.* reported attempts to prepare such fascinating materials using metal-mediated Hay-coupling procedures.[157] Analysis of the resulting black solids revealed that alkyne hydration occurred during the dehydropolymerization process.

6.2 Tetraethynylsilane or *carbo*-SiH_4

The syntheses of tetraethynylsilane and tetraethynylgermane were first reported in 1966, using sodium acetylide and ZCl_4 (Z = Si, Ge) in THF.[158] They are solids with high vapor pressures and sublime in closed tubes even at room temperature. As the first homologue, tetrapropynylsilane was obtained by Cadiot and co-workers by addition of propynylmagnesium bromide to $SiCl_4$.[159a] This compound has been later prepared from Si_2Cl_6 and propynyllithium allowing for complete characterization by X-ray diffraction and solid-state ^{13}C magic angle spinning NMR analyses.[159bc] It was also shown that dissolving this molecule in nematic liquid crystal lead to appearance of linear dichroism due to a lowering of symmetry from T_d to D_{2d} or C_{3v}.[159d]

In 1990, tetrakis(trimethylsilylethynyl)silane, germane and stannane were prepared from lithium trimethylsilylacetylide and ZCl_4.[160] The ability of group **14** elements (Si, Ge, Sn) to stabilize vinyl cation intermediates was discussed, concluding that the protonation of a ''dimetallated'' acetylene proceeds *via* the more stable β-carbocation (stronger β-effect) and leads, after loss of the better stabilizing group, to a ''monometallated'' acetylene (Scheme 42).

The β-cation stabilization varies in the order: Sn > Ge > Si, but also depends on the substituents. For a given metal, the β-effect is reduced by the substituents in the order $sp^3 > sp^2 > sp$. These trends correspond to the relative electronegativity order.

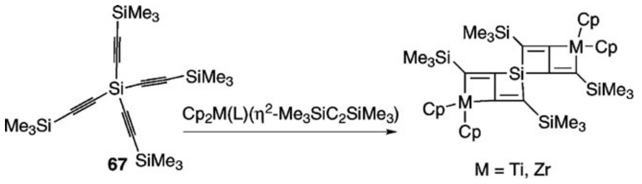


M = Si, Ge, Sn
AH = CF_3SO_3H, $MeSO_3H$, CF_3CO_2H, CCl_3CO_2H, $CHCl_2CO_2H$, CH_2ClCO_2H

Scheme 42 Competitive protonation of ''dimetallated'' acetylenes.[160]

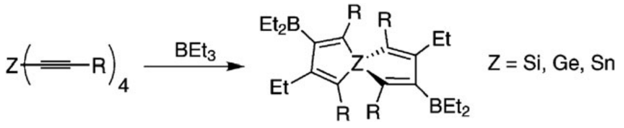
The coordinating ability of the triple bonds of tetrakis-trimethylsilylethynyl Z (Z = Sn, Ge, Si) was also examined in order to determine if a $Co_2(CO)_6$ moiety would facilitate the cleavage of the Si–C bond. The proximity of several alkynes influences the feasibility and reactivity of the $Co_2(CO)_6$ complexes. For Z = Ge and Si, the Z–C bonds are shorter, and only two dicobalt hexacarbonyl units can be coordinated. For Z = Sn, all the four triple bonds can be complexed.[161]

In 2000, Rosenthal also reported on the coordination chemistry of the TMS-protected tetraethynylsilane **67** with two metallocene sources, $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ and $Cp_2Zr(THF)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ was reported (Scheme 43).[162]



Scheme 43 Coordination of **67** with titanium and zirconium complexes.[162]

Wrackmeyer *et al.* reported the organoboration of tetra-alkynylsilanes,[163] or hexaalkynyldisilanes,[159b] giving 1,1-spirobissilole derivatives. The general method has been recently reviewed (Scheme 44).[164]



Scheme 44 Organoboration of tetraalkynyl–Z (Z = Si, Ge, Sn).[164]

Finally, a theoretical study of the structure and vibrational analysis of tetraethynylsilane must be mentioned.[165]

6.3 Tetraethynylgermane or *carbo*-GeH_4

After the first synthesis of tetraethynyl-germane and -silane in 1966,[158] TMS-protected tetraethynylgermane **68** was prepared by Corriu and co-workers in 1988 from a dianionic germanium complex **69** which proved to be more reactive than $GeCl_4$ or $GeBr_4$ (Scheme 45).[166]

In 1993, the simpler procedure previously mentioned for silicon[160] was reported by Brook and co-workers to give good yields of tetraalkynylgermanes from the corresponding lithium alkynylides and germanium tetrachloride.[167] Wrackmeyer and co-workers studied the reaction of tetraalkynylgermanium derivatives (R = Me, Ph) with triethylborane, giving spirogermanes as was observed with silicon (Scheme 44).[168]

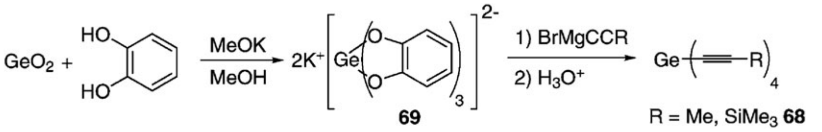
The structure and vibrational analysis of tetraethynylgermane were also studied at the theoretical level.[169]

6.4 Tetraethynylstannane or *carbo*-SnH_4

In 1990, TMS-protected tetraethynylstannane was prepared according to the procedure previously described for Si and Ge analogues.[160] Le Quan and Cadiot reported earlier the preparation of tetrapropynylstannane by reaction of sodium alkylidyne and $SnCl_4$ in refluxing hexane.[170] The *tert*-butylethynyl substituted derivative was also reported.[171]

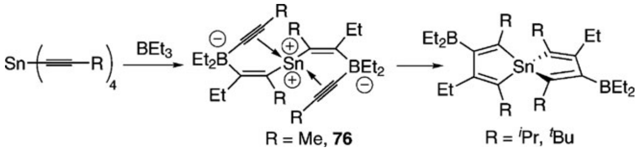
In 2002, Wrackmeyer *et al.* reported that exchange reactions occurred when mixing tetrakis-trimethylsilylethynylstannane **70** with $SnCl_4$ or $SnBr_4$, giving mixtures mainly containing dihalogeno-bis(trimethylsilylethynyl)stannanes.[172] Treatment of these mixtures with triethylborane afforded borylstannoles **71** and boryl alkenes **72** *via* halo intermediates **73** and **74**, respectively (Scheme 46). A slow precipitation of tin(II) halides was observed, thus indicating the weakness of the Sn–C bonds. Similarly, the reaction of **70** with neopentyl-9-BBN gave spirotin **75** (Scheme 46), whose structure was determined by X-ray diffraction analysis:[173] the tin atom lies in an extremely distorted tetrahedral environment. Because of the bulkiness of the substituents, the stannole rings deviate slightly from planarity.

The same procedure applied to non-protected tetraethynylstannane gave an intractable mixture of products.[164] From tetrapropynylstannane, a bis-zwitterionic intermediate **76** was formed, but decomposed above −20 °C to give a mixture containing stannole derivatives (Scheme 47).[174] With more bulky substituents (R = ^{i}Pr, ^{t}Bu), the 1,1′-spiro-bistannoles



Scheme 45 Preparation of tetraalkynylgermanes from a dianionic germanium complex.[166]

Scheme 46 Exchange reactions and reactivity of alkynylstannane derivatives.[172,173]



Scheme 47 From tetraalkynylstannanes to 1,1′-spiro-bistannoles.[174,175]

were obtained in very good yields, as it was observed for silicon and germanium analogues.[175]

In 2003, Napolitano *et al.* reported a theoretical study of the energetic consequences of the coordination geometry at Pd and Sn on the Stille transmetallation.[176] As a model system, the transfer of an ethynyl group from tetraethynylstannane to $PdBr(PH_3)_2(CCH)$ was selected. These investigations strongly support the π-complexation of a stannane triple bond at the Pd center, after displacement of the phosphine or bromine ligand.

As for Si and Ge, Jensen's theoretical study also dealt with vibrational frequencies and structural determination of tetraethynylstannane.[177]

6.5 Tetraethynyllead or *carbo*-PbH_4

Tetraethynyl lead derivatives are poorly documented. In 1967, the first synthesis of tetrasilylated tetraethynyllead was based on the use of $Pb(OAc)_4$ and trimethylsilylethynylmagnesium bromide.[178] Tetra-*tert*-butylethynyllead was also prepared by reaction of lithium acetylide and $PbCl_4$,[171] while the tetrapropynyllead was obtained from K_2PbCl_6 and propynyl lithium.[179] Its IR and Raman spectra were also described.[180]

The four tetrakis-trimethylsilylethynyl-M analogues (M = Si, Ge, Sn and Pb) were examined using NMR techniques. This study gave evidence of electronic π-interactions through the acetylene wire connecting Si with Pb, Sn, Ge or Si.[167]

7 *Carbo*-mers of unsaturated functional groups

After having considered the *carbo*-mers of atom-centered functions, the *carbo*-mers of common bond-centered functions is now surveyed.

7.1 Cumulenones or "*carbo*-ketones"

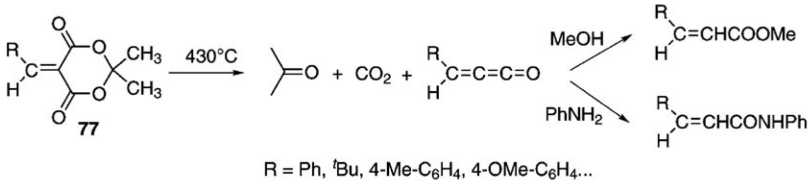
Alkylidene- or arylmethylidene-ketenes have been postulated on several occasions as reaction intermediates, but they had never been evidenced before 1974 when they were exemplified by FVP of substituted Meldrum's alkenes **77** (Scheme 48).[181] These highly reactive species were trapped with methanol or aniline. Nevertheless, the IR spectra of the FVP mixture showed a strong absorption at about 2090 cm^{-1} which was attributed to the cumulenone moiety.

One year later, Chapman *et al.* reported the formation of methylene ketenes in an attempt to prepare benzyne **81** by irradiation of 3-diazobenzofuranone **78** at low temperature.[182] Two primary products in photochemical interconversion were described, one of them being the methylene ketene **79** (favored at short wavelength: 254 nm), and the other the ketene **80** (favored at longer wavelengths: >350 nm) (Scheme 49).

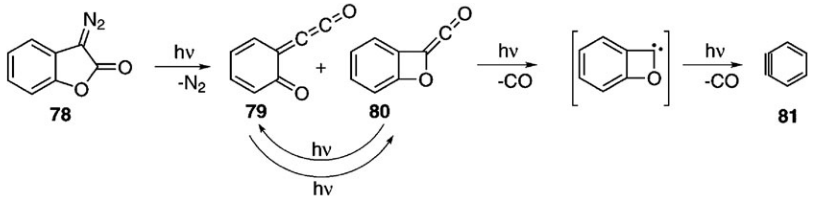
Continuing irradiation at short wavelength resulted in the decarbonylation of the ketene in a putative carbene, which decarbonylates to give benzyne **81**. The irradiation products were identified by UV, IR and mass spectrometries. This report also mentions the first observation of the carbon–carbon triple bond stretching frequency of benzyne (2085 cm^{-1}). Later, cumulenones were observed by many authors in their attempts to generate benzyne or didehydronaphthalene from anhydrides.[183]

Photolysis of the same 3-diazobenzofuranone **78** under matrix isolation conditions gave the methylene ketene **79** as the sole photoproduct,[184] in the absence of **80**. Furthermore, DFT calculations predicted a high barrier of about 156 kJ/mol between the cumulenone **79** and the ketene **80**. The carbene-like reactivity of cumulenone **79** can be illustrated by the rate-determining protonation of the cumulenone moiety at the β-carbon atom, leading finally to 3-hydroxy-3*H*-benzofuran-2-one **82** (Scheme 50).[184]

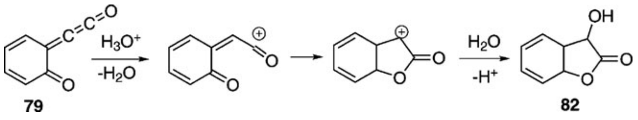
When irradiation of 3-diazobenzofuranone **78** was performed in aprotic solvents such as acetonitrile or hexane, a mixture of dimers was obtained (Scheme 51). The facile addition–cyclization reaction of the cumulenone involves the formation of a C═C double bond and two C–O bonds, leading to heteropolycycles **83**, **84** and **85**. No intermediates could be detected by FVP.



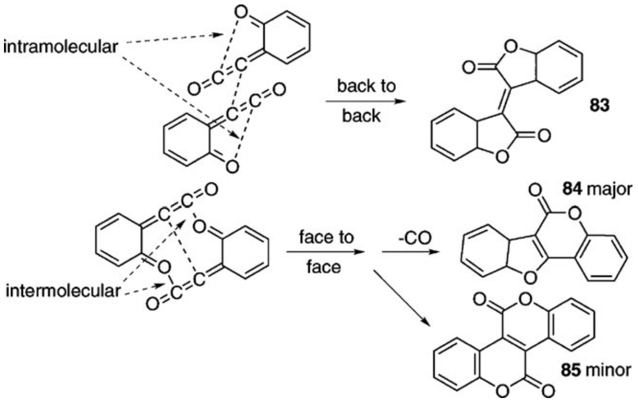
Scheme 48 First evidence of methylene ketene derivatives.[181]



Scheme 49 Chapman's photochemical generation of a methylene ketene **79** as an isomer of a benzyne precursor.



Scheme 50 Carbene-like reactivity of a cumulenone.[184]



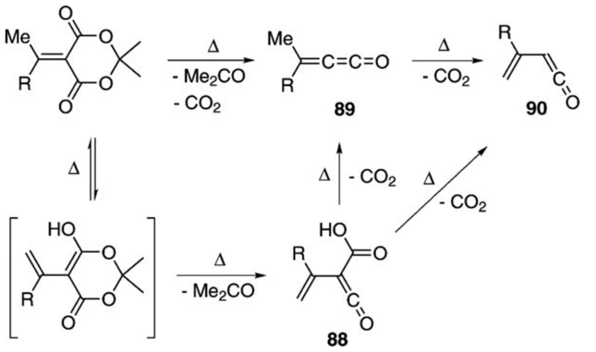
Scheme 51 Addition-cyclization of cumulenones in aprotic solvents.[184]

Tomioka and co-workers used the same photochemical method to prepare cumulenones from diazo ketones.[185] These precursors can also produce methylene ketenes by FVP.[186]

Before 1986, all the known methylene ketenes were observed as intermediates in the gas-phase or in low temperature matrices.[187] The first "stable" cumulenone was synthesized by FVP of a Meldrum's acid derivative at 450 °C/10^{-4} mm Hg.[188] Beside acetone, the sole product observed by ^{13}C NMR at −40 °C was *N*-methyl-2-pyrrolidinylidenemalonic anhydride **86**, which decarbonylates to methylene ketene **87** upon warming to −20 °C (Scheme 52). The IR absorption at 2080 cm^{-1} assigned to **87** was found to persist at room temperature.

The structure of **87** is stabilized through several canonical forms. Whereas simple alkyl- and aryl-methylene ketenes are only detectable at low temperature or in the gas phase, this result shows that electron donating substituents such as amino groups strongly stabilize these species. Similarly, alkythio- and alkoxy-methylene ketenes were reported to be stable at or near room temperature.

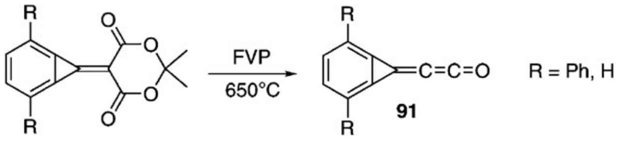
The synthesis of a cumulenone by FVP of Meldrum's acid derivatives[189a] involves the formation of a carboxy ketene intermediate **88**,[189b] which subsequently decarboxylates to methylene ketene **89** and/or vinyl ketene **90**. At higher temperatures, **89** also produces vinyl ketene **90** (Scheme 53).[189a]



Scheme 53 Mechanism of the formation of cumulenones by FVP of Meldrum's acid derivatives.[189a]

A mechanistic rationale of these reactions has been proposed on the basis of DFT calculations.[189c]

Very recently, IR characterization of the cyclopropabenzenylidenethenone **91** produced by FVP was reported by Wentrup and co-workers (Scheme 54).[190]



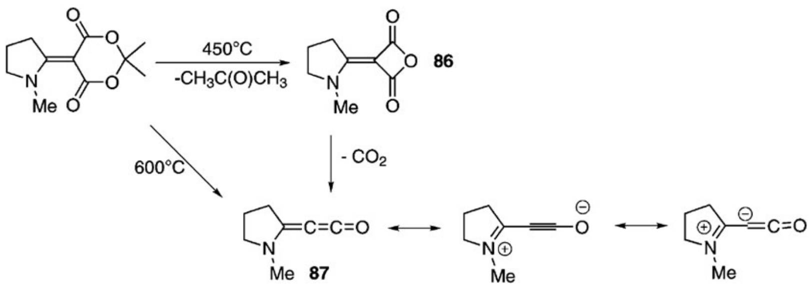
Scheme 54 Route to cyclopropabenzenylidenethenone **91**.[190]

This result confirmed a previous hypothesis by Tomioka and co-workers who postulated **91** as one of the products obtained by irradiation of a bis-diazo ketone.[185]

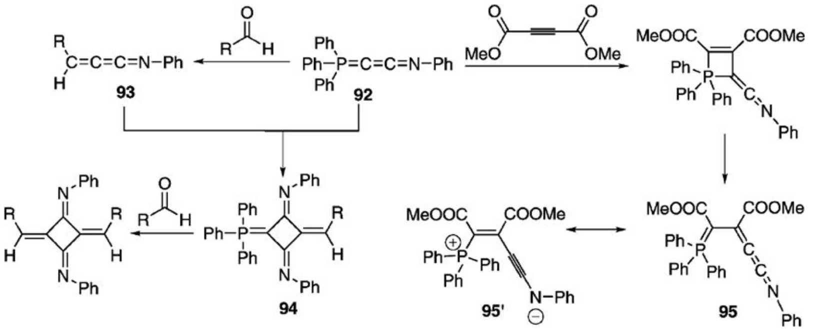
Several theoretical studies focussed on the geometry of propadienone and derivatives thereof and most of them concluded that cumulenones adopt a kinked structure.[191]

7.2 Alkylideneketenimines or "*carbo*-imines"

In 1974, alkylideneketenimines were identified as key-intermediates in the reaction of a keteniminylidene phosphorane **92** with aldehydes (Scheme 55).[192] The authors proposed that an initial Wittig reaction affords the alkylidene ketenimine **93**, which immediately undergoes a cyclodimerization to form the heteroradialenic ylide **94**. One year later, the same group reported the preparation of the first stable alkylideneketenimine **95** by reaction of **92** with dimethylacetylene dicarboxylate.[193] The stability of **95** was interpreted by a resonance with the zwitterionic form **95′**.



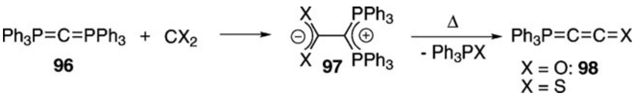
Scheme 52 Synthesis of the first stable methylene ketene derivative.[188]



Scheme 55 Preparation of alkylideneketenimine derivatives.[192,193]

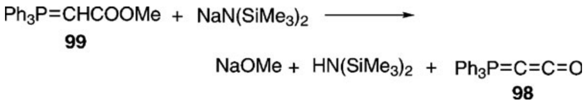
7.3 (Thio)ketenylidene phosphoranes or "*carbo*-(thio)phosphine oxide"

In 1966, the first ketenylidenetriphenylphosphorane and its thio analogue were prepared by reaction of hexaphenylcarbodiphosphorane **96** with CO_2.[194] The resulting zwitterionic intermediate **97** then underwent thermolysis to give triphenylphosphine oxide and $\mathrm{Ph_3P{=}C{=}C{=}O}$ **98** (Scheme 56).



Scheme 56 First synthesis of a phosphacumulenone derivative and its thio analogue.

Alternative methods for the preparation of **98** were later proposed. In particular, a 80% yield was obtained by reaction of $\mathrm{Ph_3P{=}CHCOOMe}$ **99** with bistrimethylsilyl sodium amide (Scheme 57).[195] The synthesis and reactivity of **98** was reviewed by Bestmann in 1977.[196]

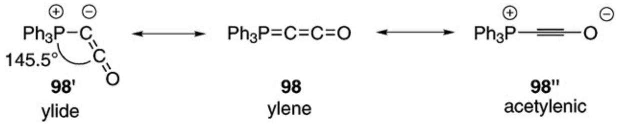


$$\underset{\mathbf{99}}{\mathrm{Ph_3P{=}CHCOOMe}} + \mathrm{NaN(SiMe_3)_2} \longrightarrow \mathrm{NaOMe} + \mathrm{HN(SiMe_3)_2} + \underset{\mathbf{98}}{\mathrm{Ph_3P{=}C{=}C{=}O}}$$

Scheme 57 An efficient synthesis of ketenylidenetriphenylphosphorane **98**.[195]

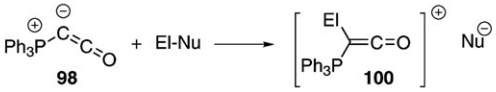
The same procedure was applied to the synthesis of the thio analogue of **98**.[197] The alternative use of $NaNH_2$ as a base was also reported in 1988.[198]

$\mathrm{Ph_3P{=}C{=}C{=}O}$ **98** is stable when stored under dry nitrogen, but slowly decomposes when dissolved in chlorinated solvents. Its X-ray crystal structure was reported in 1966,[199] showing that the P–C–C–O chain is not linear, thus evidencing the contribution of the α-ylidic canonic form **98′** (Scheme 58). The P–C_{sp} bond is however shorter (1.648 Å) than the P–Ph distances, thus indicating a partial double bond character. The C═C bond is shorter than normal carbon–carbon double bonds thus suggesting the contribution of the acetylenic zwitterionic form **98″**. The C═O bond is in the classical range for organic carbonyl groups.



Scheme 58 Canonic forms of the ketenylidenetriphenylphosphorane **98**.[199]

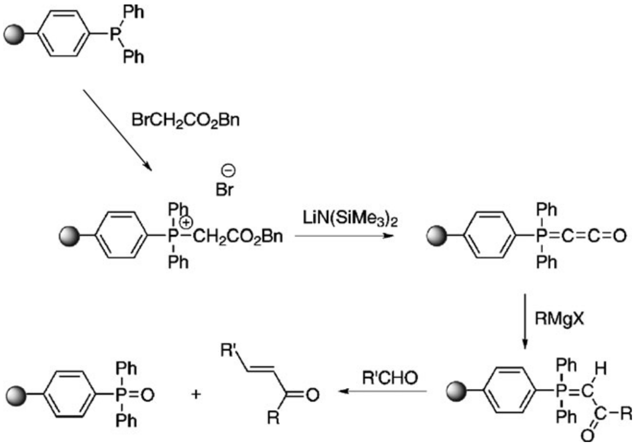
The reactivity of **98** has been widely studied and reviewed in 2003,[200] and is quite different from that of a ketene. Indeed, the C^+–O^- dipolar character of ketenes, which accounts for their propensity to undergo dimerization or cycloaddition reactions, is absent in $\mathrm{Ph_3P{=}C{=}C{=}O}$. Instead, **98** reacts with protonating or alkynylating reagents (such as alcohols, thiols, amines, HX and RX derivatives where X is an halogen. . .), leading phosphonium salts **100** (Scheme 59).



Scheme 59 Reactivity of ketenylidenetriphenylphosphorane **98′** ↔ **98**.[200]

The phosphonium cation **100** can be regarded as a "true" ketene, with the typical chemistry of ketenes. If Nu^- is strongly nucleophilic, it attacks the carbonyl carbon to give a carbonyl-stabilized ylide. If Nu^- is a weaker nucleophile, a stronger nucleophile can attack the "ketene" carbonium center.[200]

The ylidic carbon of $\mathrm{Ph_3P{=}C{=}C{=}O}$ is strongly nucleophilic and attacks electrophilic metal centers just as do



Scheme 60 Application of supported phosphacumulenones in organic synthesis.[202]

classical phosphorus ylides. Despite the paucity of reports on its reactivity with main group elements,[201] numerous contributions dealt with its reactivity with transition metals. This point is comprehensively documented in the Bertani's review and will not be developed here.[200]

Recently, polystyrene-bound $Ph_3P{=}C{=}C{=}O$ was prepared and reacted with Grignard derivatives to give acyl, amide or ester ylides (Scheme 60), and then the corresponding alkenes *via* Wittig reactions.[202] This supported methodology allowed to facilitate the purification, the Ph_3PO by-product remaining bound to the resin.

The reverse protocol based on the use of resin-bound amino- or hydroxy-carbonyl derivatives with free $Ph_3P{=}C{=}C{=}O$ in solution was previously described by the same authors.[203]

Conclusion

The above survey of the *carbo*-meric functions remains descriptive, but it sets up the basis for novel challenges in acetylenic chemistry. As just an illustrative example, the lack of investigation on bis- and trisalkynylamines is quite intriguing. Beyond the academic challenge, the handling of such *carbo*-meric functions is a basic requirement for the synthesis of ring *carbo*-mers of pyridine, a "functional" aromatic ring.[10] Since pyridine exhibit many essential properties (aromaticity, basicity, ligand-to-metal charge transfers in coordination complexes,...), and since preliminary DFT calculations of its ring *carbo*-mer demonstrated its unique aromatic character, the experimental synthesis of *carbo*-pyridine is now a natural issue to be addressed. Let us indeed remind the more general legitimate question: why do *carbo*-mers deserve a peculiar consideration? and the natural answer we propose: because they can exist, just as *stereo*isomers can.

Acknowledgements

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