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A novel twist on an old theme: β -Halovinylsilanes, a new elimination approach to oligoynes assembly

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Abstract

This article summarises our recent efforts towards using β -halovinylsilanes in a new approach to oligoynes assembly. β -Halovinylsilanes are particularly useful masked alkynes since the free alkyne can be released under mild reaction conditions by treatment with fluoride. To this end, β -chlorovinylsilane and β -fluorovinylsilane motifs have been incorporated into a 1-trimethylsilyl-hexa-3-en-1,5-diyne scaffold. Oxidative dimerisation of this masked triyne provides a centrosymmetric masked hexayne, which serves as our building block for oligoynes assembly. We have assembled a masked dodecayne using this methodology and shown that treatment of the masked dodecayne with fluoride effects a four-fold dechlorosilylation to provide the corresponding dodecayne, which is the longest aryl end-capped oligoynes reported to date. This long-chain oligoynes proved to be highly unstable. Molecular encapsulation provides a potential solution to the problem of instability associated with long-chain oligoynes, and preliminary results where one of our masked hexaynes was modified in order to form an insulated system are presented. **To cite this article:** *M. D. Weller, L. R. Cox, C. R. Chimie 12 (2009).*

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Résumé

Cet article présente notre nouvelle approche vers l'assemblage d'oligoynes à partir de β -halovinylsilanes. Les β -halovinylsilanes sont d'utiles alcynes masqués puisque ceux-ci peuvent être libérés dans des conditions douces par un traitement à l'ion fluorure. Pour cette raison, les motifs β -chlorovinylsilanes et β -fluorovinylsilanes ont été incorporés dans la structure η -enediynique. La dimérisation oxydante de ce triyne masqué fournit un hexayne masqué centrosymétrique pour servir de brique d'assemblage pour la préparation d'oligoynes. Nous avons utilisé cette méthodologie pour construire un dodecayne masqué. Quatre dechlorosilylations sont effectués par traitement avec l'ion fluorure pour donner le dodecayne correspondant, qui est le plus long oligoynes terminé par des groupements aryles reporté à ce jour. Cet dodecayne s'est avéré hautement instable. L'encapsulation moléculaire est une solution potentielle à ce problème d'instabilité due à la longue chaîne oligoynique; les résultats préliminaires concernant la modification d'un de nos hexaynes masqué pour former un système isolé sont présentés. **Pour citer cet article :** *M. D. Weller, L. R. Cox, C. R. Chimie 12 (2009).*

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Mots-clés : Elimination ; Alcyne ; Oligoynes ; Vinylsilane ; Halogénure de vinyle ; Système conjugué ; Encapsulation moléculaire

1. Introduction

The alkyne functionality occurs widely in natural products [1], and increasingly as a component of highly π -conjugated organic polymers [2], which are finding application in advanced materials. Moreover, since alkynes are amenable to elaboration, they are also used widely as intermediates for further synthesis. Although a number of alkyne building blocks are commercially available, *de novo* routes to this functionality from other starting materials are still very commonly used. In this perspective, we wish to review an elimination strategy to alkynes, which we have developed over the past five years and applied to oligoynes assembly. Our approach has required the development of a new method for synthesising β -halovinylsilanes, which act as our alkyne precursors. The elimination route to alkynes, however, has a long history and before we describe our own contribution to this field, we provide a brief overview of existing elimination approaches to alkynes, which will place our own work into its wider context.

1.1. Elimination approaches to alkynes

Elimination strategies offer a particularly attractive approach to alkynes [3]. Of the many variants that are available, the base-mediated dehydrohalogenation of vinyl halides is one of the oldest and still most widely used (Scheme 1a) [4]. The two-fold dehydrohalogenation of vicinal [5] and geminal [6] dihalides provides a useful variant (Scheme 1b), and in a related approach, a 1,4-dehydrohalogenation of 1-bromo[3]-cumulenes has been used to prepare 1,3-diynes (Scheme 1c) [7].

Although halogen substituents are the most common nucleofuges in elimination precursors, a wide range of other leaving groups has been employed including sulfones [8], sulfonates [9] and stannanes [10]. Enol phosphates, such as **1** also undergo elimination to the corresponding alkyne **2** on treatment with base (Scheme 2a) [9d,f,11]. Moreover, since this alkyne precursor is generated from the corresponding ketone enolate, this approach provides a useful route to alkynes from readily obtained carbonyl compounds. In an attractive variant on this strategy, Fleming and

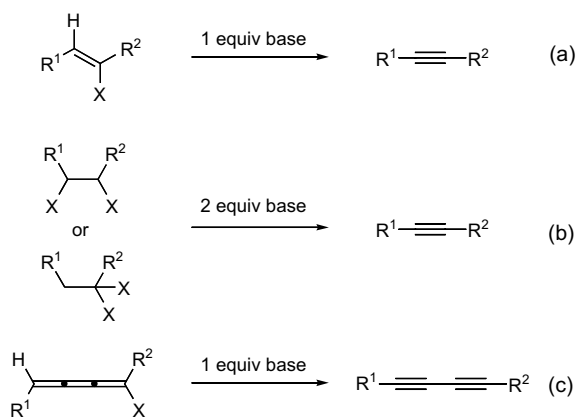
Ramarao reported a decarboxylative elimination route to alkynes (Scheme 2b) [12]. The enol triflate precursor **3** was readily prepared from the corresponding β -ketoester **4**. Subsequent acid-mediated hydrolysis of the *tert*-butyl ester in **3**, followed by treatment with base, generated the corresponding carboxylate **5**, which underwent decarboxylative elimination to provide the desired alkyne **6** in good yield. A related approach has also been reported by Zard [13]. More recently, Dudley and Tummatorn reported a related ring opening/fragmentation of dihydropyrones **7** for the synthesis of homopropargyl alcohols **8** (Scheme 2c) [14].

Reductive elimination of vinyl anions possessing a vicinal heteroatom provides another important variant on this approach to alkynes [15]. In the case of 1,2-dihaloalkene precursors, treatment with a metal, such as Zn [16], Sm [17], or SmI₂ [18] likely generates an intermediate vinylmetal species¹, which undergoes β -elimination to provide the corresponding alkyne (Scheme 3a). Ene-1,2-disulfides also undergo a similar reaction on exposure to lithium naphthalenide (Scheme 3b) [19].

Most of the elimination strategies described so far likely proceed through an *anti*-elimination pathway; however, *syn*-elimination processes have also been used to access alkynes [20]. For example, β -silylvinylsulfoxide **9** underwent a *syn*-specific elimination on thermolysis to provide alkyne **10** (Scheme 4a) [20b]. The silyl group in the alkyne precursor was important in this case for isolating the alkyne product: a similar reaction with the non-silylated vinylsulfoxide **11** provided the vinylsulfoxide regioisomer **12**, resulting from addition of the phenyl sulfenic acid elimination by-product to the intermediate alkyne (Scheme 4b).

The *syn*-elimination of vinyl sulfoxides summarised in Scheme 4 nicely illustrates the potential improvements that can be achieved in elimination reactions by replacing the most commonly employed hydrogen electrofuge for a silyl group, and conveniently serves as an introduction to our own work where we have focused on developing a mild and chemoselective elimination route to alkynes, which is amenable to oligoynes assembly.

¹ Radical intermediates may also be involved here.



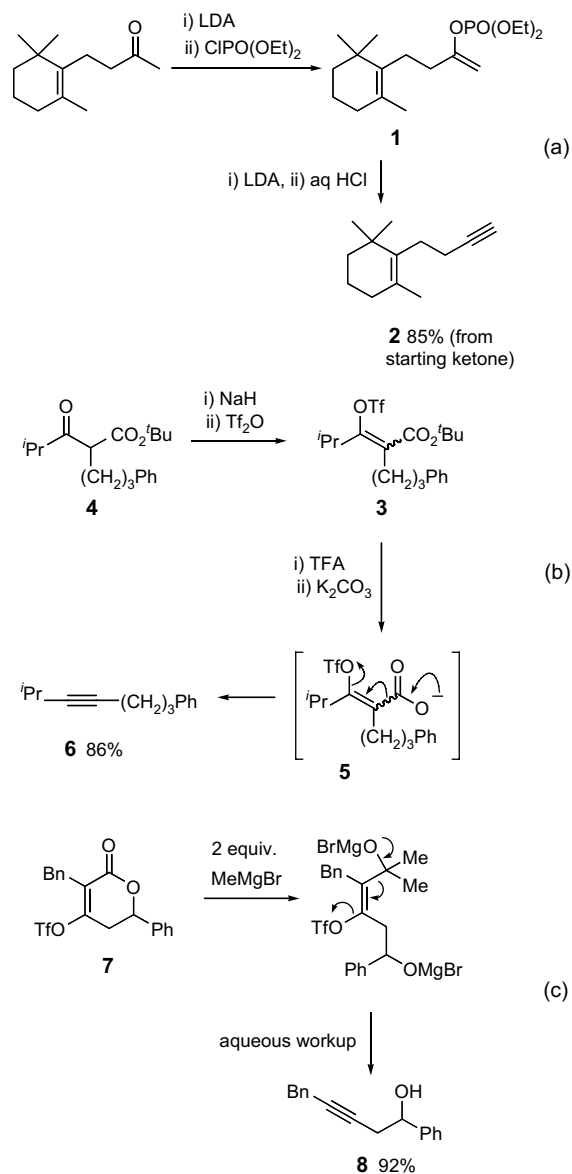
Scheme 1. Base-mediated dehydrohalogenation provides a traditional route to alkynes.

2. Elimination strategies for oligoyne assembly

Many of the available methods of alkyne synthesis, including most elimination approaches, are not conducive to long-chain oligoyne assembly; the reaction conditions are often too harsh and lead to decomposition of the oligoyne product. Although elimination strategies have only occasionally been used to prepare oligoynes [21], we were attracted to the potential simplicity of employing such an approach. To this end, we considered the possibility of employing a β -halovinylsilane motif within a masked oligoyne (Scheme 5). Treatment with a fluoride source would effect dehalosilylation and release the oligoyne chemoselectively, and importantly, under mild conditions. The ability to incorporate a range of silyl groups and halo substituents into the masked alkyne was also attractive since this would allow us to modulate a number of parameters including the solubility and stability of the oligoyne precursor, and the conditions under which unmasking of the oligoyne could be effected. The silyl substituents might also provide a handle for developing potential encapsulation strategies for the conjugated framework (see Section 2.5).

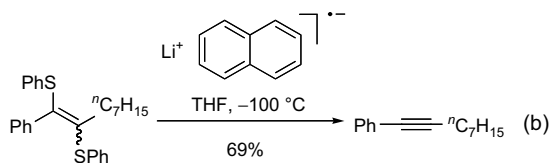
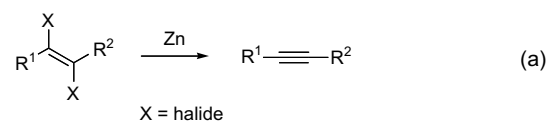
2.1. β -Halovinylsilanes as masked alkyne precursors

Whilst there are many examples where silanes possessing a halide leaving group in the β -position have been used for alkene synthesis [22], when we first set out on this project, only a small number of β -halovinylsilanes had been reported, and even fewer had been used purposefully for alkyne synthesis [23]. Moreover, all the available methods for synthesising β -halovinylsilanes were unsuitable for the



Scheme 2. Enol phosphates and triflates, and dihydropyrones serve as useful alkyne precursors.

tetrasubstituted systems that we would need for our purposes (see below). For example, in an early report, Cunico and Dexheimer prepared (*E*)- and (*Z*)- β -chlorovinyltrimethylsilane from the corresponding β -chlorovinyltrichlorosilanes, which were obtained from the pyrolysis of 1,2-dichloroethene and trichlorosilane [24]. They went on to show that both (*E*)- and (*Z*)- β -chlorovinyltrimethylsilane undergo elimination to provide acetylene on exposure to a fluoride source (Scheme 6a,b) [23a]. Some years later, Danheiser et al. identified the terminal β -chlorovinylsilane **13** as a side-product in the TiCl₄-mediated

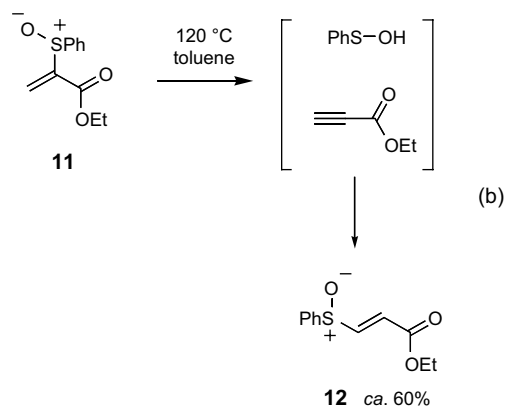
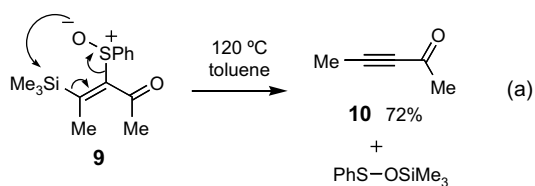


Scheme 3. Vinyl anions possessing a vicinal heteroatom undergo elimination to provide alkynes.

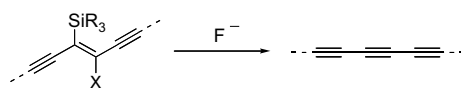
addition of allenyltrimethylsilane into a range of aldehydes, and again demonstrated that this side-product could be converted to the desired homopropargylic alcohol **14** on treatment with fluoride (Scheme 6c) [25]. A similar strategy has also been used by Marshall and Maxson [26].

2.2. A masked triyne target provides a general route to a masked hexayne

Thus with limited, although encouraging, precedent, we set about designing a β -halovinylsilane building block, which could be used for oligoyne assembly. We were attracted to the possibility of incorporating this masked alkyne into an enediynes framework **15**, since

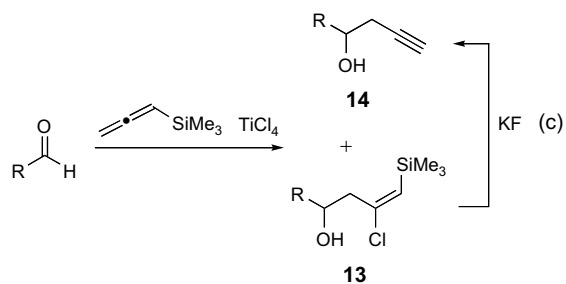
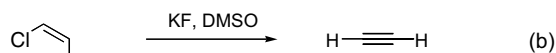
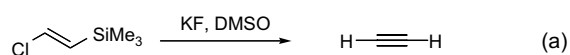


Scheme 4. *Syn*-elimination strategies have been used to prepare alkynes.

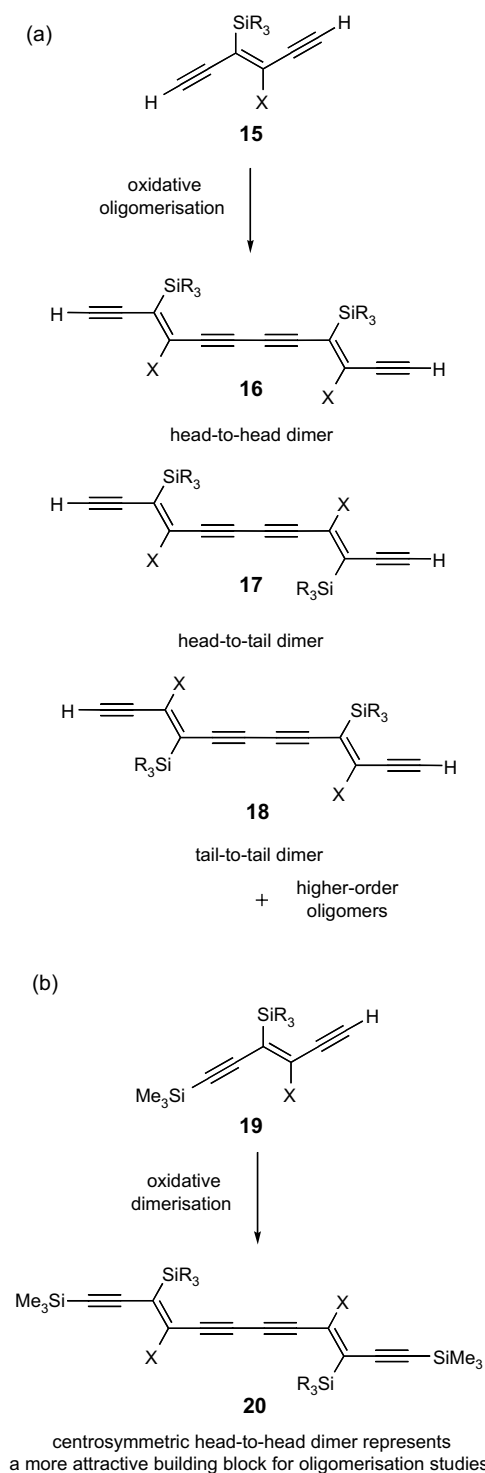


Scheme 5. A β -halovinylsilane would provide a novel masked alkyne for oligoyne assembly.

this would provide an interesting building block in its own right for assembling a novel class of oligo (triacetylene)s containing heteroatom substitution off the conjugated scaffold (Scheme 7) [27]. We envisaged oligomerisation of enediynes **15** could be effected under Eglinton–Glaser–Hay conditions [28]. However, owing to the unsymmetrical nature of the starting monomer, each oligomer would likely be formed as a mixture of constitutional isomers owing to the possibility of head-to-tail (e.g. **16**), head-to-head (e.g. **17**), and tail-to-tail coupling (e.g. **18**); the dimer, for example, would be formed as a mixture of three constitutional isomers **16**, **17** and **18** (Scheme 7a). Whilst this information would be lost on unmasking the oligoyne, we proposed a modification to our building block, which would circumvent this issue and also confer some additional attractive features. Protection of one of the alkyne termini in **15** with a trimethylsilyl group would provide a new masked triyne **19**, which on oxidative homocoupling, would afford the corresponding masked hexayne dimer **20** (Scheme 7b). Providing the trimethylsilyl end-capping groups in **20** could be removed without effecting premature dehalosilylation, the masked hexayne **20** could now be used as a new monomer unit for



Scheme 6. Literature precedent revealed that simple β -halovinylsilanes could be converted into the corresponding alkynes.

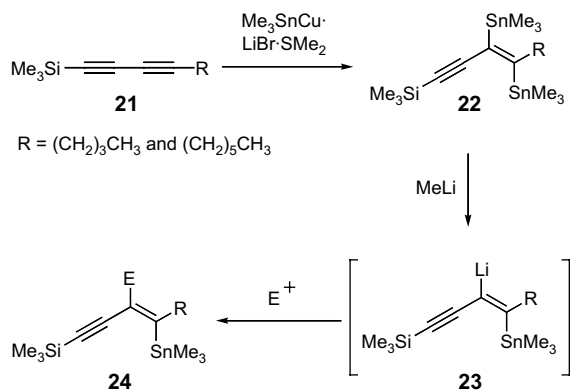


Scheme 7. Centrosymmetric masked hexayne **20** provided an attractive monomer for oligomerisation studies.

oligomerisation studies. Since this masked hexayne is centrosymmetric, each oligomer in the series would be formed as a single constitutional isomer, which would greatly facilitate characterisation. Moreover, by using a relatively large repeat unit, we hoped the large difference in size between the oligomers in the series (the monomer, dimer and trimer in the series would be masked hexaynes, dodecaynes and octadecaynes, respectively) would facilitate their separation by size-exclusion chromatography.

Our first target therefore became masked triyne **19**. In analysing this molecule, we set ourselves a number of design criteria which any synthetic strategy would have to satisfy. First, we wanted to prepare the β -halovinylsilane motif as a single stereoisomer to avoid obtaining mixtures of double bond isomers in our oligomer series. At the outset, we were not too concerned whether this was the (*E*)- or the (*Z*)-stereoisomer, as Cunico and Dexheimer had demonstrated that both could be used as masked alkynes [23a]; however, we expected the (*E*)-stereoisomer would undergo elimination under milder conditions and therefore was our preferred target. Second, we wanted a method that would allow us to incorporate a wide range of silyl groups into the β -halovinylsilane. This would not only be important for modulating the stability of the masked alkyne motif, and the conditions under which elimination would be effected, but as will be discussed later (see Section 2.5), we were keen to investigate the possibility of using the substituents appended off the silicon atom in some form of encapsulation strategy, which we believe is likely to be important for stabilising particularly long-chain oligoynes.

Masked triyne **19** represented an interesting synthetic problem. The most challenging task would involve the stereoselective synthesis of the internal tetrasubstituted olefin. Efficient methods for accessing heavily substituted olefins in a completely stereoselective fashion are scarce [29], and at the outset of this project, a suitable route to a fully substituted olefin containing vicinal silyl and halo substituents had not been developed. A search of the literature uncovered a potentially attractive solution to this problem. In 1987, Zweifel and Leong reported a completely regio- and stereoselective metallometallation of 1-trimethylsilyl-substituted 1,3-butadiene **21** using a stannylcopper reagent that was prepared from equimolar quantities of Me_3SnLi and $\text{CuBr}\cdot\text{SMe}_2$ complex (Scheme 8) [30]. On their limited set of substrates, the group went on to demonstrate that treatment of the bis-vinylstannane **22** product with MeLi effected selective



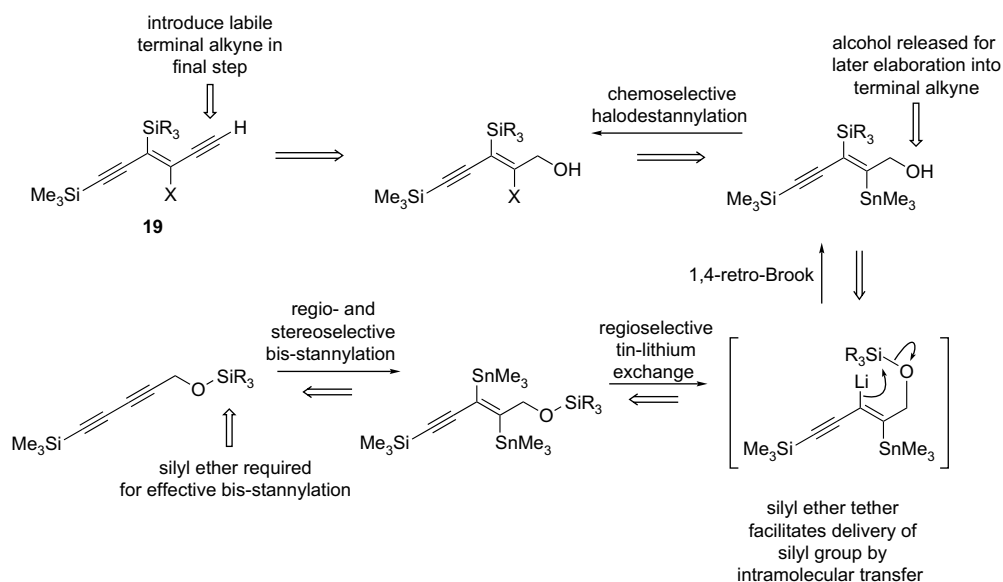
Scheme 8. A 1,2-bis-vinylstannane provides a potential precursor to a β -halovinylsilane.

tin–lithium exchange of the tin residue proximal to the remaining alkyne, to generate a reactive vinyl lithium intermediate **23**, which could be quenched with a small selection of electrophiles to provide vinylstannane **24** (Scheme 8).

We postulated that the two vinylstannane moieties in eneyne **22** could be manipulated sequentially into the vinylsilane and vinylhalide units of our desired β -halovinylsilane. For our purposes, we would need to employ silyl electrophiles to install the vinylsilane motif, after which, we expected the remaining vinylstannane would be used to introduce the vinylhalide through a halodestannylation process [31]. Were the halo substituent to be introduced first, converting the remaining vinylstannane into a vinylsilane, presumably

via a tin–lithium exchange process, would be beset with problems associated with β -halo elimination (see Scheme 3), which would simply return the starting diyne precursor **21**.

Although Zweifel and Leong had shown that a small selection of (reactive) electrophiles could be used to quench the vinyl lithium intermediate **23** [29,32]. We were not confident that this intermolecular trapping strategy would satisfy our needs. Fortunately, work we were carrying out on a different project using silyl tethers to deliver nucleophiles in an intramolecular fashion showed us a potential way forwards [33]. Our retrosynthesis of masked triyne **19** is summarised in Scheme 9. We had already identified a butadiyne containing a hydroxymethyl substituent, as a suitable precursor to our masked triyne. The internal alkyne would serve as the β -halovinylsilane precursor whilst the alcohol functionality would be elaborated into the terminal alkyne; anticipating the masked triyne end-product might exhibit poor stability, this would be done in a final step. Early on, we had shown that it would be necessary to protect the alcohol in our starting butadiyne in order to effect an efficient bis-stannylation reaction. We therefore postulated that if we protected the alcohol as a silyl ether, then this protecting group could serve a second role acting as a tethered silyl electrophile for introducing the vinylsilane through a 1,4-retro-Brook rearrangement [34] using Zweifel's tin–lithium exchange chemistry (Scheme 9). We expected this approach would have profound benefits for preparing systems containing bulky silyl groups,



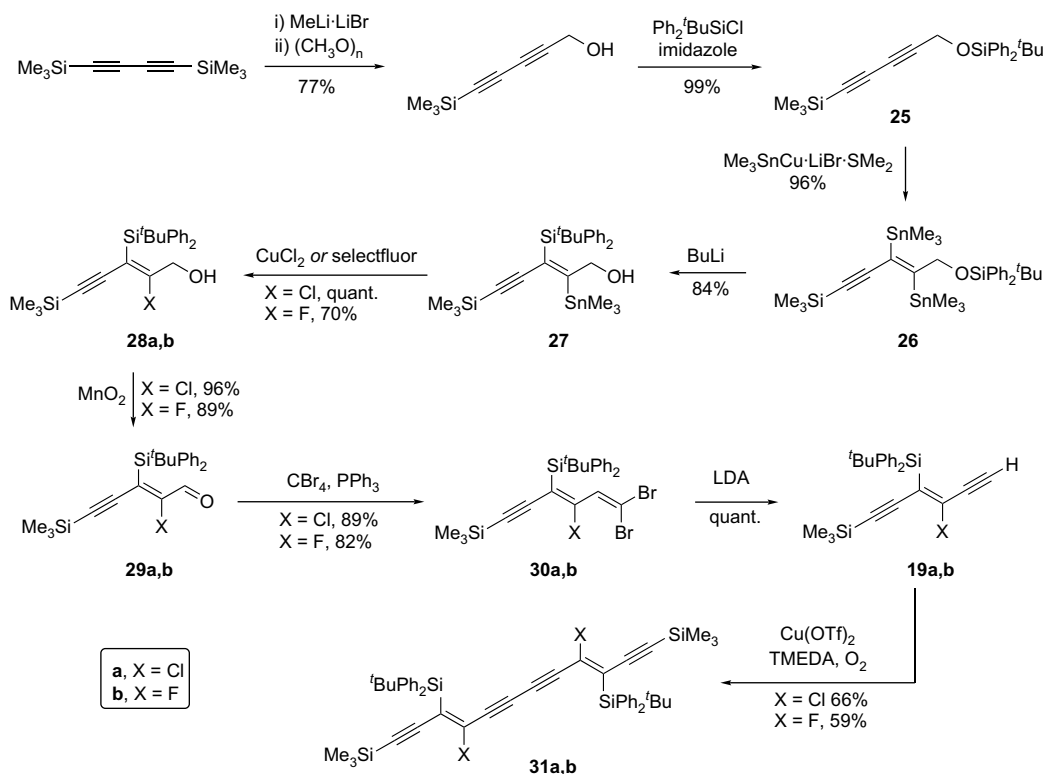
Scheme 9. Retrosynthesis of masked triyne **19**.

which would otherwise be difficult to incorporate were we forced to rely on an intermolecular reaction for introducing these motifs. Further elaboration into our masked triyne target would then be straightforward (Scheme 9).

Since one of our principal research goals was to access long-chain oligoynes, our first target was masked triyne **19a**, which contains a trimethylsilyl-substituted alkyne that would allow further elaboration (see Section 2.4). We have reported the synthesis of masked triyne **19a**, which is summarised again in Scheme 10 [35].

The key bis-stannylation of 1,3-butadiyne **25** proceeds with complete regiocontrol and in excellent yield, providing bis-vinylstannane **26** as a single (*E*)-stereoisomer. The reaction also works well using the (less toxic) tributylstannylcopper reagent although subsequent processing of the two tributylstannyl functionalities is far less efficient [36]. We do not fully understand the origins of the regioselectivity in this key reaction. One could argue that the bulky trimethylsilyl substituent controls the regiochemistry for steric reasons; however, since replacing this silyl end-cap with an aryl substituent also leads to the same regiochemical outcome, we tentatively propose that the

trimethylsilyl or aryl substituents exert a mesomeric directing effect, which leads to the observed regioselectivity. That bulky silyl groups, which generally disfavour coordination of metals to the Lewis basic oxygen centre, also give the same regiochemical outcome, suggests a coordinative directing effect from the silyl ether is probably not important. Treatment of bis-stannane **26** with BuLi effects the planned 1,4-retro-Brook rearrangement and transfers the silyl group contained within the silyl ether to an internal position. Although we show the formation of the TBDPS derivative **27** in Scheme 10, this reaction works well for a range of silyl groups, including systems containing bulky ligands, which would have undoubtedly been difficult to install using an intermolecular trapping of the intermediate vinylolithium species with a silyl electrophile. Converting the remaining vinylstannane in **27** to a vinylhalide is straightforward. Most of our work to-date has focused on using β -chlorovinylsilanes as masked alkynes as we initially argued these would be sufficiently stable to avoid premature dechlorosilylation, and yet would still undergo the desired elimination under mild conditions when required. The vinylchloride in **28a** is readily obtained by treatment with CuCl₂. This reaction proceeds with



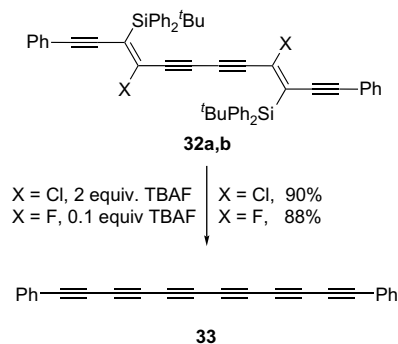
Scheme 10. Synthesis of masked triyne **19** and centrosymmetric masked hexayne **31**.

retention of configuration, which has been confirmed by X-ray crystallography [35]. More recently we have also explored the introduction of other halogen substituents and shown that vinylstannane **27** can be converted to the corresponding fluoride, bromide and iodide [31]. The bromo and iodo derivatives proved to be too labile to be useful candidates for further investigation; however, the β -fluorovinylsilane **28b**, which is obtained by treating **27** with selectfluor[®], has led to a particularly useful development, about which more will be said in Section 2.3. The 1,4-retro-Brook rearrangement releases an alcohol functionality in **27**, which is then elaborated to a terminal alkyne in three straightforward steps: allylic oxidation of **28** affords an intermediate aldehyde **29**, which is then converted to 1,1-dibromoolefin **30** [37]. Finally, exposure of dibromide **30** to an excess of LDA effects a Fritsch–Buttenberg–Wiechell-like reaction to provide a lithiated alkyne, which can be manipulated in a number of ways. Protolytic work-up affords our masked triyne target **19**; however, other electrophiles including TMSCl and acetone have also been used to provide different end-caps. Whilst we have not investigated its application in further synthesis, dehydrobromination in dibromoolefin **30a** using NaHMDS provides a bromoalkyne that could potentially be used in Cadiot–Chodkiewicz-style couplings.

Masked triyne **19** containing a free terminal alkyne is not particularly stable and for this reason, we invariably use this directly in an oxidative dimerisation to afford our second target, namely centrosymmetric masked hexayne **31**. This reaction proved to be an unexpectedly troublesome step and required careful optimisation. The source of copper catalyst seems to be the most important variable for obtaining optimal yields of the dimer, with copper salts containing non-nucleophilic counteranions, in particular Cu(OTf)₂, providing the best results. In summary, our route outlined in Scheme 10 is robust and flexible and allows the introduction of a range of silyl and halo substituents as well as end-capping groups to suit our needs.

2.3. Unmasking the oligoyne

Whilst silyl end-capped masked hexaynes are needed for oligomerisation studies, aryl end-capped masked hexaynes were more useful for investigating unmasking conditions since these end-caps would ensure that relatively stable hexayne products are produced on unmasking. Aryl-substituted masked hexaynes are readily prepared from the corresponding aryl-substituted butadiyne according to Scheme 10. For



Scheme 11. Oligoyne products are released upon treatment with fluoride.

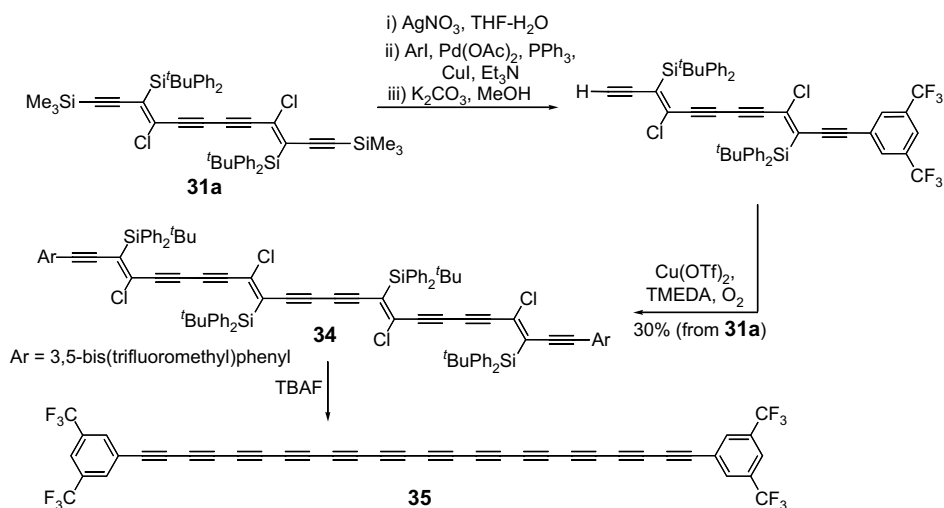
hexaynes containing two β -chlorovinylsilane units (e.g. **32a**), treatment with two equivalents of TBAF (one equivalent per β -chlorovinylsilane) provides the free hexayne **33** in excellent yield (Scheme 11). The reaction is rapid and proceeds at room temperature or below. As described in Section 2.2, we have recently shown that masked hexaynes **32b** containing two β -fluorovinylsilanes can also be prepared. This modification to the masked hexayne framework is particularly appealing because unmasking is now fluoride-catalysed rather than fluoride-mediated [38]. For example, phenyl end-capped hexayne **33** can be prepared from **32b** in excellent yield using just 10 mol% TBAF (Scheme 11) [31].

2.4. Application to the synthesis of an aryl end-capped dodecayne

One of our research goals is to prepare long-chain oligoynes, which provide clipped analogues of a fourth allotrope of carbon known as carbyne (a poly(alkyne)). To this end, we recently dimerised masked hexayne **31a** to afford the corresponding masked dodecayne **34** (Scheme 12). Exposure of **34** to TBAF provided the corresponding dodecayne **35**, which represents the longest aryl end-capped oligoyne reported to date [39]. Dodecayne **35** proved to be highly unstable, even under the very dilute reaction concentrations which were used to effect unmasking; however, this oligoyne was characterised by UV–vis spectroscopy and MALDI-TOF mass spectrometry.

2.5. An encapsulation strategy for stabilising longer chain oligoynes

With some notable exceptions [40], oligoynes (triyne and longer) with hydrogen substituents at the termini exhibit very poor stability in solution as well as



Scheme 12. Using a β -chlorovinylsilane to synthesise the longest aryl end-capped oligoyne reported to date.

in the solid state, where topochemical polymerisation degradation pathways can be a particular problem. One method for stabilising the conjugated scaffold in oligoynes is to incorporate sterically bulky end-caps on the termini [41]; however, as the length of the oligoyne increases, and the end-caps constitute an ever-decreasing component of the system, this method of stabilisation becomes increasingly unsatisfactory. The instability of dodecayne **35** does not bode well for the trimer in this series, which is an octadecayne and represents our next target. For such long-chain systems, a method for providing some form of insulation along the entirety – as opposed to just the termini – of the conjugated carbon chain would be desirable, and indeed some progress has been made in recent years along these lines [42]. We postulated that the silyl substituents appended at regular intervals along the conjugated framework in the masked oligoyne precursor could provide a handle for constructing a macrocycle that encapsulates the conjugated chain. A crystal structure of the phenyl end-capped masked hexayne **32a** suggested a potential strategy for achieving this (Fig. 1) [43].

Of particular interest in the structure of **32a** is the position of the two TBDPS substituents, which occupy opposite sides of the conjugated framework. Even more interesting is the orientation of the phenyl groups within each silyl substituent, which sandwich the conjugated framework. The average distance between the eclipsing carbons in the phenyl rings that make up the sandwich is 6.8 Å, which is less than the sum of the van der Waals radii of the carbon atoms involved ($\text{C}(\text{sp}) = 1.78 \text{ \AA}$, $\text{C}(\text{sp}^2) = 1.77 \text{ \AA}$). We tentatively

propose that this conformation, at least in the solid state, is a consequence of the electron-withdrawing nature of the two chloro substituents, which renders the internal region of the π -conjugated framework electron-deficient. The polarisable nature of the π -cloud within the phenyl substituents then compensates for this through π -stacking. Assuming the crystal structure of **32a** represents a low-energy conformation for this type of masked hexayne, we have used this structural information to advance a novel encapsulation strategy,

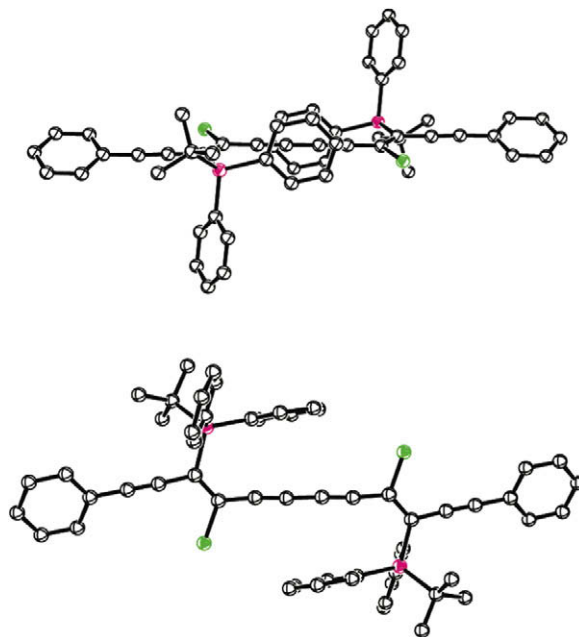
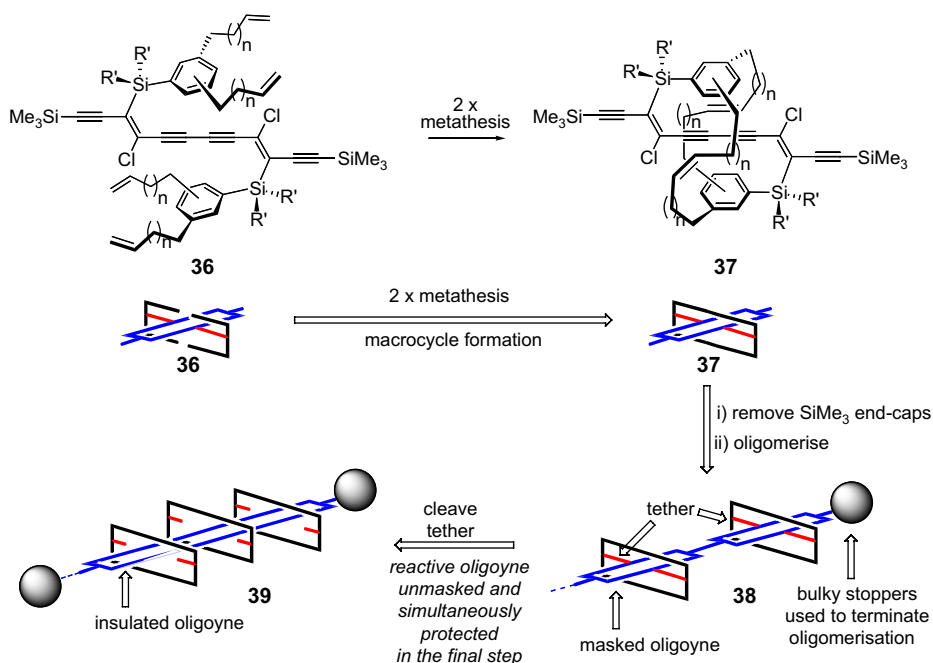


Fig. 1. Crystal structure of masked hexayne **32a**.

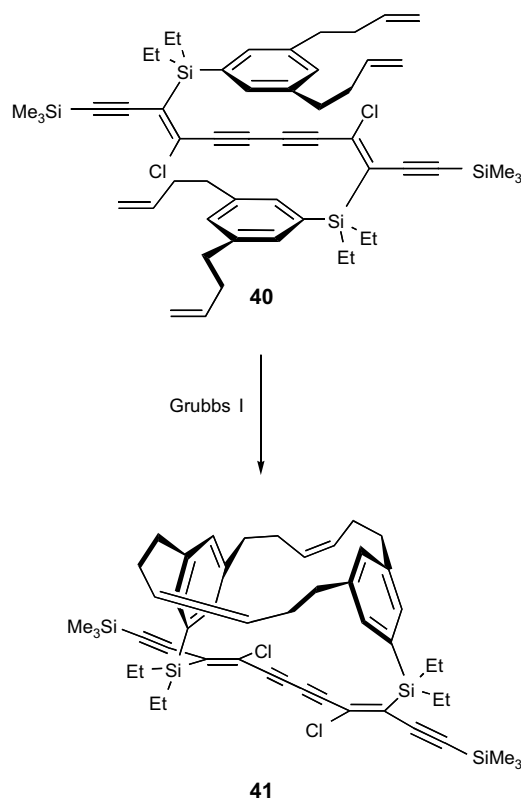


Scheme 13. A novel oligoyne encapsulation strategy.

which would ultimately lead to a rotaxanated oligoyne. Our idea is outlined in cartoon form in Scheme 13.

A phenyl group in the vinylsilane substituents would be functionalised with two alkenyl side-chains. The resulting masked hexayne **36** would then be assembled as outlined in Scheme 10. We then hypothesised that reaction of **36** in the presence of Grubbs' catalyst should effect a double metathesis operation to generate a macrocycle [44]. If the reactive conformation of **36** is similar to that found in the crystal structure of masked hexayne **32a** (Fig. 1), then the macrocycle might encapsulate the conjugated enediyne framework to provide masked hexayne **37** (Scheme 13). Removal of the trimethylsilyl end-caps in **37** and oxidative coupling would generate a series of oligomers. Terminating the oligomerisation with bulky end-capping groups would provide the masked oligoyne **38**. Finally, treatment with fluoride would unmask the oligoyne and simultaneously release the insulating macrocycles (one per six alkynes). Providing the end-caps are sufficiently large, the resulting macrocycles will remain around the oligoyne to afford rotaxane product **39**. This insulation approach is an attractive one in that the unstable oligoyne is only generated in the final step when it is already protected by encapsulation.

In a first attempt, we have prepared masked hexayne **40** in which butenyl substituents were incorporated into the 3- and 5-positions of the aromatic group in the vinylsilane [43]. We were pleased to observe that



Scheme 14. A first attempt at molecular encapsulation of the masked hexayne framework proved unsuccessful.

exposing **40** to Grubbs' catalyst effected a double metathesis operation. Unfortunately in this case, a crystal structure of the product **41** revealed that the macrocycle was crowning rather than encapsulating the enediyne framework (Scheme 14) [43]. Whilst this outcome was disappointing, it is encouraging to observe that (i) the unsaturated enediyne framework is stable under the metathesis reaction conditions and (ii) that a macrocycle was formed. Efforts are now underway to modify the structure of the macrocycle precursor to encourage it to adopt a conformation that is more conducive to threading the conjugated framework.

3. Conclusion and future directions

Whilst oligoynes have been synthetic targets for many years, the synthesis of long-chain systems still represents a state-of-the-art challenge. Since Bohlmann's [21a–d] and Jones' [21e–g] pioneering studies in the 1950s, and Walton's important contributions in the 1970s [45], the last ten years have seen great advances in modern synthetic methods that have provided significant developments in oligoynes assembly, most notably from Hirsch et al. [46], Gladysz et al. [47] and Tykwinski [48]. Our elimination route to oligoynes provides a new approach to oligoynes assembly. The next challenges for us will involve the synthesis of even longer chain systems using molecular encapsulation methods to stabilise the entire length of the labile π -conjugated framework.

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