Comparative Cyclotrimerisation of Enantiopure *vic*-Bromo(trimethylstannyl)bicycloalkenes Derived from (+)-Camphor, (+)-Fenchocamphorone and (−)-Epicamphor: Effect of the Bridgehead Methyl Group on the *syn*/*anti* Product Ratios

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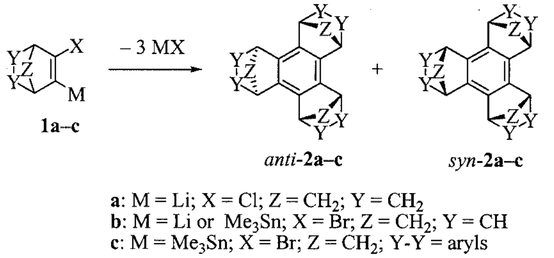
The influence of the bridgehead methyl group on *syn/anti* diastereoselectivity in the cyclotrimerisation of polycyclic alkenes was investigated. To this end, three different enantiopure *vic*-bromo(trimethylstannyl)-substituted bicyclic olefins were prepared and used as probes. The effects of different copper(II) or -(I) salts were studied, and most dimeric intermediates were independently synthesised and characterised. Some indications of the mechanism of cyclotrimerisation were furnished by experiments aimed at determining the relative rates of dimerisation. The results gave useful indications of how to achieve highly effective *syn*-cyclotrimerisation reactions.

Introduction

In the last decade great interest has been focused on cyclotrimerisations of bicyclic olefins and related cyclotrimers.[1−5] The latter compounds serve as models for the Mills-Nixon effect,[6] and can be viewed as attractive scaffolds for the construction of subunits of fullerenes[3a,3i,3j] or as hosts in supramolecular chemistry.[2e,3e,4h−4i] Of course, the most valuable cyclotrimers for these applications are the C_3-symmetric ones (i.e. the *syn* isomers), which are obtained by connecting three C_s olefinic subunits to form the aromatic ring. Unfortunately, cyclotrimerisation reactions of such kinds of substrates generally result in the formation of statistical 1:3 mixtures of *syn*/*anti* diastereomers (Scheme 1).[2,3]



1a–c

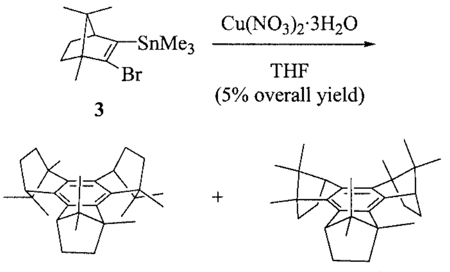
anti-**2a–c**

syn-**2a–c**

a: M = Li; X = Cl; Z = CH$_2$; Y = CH$_2$
b: M = Li or Me$_3$Sn; X = Br; Z = CH$_2$; Y = CH
c: M = Me$_3$Sn; X = Br; Z = CH$_2$; Y-Y = aryls

Scheme 1

As a first hypothesis, cyclotrimerisation reactions of bromo(stannyl) derivatives **1b−c** were postulated to be completely selective couplings between the carbon atoms bearing the metal and the halogen atoms. In this case, the cyclotrimerisation of an enantiopure substrate should exclusively produce only the *syn* cyclotrimer. Disappointingly, initial experiments with an enantiopure substrate derived from (+)-camphor furnished a 9:1 *anti*/*syn* mixture of isomers (Scheme 2).[2f]



3

anti-**4**

syn-**4**

Scheme 2

This unexpected result was even more puzzling because in isomer *anti*-**4** two bridgehead methyl groups are pointing towards each other, whereas in isomer *syn*-**4** this negative feature is missing. We thus investigated the role of the methyl group at the bridgehead position, in order to gain indications of its role in the mechanistic pathway and possibly to invert the unfavourable stereoselective outcome of the reaction. The investigations were performed on **3**, **5** and **6** and are reported here.

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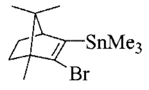

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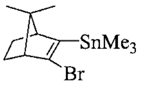

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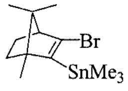

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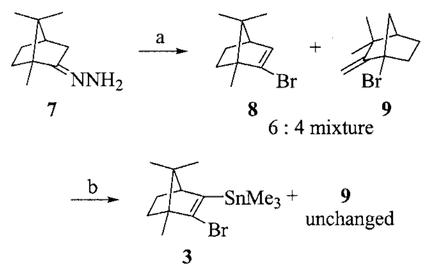
Results and Discussion

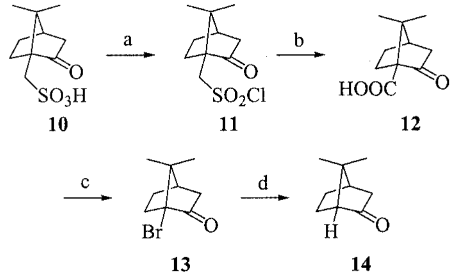
Preparation of Substrates and Intermediates

The synthesis of olefins **3**, **5** and **6** began with the conversion of ketones derived from the chiral pool into vinyl bromides. The subsequent stannylation can be accomplished by metallation with lithium diisopropylamide and substitution with trimethyltin chloride. In the case of (+)-camphor, bromo olefin **8** was obtained by a Shapiro reaction with the tosylhydrazone of (+)-camphor[7] or, more conveniently, by bromination of the corresponding hydrazone[8] by the methodology described by Pross and Sternhell.[9] The reaction furnished a 1:1 mixture of 2-bromoborn-2-ene (**8**) and 1-bromocamphene (**9**), a Meerwein rearrangement product, in a 67% overall yield. Inverse addition of a diluted (0.2 M in diethyl ether) solution of hydrazone to a previously prepared mixture obtained by addition of a 0.2 M solution of bromine (2 equiv.) to a 0.5 M solution of pyridine (10 equiv.) improved both yields and ratio (77% and 6:4, respectively) (Scheme 3). The separation of the mixture of isomers was a tedious and troublesome operation, and for this reason the mixture of isomers was used in the subsequent transformation. In fact, the use of excess lithium diisopropylamide, necessary to effect the lithiation of the 2-bromoborn-2-ene (**8**), did not affect 1-bromocamphene (**9**), which was readily removed from the desired 2-bromo-3-(trimethylstannyl)-born-2-ene (**3**) by evaporation.[2f]



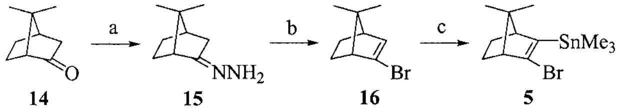
Scheme 3. Reagents and conditions: a: Br_2, Py, Et_2O, room temp. (77%); b: LDA, Me_3SnCl, THF, room temp. (66%)

The synthesis of the camphor derivative in which the methyl group in the 1-position is replaced by an unhindered hydrogen atom [fenchocamphorone (**14**)], consists of four steps starting from (+)-camphorsulfonic acid (**10**) according to the procedure by Paquette and co-workers (Scheme 4).[10]



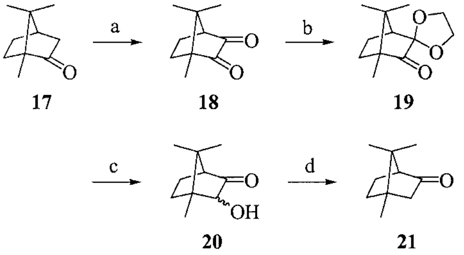
Scheme 4. Reagents and conditions: a: $SOCl_2$, neat, Δ (40%); b: $KMnO_4$, Na_2CO_3, H_2O, Δ (40%); c: Br_2, HgO (red), $MgSO_4$, CH_2Cl_2, Δ (76%); d: $n Bu_3SnH$, AIBN, PhH, Δ (87%)

The resulting demethylated camphor derivative **14** was transformed into its hydrazone **15** by heating at reflux in *n*-butanol with an excess of hydrazine hydrate and a catalytic amount of sulfuric acid.[8] The resulting oil was purified by bulb-to-bulb distillation and was converted into the 2-bromo-7,7-dimethylborn-2-ene (**16**) by addition of pyridinium perbromate[11] in the presence of pyridine as proton scavenger. Although no Meerwein rearrangement products were detected in the crude product, the yields were modest (51%), probably because of the high volatility of the product. The vinyl bromide **16** was stannylated by a well-established procedure[2f] involving lithiation with excess of lithium diisopropylamide and quenching with trimethylstannyl chloride, to give **5** in 70% yield (Scheme 5).



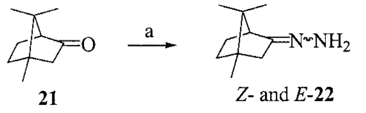
Scheme 5. Reagents and conditions: a: $NH_2NH_2{\cdot}H_2O$, nBuOH, H_2SO_4 (cat.), Δ (84%); b: $PyHBr_3$, Py, Et_2O, room temp. (51%); c: LDA, Me_3SnCl, room temp. (70%)

The third substrate that we considered (i.e., **6**) bears the trimethylsilyl moiety close to the bridgehead methyl group and the bromine atom at the opposite position of the vinyl group. To obtain this molecular arrangement we needed (−)-epicamphor, which was prepared in four steps from (+)-camphor according to the methodology by Baker and Davis (Scheme 6).[12]



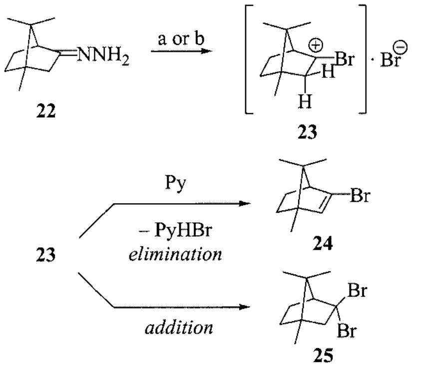
Scheme 6. Reagents and conditions: a: SeO_2, Ac_2O, Δ (85%); b: $HOCH_2CH_2OH$, APTS (cat.), PhMe, Δ (50%); c: (i) LAH, THF, Δ, (ii) 37% HCl, room temp. (94%); 4% Na/Hg, EtOH, room temp. (48%)

The conversion of (−)-epicamphor (**21**) into the bromo(stannyl)alkene required a different treatment of the starting ketone. In fact, even a short reflux time in *n*-butanol with hydrazine hydrate gave complex mixtures. The use of the methodology reported by Marchand and co-workers[13] proved to be slow but extremely efficient, and clean conversion of epicamphor (**21**) into the relative hydrazone **22** was achieved, the product being isolated as a 2:1 mixture of inseparable isomers.



Scheme 7. Reagents and conditions: a: $H_2NNH_2{\cdot}H_2O$, MeOH, molecular sieves (4 Å), room temp. (75%)

The mixture of hydrazones **22** was brominated with pyridinium perbromate and an excess of pyridine, furnishing a crude product of 3-bromoborn-2-ene (**24**) containing non-negligible amounts of 3,3-dibromobornane (**25**). It was not possible to obtain a pure sample of **25**, which always resulted in contamination of the desired olefin (Scheme 8). The structure of **25** was assigned from the analysis of ^1H NMR spectra, showing a doublet of doublets with $J = 15.8$, 2.4 Hz at $\delta = 3.09$ ppm (2-H_{exo}) and a doublet with $J = 15.8$ Hz at $\delta = 2.64$ ppm (2-H_{endo}). These resonances are diagnostic of a methylene system deshielded by the vicinal *gem*-dibromide moiety in which the *exo*-hydrogen atom displays a long-range ^4J coupling with 6-H_{exo} owing to the rigid W displacement of the four bonds connecting the two nuclei. In addition, GC-MS data of the mixture displayed a peak, more strongly retained than authentic 3-bromobornene, with highest $m/z = 215-217$, corresponding to the peak for $[M^+ - Br]$ of the dibromide.

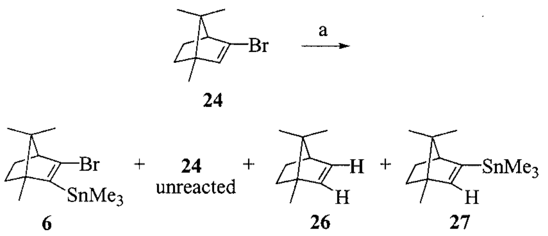


Scheme 8. Reagents and conditions: a: $PyHBr_3$, Py, Et_2O, room temp. (52% yield of **24**); b: NBS, Py, 0 °C (68% yield of **24**)

The formation of this dibromide results from a nucleophilic addition of a bromide ion on the carbocation generated from the decomposition of the diazonium salt. It appears to us that this side-reaction is more preferred than in the cases of **8** and **16**, probably because of the higher steric hindrance around the hydrogen atom at C-2 (which prevents efficient abstraction by the base), the lower hindrance of C-3 and the use of pyridinium perbromate, which increases the bromide ion concentration. It is noteworthy that, even in this case, no Meerwein rearrangement products were observed in the crude product of the reaction. In fact, the absence of the bridgehead methyl group close to the carbocation should result in a destabilised secondary carbocation vs. a tertiary one in the case of **7**.

In order to minimise the formation of by-product **25**, the reaction was carried out according to the methodology reported by Bourgeois and co-workers,[14] with *N*-bromosuccinimide in pyridine as solvent (Scheme 8). Use of this route resulted in the clean formation of the desired product **24**, free of dibromide **25**.

The presence of dibromide **25** was not a serious drawback for the next step, since previous experiments had demonstrated that lithium diisopropylamide dehydrobrominated **25**, resulting in the formation of clean vinyl compound **24**. For this reason a mixture of **24** and **25** was treated with excess LDA and a stoichiometric amount of trimethyltin chloride to afford 3-bromo-2-(trimethylstannyl)born-2-ene (**6**) (Scheme 9).

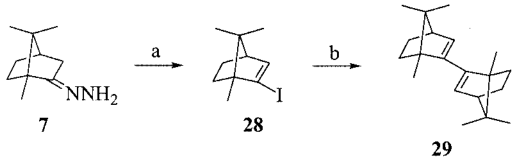


Scheme 9. Reagents and conditions: a: LDA, Me_3SnCl, THF, room temp. (4%)

This reaction did not go to completion (60%), and low yields of the stannyl derivative **6** were obtained, together with large amounts of unexpected products, such as bornene (**26**) and 3-(trimethylstannyl)bornene (**27**),[15] as revealed by GC-MS and ^1H NMR analysis. The poor reactivity and the formation of side-products can be explained, even in this case, by the steric hindrance of the bridgehead methyl moiety, which prevents the quenching of the lithiated olefin with the electrophilic tin atom.

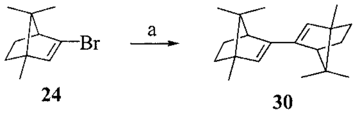
Dimerisations

In order to gain a deeper insight into the mechanistic path of the cyclotrimerisation reactions, we synthesised the three dimers of 2-bornene, present in many cyclotrimerisation reactions. In addition, the resulting dimers are enantiopure conjugated dienes that can be subjected to further reactions to afford interesting derivatives.[4g,5d,16,17] 2,2′-Bi(born-2-ene) (**29**) was obtained in good yields from 2-iodoborn-2-ene (**28**)[9,18] by metallation with a two-fold excess of *tert*-butyllithium followed by copper(I)-mediated coupling (Scheme 10).[19]



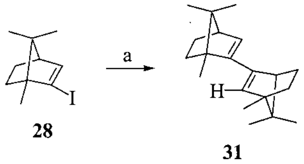
Scheme 10. Reagents and conditions: a: I_2, *N*,*N*,*N'*,*N'*-tetramethylguanidine, Et_2O, room temp. (53%); b: *t*BuLi, CuI, THF, pentane, room temp. (85%)

The isomeric C_2-symmetric dimer **30** was obtained by a similar methodology, through homo-coupling of 3-bromoborn-2-ene (**24**) (Scheme 11).



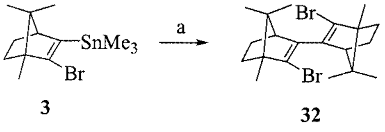
Scheme 11. Reagents and conditions: a: *t*BuLi, CuI, THF, pentane, room temp. (40%)

Finally, the head-to-tail-coupled bornene **31** was isolated in good yields from a Heck-type coupling of 2-iodobornene **28**, as reported in a previous communication (Scheme 12).[2g]



Scheme 12. Reagents and conditions: a: $Pd(OAc)_2$, PPh_3, DABCO, nBu_4NBr, molecular sieves (4 Å), DMF (90%)

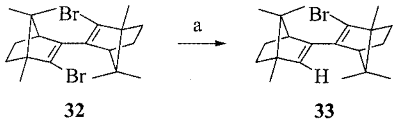
A synthetically interesting functionalised dimer was also obtained through copper-mediated tin−tin coupling of 2-bromo-3-(trimethylstannyl)born-2-ene (**3**). The procedure aimed at the synthesis of cyclotrimers is a modification of Piers' methodology,[20,21] consisting of the use of copper(I) chloride in DMF in the presence of lithium chloride[22] and 1,2-dimethoxyethane as a chelating ligand. In contrast with what had been observed with less hindered substrates, which gave good yields of *syn* cyclotrimers,[3h] application of this methodology to olefin **3** furnished good yields of dibromodiene **32** (Scheme 13).



Scheme 13. Reagents and conditions: a: LiCl, CuCl, DME, DMF, room temp. (76%)

Dibromide **32** is of particular interest because of the potential for metallation of the termini of the diene moiety. The resulting double nucleophile can react with a variety of electrophilic carbon atoms or heteroatoms,[17] resulting in the formation of new highly symmetric enantiopure molecules.

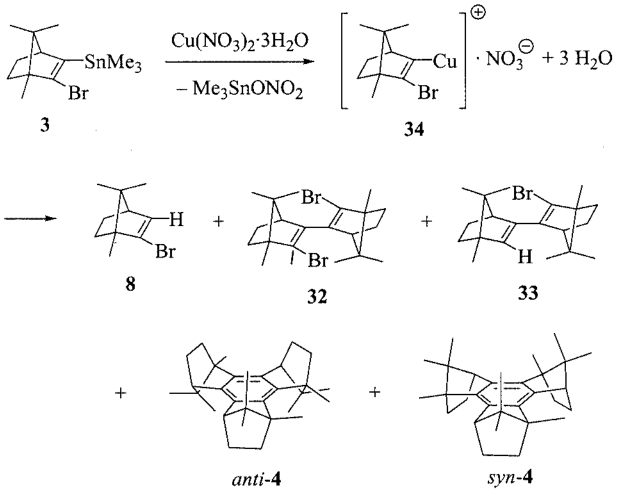
The common intermediate **33** was obtained in satisfactory yields by metallation of **32** with *tert*-butyllithium, followed by quenching with water (Scheme 14).



Scheme 14. Reagents and conditions: a: *t*BuLi, THF, −78 °C, H_2O (63%)

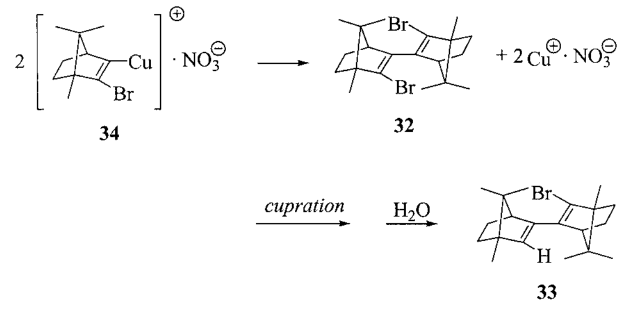
Cyclotrimerisations

The first reaction carried out with the enantiopure substrate **3** involved the use of copper(II) nitrate trihydrate and furnished poor yields (5%) of cyclotrimers in an unfavourable 9:1 *anti*/*syn* ratio (Scheme 2).[2f] The biggest drawback of the reaction was the formation of a large amount of 2-bromoborn-2-ene (**8**). This compound could result from a copper/tin exchange, presumably driven by the formation of trimethyltin nitrate,[23] followed by a proto-destannylation reaction effected by the crystal lattice water in copper(II) nitrate (Scheme 15).



Scheme 15

The other by-products of the reaction are mainly the dibromo dimer **32**, the result of heterocoupling of the bornene moiety.[24] The oxidative coupling of the cuprate is attested to by the colour of the reaction mixture, which rapidly fades from deep blue to pale green, because of the generation of copper(I). Copper(I) nitrate becomes unstable in the absence of strong ligands, such as phosphanes or arsanes,[25] and the bromo diene **33** could arise from copper/halide exchange caused by copper(I)[26] and dibromide **32**, followed by quenching with water (Scheme 16). This cuprate is very probably the intermediate in the process leading to the formation of trimer *anti*-**4**.



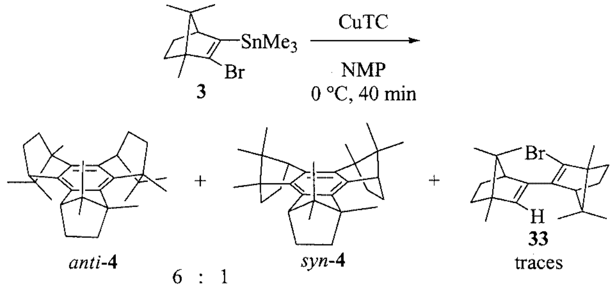
Scheme 16

In order to minimise the negative influence of water, the reaction was carried out in the presence of triturated molecular sieves (4 Å), but with little or no effect, probably because the molecules of water remain coordinated to the copper ion during the course of the reaction and can eventually be cleaved only by the organocuprate. In an experiment aimed at determining the minimum amount of tetrahydrofuran necessary to dissolve the salt and to start the cyclotrimerisation reaction, it was noticed that the reaction started only when 2 equiv. of THF were added to the 1:1 mixture of copper salt and substrate. Under these conditions, minor amounts of bromoalkene **8** were observed in the crude products, concomitantly with an enhancement of the yields of cyclotrimers, balanced by the presence of several by-products.

Anhydrous copper(II) nitrate can be obtained only by nontrivial methodologies,[27] while anhydrous copper(II) triflate is commercially available.[28] The latter reagent was tested under similar conditions and furnished a 1:6 *syn*/*anti* mixture of cyclotrimers in 44% overall yields. The dibromo dimer **32** was also isolated in the mixture, in 43% yield. This result prompted us to investigate the use of other anhydrous copper salts, investigating the effect of the oxidation state in the diastereoselectivity of the reaction. Copper(I) chloride had been reported to promote both homocoupling of tin derivatives[20] and heterocoupling of stannyl compounds with halides.[21,22] The original methodology involving the use of copper(I) chloride in DMF did not furnish any product, and reagent **3** was recovered unchanged. The addition of excess of lithium chloride[3h,22] dramatically changed the reactivity of the copper salt, furnishing a 50% yield of dibromide **32**, with only traces of trimer *anti*-**4** detected in the crude products. The use of a chelating ligand such as 1,2-dimethoxyethane[3h] increased the yields of **32** to 70% and in this case trimers were undetected in the mixtures. As described above, this procedure represents the best methodology so far for the synthesis of dibromide **32**.

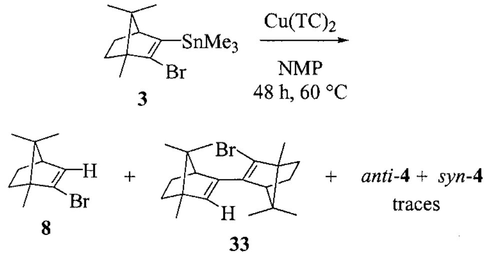
Anhydrous copper(I) triflate[29] is commercially available as a benzene complex and it had been reported to promote cyclotrimerisation of unsubstituted cycloalkenes through the formation of a π complex.[30] Treatment of **3** with 1.2 equiv. of CuOTf·PhH in dry THF furnished *syn*- and *anti*-**4** in 49% overall yields and 1:5 ratio, and only 10% of **32**.

Liebeskind and other researchers have described the use of copper(I) thiophene-2-carboxylate (CuTC) as a promoter of couplings between stannanes and halides[31] or between halides[26i,26j] under very mild conditions. This reagent is an air-stable, non-hygroscopic, inexpensive and easy to prepare[31a] copper salt with exceptionally high activity in polar solvents such as *N*-methylpyrrolidin-3-one. The reaction carried out on substrate **3** in NMP in the presence of 1.2 equiv. of CuTC afforded almost quantitative yields of cyclotrimers *syn*- and *anti*-**4** in a 1:6 ratio with a negligible amount of **33** (Scheme 17).[2h] The high efficiency of the salt allowed us to perform the reaction even at lower temperature (−20 °C), with insignificant effect upon the ratio of the diastereoisomers.



Scheme 17

Cu(TC)$_2$ [32] displayed lower reactivity than CuTC in NMP. In fact, the reaction was completed in 2 d at 60 °C, resulting in the formation of proto-destannylated olefin **8** (60%), diene **33** (30%) and only traces of trimers **4** (Scheme 18).

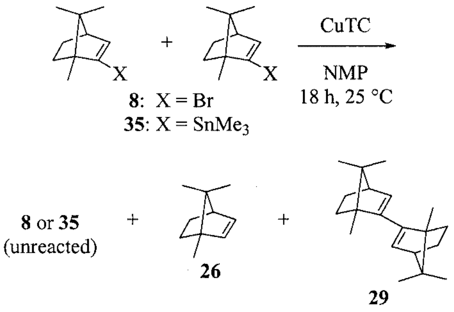


Scheme 18

The unfavourable *anti*/*syn* ratios obtained so far with any copper salt used prompted us to assume that the diastereoselectivity of the process was exclusively driven by the substrate. The presence of variable amounts of **32** and **33** in the reaction mixtures enforces these considerations.

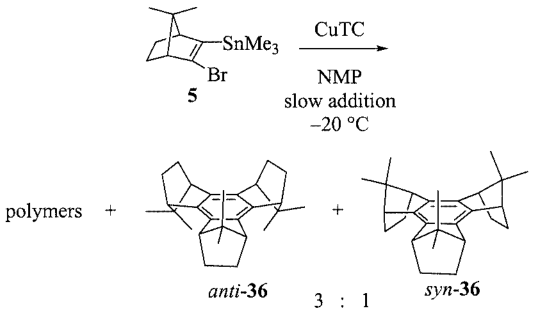
To confirm this assumption we carried out two experiments aimed at defining the relative ease of cupration and coupling of bromide **8** and tin compound **35**[15] by use of either one of the reagents alone. When a 1.0 M solution of the stannyl derivative **35** in dry NMP was mixed with 1.0 equiv. of CuTC (Scheme 19), a mixture of the proto-destannylated olefin **26** (47%), dimer **29** (14%) and unchanged **35** was obtained at room temperature after 18 h. After the same period of time under the same reaction conditions, most of the bromoalkene **8** was recovered virtually unchanged, together with **26** (15%) and the dimer **29** (2%).

Since the bromo(stannyl) reagent **3** reacts in a much shorter time, we can estimate that the presence of both tin and bromine atoms has a synergistic effect on the reaction rate and that the bridgehead methyl group exerts a negative effect in the coupling of the nearest olefinic carbon atom.



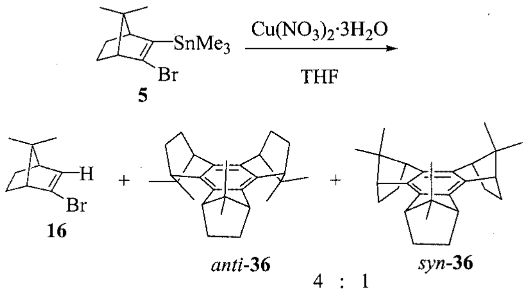
Scheme 19

To confirm these findings we carried out the cyclotrimerisation on enantiopure substrate **5**, in which the steric hindrance is the same on both sides of the olefin moiety. When the reaction was carried out with CuTC in NMP by the usual methodology, large amounts of a dark red polymeric material were obtained. In order to minimise the formation of this by-product it was necessary to add a slurry of CuTC in dry NMP to the substrate at low temperature (−20 °C) over a long period (4 h) with the aid of a syringe-pump (Scheme 20). Nevertheless, the red tar was still formed in non-negligible amounts and before the usual flash chromatography it was necessary to decompose the polymer, with the crude product, adsorbed on silica gel, being exposed to air. Cyclotrimers *syn*- and *anti*-**36** were isolated in 20% yields and a 1:3 ratio.



Scheme 20

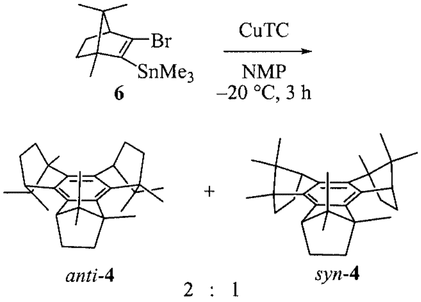
The reaction performed with $Cu(NO_3)_2{\cdot}3H_2O$ in THF did not produce polymeric materials but, as expected, furnished large amounts of proto-destannylated **16** (60% yield). Cyclotrimers *syn*- and *anti*-**36** were isolated in 30% yields and in a 1:4 ratio (Scheme 21), which is in accordance with the CuTC/$Cu(NO_3)_2{\cdot}3H_2O$ behaviour of substrate **3**.



Scheme 21

The *syn*/*anti* ratios observed in the reaction with enantiopure **5** are close to the statistical distributions observed in cases of cyclotrimerisations of racemic *vic*-bromo(stannyl)alkenes so far reported.[2,3] These data not only confirm the role of the bridgehead methyl group in determining the formation of large amounts of *anti* isomer, but appear to be a deterrent to any attempt to obtain *syn* diastereoselectivity by the use of enantiopure bicycloalkenes bearing hydrogen atoms at both bridgehead position.

Finally, the cyclotrimerisation reaction was performed with enantiopure substrate **6**. In this compound the steric hindrance of the 1-methyl moiety is exerted on the side of the olefin bearing the trimethylstannyl residue, with the double advantage of slowing down the transmetallation process and of favouring the coupling between the congested cuprate and the uncongested side of the olefin bearing the bromine atom. Treatment of **6** with 1.5 equiv. of CuTC in dry NMP afforded cyclotrimers *syn*- and *anti*-**4** in a 1:2 ratio, confirming the beneficial influence of the methyl group when close to the trimethylstannyl moiety (Scheme 22).



Scheme 22

On the other hand, treatment of **6** with $Cu(NO_3)_2{\cdot}3H_2O$ in THF afforded the proto-destannylated product **24** in quantitative yield, confirming the deleterious effect of the water of crystallisation upon the cuprate, a consequence of reduced reactivity owing to steric congestion.

Conclusions

This paper describes the use of several copper salts capable of promoting the cyclotrimerisation of various enantiopure *vic*-bromo(stannyl)alkenes. Although a full interpretation of the reaction still awaits, some conclusions may be drawn: (i) as a general trend, copper(I) salts gave better *syn*/*anti* ratios, and higher yields than those of copper(II), probably because the dimerisation of the cuprate resulting from the copper/tin exchange is less favoured in the first case, (ii) bromo- or trimethylstannyl-substituted olefins react slowly to afford dimers, whereas alkenes bearing both substituents behave in a different fashion to produce mainly benzocyclotrimers in a shorter time, (iii) the formation of minor amounts of the *anti* isomer when the methyl group is close to the trimethylstannyl group seems attributable to disfavoured tin−tin coupling in the first step of the process, and (iv) as a consequence of the limited but definite effect of the methyl group, the hypothesis of the formation of strained alkynes[1b,2a,4d,5b,5c] as intermediates seems to be less plausible in the case of cyclotrimerisation of *vic*-bromo(trimethylstannyl)alkenes with copper salts.

Experimental Section

General: Reactions were carried out by standard techniques in flame-dried glassware cooled under argon. Commercial high-purity reagents were employed without further purification. Dry THF and 1,2-dimethoxyethane were distilled from sodium/benzophenone prior to use. Dry diisopropylamine, DMF and NMP were distilled from calcium hydride prior to use. The progress of the reactions was monitored by TLC, GC-MS or ^{1}H NMR spectroscopy. Gas-chromatographic analyses were performed with a 30-m, 0.25-mm (i.d.) Rtx-5MS capillary column (diphenyl-/dimethyl-polysiloxane, 5:95). Flash-chromatographic purifications were performed with 230−400 mesh silica gel (Merck 60). Melting points are uncorrected. Optical rotations were observed in a 10-cm cell.

Preparation of (−)-Fenchocamphorone Hydrazone (15): A mixture of **14** (8.0 g, 58.0 mmol), hydrazine hydrate (15 mL, 469 mmol) and concd. H_2SO_4 (2 drops) in *n*BuOH (25 mL) was heated at reflux using a Dean−Stark trap filled with molecular sieves (4 Å) for 18 h. The resulting solution was cooled, allowing the sulfate salts to settle on the bottom of the flask, and the supernatant was filtered by suction, the salts being washed with small amounts of Et_2O (2 × 5 mL). The filtrate was concentrated in vacuo to afford a colourless oil (7.4 g, 84% yield) pure enough for the next steps. An analytical sample of **15** was obtained by bulb-to-bulb distillation, b.p. 70 °C/7.5·1042 Torr. $[\alpha]_D^{22} = -71.2$ ($c = 1.6$, $CHCl_3$). IR (film): $\tilde{\nu} = 3361, 2955, 799$ cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 4.42$ (br. s, 2 H), 2.36 (dt, $J = 14.3, 4.0$ Hz, 1 H), 2.17 (d, $J = 4.2$ Hz, 1 H), 2.05−1.82 (series of m, 3 H), 1.74 (d, $J = 14.3$ Hz, 1 H), 1.50−1.20 (series of m, 2 H), 1.02 (s, 3 H), 0.92 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 165.7$, 52.1, 46.3, 43.8, 32.8, 28.1, 25.7, 21.4, 20.7 ppm. MS (EI, 70 eV): *m/z* (%) = 152 (100) [M$^+$], 137 (70), 120 (30), 109 (74). $C_9H_{16}N_2$ (152.24): calcd. C 71.01, H 10.59; found C 70.00, H 10.62.

Preparation of Epicamphor Hydrazones [(*E*)- and (*Z*)-22]: Hydrazine hydrate (30 mL, 489 mmol) was added by syringe at room temp. under argon to dry MeOH (150 mL) and powdered molecular sieves (4 Å) (5.0 g). The mixture was stirred for 20 min, and **21** (4.5 g, 29.6 mmol) was added in one portion. The resulting slurry was maintained with vigorous stirring for 72 h, and was then filtered through a Celite pad, which was washed with Et_2O. Concentration in vacuo furnished a semi-solid material that was taken up with pentane, filtered and concentrated in vacuo to afford the epicamphor hydrazones, as two isomers (3:1 ratio, 3.7 g, 75% yield), as a colourless oil.

Major Isomer: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 4.67$ (br. s, 2 H), 2.26 (d, $J = 4.7$ Hz, 1 H), 2.10 (dd, $J = 16.6, 4.7$ Hz, 1 H), 1.98−1.86 (m, 1 H), 1.77 (d, $J = 16.6$ Hz, 1 H), 1.70−1.60 (m, 1 H), 1.48−1.25 (m, 2 H), 0.98 (s, 3 H), 0.90 (s, 3 H), 0.82 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 162.5$, 54.2, 47.4, 46.2, 38.7, 35.1, 24.8, 19.2, 18.0, 15.3 ppm. MS (EI, 70 eV): *m/z* (%) = 166 (100) [M$^+$], 151 (83), 123 (78), 110 (83).

Minor Isomer: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 4.80$ (br. s, 2 H), 2.63 (d, $J = 4.7$ Hz, 1 H), 2.29 (dd, $J = 16.6, 4.7$ Hz, 1 H), 1.1.94 (d, $J = 16.6$ Hz, 1 H), 1.96−1.84 (m, 1 H), 1.70−1.60 (m, 1 H), 1.48−1.25 (m, 2 H), 0.95 (s, 3 H), 0.90 (s, 3 H), 0.86 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 155.9$, 47.1, 44.4, 46.6, 45.2, 35.0, 23.2, 19.5, 17.9, 15.0 ppm. MS (EI, 70 eV): *m/z* (%) = 166 (100) [M$^+$], 151 (58), 123 (50), 110 (60). $C_{10}H_{18}N_2$ (166.26): calcd. C 72.24, H 10.91; found C 72.27, H 10.88.

General Procedures for the Bromination of Hydrazones 15 and (*E*/*Z*)-22

Method A: A solution of hydrazone (24.9 mmol) in Et_2O (200 mL) was added dropwise to a well-stirred slurry of $PyHBr_3$ (16.0 g, 49.9 mmol) and Py (8.0 mL, 100 mmol) in Et_2O (100 mL). Evolution of gas (N_2) during the addition was observed with the aid of a bubbler. The mixture was stirred for an additional 15 min after the addition was complete, H_2O (100 mL) was added, and the layers were separated. The organic layer was washed with hydrochloric acid (2 M, 3 × 50 mL) and saturated NaCl (50 mL) and was dried with $MgSO_4$. The resulting solution was distilled to remove volatile materials and the residue was purified by flash chromatography (eluent pentane).

Method B: A solution of hydrazone (12.0 mmol) in dry pyridine (10 mL) was added at 0 °C under Ar to a solution of NBS (4.28 g, 24.1 mmol) in dry pyridine (30 mL). Evolution of gas during the addition (N_2) was observed with the aid of a bubbler. The mixture was stirred for an additional 45 min after the addition was complete, H_2O (300 mL) was added, and the mixture was extracted with pentane (3 × 50 mL). The combined organic layers were washed with hydrochloric acid (2 M, 3 × 50 mL) and saturated NaCl (50 mL) and were dried with $MgSO_4$. The resulting solution was distilled to remove volatile materials and the residue was purified by flash chromatography (eluent pentane).

(−)-2-Bromo-7,7-dimethylbicyclo[2.2.1]hept-2-ene (16): 51% yield by method A, as a colourless oil. $[\alpha]_D^{22} = -23.1$ ($c = 2.3$, $CHCl_3$). IR (film): $\tilde{\nu} = 2958, 1581, 1025$ cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 5.99$ (d, $J = 4.4$ Hz, 1 H), 2.32 (br. s, 2 H), 1.92−1.81 (m, 2 H), 1.17−1.07 (m, 2 H), 1.06 (s, 3 H), 0.90 (s, 3 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 134.2$, 125.3, 58.9, 56.1, 52.6, 25.2, 23.7, 21.8, 21.3 ppm. MS (EI, 70 eV): *m/z* (%) = 200−202 (28) [M$^+$], 185−187 (20), 172−174 (14), 157−159 (28), 121 (87), 105 (64), 91−93 (87), 77 (100). $C_9H_{13}Br$ (201.10): calcd. C 53.75, H 6.52; found C 53.75, H 6.54.

(+)-3-Bromo-1,7,7-trimethylbicyclo[2.2.1]hept-2-ene (24): 52% yield (method A), 68% (method B), as a colourless oil. $[\alpha]_D^{22} = +14.9$ ($c = 1.4$, $CHCl_3$). IR (film): $\tilde{\nu} = 2955, 2869, 1584, 810$ cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 5.73$ (s, 1 H), 2.36 (d, $J = 3.7$ Hz, 1 H), 1.82 (td, $J = 8.5, 3.7$ Hz, 1 H), 1.62 (dd, $J = 10.0, 1.8$ Hz, 1 H), 1.26 (m, 2 H), 1.04 (s, 3 H), 0.93 (s, 3 H), 0.77 (s, 3 H) ppm.

^{13}C NMR (50 MHz, CDCl$_3$): δ = 138.0, 124.5, 60.6, 57.1, 55.6, 32.6, 24.2, 19.2, 19.0, 13.0 ppm. MS (EI, 70 eV): *m*/*z* (%) = 214−216 (10) [M$^+$], 199−201 (19), 188−190 (11), 171−173 (9), 107 (80), 91 (100). $C_{10}H_{15}Br$ (215.13): calcd. C 55.83, H 7.03; found C 53.72, H 6.50.

General Procedure for the Stannylation of Bromoalkenes 8, 16 and 24: *n*BuLi (5.0 mL, 2.5 M solution in hexanes, 12.5 mmol) was added dropwise at 0 °C under Ar to a solution of dry diisopropylamine (1.6 mL, 12.5 mmol) in dry THF (12 mL) and the mixture was kept at 0 °C for 15 min. Bromoalkene **8** (containing **9**), **16** or **24** (containing **25**) (5.0 mmol) was added by syringe, and the mixture was stirred for an additional 15 min. Trimethyltin chloride (1.0 g, 5.0 mmol) was added in one portion, and the mixture was warmed to room temp. overnight. After 20 h, the resulting solution was poured into water (25 mL) and extracted with Et$_2$O (3 × 15 mL). The combined organic extracts were washed with H$_2$O (15 mL) and saturated aqueous NaCl (15 mL), dried with MgSO$_4$ and concentrated in vacuo to afford a pale yellow oil that was purified by flash chromatography (eluent hexanes).

(−)-2-Bromo-1,7,7-trimethyl-3-(trimethylstannyl)bicyclo[2.2.1]hept-2-ene (3): 66% yield, as a colourless oil. $[\alpha]_D^{22}$ = −4.0 (*c* = 1.5, CH$_2$Cl$_2$). IR (film): $\tilde{\nu}$ = 2954, 2870, 773 cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ = 2.44 (d, *J* = 3.6 Hz, 1 H), 1.87−1.71 (m, 1 H), 1.61−1.45 (m, 1 H), 1.19−0.94 (m, 2 H), 1.0 (s, 3 H), 0.85 (s, 3 H), 0.81 (s, 3 H), 0.22 (s, 9 H) ppm. ^{13}C NMR (50 MHz, CDCl$_3$): δ = 146.0, 142.8, 58.5, 57.9, 56.2, 30.7, 25.0, 20.2, 19.4, 12.9, −9.7 ppm. MS (EI, 70 eV): *m*/*z* (%) = 376 (10) [M$^+$ − Me], 283 (14), 229 (56), 133 (87), 119 (100). $C_{13}H_{23}BrSn$ (377.94): calcd. C 41.31, H 6.13; found C 41.29, H 6.14.

(−)-2-Bromo-7,7-dimethyl-3-(trimethylstannyl)bicyclo[2.2.1]hept-2-ene (5): 70% yield, as a colourless oil. $[\alpha]_D^{22}$ = −1.36 (*c* = 2.2, CHCl$_3$). IR (film): $\tilde{\nu}$ = 2953, 1554, 771 cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ = 2.39−2.30 (m, 2 H), 1.92−1.75 (m, 2 H), 1.14 (t, *J* = 8.7 Hz, 1 H), 1.05 (s, 3 H), 0.95 (d, *J* = 8.8 Hz, 1 H), 0.90 (s, 3 H), 0.22 (s, 9 H) ppm. ^{13}C NMR (50 MHz, CDCl$_3$): δ = 147.0, 137.2, 60.7, 57.8, 56.1, 24.9, 23.7, 21.8, 21.4, −9.5 ppm. MS (EI, 70 eV): *m*/*z* (%) = 364 (15) [M$^+$], 347−349 (55), 267 (57), 227 (62), 199 (55), 119 (100). $C_{12}H_{21}BrSn$ (363.91): calcd. C 39.61, H 5.82; found C 39.60, H 5.85.

(+)-3-Bromo-1,7,7-trimethyl-2-(trimethylstannyl)bicyclo[2.2.1]hept-2-ene (6): 4% yield, as a colourless oil. $[\alpha]_D^{22}$ = +11.6 (*c* = 1.7, CHCl$_3$). IR (film): $\tilde{\nu}$ = 2960, 2871, 1551, 772 cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ = 2.36 (d, *J* = 3.7 Hz, 1 H), 1.88−1.70 (m, 1 H), 1.56 (t, *J* = 9.8 Hz, 1 H), 1.25−0.98 (m, 2 H), 1.08 (s, 3 H), 0.93 (s, 3 H), 0.78 (s, 3 H), 0.25 (s, 9 H) ppm. ^{13}C NMR (50 MHz, CDCl$_3$): δ = 149.6, 137.2, 62.6, 60.9, 56.8, 32.6, 24.2, 19.4, 19.2, 15.1, −7.8 ppm. MS (EI, 70 eV): *m*/*z* (%) = 378 (2) [M$^+$], 363 (12), 283 (24), 229 (65), 133 (100). $C_{13}H_{23}BrSn$ (377.94): calcd. C 41.31, H 6.13; found C 41.34, H 6.11.

General Procedure for the Dimerisation of 28 and 30 with Copper(I) Iodide: A solution of *t*BuLi in pentane (1.7 M, 8.2 mL, 7.0 mmol) was added at −20 °C under argon to a solution of **28** or **30** (3.18 mmol) in pentane (1 mL). The temperature was allowed to rise to room temp., with the formation of a white precipitate. Copper(I) iodide (660 mg, 3.50 mmol) and dry THF (0.5 mL, 6.36 mmol) were added, and the mixture was vigorously stirred at room temp. for 3 d. The resulting dark slurry was taken up with pentane, filtered through a silica gel pad and concentrated.

(1*R*,4′*R*,1′*R*,4*R*)-1,1′,7,7,7′,7′-Hexamethyl-2,2′-bi(bicyclo[2.2.1]hept-2-ene) (29): 85% yield, as a colourless oil. $[\alpha]_D^{22}$ = −98.0 (*c* = 2.0, CHCl$_3$). IR (film): $\tilde{\nu}$ = 2985, 2951, 2870, 1384 cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ = 5.66 (d, *J* = 3.2 Hz, 2 H), 2.29 (t, *J* = 3.2 Hz, 2 H), 1.96−1.74 (m, 4 H) 1.60−1.43 (m, 4 H), 1.05 (s, 6 H), 0.83 (s, 6 H), 0.77 (s, 6 H) ppm. ^{13}C NMR (50 MHz, CDCl$_3$): δ = 144.5, 128.0, 55.5, 54.9, 51.5, 31.7, 26.3, 19.8, 19.7, 12.5 ppm. MS (EI, 70 eV): *m*/*z* (%) = 270 (21) [M$^+$], 255 (18), 242 (38), 227 (84), 91 (67), 41 (100). $C_{20}H_{30}$ (270.45): calcd. C 88.82, H 11.18; found C 88.83, H 11.20.

(1*S*,4*R*,1′*S*,4′*R*)-1,1′,7,7,7′,7′-Hexamethyl-3,3′-bi(bicyclo[2.2.1]hept-2-ene) (30): 40% yield, as colourless crystals m.p. 88−90 °C (from hot MeOH). $[\alpha]_D^{22}$ = +220 (*c* = 1.2, CHCl$_3$). IR (KBr): $\tilde{\nu}$ = 2954, 2867, 1385, 793 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 5.43 (s, 2 H), 2.37 (d, *J* = 3.4 Hz, 2 H), 1.83−1.63 (m, 6 H), 1.11 (td, *J* = 10.1, 2.8 Hz, 2 H), 1.05 (s, 6 H), 0.84 (s, 6 H), 0.80 (s, 6 H) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = 143.1, 131.9, 55.1, 53.4, 52.4, 34.5, 24.6, 19.5, 19.4; 13.4 ppm. MS (EI, 70 eV): *m*/*z* (%) = 270 (86) [M$^+$], 255 (100), 227 (91), 199 (48), 187 (46). $C_{20}H_{30}$ (270.45): calcd. C 88.82, H 11.18; found C 88.81, H 11.15.

Preparation of (1*R*,4*S*,1′*R*,4′*S*)-2,2′-Dibromo-1,1′,7,7,7′,7′-hexamethyl-3,3′-bi(bicyclo[2.2.1]hept-2-ene) (32): Dry LiCl (2.69 g, 63.5 mmol) was flame-dried three times in vacuo in a two-necked round-bottomed flask, with argon purging during the cooling stages. Dry DMF (26 mL) and **3** (2.00 g, 5.29 mmol) were added, and the mixture was stirred at room temp. for 15 min. Dry CuCl (2.60 g, 26.3 mmol) and dry 1,2-dimethoxyethane (5.5 mL, 52.9 mmol) were added in sequence and the mixture was stirred at room temp. for 48 h. Water (150 mL) was added, and the mixture was extracted with an Et$_2$O/hexanes mixture (1:1, 3 × 50 mL). The combined organic extracts were washed with a 5% aqueous NH$_3$ solution, dried with MgSO$_4$, concentrated and purified by flash chromatography (eluent *n*-hexane) to afford **32** (1.12 g, 76% yield) as a colourless oil that crystallised upon standing; m.p. 52−53 °C. $[\alpha]_D^{22}$ = +214 (*c* = 2.3, CHCl$_3$). IR (KBr): $\tilde{\nu}$ = 2956, 2867, 1273, 991 cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ = 2.90 (d, *J* = 3.6 Hz, 2 H), 1.95−1.84 (m, 2 H), 1.65−1.53 (m, 2 H), 1.45−1.33 (m, 2 H), 1.26−1.14 (m, 2 H), 1.04 (s, 6 H), 0.90 (s, 6 H), 0.85 (s, 6 H) ppm. ^{13}C NMR (50 MHz, CDCl$_3$): δ = 140.0, 127.0, 58.2, 55.4 (2 overlapping signals), 31.3, 25.8, 19.9, 19.3, 13.2 ppm. MS (EI, 70 eV): *m*/*z* (%) = 426−428−430 (64) [M$^+$], 398−400−402 (27), 383−385−387 (27), 347−349 (65), 319−321 (100). $C_{20}H_{28}Br_2$ (428.24): calcd. C 56.09, H 6.59; found C 56.06, H 6.57.

Preparation of (1*R*,4*S*,1′*S*,4′*S*)-2-Bromo-1,1′,7,7,7′,7′-hexamethyl-3,3′-bi(bicyclo[2.2.1]hept-2-ene) (33): A solution of *t*BuLi in pentane (1.7 M, 0.9 mL, 1.5 mmol) was added at −78 °C under argon to a solution of **32** (500 mg, 1.2 mmol) in dry THF (5 mL). The solution was kept at the same temperature for 20 min, water (10 mL) was added, and the warmed mixture was extracted with Et$_2$O (3 × 10 mL). The combined organic extracts were dried with MgSO$_4$, concentrated and purified by flash chromatography (eluent *n*-hexane) to afford **33** (260 mg, 63% yield) as a colourless oil that crystallised upon standing: m.p. 67−68 °C. $[\alpha]_D^{22}$ = +192 (*c* = 2.5, CHCl$_3$). IR (KBr): $\tilde{\nu}$(tilde) = 2987, 2954, 2868, 1479, 1452, 822 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 5.73 (s, 1 H), 3.06 (d, *J* = 3.4 Hz, 1 H), 2.48 (d, *J* = 3.6 Hz, 1 H), 1.92−1.71 (m, 2 H), 1.67−1.55 (m, 2 H), 1.37−1.14 (m, 2 H), 1.04 (s, 3 H), 1.02 (s, 3 H), 1.02−0.80 (m, 2 H), 0.86 (s, 3 H), 0.83 (s, 6 H), 0.79 (s, 3 H). ^{13}C NMR (75 MHz, CDCl3): δ = 141.8, 136.6 (2 overlapping signals), 123.2, 58.8, 55.5, 55.3, 54.1, 52.8 (2 overlapping signals), 33.5, 31.9, 25.6, 24.4, 19.9, 19.6, 19.3, 19.1, 13.4, 13.1. MS (EI, 70 eV): *m*/*z* (%) = 348−350 (32) [M$^+$], 320−322 (35), 305−307 (100), 269 (65), 213 (75), 91 (88). $C_{20}H_{29}Br$ (349.35): calcd. C 68.76, H 8.37; found C 68.79, H 8.39.

General Procedure for the Cyclotrimerisation with $Cu(NO_3)_2\cdot 3H_2O$, $Cu(OTf)_2$ or CuOTf·PhH in THF: The appropriate copper salt (1.5 mmol) was added in one portion to a solution of a *vic*-bromo(trimethylstannyl)bicycloalkene (1.0 mmol) in THF (2.5 mL). The mixture was stirred at room temp. for 5 h, a 20% aqueous NH_3 solution (10 mL) was added, and the resulting slurry was extracted with Et_2O (3 × 10 mL). The combined organic extracts were washed with H_2O (2 × 10 mL) and saturated aqueous NaCl (10 mL), dried with $MgSO_4$ and concentrated in vacuo to afford a pale yellow oil that was analysed (^{1}H NMR, GC-MS) and purified by flash chromatography (eluent pentane).

General Procedure for the Cyclotrimerisation with CuTC in NMP: Copper(I) thiophenecarboxylate (1.5 mmol) was added at −20 °C under argon, in one portion for **3** and **6** and by injection by syringe pump for **5**, to a solution of the *vic*-bromo(trimethylstannyl)bicycloalkene (1.0 mmol) in dry NMP (2.5 mL). The mixture was warmed to room temp. over 2 h, aqueous NH_3 solution (20%, 10 mL) was added, and the resulting slurry was stirred for 30 min and extracted with Et_2O (3 × 10 mL). The combined organic extracts were washed with H_2O (2 × 10 mL) and saturated aqueous NaCl (10 mL), dried with $MgSO_4$ and concentrated in vacuo to afford a pale yellow oil that was analysed (^{1}H NMR, GC-MS) and purified by flash chromatography (eluent pentane). Flash chromatography (eluent pentane) of the trimerisation mixtures from **3** and **6** furnished (+)-*anti*-**4** as the first eluate.

(+)-(1*R*,4*S*,5*R*,8*S*,9*S*,12*R*)-2,3,4,6,7,8,9,10,11-Nonahydro-1,5,12,13,13′,14,14′,15,15′-nonamethyl-1,4:5,8:9,12-trimethanotriphenylene (*anti*-4): Waxy solid. $[\alpha]_D^{22}$ = +52.0 (*c* = 1.2, $CHCl_3$). IR (film): $\tilde{\nu}$ = 2952, 2871, 1474, 1382 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.98 (d, *J* = 4.0 Hz, 1 H), 2.65 (d, *J* = 3.9 Hz, 1 H), 2.61 (d, *J* = 3.8 Hz, 1 H), 2.01−1.90 (m, 3 H), 1.78−1.68 (m, 3 H), 1.34 (s, 6 H), 1.30 (s, 3 H), 1.29−1.20 (m, 2 H), 1.13−0.94 (m, 4 H), 0.90 (s, 3 H), 0.87 (s, 3 H), 0.86 (s, 3 H), 0.53 (s, 3 H), 0.46 (s, 3 H), 0.42 (s, 3 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 140.5, 140.0, 138.3, 138.1, 137.5, 136.1, 56.2, 56.1, 55.9, 53.4, 53.2, 52.2, 50.2, 49.9, 50.0, 34.0, 33.9 (2 overlapping signals), 26.9, 26.6, 26.5, 20.3 (2 overlapping signals), 20.2, 19.4 (2 overlapping signals), 19.0, 16.7, 16.6, 14.4 ppm. MS (EI, 70 eV): *m*/*z* (%) = 402 (45) [M$^+$], 374 (28), 359 (100), 109 (47), 83 (100). $C_{30}H_{42}$ (402.65): calcd. C 89.49, H 10.51; found C 89.48, H 10.54.

The second eluate, containing an inseparable mixture of *syn*-**4** and **32**, was dissolved under Ar in a minimum amount of dry THF and was treated with an excess of 2.5 M *n*BuLi at 0 °C for 30 min. Silica gel was added to the resulting mixture, and the volatile materials were removed in vacuo to afford a solid material that was subjected to flash chromatography (eluent pentane) to afford *syn*-**4** as a waxy solid.

(+)-(1*R*,4*S*,5*R*,8*S*,9*R*,12*S*)-2,3,4,6,7,8,10,11,12-nonahydro-1,5,9,13,13′,14,14′,15,15′-nonamethyl-1,4:5,8:9,12-trimethanotriphenylene (*syn*-4): $[\alpha]_D^{22}$ = +10.2 (*c* = 1.8, $CHCl_3$). IR (film): $\tilde{\nu}$ = 2956, 2871, 1482, 1386 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.98 (d, *J* = 4.0 Hz, 3 H), 1.99−1.91 (m, 3 H), 1.76−1.68 (m, 3 H), 1.29 (s, 9 H), 1.16−1.00 (m, 6 H), 0.89 (s, 9 H), 0.55 (s, 9 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 138.9, 136.2, 56.0, 52.2, 49.7, 33.8, 26.1, 20.3, 19.1, 14.3 ppm. MS (EI, 70 eV): *m*/*z* (%) = 402 (24) [M$^+$], 374 (32), 359 (60), 109 (65), 83 (100). $C_{30}H_{42}$ (402.65): calcd. C 89.49, H 10.51; found C 89.52, H 10.49.

The trimerisation mixture with CuTC from **5** was a dark red tar, which was dissolved in hexanes (50 mL) and stirred with silica gel (5 g) until the solution became pale yellow (ca. 3 h). The mixture was filtered and the filtrate was concentrated to afford an oil that was analysed (^{1}H NMR, GC-MS) and purified by flash chromatography (eluent hexanes).

First Eluate. *anti*-1,2,3,4,5,6,7,8,9,10,11,12-Dodecahydro-13,13′,14,14′,15,15′-hexamethyl-1,4:5,8:9,12-trimethanotriphenylene (*anti*-36): Waxy solid. IR (film): $\tilde{\nu}$ = 2953, 2924, 2850, 1470 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.63 (dd, *J* = 1.8, 1.6 Hz, 6 H), 2.09−1.98 (m, 6 H), 1.10−1.03 (m, 6 H), 1.04 (s, 9 H), 0.67 (s, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.50, 137.46, 137.14, 55.31 (2 overlapping signals), 54.80, 50.04, 49.98, 49.92, 26.92, 26.70, 26.48, 22.57, 22.43 (2 overlapping signals), 21.73 (2 overlapping signals), 21.70 ppm. MS (EI, 70 eV): *m*/*z* (%) = 360 (22) [M$^+$], 317 (88), 289 (9), 235 (25), 95 (100). $C_{27}H_{36}$ (360.57): calcd. C 89.94, H 10.06; found C 89.97, H 10.08.

Second Eluate. *syn*-1,2,3,4,5,6,7,8,9,10,11,12-Dodecahydro-13,13′,14,14′,15,15′-hexamethyl-1,4:5,8:9,12-trimethanotriphenylene (*syn*-36): Waxy solid. IR (KBr): $\tilde{\nu}$ = 2966, 2945, 1466 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.62 (dd, *J* = 1.8, 1.6 Hz, 6 H), 2.08−2.00 (m, 6 H), 1.12 (d, 3 H, 1/2 AB, *J* = 4.4 Hz), 1.08 (d, 1/2 AB, *J* = 4.4 Hz, 3 H), 1.04 (s, 9 H), 0.70 (s, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 136.86, 55.68, 49.86, 26.27, 22.32, 21.74 ppm. MS (EI, 70 eV): *m*/*z* (%) = 360 (36) [M$^+$], 317 (100), 289 (15), 235 (37), 95 (94). $C_{27}H_{36}$ (360.57): calcd. C 89.94, H 10.06; found C 89.92, H 10.03.

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