Roots: From carbenes to allenes and coordination polymers† *Ever present never twice the same*‡§

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The purpose of this Feature Article is to demonstrate that recognizing the similarities in different areas of chemistry allows the prediction of potential results in related fields. For instance, during our investigations of 2,2-diethoxyvinylidene-triphenylphosphorane we became interested in 2,2-diethoxydiazoethene. In order to obtain diazoethenes, we studied vinyl-diazonium salts and geminal vinyl-diazides as precursors. In the course of these investigations, we realized their synthetic potential to produce, *via* substituent-dependent 1,5-, 3,5-, or 1,5'-cyclization, a whole variety of heterocycles. However, more importantly, we became familiar with the chemistry of carbenes, which prompted an investigation of the carbene-like character of push–pull substituted allenes. Due to the ambiphilicity of their central carbon atom, they readily dimerized. Consequently, our strong interests in push–pull substituted allenes drew our attention to tetradonor substituted allenes, and as a result, we employed tetraethoxyallene as a synthetic equivalent to the fictitious malonic ester 1,1-/1,3-dianion synthon. This concept led to the synthesis of heterocumulenes and to the *transallenation* reaction to give allenecarboxanilides, which was further developed as a *cumuhomologation* for the synthesis of butatrienes *via* haloallenes from propargyl alcohols. The Diels–Alder reaction and intramolecular domino cyclization of multi-functional allenecarboxanilides yielded complex fused heteroarenes. Finally, the 1,5-cyclization of vinyl-azides, reported earlier, provided tetrazolylidene ligands, triggering our interest in supramolecular coordination chemistry, for example, the synthesis of one-, two- and three-dimensional coordination polymers.

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§ Dedicated to Professor Dr. Alfred X. Trautwein on the occasion of his 65th birthday.

Rolf W. Saalfrank

Rolf W. Saalfrank studied chemistry at the University Erlangen-Nürnberg and received his PhD in 1970 for studies of cumulated phosphoranes. After spending one year as a postdoctoral research fellow with Professor Donald G. Farnum (Michigan State University, East Lansing, Michigan, USA), he moved to the German Cancer Research Center in Heidelberg. In 1973 he returned to Erlangen, and finished his habilitation in 1976 on push–pull substituted allenes. In 1980 he was appointed Professor of Organic Chemistry. He is an Overseas Visiting Scholar at St. John's College, University of Cambridge, UK. Since 1987 his research has generated seminal work in supramolecular coordination chemistry.

Introduction

A well-balanced integration of carefully planned strategies, combined with a straightforward evaluation of developing new points of view, has spontaneously uncovered a variety of topics, through which runs a common thread. The intention of this Feature Article is to demonstrate that chemistry needs to be viewed from different angles in order to reach the new levels necessary for progress. This mindset allows predictions not only within the borders of a specific topic, but also facilitates the crossing of frontiers and an acknowledgement of the common aspects within different fields. We relied on the synergistic effect of serendipity and rational design. This is by some means equivalent to a broader interpretation of predicting results. There is no realistic possibility of providing an exhaustive account of this field of science. Completeness is not claimed, but examples are selected and highlighted according to their originality. The illustrations are taken mainly from our own work, with credit given to a wide range of other contributors by means of citations of their original articles.

The starting point was 2,2-diethoxyvinylidene-triphenylphosphorane, generated from the corresponding vinylphosphonium salt. This result prompted us to synthesize 2,2-diethoxyethene from a 2,2-diethoxyvinyl-diazonium salt. In connection with these investigations, it became apparent that 2,2-diethoxyvinyl-diazonium salts are excellent precursors to various heterocycles. Similarly, geminal vinyl-diazides

revealed a high synthetic potential, especially on the basis of their geminal amino vinyl-azides, which readily performed substituent-dependent 1,5-, 3,5- and 1,5′-cyclization reactions.

Our studies of vinyl-diazonium salts and geminal vinyl-diazides drew our attention to carbenes, and consequently to push–pull substituted allenes, revealing carbene-like characteristics within the central carbon atom. As a result, we subsequently studied tetradonor substituted allenes with respect to their use as dianion equivalents of the fictitious 1,1-/1,3-dianion of malonic ester. The result of these investigations was the discovery of the *transallenation* reaction.

On the other hand, 1,1-acceptor allenes were prepared from propargyl alcohols and various chloro compounds *via* [2.3]- and [3.3]-sigmatropic rearrangements. The resulting haloallenes were the basis for the *cumuhomologation* reaction, leading to butatrienes, whereas the allenecarboxanilides readily underwent intramolecular consecutive Diels–Alder/skeletal rearrangement reactions or domino cyclizations. In addition, versatile heterocycles were accessible from *N*,*N*-diphenyl-1-(diethoxyphosphoryl)allene-1-carboxanilides *via* a consecutive Michael addition and Horner–Emmons reaction.

On the basis of the concept mentioned previously, the synthon strategy was also applied to enolates and silylenolethers, 1,3-dianion equivalents of 1,3-dicarbonyl compounds.

The tetrazolylidenes, originally prepared for totally different purposes, offered an additional application as chelating ligands for one-, two- and three-dimensional coordination polymers.

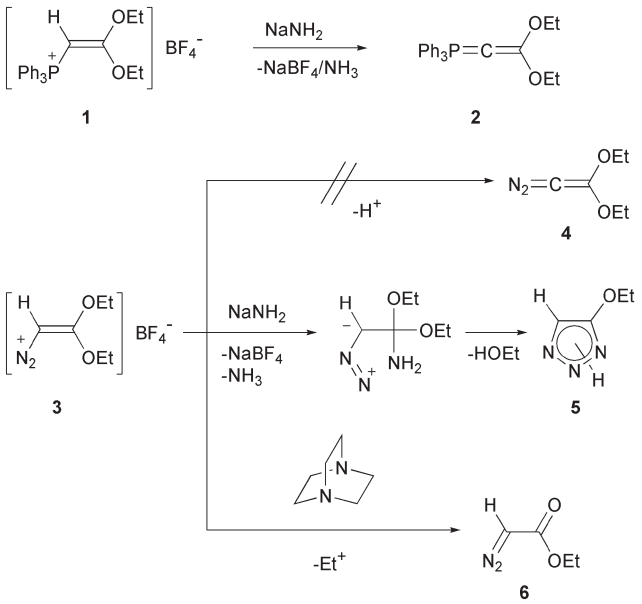
1. 2,2-Diethoxyvinylidene-triphenylphosphorane and 2,2-Diethoxydiazoethene

Deprotonation of 2,2-diethoxyvinyl-phosphonium salt **1** with sodium amide in liquid ammonia readily affords 2,2-diethoxyvinylidene-triphenylphosphorane **2**.[1] However, when 2,2-diethoxyvinyl-diazonium salt **3** was reacted with sodium amide, the anticipated 2,2-diethoxydiazoethene **4** could not be detected, but we instead isolated crystals of triazole **5**.[2,3] Likewise, the use of less nucleophilic 1,4-diaza-bicyclo[2,2,2]octane (DABCO) did not deprotonate **3** to produce **4**, but instead dealkylated **3** to form diazo acetate **6**[2] (Scheme 1).

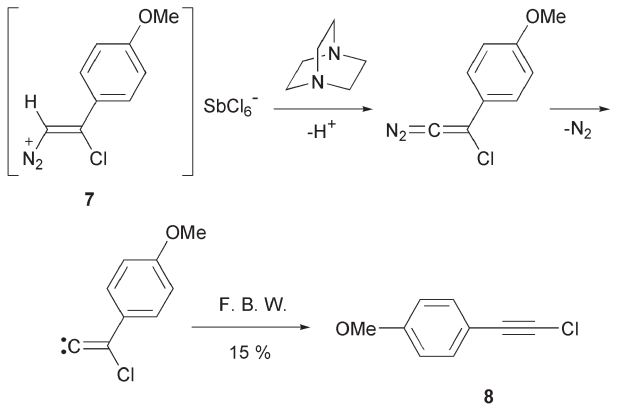
Whereas vinyldiazonium salt **3** could not be deprotonated by DABCO, we obviously succeeded in the case of 2-chloro-2-methoxyphenyl-vinyl-diazonium salt **7**, as indicated by the formation of chloro-methoxyphenyl acetylene **8**.[2] This evidence suggests the generation of an intermediate diazoethene, which loses N_2, and after a Fritch–Buttenberg–Wichel (F. B. W.) rearrangement[4] of the corresponding vinylidene, finally affords **8** (Scheme 2).

2. Vinyl-diazonium salts as synthetic building blocks

The serendipitous discovery of the formation of triazole **5**, starting from 2,2-diethoxyvinyl-diazonium salt **3** and sodium amide, prompted us to generalize this finding. Consequently, we reacted the vinyl-diazonium salts **9** with a variety of primary amines[5,6] or diamines[7] and isolated the corresponding substituted triazoles **10** or **11** in good yields. On the contrary,



Scheme 1



Scheme 2

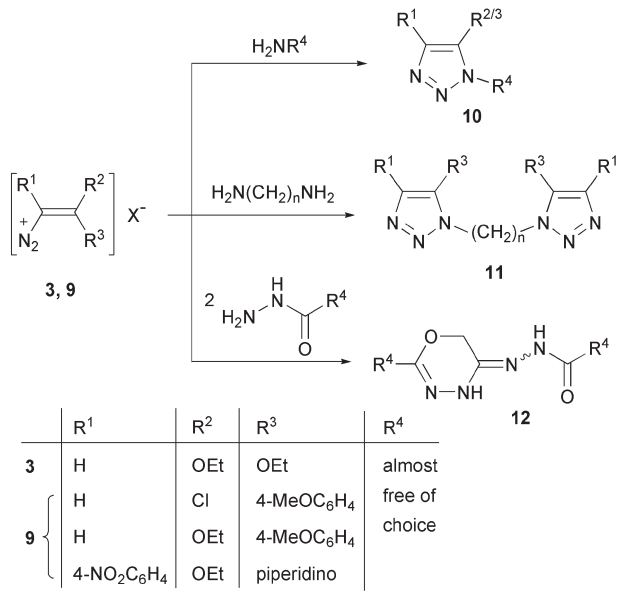
2,2-diethoxyvinyl-diazonium salt **3** and hydrazides[2b,8,9] reacted to yield oxadiazinhydrazones **12**, which turned-out to be versatile precursors for a variety of heterocycles (Scheme 3).

Scheme 4 presents a summary of the various heterocycles accessible from vinyl-diazonium salts.

3. Geminal vinyl-diazides

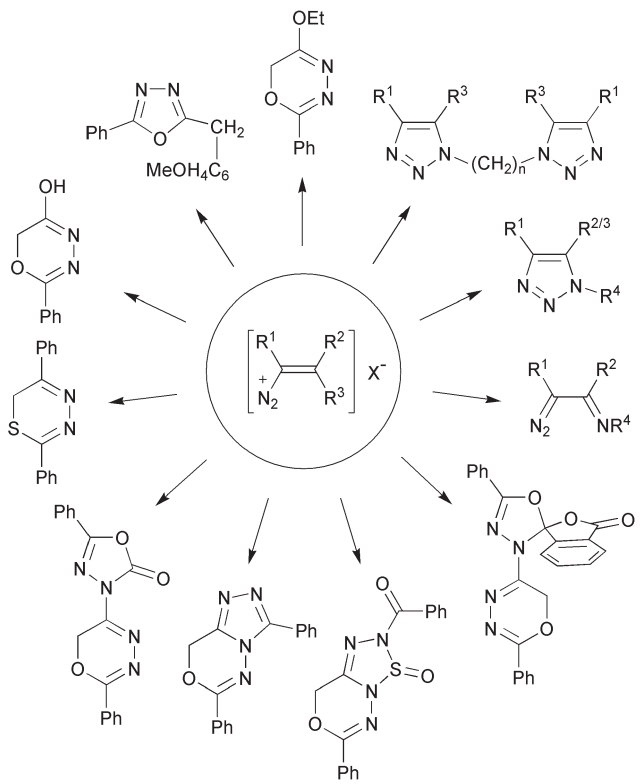
Potential precursors of functionalized vinylidenes

Above, we demonstrated that 2-chloro-2-methoxyphenyl-vinyl-diazonium salt **7** is deprotonated by DABCO and acetylene **8** is generated *via* the intermediate diazoethene and vinylidene. Correspondingly, geminal vinyl-diazides **13** seem to open up another feasible route for the generation of further heterosubstituted or functionalized diazoethenes or vinylidenes.[10] Upon addition to methanol at just below its boiling point, the geminal vinyl-diazide **13** decomposes with the vigorous loss of N_2 to give methoxy methylester **15** (70%). We assume that on heating, **13** initially undergoes a 3,5-ring closure with N_2 elimination. The resulting azido-azirine then



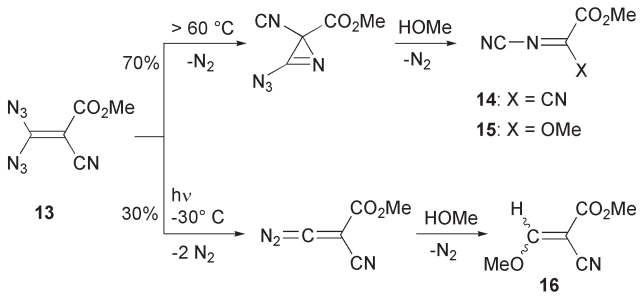
	R^1	R^2	R^3	R^4
3	H	OEt	OEt	almost free of choice
9	H	Cl	4-$MeOC_6H_4$	
	H	OEt	4-$MeOC_6H_4$	
	4-$NO_2C_6H_4$	OEt	piperidino	

Scheme 3



Scheme 4

undergoes further loss of N_2 and rearrangement to the cyano methylester **14**, which, in turn, adds methanol and subsequently eliminates hydrogen cyanide to afford methoxy methylester **15**. Alternatively, irradiation of **13** in methanol at −30 °C affords **15**, together with the photoproduct **16** (30%). Olefin **16** probably results from an insertion of the intermediate vinylidene into the H–O bond of methanol. A further possible route to obtain olefin **16** is protonation of the intermediate diazoethene to give the corresponding vinyldiazonium methoxide, followed by loss of N_2 (Scheme 5).

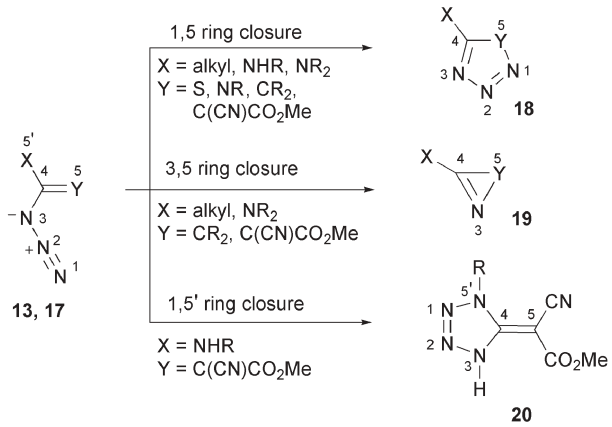


Scheme 5

4. Geminal amino vinyl-azides as synthetic building blocks

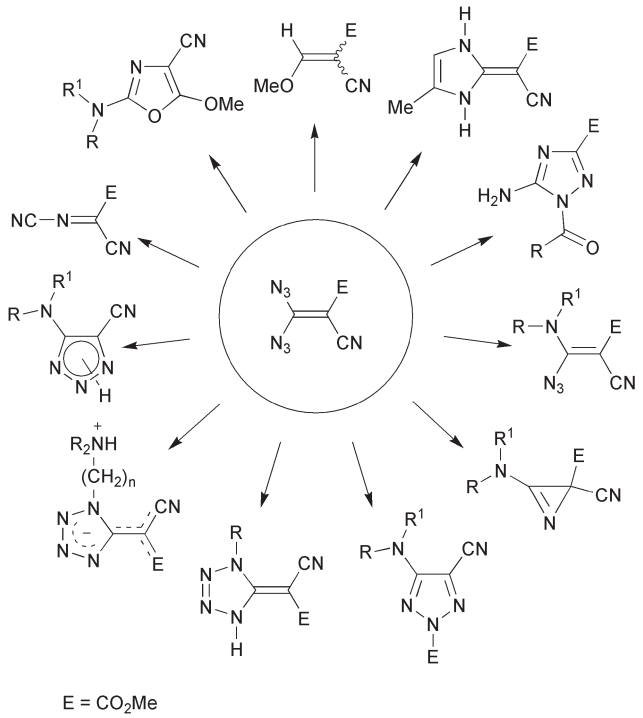
Substituent-dependent 1,5-, 3,5- and 1,5′-cyclization

In the section above we demonstrated that in methanol at just below 65 °C, the geminal vinyl-diazide **13** decomposes with vigorous loss of N_2 to give methoxy methylester **15**. On the other hand, a similar reaction proceeds with primary amines even at 35 °C. However, at temperatures below −30 °C, **13** (X = N_3, Y = $C(CN)CO_2Me$) reacts in a completely different way with amines to yield the geminal amino vinyl-azides **17** (X = NHR, NR_2, Y = $C(CN)CO_2Me$) as the first step (Scheme 6).



Scheme 6

Geminal amino vinyl-azides of general structure **17** may, in principle, undergo a 1,5-cyclization to give isomer **18**. Whether isomer **17** or **18** represents the more stable structure depends on the substituents X and Y.[11] For example, acyl azides **17** (X = alkyl, Y = O) exist exclusively in the open chain form,[11,12] whereas thioacyl azides **17** (X = alkyl, Y = S) cyclize to give 1,2,3,4-thiatriazoles **18**.[12,13] In the case of imino-azides **17** (X = alkyl, Y = NR), only electron accepting substituents R are capable of stabilizing the azide form, tetrazoles **18** being obtained otherwise.[11,14] The imino-azide/tetrazole isomerization is very well documented with numerous examples, but only a few reports are available on the vinyl-azide/triazole isomerization **17**→**18** (X = alkyl, Y = CR_2).[15]



Scheme 7

Vinyl-azides **17** (X = NHR or NR_2, Y = $C(CN)CO_2Me$) substituted with donor groups in the 4-position can undergo both 1,5- and 3,5-ring closure reactions. Depending on the substituents X and the reaction conditions, either the 4*H*-1,2,3-triazoles **18** (X = NHR or NR_2) or 2*H*-azirines **19** (X = NR_2) are formed with elimination of N_2.[16–22]

A reaction mechanism involving the 3,5-ring closure of **17** with concurrent elimination of N_2 is favoured over a pathway involving a free nitrene or one involving a 1,5-ring closure to give 4*H*-1,2,3-triazoles, followed by elimination of N_2.

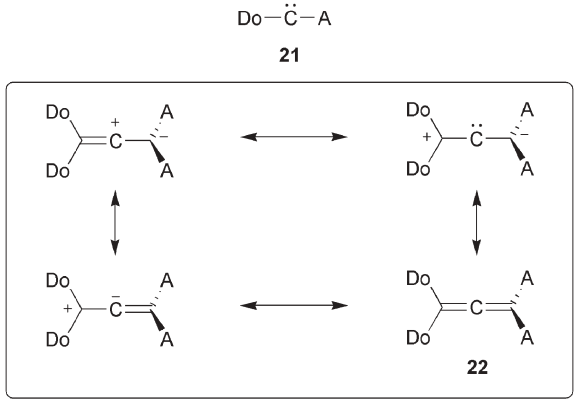
A detailed investigation of the vinyl-azides **17** (X = NHR, Y = $C(CN)CO_2Me$) revealed that, in this case, a 1,5′-ring closure reaction strongly dominates over a 1,5-cyclization to afford tetrazolylidenes **20** (Scheme 6).[18–25]

Scheme 7 presents a summary of the various heterocycles accessible from geminal vinyl-diazides.

5. Push–pull substituted allenes

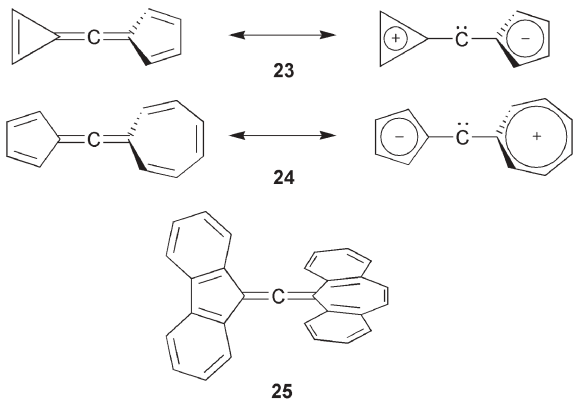
Over the course of our ongoing studies on vinylidenes, the need to study push–pull substituted allenes with respect to their carbene character loomed large.

Ambiphilic carbenes **21**, like chloro(methoxy) carbene, exhibit electrophilic and nucleophilic selectivity towards electron rich and electron deficient olefins, respectively.[26] Consequently, a formal replacement of the donor substituent (Do) in an ambiphilic carbene **21** by a stabilized anion and the acceptor substituent (A) by a stabilized cation leads to the dipolar carbenoid mesomeric structure of allene **22** (Scheme 8). In this section, we will demonstrate that such push–pull substituted allenes are likewise ambiphilic, *i.e.* they react at the central atom (C-2) both electrophilically and nucleophilically. Furthermore, allenes of type **22** are able to perform carbene-like reactions.[27,28]



Scheme 8

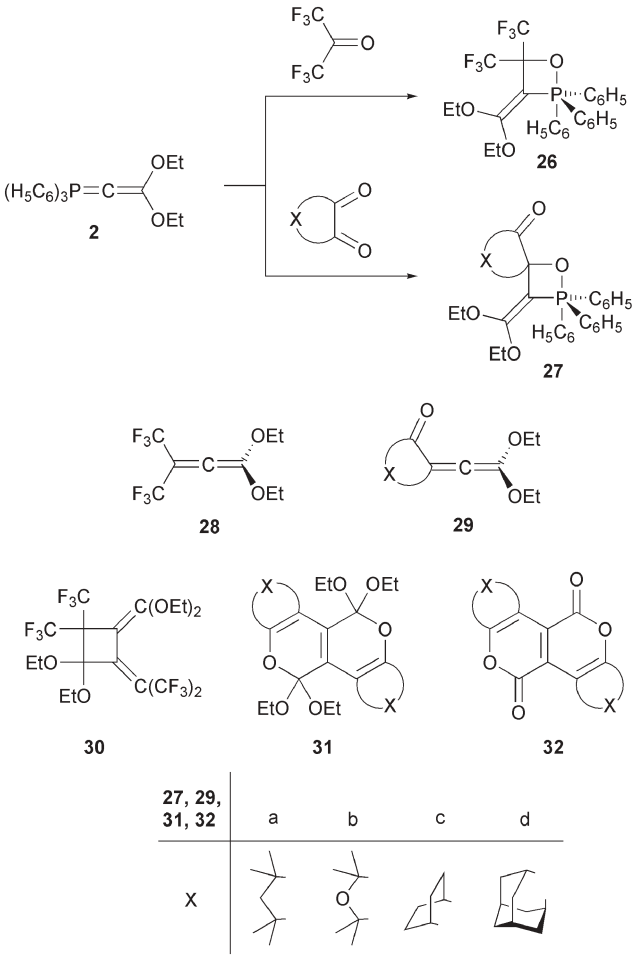
The two prototype push–pull substituted allenes (cyclopropenylidene)(cyclopentadienylidene) methane **23** and (cyclopentadienylidene)(cycloheptatrienylidene) methane **24** remain unknown.[29] Although (fluoren-9-ylidene)(dibenzo[*a*,*d*]cyclohepten-5-ylidene)methane **25** has been synthesized, its spectroscopic data indicate no significant carbene character[30] (Scheme 9).



Scheme 9

The difficulty associated with the synthesis and isolation of push–pull substituted allenes is mainly due to their strong tendency to dimerize, as reactive groups of opposite polarity form different parts of the same molecule. However, the Wittig reaction turned out to be suitable for their generation. Reaction of hexafluoroacetone with cumulated phosphorane **2**[31] affords the surprisingly thermally-stable oxaphosphetane **26**.[32,33] Similarly, with non-enolizable 1,2-diketones the oxaphosphetanes **27** are accessible.[33,34] The ^{13}C NMR spectra of **26** and **27** display three equivalent phenyl groups, indicating fast regular ligand exchange processes, even at −40 °C. On warming (≈120 °C), **26** and **27** smoothly eliminate triphenylphosphane oxide to give the push–pull substituted allenes **28** and **29**, some of which can be isolated before dimerization. The structure of the dimers strongly depends on the nature of the substituents of the push–pull allenes. For instance, push–pull substituted 1,1-diethoxy-3,3-bis(trifluoromethyl)allene **28**, exclusively gives the head-to-tail 1,2-bis(methylene)cyclobutane derivative **30**.[33] Allene dimerizations, in which the substituents are involved in the reaction, have been little

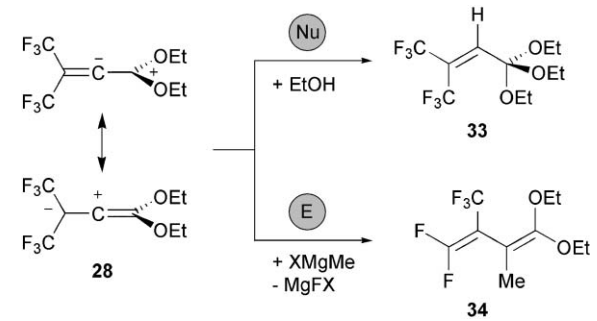
investigated.[35] The dimerization of push–pull allenes **29** is initiated by a 1,4-dipolar cycloaddition of the α,β-unsaturated keto system of one allene molecule to the ketene acetal double bond of another. Subsequently, the intermediate s-(*Z*), α,β-(*Z*) and s-(*Z*) pentadienones undergo an electrocyclic reaction that is analogous to the hexatriene–cyclohexadiene rearrangement to give the dimers **31**.[27,28,33,34,36] The diethoxy pyranes **31** are converted to the corresponding α-pyrones **32** on refluxing in glacial acetic acid. These compounds are strongly fluorescent and particularly well suited as laser dyes because of their exceptional stability[37] (Scheme 10).



Scheme 10

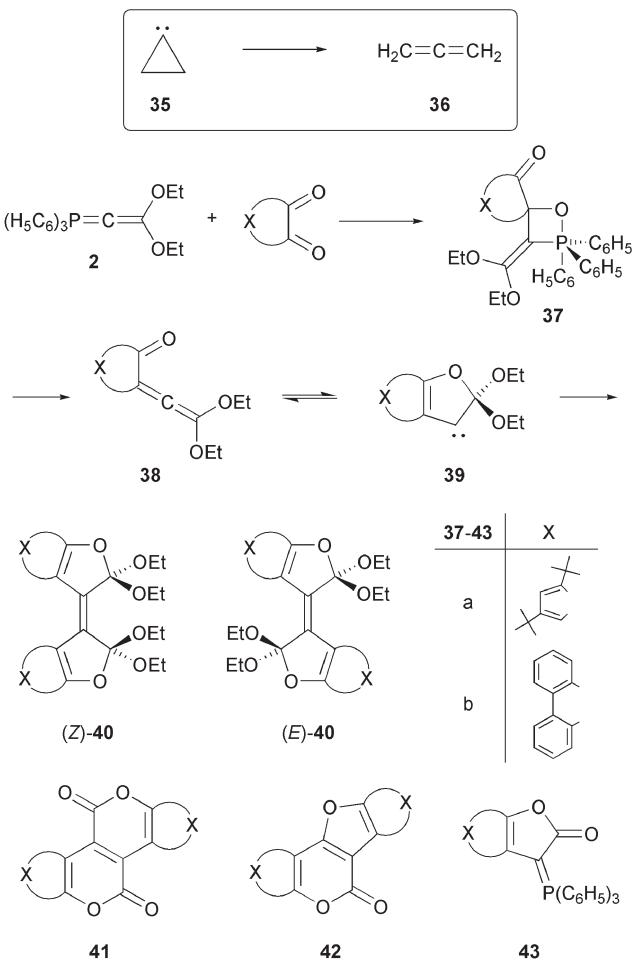
The ambiphilic character of push–pull substituted allenes is demonstrated most convincingly for 1,1-diethoxy-3,3-bis-(trifluoromethyl)allene **28**, since it reacts both as a nucleophile and an electrophile at the central carbon C-2. For instance, **28** is protonated by ethanol and alkylated by methyl Grignard at C-2 to form orthoester **33** and butadiene **34**, respectively[32] (Scheme 11).

Whereas the cyclopropylidene–allene rearrangement (**35→36**) is one of the most prominent synthetic methods for the generation of allenes,[38] this reaction is irreversible. In the case of the *ortho*-benzoquinoid push–pull allenes **38** however, a five-membered carbene **39** is conceivable. This is the case since compared with cyclopropylidene, the ring strain could be



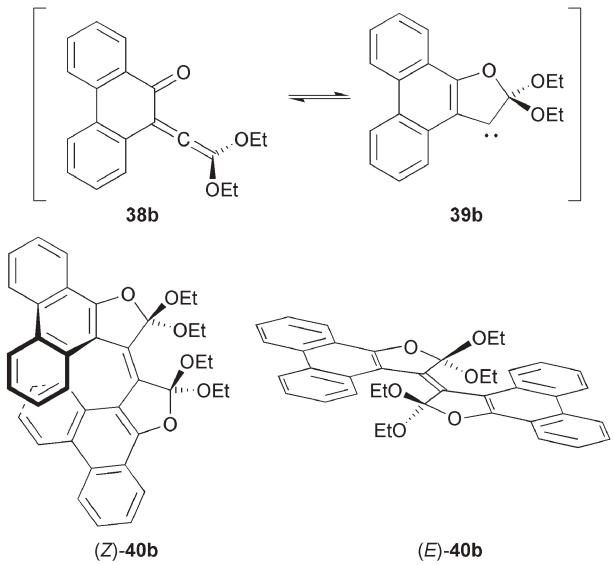
Scheme 11

neglected and even more important additional resonance energy be gained. When phosphorane **2** is reacted with *ortho*-quinones, the initially formed oxaphosphetanes **37** readily lose triphenylphosphane oxide to give the push–pull allenes **38**, which spontaneously dimerize to afford the product (*Z*/*E*)-olefins **40**.[27,28,39] Precursors to the olefins are most likely the five-membered carbene intermediates **39**. Acetic hydrolysis of the (*Z*/*E*)-diastereomers **40** yield, *via* a complex cascade of several isolable intermediates, cumarino-cumarin **41** and furo-cumarin **42**.[40] Thermolysis of the oxaphosphetanes **37** in the presence of the carbene scavenger triphenylphosphane, after elimination of diethyl ether, yields phosphorane **43**[39] (Scheme 12).



Scheme 12

The (*Z*/*E*)-olefins **40a** do not display any special ^{1}H NMR signals. However, according to the ^{1}H NMR spectra of the (*Z*/*E*)-isomers **40b**, the four ethoxy groups are only pairwise equivalent. The (*Z*)- and (*E*)-isomers therefore have C_2 molecular symmetry. The spectra in which the triplets are furthest separated are assigned to the isomer of (*E*)-configuration. In the case of (*E*)-**40b**, two of the ethoxy groups are positioned directly above the phenanthrene rings, in contrast to isomer (*Z*)-**40b**. This is in agreement with the single crystal X-ray structure of (*E*)-**40b**.[39] The racemate of helical (*Z*)-**40b** (for clarity only the (*P*)-stereoisomer is shown) was resolved by high performance liquid chromatography (HPLC) using short columns containing the optically-active charge transfer (CT) complexing agent (+)-(*R*)-2-(2,4,5,7-tetranitro-9-fluorenylideneaminooxy)propionic acid (TAPA)[41] (Scheme 13).



Scheme 13

6. Tetradonor substituted allenes

Our strong interest in push–pull substituted allenes consequently drew our attention to tetradonor substituted allenes.[27,28,42–44]

A striking property of allene ^{13}C NMR spectra is the low field shift (δ 185–216) of the central sp-hybridized carbon atom, compared to the terminal sp^2-hybridized allene carbon atoms recorded between δ 60–130.[45] The charge distribution in the allene skeleton can, at least qualitatively, be determined from the chemical shifts of their carbon atoms, and in turn, conclusions about their decisive reactivity can be drawn. A comparison of the ^{13}C NMR data of unsubstituted allene **44** with those of tetraethoxyallene **45** shows the deshielding effect on the terminal carbon atoms because of the σ-acceptor character of the oxygen substituents. On the other hand, the π-donor character of the OEt groups causes a large shift to higher field for the central carbon atom of allene **45**. These effects lead to an inversion of the order of the usual signals found in simple allenes.[45c] The central carbon atom in tetraethoxyallene **45** is more strongly shielded than its terminal ones. Consequently, C-2 in tetrakis(ethoxycarbonyl)allene **46** is strongly deshielded. On the other hand, push–pull-substituted 1,1-diethoxy-3,3-bis(trifluoromethyl)allene **28** exhibits the expected large separation of the ^{13}C signals for the two terminal carbon atoms. Most interestingly, the chemical shift of the central carbon atom of **28** almost matches that of parent allene **44**. This is because central C-2 in **28** is coupled to two π-systems of opposite polarity (Table 1).[28,45]

Table 1 ^{13}C NMR data for the allenes **28** and **44–46** (δ values relative to TMS)

$$\left(R^1\right)_2\overset{1}{C}=\overset{2}{C}=\overset{3}{C}\left(R^2\right)_2$$

	R^1	R^2	C-1/3	C-2
28	CF_3	EtO	109.4	199.6
44	H	H	72.3	211.4
45	EtO	EtO	148.1	115.2
46	EtO_2C	EtO_2C	102.5	227.4

A comparison of the He(I)-photoelectron (PE) spectra of donor–acceptor allene **28**, tetradonor allene **45** and tetraacceptor allene **46** shows that **28** occupies a position between **45** and **46**, and that it consists of electron-rich and electron-deficient π-fragments.

The HOMOs of 1,1-dimethoxy-3,3-bis(trifluoromethyl)allene, tetramethoxyallene and tetrakis(ethoxycarbonyl)allene **46** were calculated with MINDO/3, and comparisons with the first peak of the PE spectra of **28**, **45** and **46** showed excellent agreement.[46]

6.1 Heterocumulenes from tetraethoxyallene

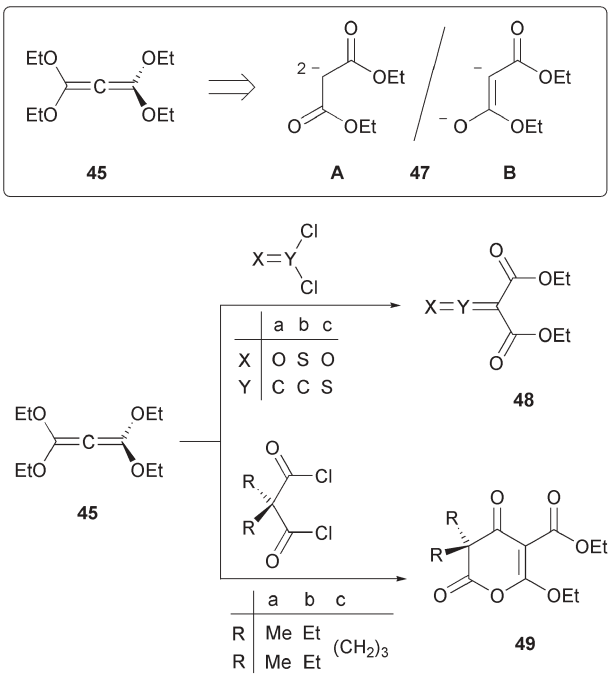
We have employed tetraethoxyallene **45** as a synthetic equivalent of the fictitious malonic ester 1,1-/1,3-dianion synthon **47**.[27,42–44] Formal removal of an ethyl cation from each of the perpendicularly-oriented ketene acetal functions of **45** transforms the terminal carbon atoms into ester functions, linked to a central double-negatively charged carbon atom.

With phosgene,[43] thiophosgene[43] and thionyl chloride,[42a] **45** reacts, with the elimination of two moles of ethyl chloride (per mole of **45**), exclusively as the 1,1-dianion synthon **47A** to give bis(ethoxycarbonyl)-ketene **48a**, bis(ethoxycarbonyl)-thioketene **48b** and diethyl thioxomalonate-*S*-oxide **48c**, respectively.

However, with dialkylmalonyl chlorides, tetraethoxyallene **45** again reacts with loss of two moles of ethyl chloride, but this time as the 1,3-dianion synthon **47B** to give the 3,4-dihydro-3,3-dialkyl-2,4-dioxo-2*H*-pyranes **49**[44,47,48] (Scheme 14).

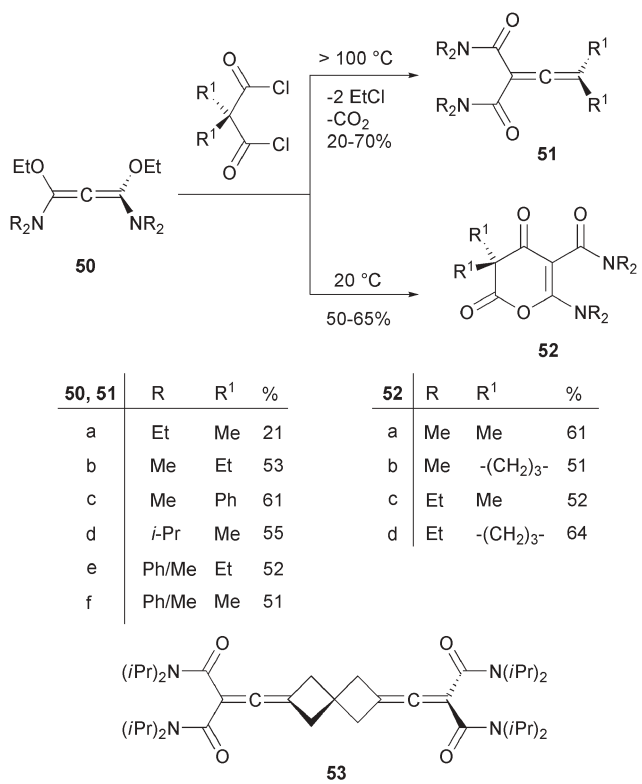
6.2 Transallenation

The educt 1,3-bis(dialkylamino)-1,3-diethoxyallenes **50** are synthesized *via* a four step procedure, involving two alternating alkylation and deprotonation steps, starting from *N*,*N*′-tetrasubstituted malonic diamides.[48,49] The readily accessible tetradonor allenes **50** react with disubstituted malonyl chlorides, *via transallenation*, to give allene-1,1-dicarboxamides **51**.[48,50,51] Previously, transallenation has not played a significant role in allene chemistry. This novel method is of



Scheme 14

general use if attention is paid to ensuring that suitable substituent combinations are used. Provided that both the substituents R and R^1 are sterically-demanding, the competing side reaction that yields the lactones **52**, is suppressed. The broad applicability of transallenation is highlighted by the synthesis of spiro bisallene **53**[47] (Scheme 15).

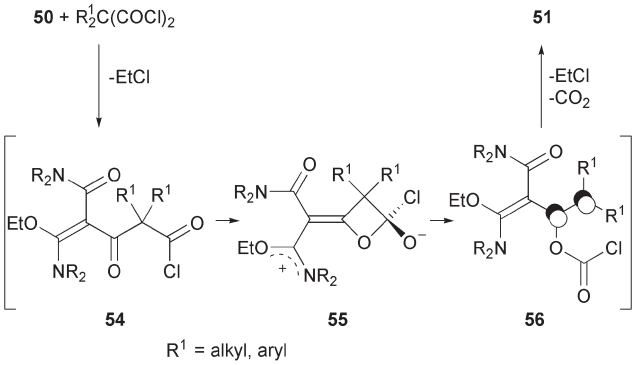


50, 51	R	R^1	%
a	Et	Me	21
b	Me	Et	53
c	Me	Ph	61
d	*i*-Pr	Me	55
e	Ph/Me	Et	52
f	Ph/Me	Me	51

52	R	R^1	%
a	Me	Me	61
b	Me	-$(CH_2)_3$-	51
c	Et	Me	52
d	Et	-$(CH_2)_3$-	64

Scheme 15

Concerning the reaction mechanism of the transallenation, we propose the initial formation of ketene-*O*,*N*-acetal **54**, followed by cyclization to give oxetane **55**, and rearrangement of the latter, initiated by a carbon–carbon bond cleavage,[27,44,52] to give key intermediate chlorocarbonic vinylester **56**. Simultaneous loss of ethyl chloride and carbon dioxide from the carbonic acid derivative **56** finally yields the allenes **51** (Scheme 16).



Scheme 16

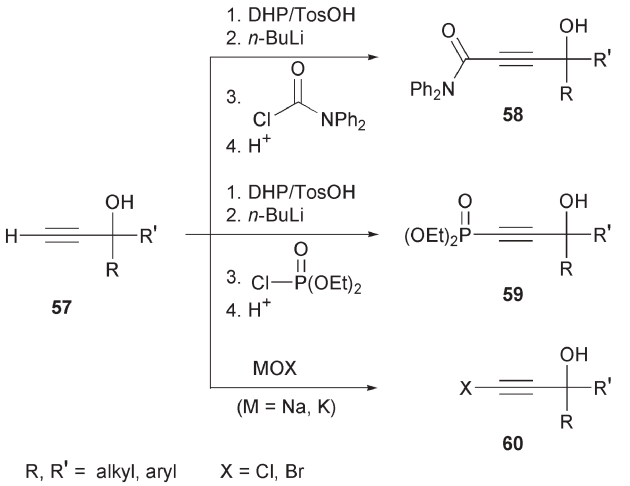
In summary, in the transallenation process, the 1,3-bis(dialkylamino)-1,3-diethoxyallenes **50** act as synthetic equivalents of 1,1-dianions of malondiamides, and the disubstituted malonyl chlorides as equivalents of 1,1-vinylidene dications. In the lactonization process however, the allenes **50** behave as synthetic equivalents of 1,3-dianions of malondiamides, and the malonyl chlorides simply act as equivalents of 1,3-dications.

Tetraethoxyallene **45** transallenates only when it reacts with diphenylmalonyl chloride.[50b] In all other cases investigated so far, tetraethoxyallene **45** generates lactones with dialkylmalonyl chlorides.

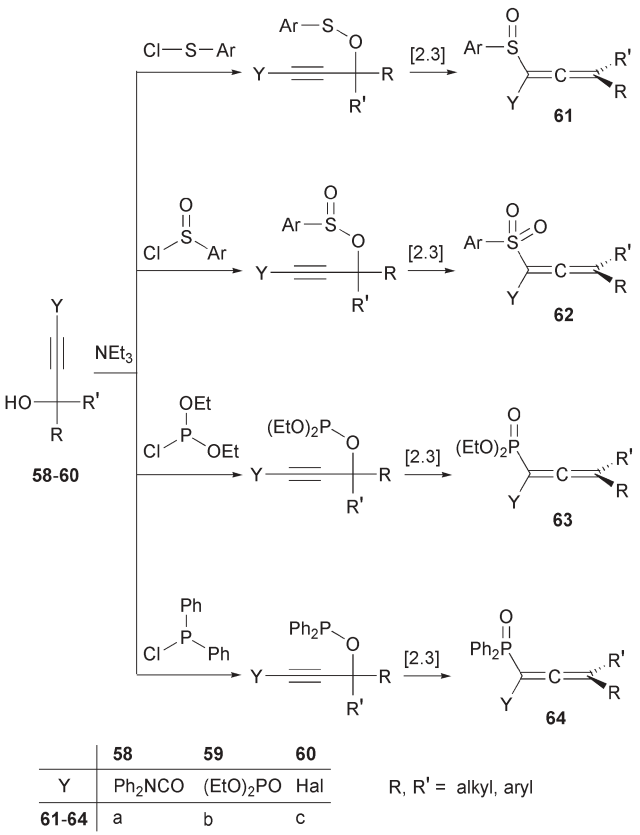
7. 1,1-Functionalized allenes from propargyl alcohols *via* [2.3]-sigmatropic rearrangement

Some of the alkynols **57** used here are commercially available. Less common derivatives are obtained by deprotonation of trimethylsilyl acetylene with ^{n}BuLi, followed by reaction with carbonyl compounds[53] and cleavage of the silyl group with potassium carbonate.[54] Alkynol-*N*-diphenylanilides **58** and diethyl hydroxyalkynylphosphonates **59** can be obtained by protection of the alkynols **57** with dihydropyrane (DHP), deprotonation with ^{n}BuLi, reaction of the acetylides thus generated with diphenylcarbamoyl chloride or phosphoric acid diethylester chloride, and a subsequent acidic hydrolysis.[51,55] Reaction of the alkynols **57** with alkaline sodium hypochlorite or potassium hypochlorite solutions leads to the halo alkynols **60**[56] *via* proton/halogen exchange (Scheme 17).

The alkynols **58–60** readily react in the presence of triethylamine with arylsulfenyl chlorides, arylsulfinyl chlorides, diethoxychlorophosphane or diphenylchlorophosphane to give the corresponding alkynyl esters, some of which are thermally quite stable. However, on heating in toluene at 80 °C they isomerize quantitatively *via* a [2.3]-sigmatropic rearrangement[57] to give the allylic sulfoxides **61**, allenesulfones **62**, allylic phosphoric acid esters **63** or allylic phosphane oxides **64**[51,55,58] (Scheme 18).



Scheme 17

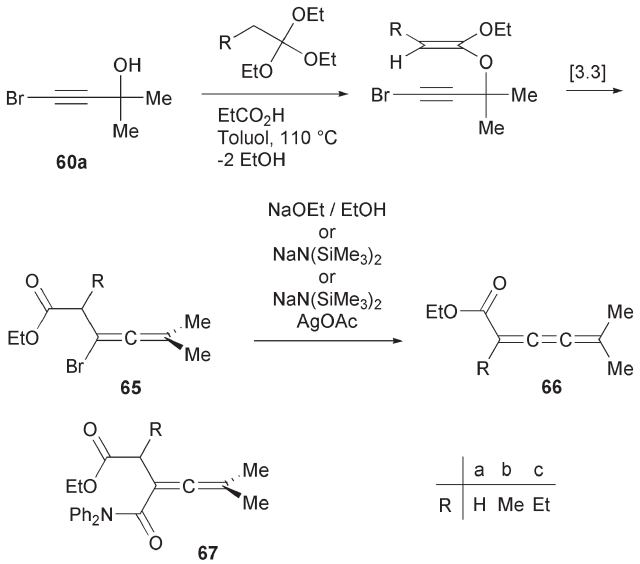


	58	59	60
Y	Ph_2NCO	$(EtO)_2PO$	Hal
61-64	a	b	c

Scheme 18

8. Cumuhomologation: Butatrienes from halo allenes *via* [2.3]-sigmatropic rearrangement of alkynylvinyl ketene acetal ethers

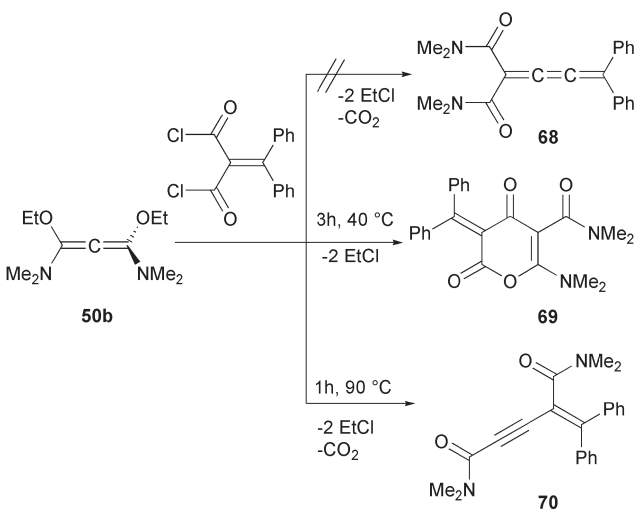
The acid catalyzed reaction of bromo alkynol **60a** with triethyl orthoesters and elimination of two moles of ethanol gives the intermediate alkynylvinyl ketene acetal ethers, which undergo a [3.3]-sigmatropic rearrangement[59] in toluene at 110 °C to yield the halo allenes **65**[55] (Scheme 19). Elimination of



Scheme 19

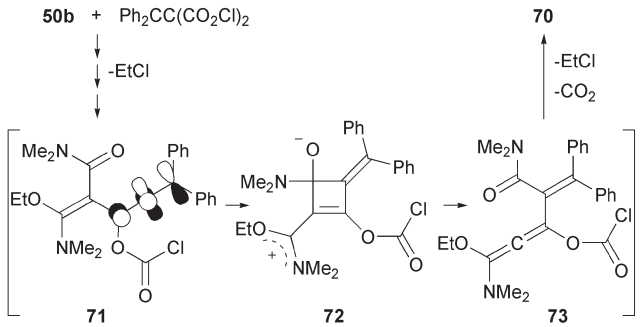
hydrogen bromide from halo allene **65a** with sodium ethoxide in ethanol affords butatriene **66a**. In the contrast, elimination of hydrogen bromide from allene **65b** to give butatriene **66b** is accomplished by sodium bis(trimethylsilyl)amide, whereas halo allene **65c** is dehydrohalogenated to butatriene **66c** by sodium bis(trimethylsilyl)amide in combination with silver acetate.[60] The *cumuhomologation* reaction of propadienes **65** to give butatrienes **66** is impressive due to its simplicity and high yields. Analogously, starting from propargylalcohol **58** (Scheme 17 and Scheme 19), we obtained with triethyl orthoesters the corresponding alkynylvinyl ketene acetal ethers, which, after [3.3]-sigmatropic rearrangement, yielded the carboxanilide allenes **67**.[58]

Our attempts to extend the transallenation of tetradonor-substituted allenes **50** with dialkyl malonyl chlorides to the cumuhomologation of allenes **50** with alkylidene malonyl chlorides failed hitherto. Instead of the expected butatrienes **68**, depending on the reaction conditions, we isolated 2,4-dioxo-pyrane **69** or vinyl acetylene **70** (Scheme 20).[61]



Scheme 20

For the mechanism of forming vinyl acetylene **70**, we propose initially exactly the same steps as discussed for the transallenation shown in Scheme 16. Therefore, similar to the key intermediate **56** of the transallenation reaction, the key intermediate of the cumuhomologation reaction of 1,3-bis(dimethylamino)-1,3-diethoxyallene **50b** with an alkylidene malonyl chloride is the chlorocarbonic allenylester **71**. The intermediate allene **71** then isomerizes *via* cyclobutene **72** with carbon–carbon bond cleavage[48,52] to give 1,1-bis-donor allene **73**. Isomer **73**, compared to **71**, again a carbonic acid derivative, finally eliminates ethyl chloride and carbon dioxide to give the product vinyl acetylene **70**.[27,61] In contrast to **56** of the transallenation mechanism, it is the extra in-plane π-orbital of **71** that allows the isomerization step **71**→**73**, prevents the cumuhomologation and leads to vinyl acetylene **70** as the end product (Scheme 21).



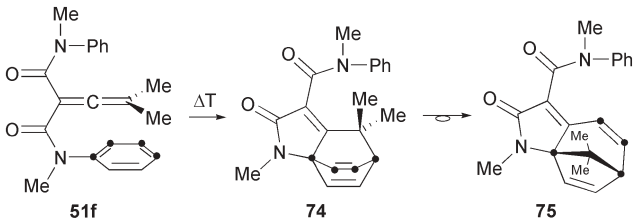
Scheme 21

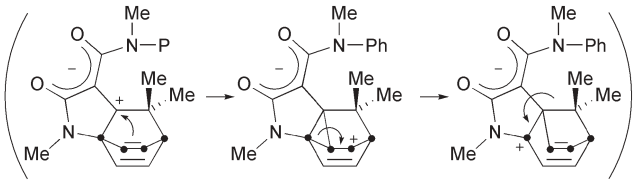
Furthermore, the 1-haloallenes **65** turned out to be useful synthetic building blocks for reacting with trimethylstannyl acetylenes *via* palladium-mediated carbon–carbon coupling reactions to give yne-allenes.[62,63]

9. Intramolecular Diels–Alder reactions of allenecarboxanilides

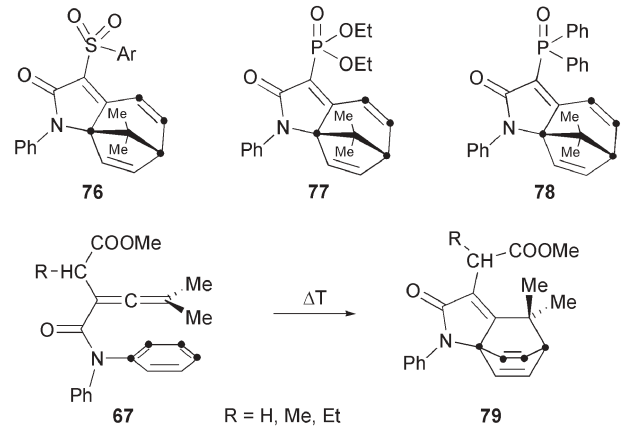
Allenecarboxanilides generally undergo intramolecular Diels–Alder reactions.[50,51,64–67] This is also true for the readily available allene-1,1-dicarboxanilides **51f**, **62a–64a** and **67**. For instance, when *N*,*N*′-dimethyl-allene-1,1-dicarboxanilide **51f** is heated neat or in DMSO to 150–200 °C, an intramolecular Diels–Alder reaction of the *N*-phenyl ring and the terminal allene double bond generates the [2.2.2]-bicycle **74**, which spontaneously isomerizes to give [3.2.1]-bicycle **75**. The bicyclo[2.2.2] → bicyclo[3.2.1] skeletal rearrangement probably proceeds *via* the rearrangement of a homoallyl cation (part of the zwitterion) to the corresponding cyclopropyl-methyl cation, followed by a *N*-stabilized allyl cation and a final 1.2-alkyl shift (Scheme 22).

Similarly, the allenecarboxanilides **62a**, **63a** and **64a** on heating undergo intramolecular Diels–Alder reactions and isomerization to give the [3.2.1]-bicycles **76**, **77** and **78** in good yields (60–70%).[50,51] It is worthy noting, however, that we succeeded only in the case of *N*-phenyl-allene-1-carboxanilide **67** to isolate the initial [2.2.2]-bicyclic Diels–Alder product **79**[51] (Scheme 23).





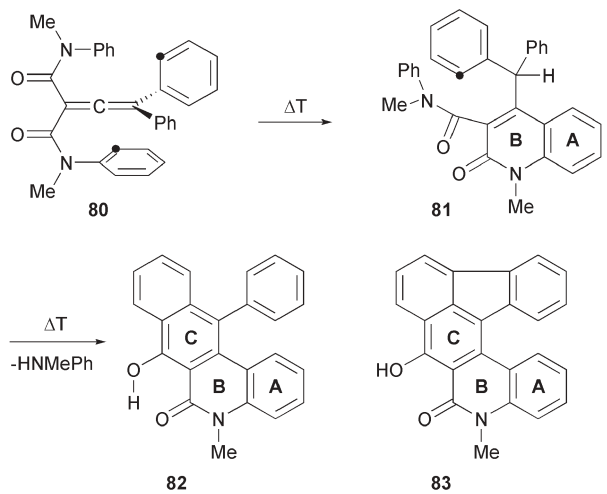
Scheme 22



Scheme 23

10. Intramolecular domino cyclizations of allenecarboxanilides

When *N*,*N*′-dimethyl-allene-1,1-dicarboxanilides containing aryl substituents in the 3-position are heated in DMSO, they react completely differently to those containing simple alkyl substituents (Scheme 23 and Scheme 24). Whereas the

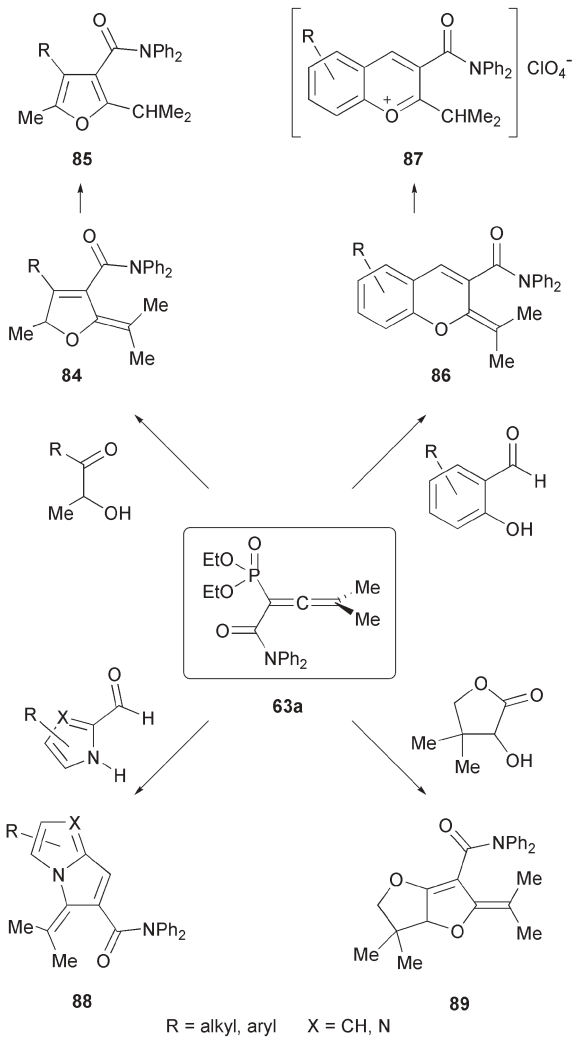


Scheme 24

alkyl-substituted derivatives readily undergo, as expected, intramolecular Diels–Alder reactions followed by profound rearrangements of the molecular skeleton, in 3,3-diphenyl-*N*,*N*′-dimethyl-allene-1,1-dicarboxanilide **80** the phenyl groups are involved in the rearrangement process. On heating **80** in DMSO to 80 °C, electrophilic attack of the central allene carbon on the *ortho*-position of one of the anelide phenyl rings, followed by a 1.3-hydrogen shift, yields 2-chinolinon **81**. Further cyclization of **81** *via* electrophilic attack of the amide carbonyl carbon at one of the originally terminal allene phenyl groups in the *ortho*-position and subsequent aromatization by loss of *N*-methyl aniline affords phenanthridone derivative **82**. The fluorenylidene analog of **80** is a precursor of **83**[50a,51,64a] (Scheme 24). The phenanthridone skeleton is part of numerous natural products such as oxysanguinarine, a substance produced by *Amaryllis deceae*.[68]

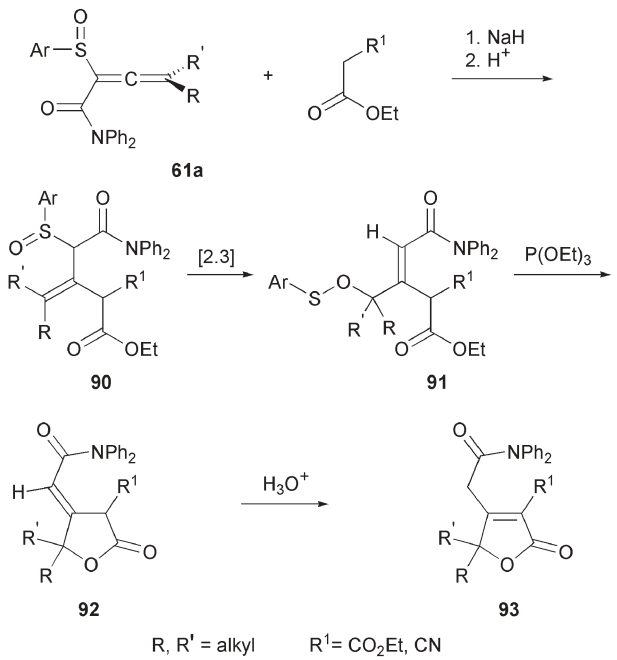
11. Heterocycles from *N*,*N*-diphenyl-1-(diethoxyphosphoryl)allene-1-carboxanilide *via* consecutive Michael addition and Horner–Emmons reaction

Michael addition of α-hydroxyketones to (diethoxyphosphoryl)allene **63a** and a subsequent Horner–Emmons reaction affords alkylidene-dihydro furans **84**, which isomerize to furans **85** under base catalysis (Scheme 25). Similarly, *ortho*-hydroxybenzaldehydes first lead to the alkylidene chromenes **86**, which were protonated by perchloric acid to give benzopyrylium salts **87**. Interesting heterocycles **88** are accessible from **63a** and pyrrole- or imidazole-aldehydes. The reaction sequence Michael addition/Horner–Emmons reaction proceeds even with α-hydroxylactones, as demonstrated by the formation of alkylidene dihydrofuran **89**.[51]



Scheme 25

Similarly, allylic sulfoxides such as **61a** react with CH-acidic compounds in the presence of sodium hydride, with subsequent protonation giving Michael products **90** after the first step (Scheme 26). These allylic sulfoxides readily undergo a two step reaction cascade ([2.3]-sigmatropic shift, sulfenic acid ester/butyrolactonization) to generate the lactones **92** *via* **91** and a subsequent cyclization. Tautomerization of lactones **92** yields the butenolides **93** as the final products.[51] In some cases, this transformation has to be supported by thiophiles such as triethyl phosphite.[69]

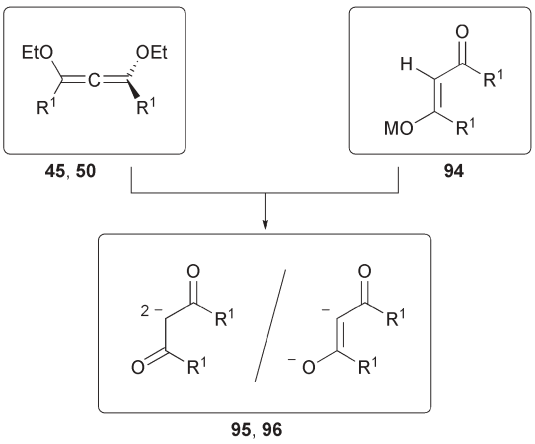


Scheme 26

12. Impact

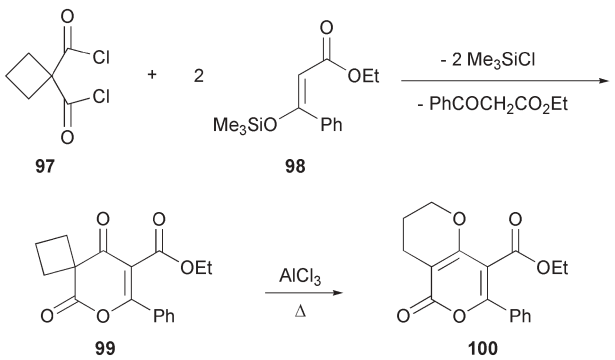
12.1 Synthon strategy

The synthon strategy proved to be very successful for the development of new synthetic methods.[70] In this context, our attention was drawn to the tetradonor substituted allenes **45** (R^1 = OEt) and **50** (R^1 = NR_2), which act as 1,1-/1,3-dianions **95/96** of malonic esters or malonamides.[42a,48,50a,61,71] On the basis of this concept, we used enolates and silylenolethers **94** (M = Li, $SiMe_3$) of 1,3-dicarbonyl compounds, as well as 1,3-dianion equivalents **96** (R^1 = OEt, alkyl, aryl)[47,72,73] (Scheme 27).



Scheme 27

For example, reaction of cyclobutane-1,1-dicarbonyl dichloride **97** with two equivalents of silylenolether **98** affords 2,4-dioxo-2*H*-pyran **99**. Spiro compound **99** isomerizes on heating with aluminum trichloride to 2-pyrone **100**[47] (Scheme 28).

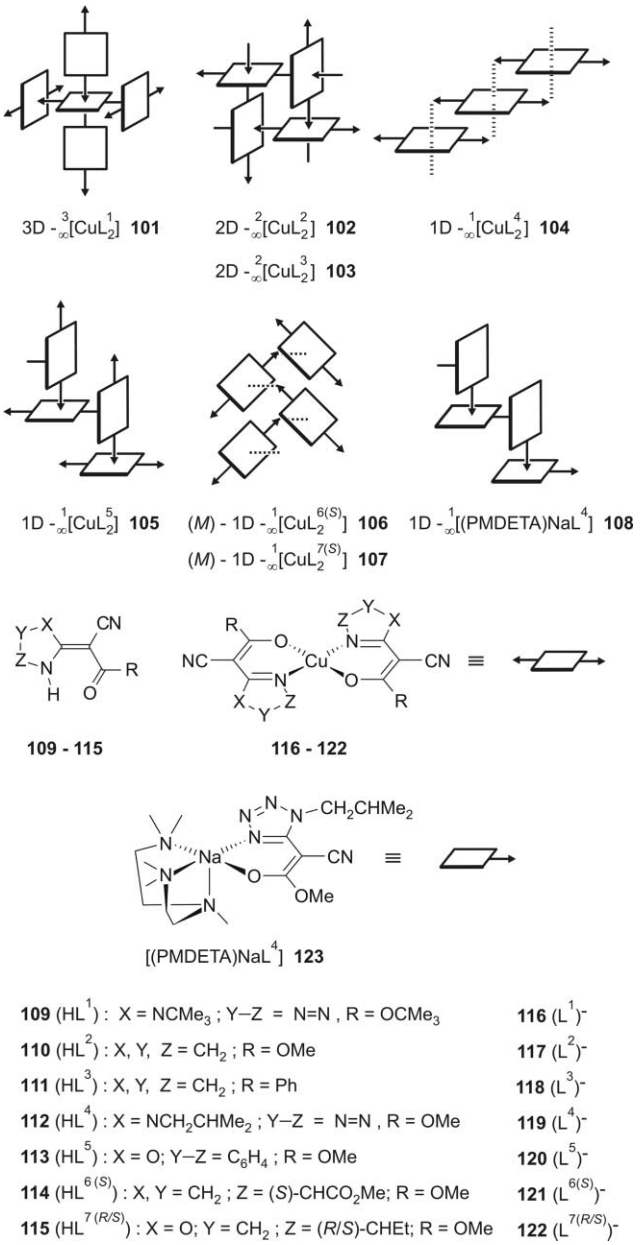


Scheme 28

12.2 One-, two- and three-dimensional coordination polymers

In Section 4, we discussed the 1,5′-cyclization of vinyl-azides **17**, affording tetrazolylidenes **20**. With completely different aims in mind, we realized that **20** is an excellent ligand for iron and copper. In this section we demonstrate that compounds similar to **20**, like **109–115** (HL^{1-7}),[74] allow the construction of various coordination polymers.[75–88] In principle, the monoanionic bidentate ligands $(L^{1-7})^-$ give rise to the neutral, coordinatively-unsaturated building blocks **116–122** with two extra CN-donor groups. Thus, the monomers **116–122** are self complementary and consist of both coordinatively-unsaturated metals and bidentate CN-ligands that yield various 1D-, 2D- and 3D-coordination polymers **101–108** (Scheme 29, Fig. 1).

We have shown that the reaction of a methanolic solution of copper(II) acetate with tetrazole **109** (HL^1) leads to the formation of the three-dimensional coordination polymer 3D-$^3{}_\infty[CuL^1{}_2]$ **101**,[78,81] whereas, under identical reaction conditions, the pyrrolidines **110** (HL^2) and **111** (HL^3) form



109 (HL^1) : X = $NCMe_3$; Y–Z = N=N , R = $OCMe_3$ — **116** $(L^1)^-$

110 (HL^2) : X, Y, Z = CH_2 ; R = OMe — **117** $(L^2)^-$

111 (HL^3) : X, Y, Z = CH_2 ; R = Ph — **118** $(L^3)^-$

112 (HL^4) : X = NCH_2CHMe_2 ; Y–Z = N=N , R = OMe — **119** $(L^4)^-$

113 (HL^5) : X = O; Y–Z = C_6H_4 ; R = OMe — **120** $(L^5)^-$

114 ($HL^{6(S)}$) : X, Y = CH_2 ; Z = (*S*)-$CHCO_2Me$; R = OMe — **121** $(L^{6(S)})^-$

115 ($HL^{7(R/S)}$) : X = O; Y = CH_2 ; Z = (*R*/*S*)-CHEt; R = OMe — **122** $(L^{7(R/S)})^-$

Scheme 29

two-dimensional coordination polymers 2D-$^2{}_\infty[CuL^2{}_2]$ **102**[77,83] and 2D-$^2{}_\infty[CuL^3{}_2]$ **103**, respectively.[75]

Unexpectedly, reaction of methanolic copper(II) acetate solution with tetrazole **112** (HL^4) furnishes the one-dimensional coordination polymer 1D-$^1{}_\infty[CuL^4{}_2]$ **104**.[75,82,88,89] In the case of **104**, a parallel rather than a perpendicular orientation of the building blocks **119** leads to the one-dimensionality. A one-dimensional zigzag coordination polymer 1D-$^1{}_\infty[CuL^5{}_2]$ **105** was also obtained starting from benzoxazolidine **113** (HL^5). The reduced dimensionality of **105** allows monoanion **120** $(L^5)^-$ to coordinate to copper(II) through one cyano group only.[75]

In contrast to the C_{2h}-symmetric monomers **116–120** , the C_2-symmetric building block (*S*,*S*)-**121** $(L^{6(S)})^-$, generated from (*S*)-methoxycarbonylpyrrolidine **114** ($HL^{6(S)}$), is sterically shielded on one side and thus couples only through one

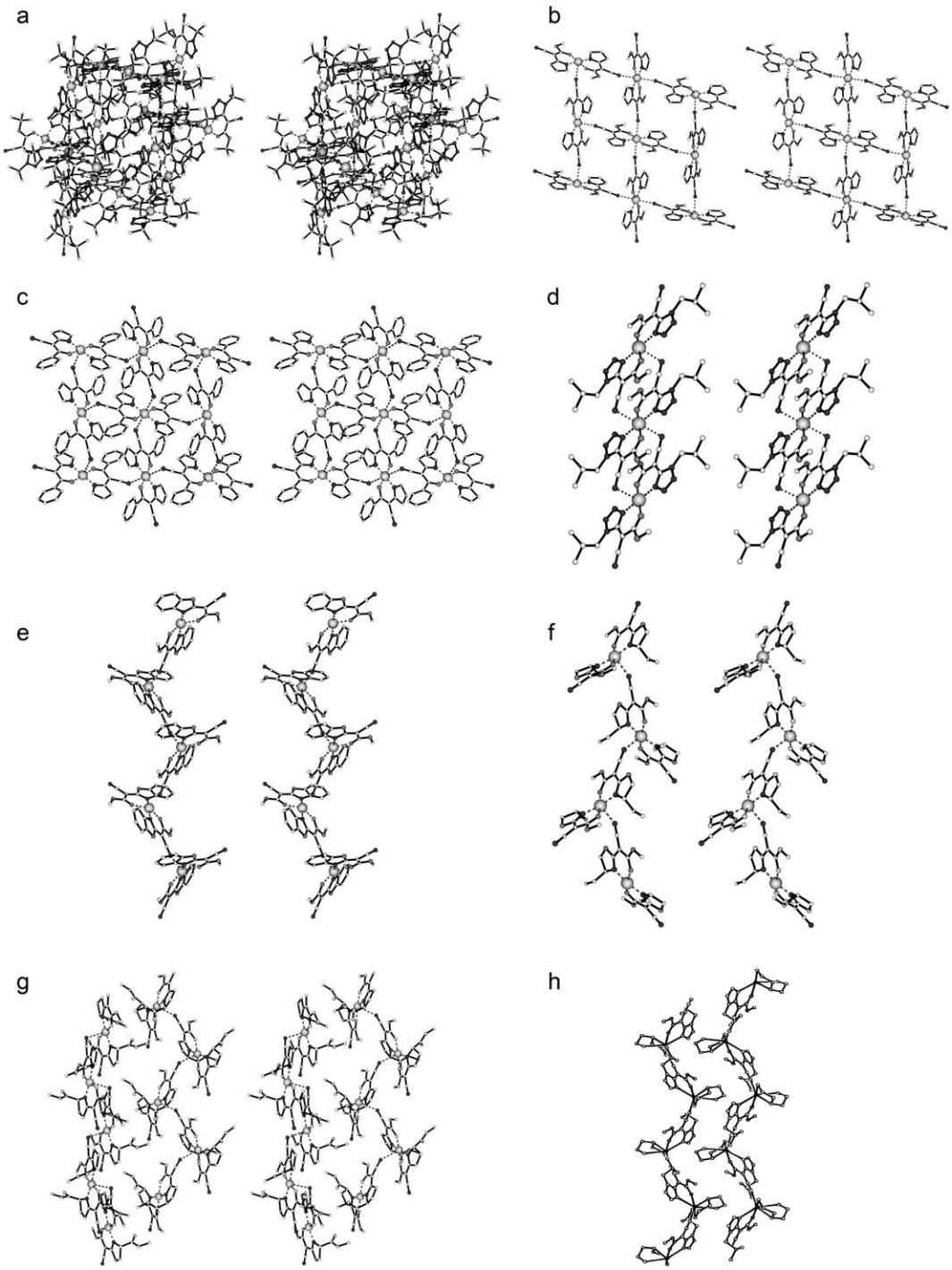


Fig. 1 Molecular structures of **101–108** in the crystal ((a)–(g) Stereoviews: POVRAY presentations): (a) 3D-$^{3}_{\infty}$[CuL^{1}_{2}] **101**, (b) 2D-$^{2}_{\infty}$[CuL^{2}_{2}] **102**, (c) 2D-$^{2}_{\infty}$[CuL^{3}_{2}] **103**, (d) 1D-$^{1}_{\infty}$[CuL^{4}_{2}] **104**, (e) 1D-$^{1}_{\infty}$[CuL^{5}_{2}] **105**, (f) (*P*)-1D-$^{1}_{\infty}$[$CuL^{6(S)}_{2}$]/(*M*)-1D-$^{1}_{\infty}$[$CuL^{6(S)}_{2}$] **106**, (g) (View: PLUTON presentation): (*M*)-1D-$^{1}_{\infty}$[$CuL^{7(S)}_{2}$] **107**, (h) 1D-$^{1}_{\infty}$[(PMDETA)NaL^{4}] **108**.

cyano group. This leads to the helical one-dimensional coordination polymer 1D-$^{1}_{\infty}$[$CuL^{6(S)}_{2}$] **106**. According to the X-ray diffraction analysis, the crystal is composed of two almost identical strands, (*P*)-1D-$^{1}_{\infty}$[$CuL^{6(S)}_{2}$] **106** and (*M*)-1D-$^{1}_{\infty}$[$CuL^{6(S)}_{2}$] **106**, which creates pairs of diastereoisomers.[79] It is worthy to note that the stereogenic centers in (*S*,*S*)-**121** do not lead to asymmetric induction. However, when enantiomerically pure oxazolines **115** ($HL^{7(R/S)}$) were reacted with copper(II) acetate, X-ray analysis of the resulting crystals revealed the formation of one-dimensional strands of either (*P*)-1D-$^{1}_{\infty}$[$CuL^{7(R)}_{2}$] **107** or (*M*)-1D-$^{1}_{\infty}$[$CuL^{7(S)}_{2}$] **107** helicity.[76,90] Each cylindrical strand was formed by a set of C_2-symmetric copper(II) building blocks (*R*,*R*)-**122** or (*S*,*S*)-**122**.

Another strategy (aside from steric hindrance), in which reduced dimensionality might be achieved, is to use a Group 1 metal. In such a case, regardless of steric considerations, only

one cyano donor group per monomeric **123** unit is available for coordination to another metal center. However, a prerequisite is the pre-capping of the metal. The reaction of sodium hydride with tetrazole **112** (HL^4) in the presence of PMDETA (pentamethyldiethylenetriamine) in toluene affords one-dimensional coordination polymer $1D\text{-}^1{}_\infty[(PMDETA)NaL^4]$ **108**.[80]

Summary

The purpose of this Feature Article has been to demonstrate that recognizing the similarities in different areas of chemistry allows the prediction of potential results in related fields. For instance, during our investigations of 2,2-diethoxyvinylidenetriphenylphosphorane we became interested in 2,2-diethoxydiazoethene. In order to obtain diazoethenes, we studied vinyl-diazonium salts and geminal vinyl-diazides as potential precursors. In the course of these investigations we realized their synthetic potential to produce, *via* substituent-dependent 1,5-, 3,5- or 1,5′-cyclization, a whole variety of heterocycles. However, more importantly, we became familiar with the chemistry of carbenes, which prompted an investigation of the carbene-like character of push–pull-substituted allenes. Due to the ambiphilicity of their central carbon atom, they readily dimerized. Consequently, our strong interests in push–pull-substituted allenes drew our attention to tetradonor substituted allenes, and as a result, we employed tetraethoxyallene as a synthetic equivalent to the fictitious malonic ester 1,1-/1,3-dianion synthon. This concept led to the synthesis of heterocumulenes, and to transallenation reactions to give allenecarboxanilides. 1,1-Functionalized allenes were also prepared from propargylalcohols *via* [2.3]- and [3.3]-sigmatropic rearrangements and the halo allenes were transformed *via* cumuhomologation to butatrienes. The Diels–Alder reaction and intramolecular domino cyclizations of the multifunctional allenecarboxanilides yielded complex fused heteroarenes. Finally, the 1,5′-cyclization of the vinyl-azides reported earlier provided tetrazolylidene ligands, triggering our interest in supramolecular coordination chemistry, for example the synthesis of one-, two- and three-dimensional coordination polymers.

Outlook

The preceding text has been designed to emphasise the achievements across different fields and demonstrate our straightforward evaluation of developing new synthetic aspects, through which runs a common thread. It is worth noting that our recent interests, which deal with the synergistic effect of serendipity and rational design in supramolecular coordination chemistry, are based on the experiences summarized in this Feature Article. In our up-to-date work we combine the principles of supramolecular coordination chemistry with those of single molecule magnetism. For instance, we have obtained for the first time the mixed valence inclusion complexes $[M\subset Fe^{III}{}_3(L^8)_6]$ **124** from the reaction of dialkylmalonates with methyllithium, iron(II) chloride and oxalyl chloride, followed by work-up with aqueous ammonium or alkaline salts.[91] Single molecule magnet (SMM) $\{Fe[Fe(L^9)_2]_3\}$

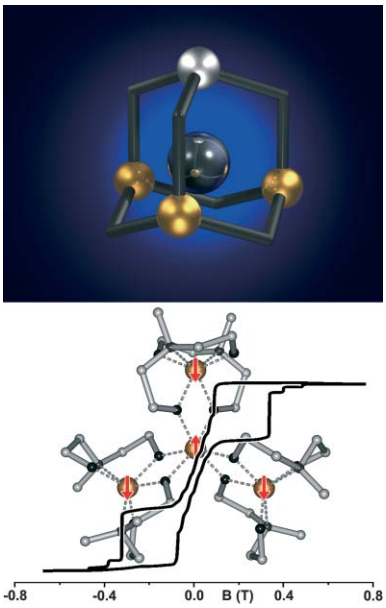


Fig. 2 Top: Schematic presentation of mixed valence, tetranuclear iron cryptate $[M\subset Fe^{III}{}_3(L^8)_6]$ **124** (colour code: $Fe^{II} \equiv$ silver, $Fe^{III} \equiv$ gold, $M(NH_4, K, Cs) \equiv$ anthracite, bracket $(L^8)^{2-} \equiv$ tetraalkyl-2,3-dioxobutane-1,1,4,4-tetracarboxylato-dianion). Bottom: Star-shaped single molecule magnet $\{Fe[Fe(L^9)_2]_3\}$ **125**, together with the hysteresis loop highlighting its SMM behaviour.

125 was formed when *N*-methyldiethanolamine (H_2L^9) was deprotonated with sodium hydride, followed by titration of $(L^9)^{2-}$ with a solution of iron(III) chloride up to an iron/ligand ratio of 1 : 1.5 (Fig. 2).[92]

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