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Journal of Organometallic Chemistry 691 (2006) 5517–5523
Journal of Organometallic Chemistry
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Note

Towards the synthesis of insulated oligoynes: A ring-closing-metathesis approach to molecular encapsulation

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Received 14 June 2006; received in revised form 24 July 2006; accepted 24 July 2006
Available online 1 August 2006

Abstract

Masked hexayne **18** was prepared in 11 steps from commercially available reagents. The four butenyl substituents contained within the two arylsilane residues in **18** have been used in a double ring-closing-metathesis operation in an attempt to encapsulate the π-conjugated framework. When **18** was treated with Grubbs' 1st generation metathesis catalyst however, double ring-closing metathesis provided macrocycle **19** as the major product in good yield. Reasons why the macrocycle in **19** crowns, rather than encapsulates, the π-conjugated framework are discussed.

Keywords: Oligoynes; Carbyne; Ring-closing metathesis; Molecular encapsulation

1. Introduction

Oligoynes represent clipped versions of carbyne [1], and as such, they serve as useful models for this elusive, fourth allotrope of carbon (Fig. 1) [2]. Although the synthesis of oligoynes up to the hexamer is relatively straightforward, higher-order oligomers exhibit increasing lability, and as a consequence, their assembly represents a state-of-the-art synthetic challenge. In order to minimise some of these lability issues, bulky groups have traditionally been used to cap the oligoyne termini [3–6]. As the degree of oligomerisation increases, however, this stabilisation strategy becomes progressively more ineffective as the end-capping groups constitute an ever-decreasing contribution to the molecular framework. Furthermore, with only the end-caps imparting useful levels of solubility on oligoynes, the handling and processing of long-chain systems can become technically demanding.

We postulated that it might be possible to better suppress intermolecular decomposition pathways by sterically preventing the close association of individual oligoyne molecules along the π-conjugated framework through some form of molecular encapsulation (rather than just relying on stabilising groups at the termini). A number of promising encapsulation approaches have been developed in recent years for a range of π-conjugated organic frameworks [7], including oligoynes [7a,7b,7c], and it is significant that the molecular insulation in these systems modulates the properties, including the lability, of the protected π-conjugated core. As an added advantage, an insulating molecular frame should also provide a means for accessing more soluble, and therefore more processible, products, which should facilitate their characterisation and analysis.

We have been investigating the use of β-chlorovinylsilanes as masked alkynes in oligoyne assembly [8]. Not only can the free alkyne be released under mild conditions upon treatment with fluoride, but the silyl groups also provide a useful handle for constructing an encapsulating macrocycle. We have previously reported a synthesis of masked triyne **1** in which the central alkyne is protected as an (*E*)β-chlorovinylsilane (Scheme 1) [8]. This unit can be dimerised to afford a masked hexayne **2**, from which we have recently prepared the masked dodecayne **3**. As expected, treatment of **3** with fluoride induces dechlorosilylation under mild

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0022-328X/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2006.07.021

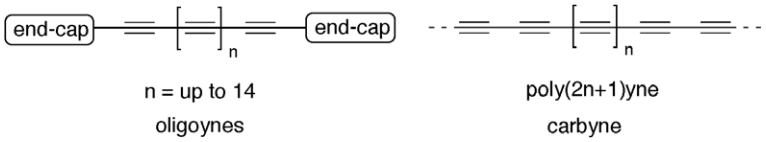


Fig. 1. Oligoynes are clipped versions of carbyne.

conditions, affording the corresponding dodecayne **4** in excellent yield. The dodecayne derived from **3** is extremely labile, and to-date, we have only been able to characterise it by UV-spectroscopy. These observations support our premise that some form of protection will be necessary if we are to stand any chance of accessing higher-order oligoynes. We now report out first attempt towards achieving this.

2. Results and discussion

A crystal structure of masked hexayne **5** provided us with a potential way forward (Fig. 2). We were particularly struck by the conformation adopted by the two *t*-butyldiphenylsilyl (TBDPS) substituents appended on the π-conjugated framework. Within each TBDPS group, one of the phenyl substituents was effectively sandwiching the internal butadiyne portion of the masked hexayne (Fig. 2). We tentatively propose that this is a consequence of the electron-withdrawing nature of the two chloro substituents rendering this 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; in effect, the π-conjugated framework is acting as a template for one phenyl substituent in each TBDPS appendage.

We postulated that it might be possible to exploit this preorganisation effect in a novel encapsulation strategy. After considering a range of options, the double ring-closing-metathesis approach outlined in Fig. 3 seemed to offer a host of particularly attractive features. Ring-closing-metathesis

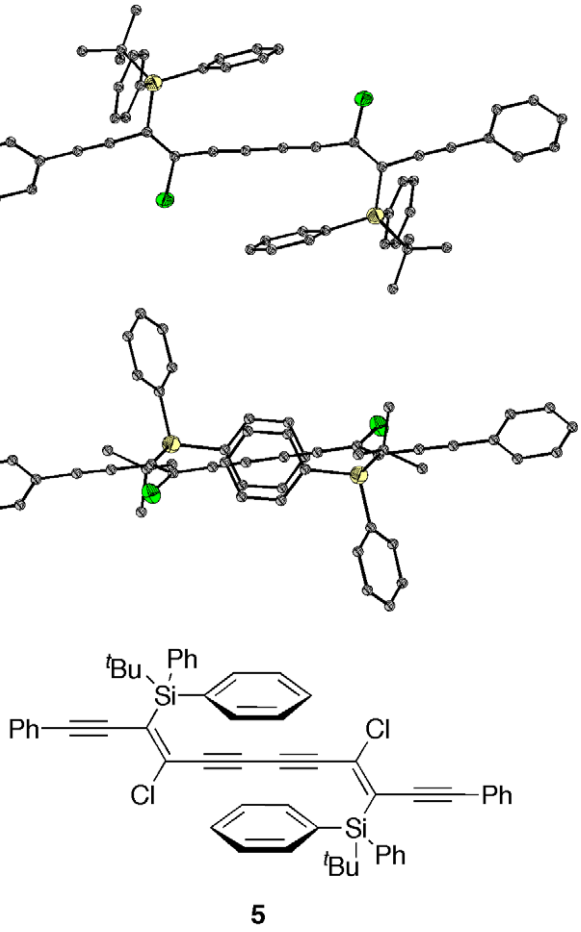
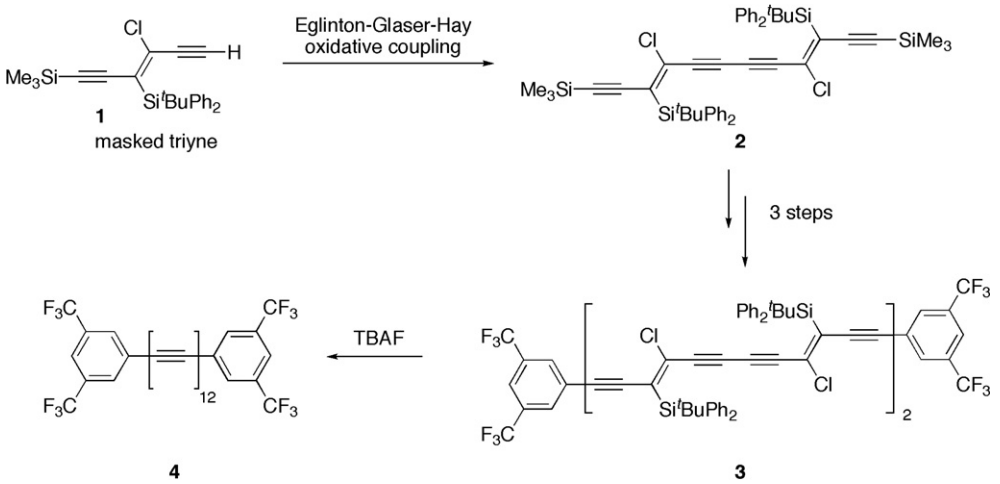


Fig. 2. Two of the phenyl substituents in the TBDPS appendages in masked hexayne **5** sandwich the π-conjugated framework.



Scheme 1. Synthesis of a masked triyne **1** allowed the preparation of dodecayne **4**.

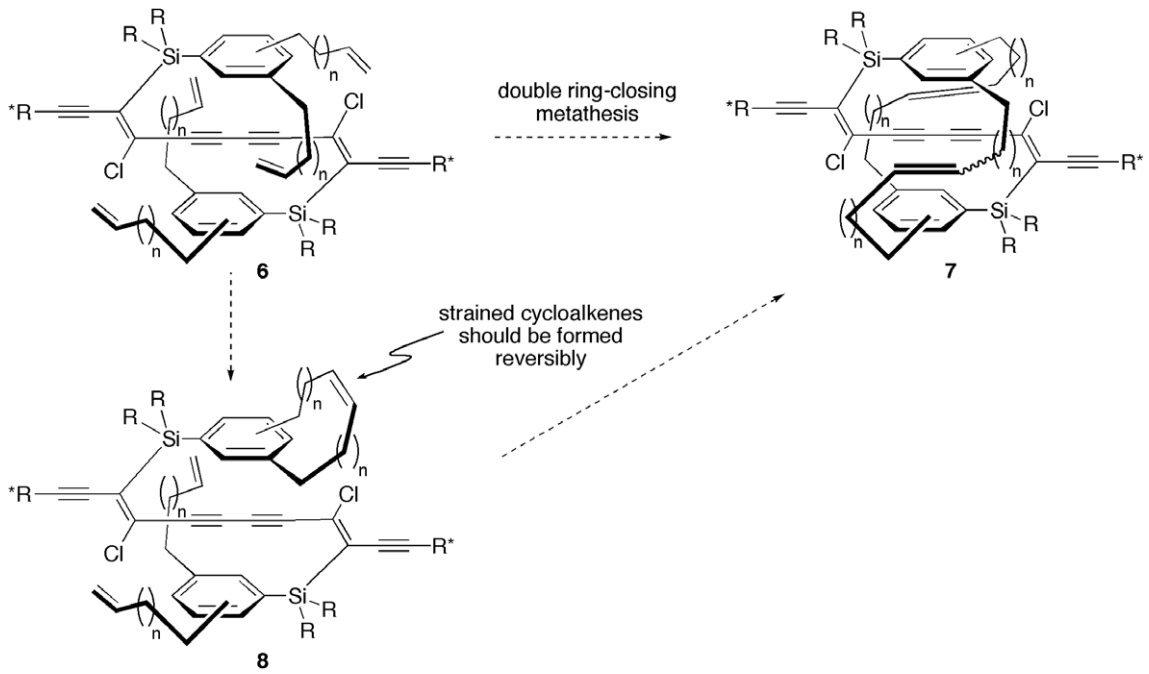


Fig. 3. A double ring-closing-metathesis operation would provide a neat method for hexayne encapsulation.

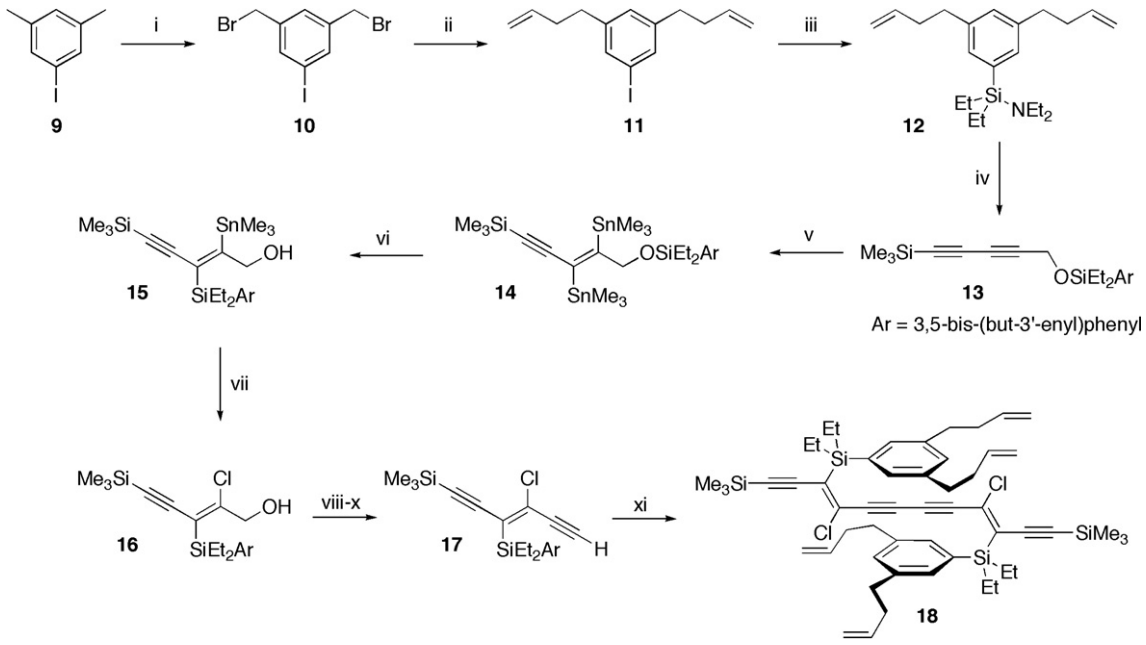
strategies now abound in synthesis, and significantly have proven their worth in the preparation of large rings [9]. Since the synthesis of the masked hexayne precursor (see Scheme 2) also involves a number of steps that employ strongly basic reaction conditions, the terminal olefin functionality required for a late-stage metathesis operation would remain unaffected in the rather uncompromising reactions required in the early stages of our synthesis.

The length of the alkyl linker connecting the aryl template and terminal olefin, and the relative substitution pattern of these groups (*i.e. ortho, meta* or *para*) on the aryl group, were clearly going to be critical to the success of the proposed double ring-closing macrocyclisation. The linker in precursor **6** would need to be long enough to generate a macrocycle in **7**, which is of sufficient size to encapsulate the conjugated framework, but at the same time, not be so long that an alternative ring-closing metathesis between two alkenes appended on the *same* aryl group (to form **8**), could become a more favourable pathway (Fig. 3).

After considering a range of possible alkenyl substituents and substitution patterns, and modelling the desired product macrocycle, we arrived at masked hexayne **18** as a first target (Scheme 2). Significantly, the use of an ethylene tether and the *meta*-substitution of the two olefins on the aryl groups, would ensure that ring-closing metathesis between alkenes in the *same* aryl group would generate a strained cycloalkene [10]. In this way, we would then be able to exploit the reversibility of metathesis operations since the reverse, ring-opening transform on **8** would return such products to our desired reaction pathway. This potential side-reaction would therefore not represent an unproductive direction. The synthesis of the ring-closing-metathesis precursor **18** is outlined in Scheme 2.

Radical bromination of 3,5-dimethyl-iodobenzene **9** afforded bis-benzyl bromide **10** [11], which reacted with (allyl)MgBr to provide aryl iodide **11** containing the two *meta*-related butenyl side-chains [12]. Lithium–halogen exchange of iodide **11** with ^{t}BuLi, followed by trapping of the resulting aryl lithium intermediate with $Et_2Si(NEt_2)Cl$ [13], provided aminosilane **12**, which was used directly in a silyletherification[14] with 5-hydroxy-1-trimethylsilyl-penta-1,3-diyne [8], to afford silyl ether **13** in excellent yield over the two steps. Silyl ether **13** was then elaborated into masked triyne **17** using our established route [8]: bis-stannylation of diyne **13** using an excess of the stannylcopper reagent derived from equimolar quantities of Me_3SnLi and $CuBr \cdot SMe_2$, provided (*E*)-bis-1,2-vinylstannane **14** with complete regio- and stereocontrol. Selective tin–lithium exchange of the internal vinylstannane in **14** effected a 1,4-retro-Brook rearrangement to install the vinylsilane **15** and at the same time, freed up the alcohol required for subsequent homologation into a second alkyne. Chlorodestannylation of the remaining vinylstannane in **15** proceeded with retention of configuration to afford vinyl chloride **16**, which was readily transformed into masked triyne **17**: allylic oxidation of the alcohol in **16** with MnO_2 provided the corresponding aldehyde, which was elaborated into masked triyne **17** in a two-step dibromoolefination–Fritsch–Buttenberg–Wiechell reaction sequence. Finally, dimerisation under our modified oxidative coupling conditions provided masked hexayne **18** in excellent yield [15].

With our macrocyclisation precursor in hand, we were ready to investigate the key, ring-closing-metathesis reaction. In light of the potential reactivity issues associated with the highly unsaturated enediyne framework taking



Scheme 2. Synthesis of macrocyclisation precursor **18**. *Note*: *Reagents and conditions:* (i) NBS (2.4 equiv.), AIBN (5 mol%), PhH, reflux, 14 h, 44%; (ii) (allyl)MgBr (3.0 equiv.), Et_2O, reflux, 15 h, 78%; (iii) ^tBuLi (2.0 equiv.), Et_2O, −78 °C, 1 h, then $Et_2Si(NEt_2)Cl$ (1.1 equiv.), Et_2O, −78 °C to RT, 14 h; (iv) 5-hydroxy-1-trimethylsilyl-penta-1,3-diyne (1.0 equiv.), CH_2Cl_2, RT, 4 h, 82% over two steps from **11**; (v) $Me_3SnCu \cdot SMe_2 \cdot LiBr$ (2.6 equiv.), THF, −50 °C to RT, 18 h, 93%; (vi) ^nBuLi (1.0 equiv.), THF, −78 °C, 45 min, 70%; (vii) $CuCl_2$ (2.2 equiv.), THF, 0 °C to RT, 90 min, 89%; (viii) MnO_2 (20 equiv.), CH_2Cl_2, RT, 5 h, 82%; (ix) CBr_4 (2.0 equiv.), PPh_3 (4.0 equiv.), CH_2Cl_2, 0 °C, 30 min, 80%; (x) LDA (6.0 equiv.), THF, −78 °C, 1 h; (xi) $Cu(OTf)_2$ (20 mol%), TMEDA (70 mol%), O_2, PhMe, 40 °C, 4 h, 80% from dibromide.

part in any metathesis operations, we elected to use the Ru alkylidene metathesis catalysts introduced by Grubbs, believing these would be eminently suitable for effecting metathesis of terminal olefins, and yet would leave the enediyne framework unscathed. A 0.01 M solution of **18** in d_2-dichloromethane was heated to 30 °C and the progress of the reaction monitored by NMR. After 6 h, all of the starting material had been converted into one major product. From the NMR data, this new compound lacked the terminal alkene substituents present in the starting material, and instead contained olefinic resonances in accordance with a 1,2-disubstituted alkene. Mass spectral analysis of the product mixture also pointed encouragingly to a product that had a molecular mass 56 a.m.u. lower than the starting material, as would be expected from the desired double ring-closing-metathesis operation. Carrying out the reaction in d_6-benzene provided similar results, and when Grubbs' 2nd generation catalyst was employed, if anything, the selectivity for the major product decreased slightly. Whilst we were now confident that **18** had undergone the desired double ring-closing-metathesis operation, we were unable to ascertain by NMR whether or not it had achieved molecular encapsulation. Fortunately, crystals of the major product, grown from hexane, proved suitable for X-ray analysis. However, whilst the metathesis operations had indeed generated the desired macrocycle, the cyclophane ring in the product **19** was crowning rather than encapsulating the conjugated framework (Fig. 4).

Although disappointed with the outcome of the macrocyclisation, the result remains significant. It confirms that the conjugated masked hexayne framework is compatible with Grubbs' ruthenium alkylidenes and the metathesis reaction conditions, and also that the double ring-closing-metathesis strategy is a viable option for generating the macrocycle. In order to understand the outcome of the reaction, and inform future structural modifications, it is necessary to consider the potential reactive conformations of the cyclisation precursor **18**.

Rotation about the central C–C bond in the internal butadiyne of masked hexayne **18** provides two conformations in which full conjugation is retained along the unsaturated chain (Fig. 5), one, the 's-*trans*' conformer **18a**, in which the silyl substituents are able to sandwich the conjugated framework, and a second, the 's-*cis*' conformer **18b**, in which the two silyl groups are on the same side of the conjugated system. It is tempting to speculate that steric interactions between the two silyl groups disfavour the 's-*cis*' conformation, and also encouraging to observe that the crystal structure of our lead molecule **5** (and **19** for that matter), shows the masked hexayne adopting the required 's-*trans*' conformation.

Rotation about the C–Si bond in the vinylsilane also needs to be considered. At the outset we proposed that a templating effect would favour the rotamer in which the aryl group in the $ArEt_2Si$ substituents sandwich the internal butadiyne, thereby generating the conformation necessary for achieving encapsulation. If this templating effect is

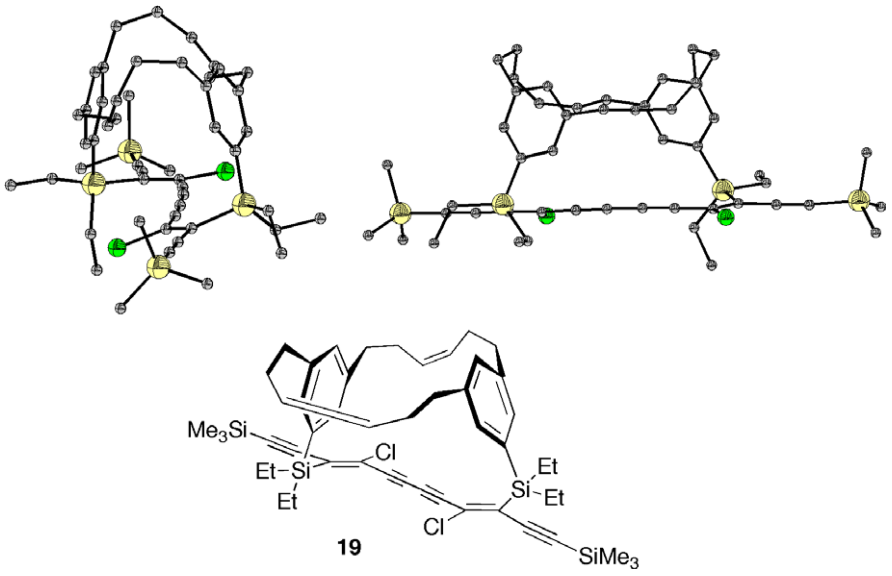


Fig. 4. Major product from the attempted encapsulation.

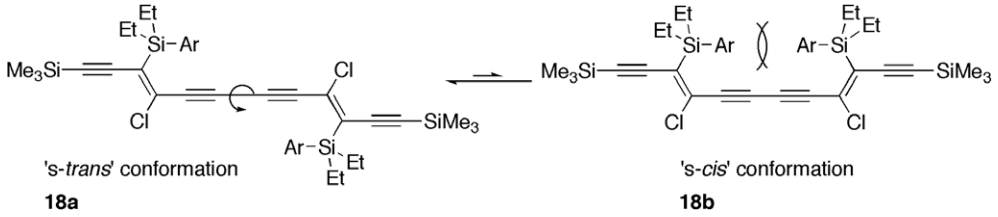
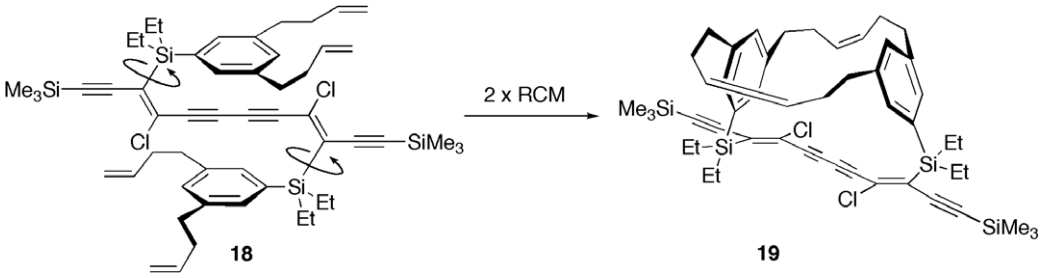


Fig. 5. Masked hexayne **18** can adopt two conformations, where full conjugation is preserved.



Scheme 3. Rotation around the C–Si bonds accounts for the formation of macrocycle **19**.

not particularly strong, then other rotamers, including those which account for the formation of the observed macrocycle **19**, will be significantly populated (Scheme 3). We currently believe that a combination of a relatively weak templating effect, and the lack of sufficient space for the ruthenium alkylidene intermediate to 'cross-link' the two aryl groups in the sandwiching 's-*trans*' conformation, rationalises the product outcome.

3. Summary

We have proposed a novel method for oligoyne encapsulation which employs two silyl groups, embedded in a masked hexayne as (*E*)β-chlorovinylsilanes, as sites from which a double ring-closing-metathesis operation can be used to form an insulating macrocycle. Whilst our first approach has proven unsuccessful, the outcome has been very instructive. Most importantly, the masked hexayne has stood up well to the metathesis conditions and Grubbs' 1st and 2nd generation catalysts. Future work will focus on designing modified macrocyclisation precursors which are 'locked' in a conformation that is conducive to encapsulation.

4. Selected experimental data

*4.1. Masked hexayne (**18**)*

A solution of alkyne **17** (363 mg, 0.8 mmol) in THF (1 mL) was treated with a pre-formed solution of copper(II) triflate (58 mg, 0.16 mmol) and TMEDA (84 μL, 0.56

mmol) in toluene (8 mL) at 40 °C under an atmosphere of O_2. After 4 h, the reaction mixture was layered on to a short silica plug and eluted with hexane–Et_2O (10:1, 3 × 10 mL). Concentration of the filtrate and purification of the residue by flash column chromatography (hexane/toluene, 9:1) provided masked hexayne **18** as an orange oil (289 mg, 80%): $R_f = 0.66$ (hexane/Et_2O/toluene; 17:1:2); λ_{max} (CH_2Cl_2)/nm 290sh (ε/dm^3 mol^{-1} cm^{-1}, 20,050), 303 (22,900), 321 (28,000), 340 (31,100), 369 (31,000), 398 (30,900); ν_{max}(film)/cm^{-1} 3077w, 2978s, 2935s, 2876s, 2113m (C≡C), 1641m, 1593w, 1502w, 1455w, 1413m, 1306w, 1249s, 1133s, 1087s, 1008m, 912s, 846s, 760m, 724s, 708s, 667s; δ_H (300 MHz, $CDCl_3$) 0.19 (18H, s, 2× Si(CH_3)$_3$), 1.01–1.12 (20H, stack, 4× CH_2CH_3), 2.34 (8H, td, *J* 7.7, 6.6, 4× CH_2CH=), 2.66 (8H, t, *J* 7.7, 4× CH_2CH_2), 4.96 (4H, d, *J* 10.4, 4× CH=CHH_{cis}), 5.02 (4H, d, *J* 17.3, 4× CH=CHH_{trans}), 5.85 (4H, ddt, *J* 17.3, 10.4, 6.6, 4× C*H*=CH$_2$), 7.02 (2H, s, 2× Ar*H*), 7.11 (4H, s, 4× Ar*H*); δ_C (75 MHz, $CDCl_3$) 141.0 (quat. C, *ipso*Ar), 138.1 (CH, Ar), 134.5 (quat. C), 133.3 (quat. C, *ipso*Ar), 132.1 (CH, Ar), 130.1 (CH, *C*H=CH$_2$), 124.6 (quat. C), 116.5 (quat. C), 114.8 (CH_2, CH=*C*H$_2$), 103.8 (quat. C), 83.5 (quat. C), 80.8 (quat. C), 35.6 (CH_2), 35.4 (CH_2), 7.3 (CH_3, CH_2CH_3), 3.8 (CH_2, *C*H$_2$CH$_3$), −0.3 (CH_3, Si(*C*H$_3$)$_3$); *m*/*z* (TOF ES+) 927.5 ([M + Na]$^+$, 100).

4.2. Double ring-closing metathesis; preparation of *19*

Bis(tricyclohexylphosphine)-benzylidene ruthenium(IV) chloride (7.5 mg, 10 mol%) was added to a solution of masked hexayne **18** (82 mg, 0.09 mmol) in CH_2Cl_2 (10 mL). The solution was stirred in the dark for 6 h and then filtered through a short plug of silica gel, eluting with hexane–Et_2O (9:1; 3 × 10 mL). The combined filtrates were then concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel (hexane/toluene; 9:1) to afford macrocycle **19** as an orange, crystalline solid (62 mg, 81%): $R_f = 0.23$ (hexane/toluene; 9:1); λ_{max} (CH_2Cl_2)/nm 287sh (ε/dm^3 mol^{-1} cm^{-1}, 2380), 305sh (10,100), 320 (12,730), 338 (12,710), 371 (11,930), 401 (12,020); ν_{max} (film)/cm^{-1} 2957s, 2933s, 2876s, 2854s, 2114m (C≡C), 1738w, 1593m, 1501m, 1455m, 1435m, 1412m, 1379w, 1354w, 1306w, 1249s, 1136s, 1088m, 1053m, 1008m, 969m, 844s, 760s, 709s, 666m, 630m; δ_H (400 MHz, $CDCl_3$) 0.28 (18H, s, 2× Si(CH_3)$_3$), 0.97–1.22 (20H, stack, 4× SiCH_2CH_3), 1.50–1.62 (4H, m, 4× CH_aH$_b$CH=), 1.83–1.95 (4H, m, 4× CH$_a$*H*$_b$CH=), 2.21–2.33 (4H, m, 4× ArCH_aH$_b$), 2.49–2.60 (4H, m, 4× ArCH$_a$*H*$_b$), 5.28–5.40 (4H, m, C*H*=C*H*), 6.81–6.98 (6H, stack, Ar*H*); δ_C (100 MHz, $CDCl_3$) 0.1 (CH_3, Si(*C*H$_3$)$_3$), 2.5 (CH_2, SiCH_2CH$_3$), 7.1 (CH_3, SiCH$_2$*C*H$_3$), 30.4 (CH_2, *C*H$_2$CH=), 35.9 (CH_2, Ar*C*H$_2$), 81.5 (quat. C), 84.4 (quat. C), 103.8 (quat. C), 116.4 (quat. C), 124.0 (quat. C), 129.0 (CH, *C*H=*C*H), 130.1 (CH, Ar), 132.6 (quat. C, *ipso*Ar), 133.1 (CH, Ar), 136.0 (quat. C), 141.0 (quat. C, *ipso*Ar); *m*/*z* (TOF ES$^+$) 869 ([M + Na]$^+$, 100); HRMS (TOF ES+). Found (M + Na)$^+$ 869.3376. $C_{50}H_{64}Cl_2NaSi_4$ requires (M + Na), 869.3360. The structure of **19** was confirmed by X-ray crystallography.

5. Crystallographic data

Compound **5**: $C_{56}H_{48}Cl_2Si_2$, FW = 848.02, T = 296(2) K, λ = 1.54178 Å, triclinic, $P\bar{1}$, a = 8.16900(10) Å, b = 11.0362(2) Å, c = 13.6405(2) Å, α = 86.3790(10)°, β = 88.7980(10)°, γ = 74.9670(10)°, V = 1185.28(3) Å^3, Z = 1, μ = 1.981 mm^{-1}, crystal size = 0.30 × 0.16 × 0.06 mm^3, 7685 reflections collected, 3961 independent reflections, R_{int} = 0.0280, 274 parameters, final R_1 = 0.0397, wR_2 = 0.1040 for $I > 2\sigma(I)$.

Compound **19**: $C_{50}H_{64}Cl_2Si_4$, FW = 848.27, T = 296(2) K, λ = 1.54178 Å, triclinic, $P\bar{1}$, a = 11.7441(15) Å, b = 18.232(3) Å, c = 26.258(4) Å, α = 70.549(8)°, β = 83.816(8), γ = 89.613(8)°, V = 5268.1(12) Å^3, Z = 4, μ = 2.194 mm^{-1}, crystal size = 0.14 × 0.14 × 0.14 mm^3, 33,717 reflections collected, 17,597 independent reflections, R_{int} = 0.0692, 1030 parameters, final R_1 = 0.0837, wR_2 = 0.1983 for $I > 2\sigma(I)$.

Data for both samples were recorded on a Bruker Smart 6000 CCD diffractometer. Structure solution by direct methods and least squares refinement on F^2 were performed using SHELXL [16] and semi-empirical absorption correction was applied.

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 610132 for **5** and No. 610131 for **19**. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1233 336033 or e-mail: deposit@ccdc.cam.ac.uk or www:http:/www.ccdc.cam.ac.uk.

Acknowledgements

We are grateful to the Leverhulme Trust (F/00 094/T) and the EPSRC (EP/C532260/1) for financial support and a post-doctoral research fellowship to S.M.E.S.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.07.021.

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