CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.201002769

1,4-Dialkynylbutatrienes: Synthesis, Stability, and Perspectives in the Chemistry of *carbo*-Benzenes

Valérie Maraval,*[a, b] Léo Leroyer,[a, b] Aya Harano,[a, b, c] Cécile Barthes,[a, b] Alix Saquet,[a, b] Carine Duhayon,[a, b] Teruo Shinmyozu,[c] and Remi Chauvin*[a, b]

Abstract: The π-electron-rich C_8-conjugated sequence of 1,4-dialkynylbutatrienes is identified as a fragile and fascinating motif occurring in *carbo*-benzene derivatives, and in Diederich's 1,4-bis(arylethynyl)- or 1,4-bis(triisopropylsilylethynyl)butatriene "capped" representatives, in particular, in tetraalkynylbutatriene. The family of symmetrical 1,4-dialkynylbutatrienes (E−C≡C)RC=C=C=CR(C≡C−E) is extended to functional caps (E = H, CH_3, C≡CPh, CPh=CHBr, or CPh=CBr_2) with non-alkynyl substituents at the sp^2 vertices (R = Ph or CF_3). The targets were selected for their potential in appealing retrosynthetic routes to *carbo*-benzenes, in which the aromatic C_{18} macrocycle would be directly generated by sequential metathesis or reductive coupling processes. The functional 1,4-dialkynylbutrienes were synthesized by either classical methods used for the preparation of generic butatrienes (R′Li/CuX-mediated reductive coupling of *gem*-dihaloenynes or $SnCl_2$/HCl-mediated reduction of 3,6-dioxyocta-1,4,7-triyne precursors). Their spectroscopic and electrochemical properties are compared and analyzed on the basis of the relative extent of total conjugation.

Keywords: alkynes · allenes · aromaticity · conjugations · UV/Vis spectroscopy

Introduction

Disregarding the effects of aromaticity,[1] which are expected to be small due to the size of the C_{18} macrocycle, the stability of *carbo*-benzene rings[2] contrasts with the high reactivity of "isolated" dialkynylbutatrienes without further π-conjugation beyond the sp carbon termini. These molecules constitute models of the three intersecting one-edge-two-vertex bis(ethyndiyl)butatriene C_8 motifs that form the Kekule structures of *carbo*-benzenic macrocycles with the same substituents at the sp^2 vertices (Scheme 1).

In their pioneering studies, Diederich, Houk, and coworkers showed that the stability of di- and tetra-alkynylbutatrienes (E−C≡C)RC=C=C=CR(C≡C−E) is determined by the presence of substituents at the sp^2 carbon atoms (R = C≡C−E versus H) and by suitable caps at the terminal sp carbon atoms (E = aryl, trialkylsilyl, and *tert*-butyl).[3] The *cis* and *trans* isomers were obtained in a ratio close to 1:1.5, and the authors provided evidence for a surprisingly facile *cis*/*trans* isomerization at room temperature ($\Delta G^{\neq}$(298 K) $\leq$ 25 kcal mol^{-1}) with a low thermodynamic preference, as expected from the weak steric interaction between the remote substituents. More generally, isomerization of generic butatrienes is fundamentally facilitated by the bispropargylic diradical form of their valence bond (VB) description (Scheme 1). This form is stabilized by the "aromaticity" of the central triple bond (as compared with the bisallylic diradical form of analogous 1,3-butadienes),[1] and correlates with a low-lying open-shell singlet transition state (TS) of the adiabatic stereoconversion though a perpendicular configuration of the sp^2 ends. The stabilization of both the ground states and TS of stereo-interconverting butatrienes naturally depends on the nature of the substituents, and it was shown that the stabilizing effect of alkynyl substituents is remarkably strong.

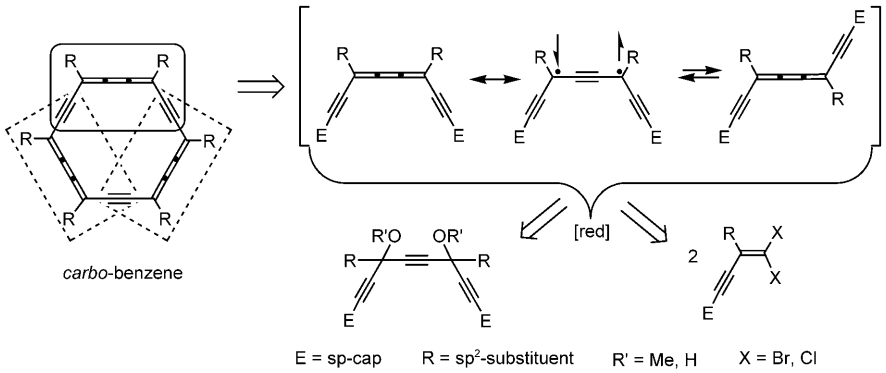
Known 1,4-dialkynylbutatrienes other than *carbo*-benzene derivatives are limited to two capped versions (E = 4-$Me_2NC_6H_4$, (iPr_3)Si) of unsubstituted diethynylbutatriene (R = H), which are less stable than the corresponding tetraalkynylbutatrienes (R = C≡C−E).[3a] The paucity of examples of 1,4-dialkynylbutatrienes thus calls for an investigation of the stability limit versus the nature of both the cap E

[a] Dr. V. Maraval, Dr. L. Leroyer, Dr. A. Harano, C. Barthes, A. Saquet, C. Duhayon, Prof. R. Chauvin
CNRS, LCC (Laboratoire de Chimie de Coordination)
205, route de Narbonne
31077 Toulouse (France)
Fax: (+33) 561-55-30-03
E-mail: vmaraval@lcc-toulouse.fr
chauvin@lcc-toulouse.fr

[b] Dr. V. Maraval, Dr. L. Leroyer, Dr. A. Harano, C. Barthes, A. Saquet, C. Duhayon, Prof. R. Chauvin
Université de Toulouse
UPS, INP, LCC, 31077 Toulouse (France)

[c] Dr. A. Harano, Prof. T. Shinmyozu
Institute for Materials Chemistry and Engineering (IMCE)
and Department of Molecular Chemistry
Graduate School of Sciences
Kyushu University, Hakozaki 6-10-1 Higashi-ku
Fukuoka 812-8581 (Japan)

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201002769.



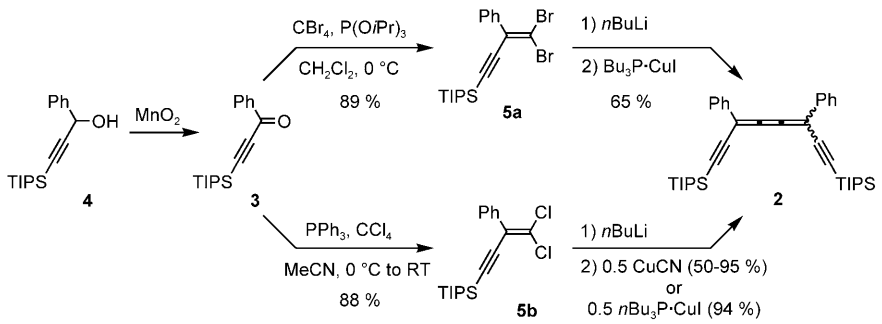
Scheme 1. Dialkynylbutatrienes as isolated models of the three intersecting one-edge-two-vertex bis(ethynediyl)butatriene C_8 motifs constituting the Kekule structure of *carbo*-benzene rings. Their electronic and stereochemical features, as well as the two main reductive retrosynthetic approaches, are illustrated.

and substituents R (Scheme 1). Caps with minimal steric and electronic demand deserve specific attention for their possible selective reactivity. For example, non-capped diethynylbutatrienes (E = H) could undergo deprotonation and electrophilic functionalization, such as Eglington–Glaser oxidative homocoupling or Sonogashira coupling with aromatic halides.[3b] Methyl-capped dialkynylbutatrienes ($E = CH_3$) can also be regarded as "functional" for homologous deprotonation/electrophilic substitution processes or alkyne metathesis (see below). Beyond (and related to) the *carbo*-benzene series, the family of functional 1,4-dialkynylbutatrienes is hereafter extended to representatives stabilized by non-alkynyl substituents, in particular, with R = Ph or CF_3. Their synthesis is undertaken by either classical methods used for the preparation of generic butatrienes,[4] that is, R′Li/CuX-mediated reductive coupling of *gem*-dihaloalkenes, or $SnCl_2$/HCl-mediated reduction of 1,4-dioxy-but-2-yne precursors (Scheme 1).

Results and Discussion

An uncapped diethynylbutatriene: Diederich and co-workers reported that protodesilylation of tris(isopropylsilyl) (TIPS)-capped 1,4-diethynylbutatrienes (with two other alkynyl substituents R) did not allow for the characterization of any product.[3b] Because no uncapped version of 1,4-diethynylbutatriene has been described, a phenyl-substituted representative **1** was targeted starting from the TIPS-capped possible precursor **2**.

*1,4-Bis(triisopropylsilylethynyl)-1,4-diphenylbutatriene (**2**; R = Ph, E = TIPS)*: The TIPS-capped reference molecule of this study (**2**) was prepared by the classical method used for the preparation of other TIPS-capped alkynylbutatrienes, consisting of a reductive homo-coupling of *gem*-dibromo olefinic precursors.[3] The parent ketone **3** was obtained in two steps from benzaldehyde and triisopropylsilylacetylene via the propargylic alcohol **4**. Dibromo-olefination of **3** was performed by a recently described procedure involving triisopropylphosphite instead of the classically used triphenylphosphane reagent, and afforded the *gem*-dibromoenyne **5a** in 89% yield (Scheme 2, top).[5] This enyne was then treated with butyllithium at −100 °C,



Scheme 2. Alternative syntheses of the TIPS-capped 1,4-diethynyl-1,4-diphenylbutatriene **2** through either *gem*-dibromoenyne **5a** (top) or *gem*-dichloroenyne **5b** (bottom).

and then with nBu$_3$P·CuI,[6] which is a soluble copper salt that was first used by Iyoda and later by Diederich to prepare butatrienes in quite good yields.[3,7] This method afforded the targeted dialkynyldiphenylbutatriene **2** in 65% isolated yield as a 50:50 mixture of *cis* and *trans* isomers (according to integration of the *o*-CH ^{1}H NMR signals of their respective phenyl groups).

In the search for methodological improvements, the same butatriene derivative **2** was also targeted through the analogous *gem*-dichloroenyne **5b**. The latter was prepared by a procedure described by Stachulski and co-workers,[8] which is based on the use of a mixture of CCl_4 and PPh_3 in acetonitrile as a specific solvent. This method was reported to be particularly efficient with ketone substrates, and here afforded the *gem*-dichloroenyne **5b** in 88% yield from ketone **3** (Scheme 2, bottom). Treatment of **5b** with *n*BuLi, and then with copper cyanide, led to the formation of butatriene **2** in poorly reproducible yields (50–95%) depending on the quality of the CuCN sample. Replacement of the latter salt by tri-*n*-butylphosphane-coordinated copper iodide resulted in

excellent and reproducible yields (94%). As illustrated in Scheme 2, the route through the "greener" dichloroalkene intermediate **5b** is thus more efficient than the classical route using the dibromo analogue **5a** and the same $Bu_3P{\cdot}CuI$ reagent (Scheme 2).

Although two distinct spots were observed on the TLC plate, the stereoisomers of **2** could not be separated by silica gel chromatography. However, the mixture (an intense yellow oil) crystallized progressively when kept at room temperature for a few hours. X-ray diffraction analysis of the crystals showed that they were composed of the pure *trans* isomer of **2** (Figure 1).

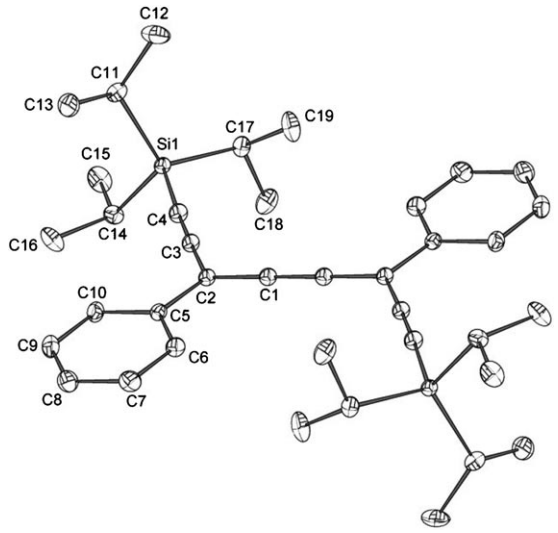
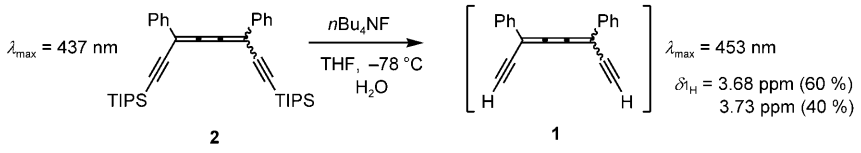


Figure 1. ORTEP diagram of the *trans* isomer of dialkynylbutatriene **2**. Distances (Å): C1−C1′ = 1.2440(13); C1−C2 = 1.3509(9); C2−C3 = 1.4249(9); C3−C4 = 1.2156(10); C2−C5 = 1.4719(10); C4−Si1 = 1.8401(7); angles (°): C1′-C1-C2 = 179.43(9); C1-C2-C3 = 117.80(6); C2-C3-C4 = 178.47(8); C3-C4-Si1 = 177.35(17); C1-C2-C5 = 121.58(6); C3-C2-C5 = 120.63(6).

Synthesis of a diethynylbutatriene (E = H, R = Ph): Deprotection of the ethynyl arms of **2** was performed with tetrabutylammonium fluoride (TBAF) in tetrahydrofuran (THF) at low temperature, affording **1** as the first characterized example of a non-capped diethynylbutatriene (Scheme 3). This compound appeared to be quite unstable, and polymerized instantaneously upon concentration. However, after flash purification of the crude reaction mixture through silica gel, the ^1H NMR spectrum of a diluted solution of pure **1** could be recorded. In the absence of the intense TIPS signals of **2** at $\delta = 1.21$ ppm, two signals at $\delta = 3.68$ and 3.73 ppm in a 60:40 ratio were assigned to the acetylenic protons of the *cis* and *trans* isomers of **1** (without configurational assignment). All attempts to record a clean ^{13}C NMR spectrum of **1** failed due to its poor stability in sufficiently concentrated solutions. Nevertheless, **1** could be kept for a few days at 4°C in pentane (approximately 3 mM, obtained after filtration through silica gel with pentane as eluent).

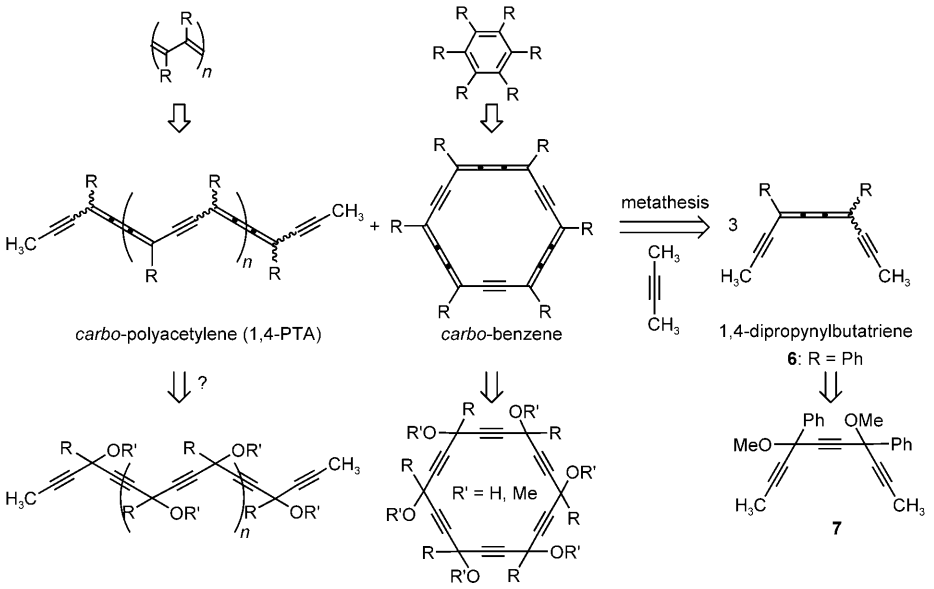


Scheme 3. Desilylation of the TIPS-capped diethynylbutatriene **2** to the uncapped version **1**.

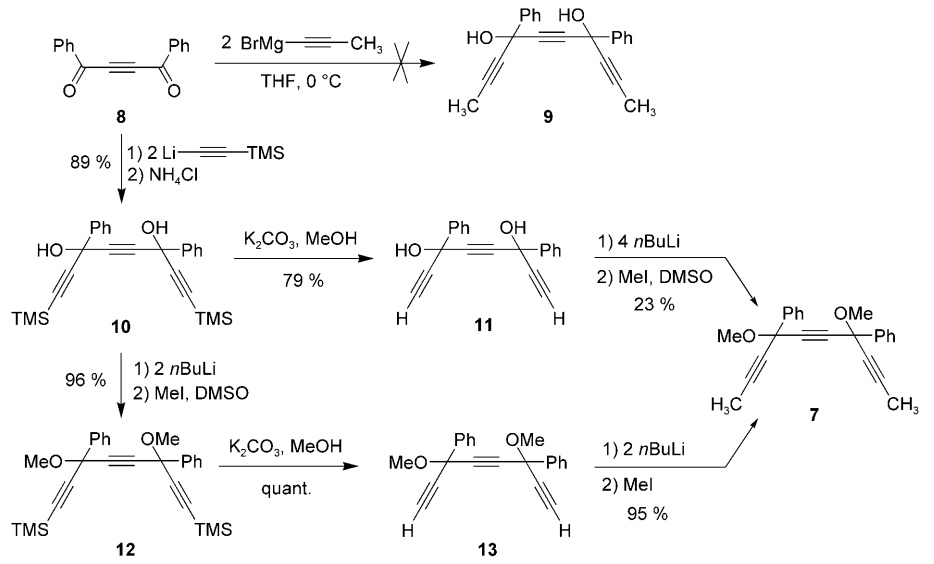
A methyl-capped diethenylbutatriene: Methyl groups are interesting caps for the 1,4-diethynylbutatriene motif (Scheme 1, $E = CH_3$) not only because of their low steric protecting effect, but also because of their functional versatility. Beyond the possibility of propargylic deprotonation and electrophilic functionalization, 1,4-dipropynylbutatrienes might undergo sequential metathesis to generate volatile but-2-yne and 1,4-poly(triacetylenes) (1,4-PTA). The latter are the chain *carbo*-mers of polyacetylenes, and the regioisomers of classical 1,2-poly(triacetylenes) (PTA = 1,2-PTA), which have attracted considerable interest for their promising conducting and optical properties.[9] Ring-closing sequences of *n* such metathesis processes might ultimately produce *carbo*-[2n]annulenes (see Scheme 4 for $n = 3$). In particular, while benzene can be obtained by cyclotrimerization of acetylene,[10] *carbo*-benzene might result from cyclotrismetathesis of 1,4-dipropynylbutatriene. Guided by our long-time ambition to develop novel strategies for the preparation of *carbo*-benzene derivatives, the synthesis of 1,4-dipropynylbutatriene key precursors was thus undertaken. Because all *carbo*-benzenes known to date have been obtained by reductive aromatization of hexaoxy[6]pericyclynes,[1,2b,11] the phenylated precursor **6** was targeted by reduction of the corresponding 3,6-methoxyocta-1,4,7-triyne precursor **7** (Scheme 4, R = Ph).

The synthesis of the dioxytriyne **7** was envisaged through double addition of acetylide derivatives to dibenzoylacetylene **8**, itself prepared from commercial *trans*-dibenzoylethene using a known two-step procedure.[12] Direct addition of two equivalents of propynylmagnesium bromide to **8**, however, failed to produce the triynediol **9**, only polymeric materials was obtained (Scheme 5).

The triyne diether **7** was then targeted from the known bis(silyl)-protected triynediol **10**, which was readily prepared by addition of two equivalents of lithium trimethylsilylacetylide to the diketone **8**.[13] Cleavage of the trimethylsilyl groups of **10** led to the formation of the bis(terminal) triyne **11** in 79% yield. However, the simultaneous quadruple methylation of **11** proved to be problematic. Under these conditions, in addition to the formation of several products resulting from partial methylation or from other side-reactions, the expected tetramethylated product **7** could be isolated in 23% yield only after a tedious chromatographic purification. A more efficient synthesis of **7** was finally achieved



Scheme 4. Retrosynthetic design of *carbo*-polyacetylenes (=1,4-poly(triacetylenes) or 1,4-PTAs) and related *carbo*-[2*n*]annulenes (*carbo*-benzene for $n=3$) based on sequential metathesis of the key target of this study, 1,4-dipropynyldiphenylbutatriene **6**.



Scheme 5. Alternative synthetic routes to the triyne diether **7**.

through an alternative, one-step longer route involving double O-methylation of the diol **10** followed by desilylation of the resulting diether **12**, giving the bis(terminal) triyne **13**.[13] Double C-methylation of **13** was achieved by treatment with *n*-butyllithium and iodomethane, giving the expected triyne-diether **7** in good yield (Scheme 5). The final product and all intermediates **10**–**13** were obtained as mixtures of *meso* and *dl* diastereoisomers. One pure stereoisomer of **7** could be separated by selective crystallization from hexane, and X-ray diffraction analysis indicated that the crystalline sample corresponded to the *meso* isomer (Figure 2), as previously observed for several other octa-1,4,7-triyn-3,6-diol derivatives.[14]

Treatment of **7** (either as the *meso*/*dl* mixture or as the pure *meso* isomer) with $SnCl_2$/HCl was carried out at low temperature in CH_2Cl_2 (Scheme 6). At −40 °C, an intense yellow coloration of the reaction mixture appeared progressively, suggesting the formation of the butatriene chromophore. Two yellow spots with very similar R_f values of similar intensity were observed by TLC analysis (AcOEt/n-heptane, 1:9), which were attributed to the *cis* and *trans* isomers of 1,4-dipropynylbutatriene **6**. After neutralization of the medium by addition of 1 N NaOH and washings with water, the organic layer was separated. When concentrated to dryness, the dipropynylbutatriene **6** appeared to be unstable. However, it could be kept in CH_2Cl_2 at 4 °C for several weeks without decomposition. The methyl-capped diethynylbutatriene **6** thus appears to be more stable than its uncapped counterpart **1** (Scheme 3). The remaining sensitivity of **6** in the dry amorphous state, however, prevented the determination of an accurate yield. Nevertheless, when the reaction was performed in a $CDCl_3$/DCl/D_2O mixture, NMR spectroscopic analysis of the $CDCl_3$ layer showed that the triyne diether **7** was completely converted and that **6** was the sole product. This was indicated by the observation of deshielded CH_3 ^{1}H NMR signals at $\delta=2.23$ and 2.26 ppm (the corresponding protons of both isomers of **7** resonate at $\delta=1.98$ ppm**)** and by the disappearance of the OCH_3 signals (the produced methanol being transferred into the aqueous layer). The two propynyl CH_3 ^{1}H NMR signals integrated in a 1:1 ratio, showing that the *cis* and *trans* isomers were formed in equal amounts.

Although the *cis* and *trans* isomers of **6** could not be separated by column chromatography, crystals were deposited by slow evaporation of concentrated CH_2Cl_2 solutions of the mixture at low temperature, and X-ray diffraction analyses showed that they corresponded to the pure *trans*-**6** isomer (Figure 3). The carbon skeleton of the molecule appears to be almost perfectly planar in the solid state. This butatriene

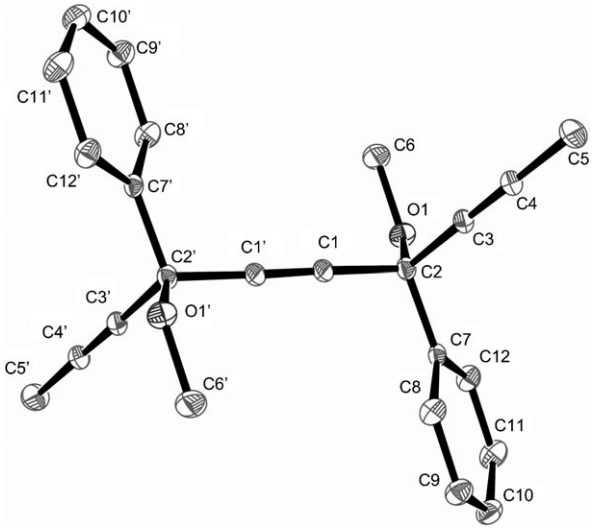


Figure 2. ORTEP diagram of the *meso* isomer of the triyne-diether **7**. Distances (Å): C1-C1′ = 1.189(2); C1-C2 = 1.4863(16); C2-C3 = 1.4756(15); C3-C4 = 1.1853(15); C4-C5 = 1.4518(16); C2-O1 = 1.4183(14); C6-O1 = 1.4208(16); C2-C7 = 1.5317(16); angles (°): C1′-C1-C2 = 178.43(16); C1-C2-C3 = 108.96(9); C2-C3-C4 = 178.35(13); C3-C4-C5 = 179.65(15); C1-C2-O1 = 110.79(9); O1-C2-C3 = 111.29(9); O1-C2-C7 = 107.85(9); C3-C2-C7 = 109.15(9); C1-C2-C7 = 108.74(9); C2-O1-C6 = 114.85(10).

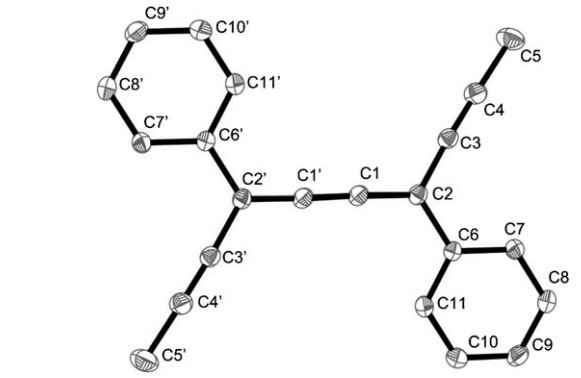
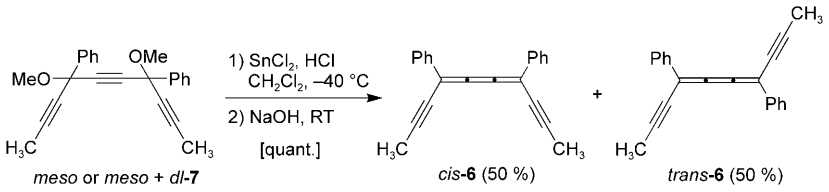


Figure 3. ORTEP diagram of the *trans* isomer of the dipropynylbutatriene **6**. Distances (Å): C1−C1′ = 1.240(3); C1−C2 = 1.3425(17); C2−C3 = 1.425(2); C3−C4 = 1.189(2); C4−C5 = 1.452(2); C2−C6 = 1.4736(18); angles (°): C1′-C1-C2 = 177.50(19); C1-C2-C3 = 119.90(12); C2-C3-C4 = 176.66(15); C3-C4-C5 = 177.20(17); C1-C2-C6 = 121.24(12); C3-C2-C6 = 118.85(11).



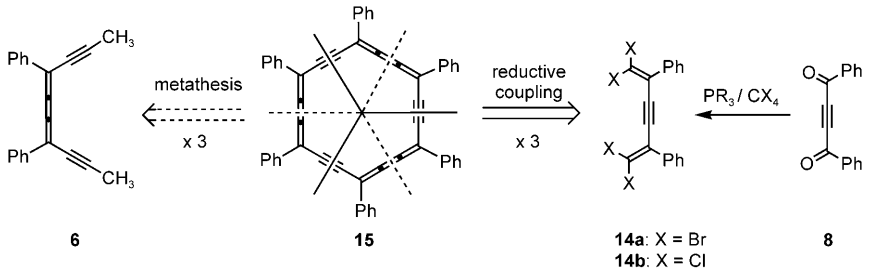
Scheme 6. Reduction of the triyne diether **7** (as either a *meso*/*dl* mixture or the pure *meso* isomer) to 1:1 mixtures of *cis*- and *trans*-1,4-diphenyl-1,4-dipropynylbutatriene (**6**).

thus adopts the configuration in which the steric repulsions are minimized, and the conformation in which the conjugation is most the efficient, with respect to coplanar phenyl rings. All attempts at recording the ^{1}H NMR spectrum of pure *trans*-**6**, however, failed because of rapid isomerization in solution at room temperature; ten minutes after the preparation of the NMR sample in $CDCl_3$, a 70:30 *trans*-**6**/*cis*-**6** mixture was observed, and, after one hour, a steady 50:50 ratio was reached. The corresponding approximate first-order kinetic constant can thus be estimated as $k = 0.00076\ s^{-1}$, which, in the Eyring model, corresponds to a free enthalpy of activation $\Delta G^{\neq}(298\ K)$ of approximately 22 kcal mol^{-1}. This value is remarkably close to the rotational energy barrier calculated at the UB3LYP/6-31G(d) level of theory for the unsubstituted diethynylbutatriene in the gas phase (R = E = H: $\Delta G^{\neq}(298\ K) = 21.2$ kcal mol^{-1}).[3c] The diphenyl derivative **6** (R = Ph, E = Me), however, appears to be configurationally less stable than the related unsubstituted dialkynylbutatrienes (R = H, E = 4-$Me_2NC_6H_4$, TIPS), the *trans* isomer of which could be resolved at room temperature (for E = TIPS) and the isomerization barrier in CD_2Cl_2 of which was estimated to be approximately 25 kcal mol^{-1}.[3c,15] These observations can be explained by the effect of the phenyl substituents of **6**, which stabilize the diradical form of the isomerization TS (Scheme 1).

The dipropynylbutatriene **6** is the first example of a fully characterized diethynylbutatriene motif that is weakly protected by caps other than the aryl, *tert*-butyl, or trialkylsilyl groups. Moreover, the reductive elimination route from the corresponding but-2-yne-1,2-diol diether proved to be compatible with the intrinsically reactive propynyl substituents.

In preliminary experiments, however, the substrate **6** was found to be surprisingly inert when submitted to alkyne metathesis conditions using standard catalysts,[16] even at high temperature (e.g., in toluene at 110 °C). Systematic studies using more sophisticated catalysts are thus planned.[17]

Alkenyl- and alkynyl-capped diethynylbutatrienes: The main challenge in the chemistry of *carbo*-benzenes is the design of a direct method allowing for the formation of the C_{18} macrocycle in its aromatic form, and thus circumventing the problematic step of reductive aromatization of [6]pericyclynic precursors (Scheme 4). In parallel to the metathesis approach aiming at the simultaneous formation of three butyne edges from the dipropynylbutatriene **6** (see above), an alternative ternary sequential route to hexaphenyl-*carbo*-benzene **15** would consist of the simultaneous formation of three butatriene edges from the *gem*,*gem*-tetrahalodienynes **14a** or **14b** (Scheme 7). Methodological investigations were first undertaken for the preparation of these key substrates from dibenzoylacetylene **8**.



Scheme 7. Alternative ternary sequential approaches to hexaphenyl-*carbo*-benzene **15** (see also Scheme 4). The key tetrahalodienyne substrates **14a** and **14b** of the reductive coupling approach (right) might be prepared from dibenzoylacetylene **8**.

Synthesis of gem,gem-*tetrahalodienynes*: The *gem*,*gem*-tetrabromodienyne **14a** was first targeted by applying the "classical" PPh_3/CBr_4 system reported by Ramirez and co-workers in 1962.[18] This method, which had been optimized for aldehyde substrates, was found to convert the diketone **8** into tetrabromodienyne **14a** in 19% yield only. Alternative *gem*-dihalo-olefination procedures were thus attempted; the results are summarized in Table 1.

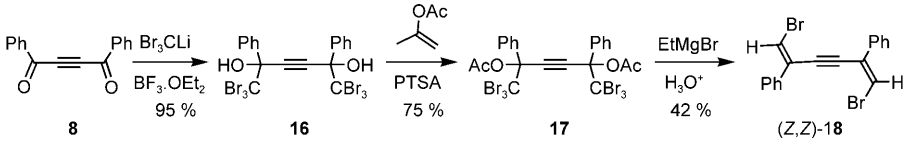
Table 1. Comparative procedures for double *gem*-dihalo-olefination of dibenzoylacetylene **8** (Scheme 7).

Entry	Reactants	Solvent	Yield in **14** [%]
1	PPh_3/CBr_4	CH_2Cl_2	19
2	PPh_3/CBr_4	toluene	<5
3	PPh_3/CBr_4	1,2-dichloroethane	<5
4	PPh_3/CBr_4 (preformed ylide)	CH_2Cl_2	19
5	$Ph_3P^+CHBr_2,Br^-$/*t*BuOK	CH_2Cl_2	0
6	PPh_3/CBr_4/Zn	CH_2Cl_2	13
7	PPh_3/CCl_4	CH_2Cl_2	0
8	PPh_3/CCl_4 (preformed ylide)	CH_2Cl_2	0
9	$PPh_3/CHCl_3$/*t*BuOK	CH_2Cl_2	0
10	PPh_3/CCl_4/Mg sonication	CH_2Cl_2	0
11	$P(NMe_2)_3/CBr_4$	CH_2Cl_2	21
12	$P(nBu_3)/CBr_4$	CH_2Cl_2	0
13	$P(OiPr)_3/CBr_4$	CH_2Cl_2	70

Improvements in the use of triphenylphosphonium reactants were first investigated. Whereas dichloromethane was found to be an optimal solvent for the generation of the tetrabromodienyne **14a** (Table 1, entries 2 and 3), pre-formation of the dibromomethylphosphonium ylide reactant from CBr_4 and PPh_3 did not result in any improvement (Table 1, entry 4),[19] and the use of alternative ylide precursors ($Ph_3P^+CHBr_2$, Br^- and *t*BuOK) failed completely (Table 1, entry 5).[19] A known procedure, allowing for a decrease in the amount of triphenylphosphane used by addition of zinc, was also attempted. Under these conditions, however, **14a** was obtained in a lower yield of 13% (Table 1, entry 6).[20] All attempts at preparing the *gem*,*gem*-tetrachlorodienyne analogue **14b** using PPh_3 and chloromethane reactants were unsuccessful (Table 1, entries 7–10).[21] Addressing these difficulties, a modification of the phosphane reagent was envisioned. The use of HMPT was reported by Jung and D'Amico,[22] and was, in this case, found to afford **14a** in a slightly better yield (21%) than obtained with triphenylphosphane (Table 1, entries 11 vs. 1). Very recently, Lautens and co-workers compared the efficiency of various phosphane reagents, including trialkylphosphanes and phosphites.[23] For dibromo-olefination of **8**, tributylphosphane was found to be inefficient (Table 1, entry 12), but triisopropylphosphite gave the tetrabromodienyne **14a** in a much improved yield of 70% (Table 1, entry 13).

Alternative multistep methods for *gem*-dibromo-olefination were attempted from diketone **8**. The first approach, described by Rezaei and Normant, proceeds in three steps.[24] The diol **16** was prepared from **8** by addition of two equivalents of the lithium salt of bromoform, and then submitted to *trans*-esterification with isopropenyl acetate to give the diester **17** in 75% yield (Scheme 8).

Addition of ethylmagnesium bromide to **17**, however, failed to produce the tetrabromodienyne **14a**, and afforded, instead, the dibromodienyne **18** as a single *Z*,*Z*-stereoisomer in 42% yield. The structure of **18** was confirmed by X-ray diffraction analysis of a single crystal (Figure 4). As in the case of the dipropynylbutatriene **6** (Figure 3), the carbon skeleton of the dienyne **18** was perfectly planar, with an optimal conjugation of the phenyl rings allowed by a 1,4-*trans-oid* conformation.



Scheme 8. Attempted procedure described by Rezaei and Normant for the three-step *gem*-dibromo-olefination of dibenzoylacetylene **8**.[24]

A two-step, *gem*-dibromo-olefination procedure reported by Nenadjenko and co-workers[25] was also attempted. This approach consists of the condensation of hydrazine with a carbonyl precursor, followed (possibly in one-pot) by treatment with CBr_4 and a copper salt (Scheme 9). In the case of the diketone substrate **8**, however, the expected dihydrazone did not form, and only the monohydrazone **19** could be iso-

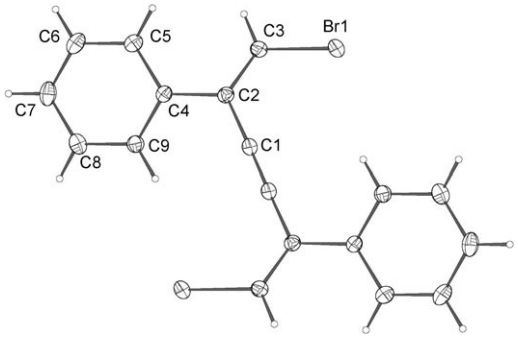
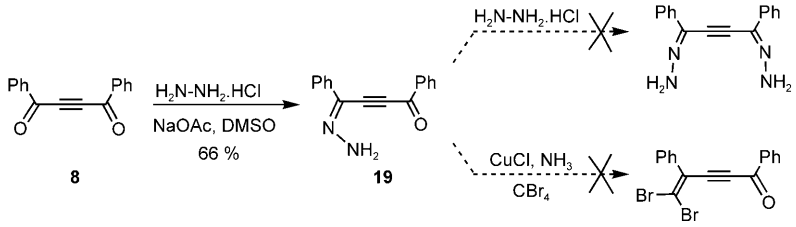


Figure 4. ORTEP view of the dibromodienyne (*Z*,*Z*)–**18**. Distances (Å): C1–C1′ = 1.196(4); C1–C2 = 1.430(3); C2–C3 = 1.342(3); C2–C4 = 1.486(2); C3–Br1 = 1.866(2); C3–H31 = 0.961; angles (°): C1′-C1-C2 = 178.9(3); C1-C2-C3 = 120.66(17); C1-C2-C4 = 117.61(16); C3-C2-C4 = 121.74(17); C2-C3-Br1 = 123.12(15); C2-C3-H31 = 122.291; Br1-C3-H31 = 114.594.

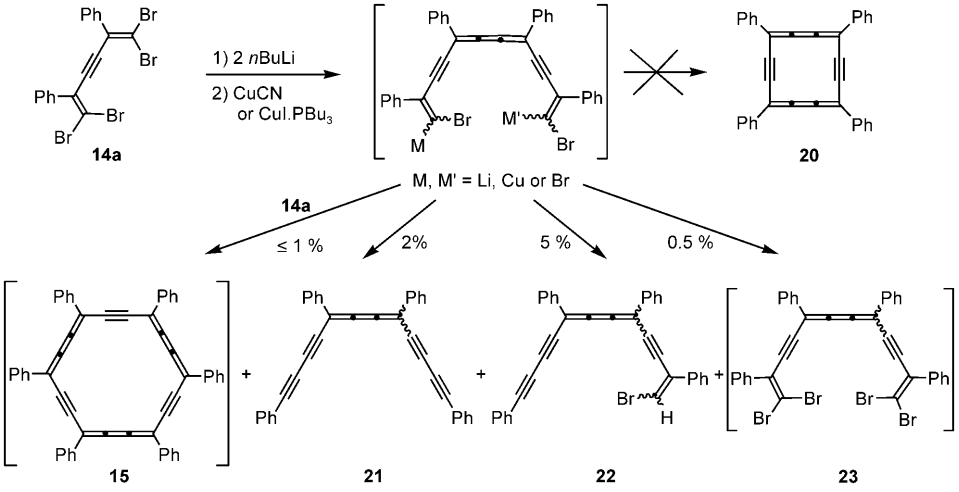


Scheme 9. Attempted procedure described by Nenadjenko and co-workers for the two-step *gem*-dibromo-olefination of dibenzoylacetylene through a hydrazone intermediate.[25]

lated (in 66% yield). The latter compound was found to be totally unreactive towards either hydrazine or the CuCl/NH_3/CBr_4 reagent; an observation which could be explained by hydrogen-bonding effects.

Coupling of gem,gem-*tetrahalodienynes*: The tetrabromodienyne **14a** was submitted to the reductive coupling conditions previously described for the preparation of the dialkynylbutatriene **2**. To prevent polymerization, quite dilute conditions were employed (Scheme 10). Two copper salts were tested and, in both cases, trace amounts of the *carbo*-benzene **15** could be detected by its characteristic apolar purple spot on the TLC plate, along with several other chromophoric products. The formation of **15** (in approximately 1% yield or less) was confirmed by its characteristic signals in the ^{1}H NMR spectrum of the crude material (at $\delta = 9.45$ and 7.99 ppm, $^3J(H,H) = 7.5$ Hz). All attempts at chromatographic purification of **15**, however, failed. Nevertheless, new chromophoric butatrienes could be separated by preparative HPLC. The less polar product eluting after **15** was found to correspond to a tetra-debromo-dimer of **14a** according to MS analysis, and the *carbo*-cyclobutadiene structure **20** was thus initially proposed. This hypothesis was, however, ruled out by the NMR data, which displayed two types of nonequivalent phenyl groups, and the structure was finally assigned to the bis(butadiynyl)butatriene **21** (Scheme 10). The pure product (which was also present as a component in other HPLC fractions) was isolated in 2% yield as a 55:45 mixture of *cis* and *trans* stereoisomers (without assignment), and was found to be surprisingly stable at room temperature. The formation of **21** formally results from a sequence of three reactions: a monocoupling of two molecules of tetrabromodienyne **14a**, generating the butatriene moiety, followed by two Fritsch–Buttenberg–Wiechell (FBW) rearrangements,[26] affording the butadiyne moieties from the remaining vinylidene functions.

The more polar, disymmetric 1,4-dialkynyl-butatriene **22** was also separated by HPLC. Although it could not be isolated in pure form (samples contained ca. 10% of impurity), the structure of **22** was confirmed by MS and NMR analyses, which indicated a mixture of four diastereoisomers (their ratio could, however, not be determined from the complex ^{1}H NMR spectrum). This product, which was isolated in 5% yield, can be considered as an intermediate in the formation of **21**, in which only one FBW rearrangement occurred, while hydrolysis of the second lithiumbromovinylidene lead to the bromoolefinic group of **22**. On the basis of MS data, the impurity present in the isolated sample of **22** was shown to correspond to the tetrabromo-derivative **23**.

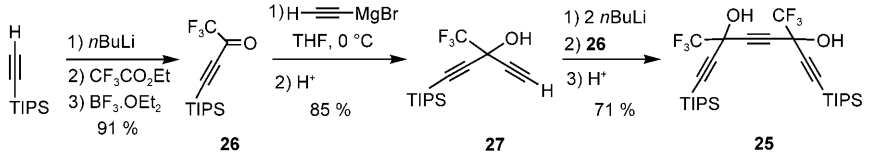


Scheme 10. Dehalo-coupling of the tetrabromodienyne **14a**.

1,4-Bis(trifluorometyl)dialkynylbutatrienes: In the weakly

polar dialkynylbutatrienes described above, or their dienyne parents, the central π system is formally cross-conjugated with two phenyl substituents. The perfectly planar conformation of the representatives **6** and **18** in the crystal state (Figures 3 and 4) thus suggests that the phenyl rings may significantly contribute to their chemical stability. To evaluate the cross-conjugation effect, replacement of the phenyl groups by trifluoromethyl groups of similar conical size[27] but without a π system was envisaged. The σ-withdrawing ability of the CF_3 groups was, however, expected to induce concentration (and thus polarization) of the π-electron cloud above the electron-deficient σ system of the butatriene unit. Overall stabilization was envisaged to occur with TIPS caps in the fluorinated target **24**.

The synthesis of **24** was first attempted by reductive elimination from the 1,4-dioxybut-2-yne **25**. Following a described procedure,[28] the ketone precursor **26** was prepared in 91 % yield by addition of lithium triisopropylsilylacetylide to ethyl trifluoroacetate in the presence of boron trifluoride (Scheme 11). Addition of ethynylmagnesium bromide to **26** at 0 °C afforded the bis(propargylic) alcohol **27** in 85 % yield. Finally, treatment of **27** with two equivalents of *n*-butyllithium followed by one equivalent of ketone **26** gave the fluorinated dioxytriynediol **25** in 71 % yield.



Scheme 11. Synthesis of the fluorinated dioxytriynediol **25**.

The triynediol **25** was obtained as a colorless oil consisting of a statistical mixture of two diastereoisomers. One of the diastereoisomers progressively crystallized at room temperature, and its X-ray diffraction analysis showed that it corresponded to the *d*/*l* isomer (Figure 5). This result is quite surprising, because all the previously described X-ray diffraction structures of related crystalline dioxytriyne derivatives were found to correspond to the *meso* isomer.[14]

The fluorinated triynediol **25** was then submitted to carefully chosen reductive elimination conditions. Among various reagents that have been proposed for this transformation, the $SnCl_2$/HCl system proved to be efficient for generation of the dipropynylbutatriene **6** (Scheme 6), and was thus selected.[29] However, no reaction occurred and **25** was quantitatively recovered after neutralization and filtration of the reaction mixture (Scheme 12).

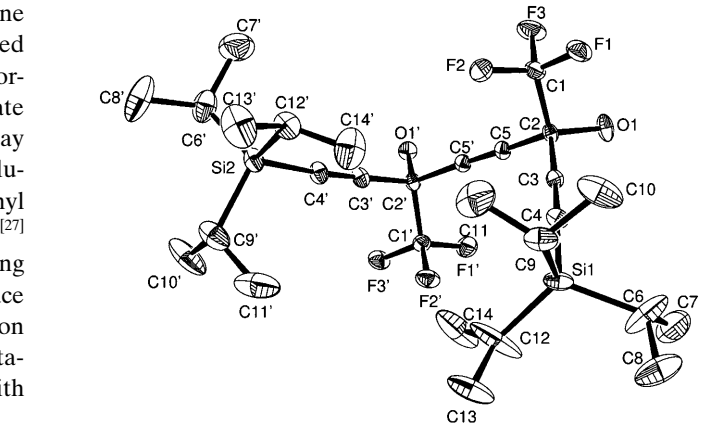
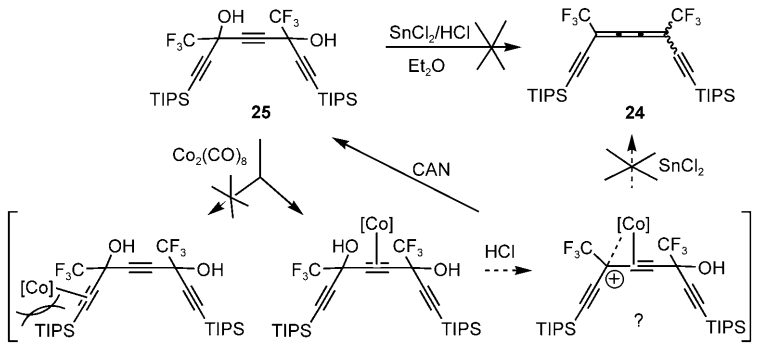


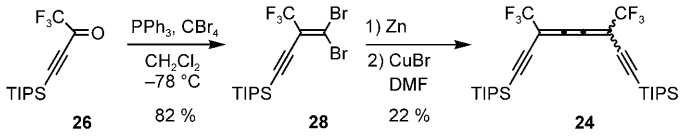
Figure 5. ORTEP diagram of the *d*/*l* isomer of the fluorinated triynediol **25**. Distances (Å): C1−C2 = 1.531(5); C2−C3 = 1.472(5); C3−C4 = 1.197(5); C4−Si1 = 1.840(4); C2−C5 = 1.477(5); C5−C5′ = 1.187(5); angles (°): C5-C2-C3 = 109.4(3); C1-C2-C5 = 108.6(3); C1-C2-C3 = 109.3(3); C2-C5-C5′ = 174.8(4); C2-C3-C4 = 178.5(4).

This result can be explained by the difficulty of protonation of the trifluoromethylated alcohols to generate the corresponding destabilized carbenium ion. The same conditions were thus applied after complexation of one of the triple bonds of **25** with a $[Co_2(CO)_6]$ unit; eliminative reduction of 1,4-dioxybut-2-yne moieties by stabilization of the propargylic carbenium intermediates as Nicholas complexes was indeed previously reported in the particular case of a hexaalkynylhexaoxy[6]pericyclyne.[30] The targeted butatriene derivative **24** was, however, not observed, and the triyne precursor **25** was recovered after treatment with cerium(IV) ammonium nitrate (CAN). To explain this failure, it can be proposed that complexation of the $[Co_2(CO)_6]$ unit occurred at the central, less hindered, triple bond (the external triple bonds are hindered by the bulky TIPS groups), and could thus block the elimination process, even if the cobalt-stabilized carbenium ion was produced (Scheme 12).



Scheme 12. Attempted preparation of the butatriene **24** by reductive elimination from the dioxytriyne **25**, and proposed explanation for the failure of the cobalt method.[30] [Co] = $[Co_2(CO)_6]$.

An alternative route based on the reductive coupling of vinylidene moieties was then envisioned. The preparation of butatrienes bearing perfluoro-alkyl or -aryl groups was previously reported from the corresponding *gem*-dibromo-olefinic precursors.[31] *gem*-Dibromo-olefination of the ketone **26** described above (Scheme 11) was first carried out using a mixture of PPh_3 and CBr_4, affording the dibromoenyne **28** in 82% yield (Scheme 13).



Scheme 13. Synthesis of the dialkynylbis(trifluoromethyl)butatriene **24**.

Reductive coupling of **28** was attempted by using the procedure described by Burton et al., which takes place through a zinc intermediate formed at room temperature under sonication, and treatment with a copper salt in situ at low temperature.[31,32] This method afforded the fluorinated butatriene **24** as the major product in the crude reaction mixture (Scheme 13). However, purification of this apolar product proved to be difficult, and it could be isolated in a pure state in only 22% yield after silica gel chromatography (eluted with pentane). The product was obtained as a 40:60 mixture of *cis* and *trans* isomers (without assignment), as indicated by integration of the two signals observed by ^{19}F NMR analysis at $\delta = -64.1$ and -64.3 ppm.

The chemical stability of **24** thus shows that cross-conjugation of the 1,4-dialkynylbutatriene motif with phenyl substituents is not a necessary condition. Desilylation of **24** was expected to afford a highly unstable and volatile product, and was thus not attempted. Nevertheless, the information gained on **24** suggests the stability of challenging trifluoromethylated *carbo*-benzene molecules.

Comparative physicochemical properties of dialkynylbutatrienes

^{13}C NMR spectroscopy: The ^{13}C NMR chemical shift of the central sp carbon atoms of symmetrical 1,4-dialkynylbutatrienes (E−C≡C)RC=C=C=CR(C≡C−E) is insensitive to the *cis* or *trans* configuration, but is expected to be primarily influenced by the nature of the substituents R at the sp^2 vertices. According to the data listed in Table 2, the influence of the cap E is indeed negligible, with ^{13}C NMR chemical shifts between $\delta = 148.0$ and 149.0 ppm for the same substituent R = Ph (Table 2, entries 2 to 4).

In contrast, the influence of the R substituents for a given cap E (= TIPS) gives rise to a marked variation in the ^{13}C NMR shifts over a range of more than 10 ppm (Table 2, entries 4–7). For π-cross-conjugated substituents (R = Ph or C≡C-TIPS), the butatrienic sp carbon atoms thus resonate at $\delta = 149$–151 ppm (Table 2, entries 4 and 7), whereas a σ-electron-withdrawing substituent ($R = CF_3$) induces an expected deshielding and a consequent shift to $\delta = 158.5$ ppm (Table 2, entry 5). It is worth noting that the most deshielded signal is observed for the unsubstituted dialkynylbutatriene (R = H) described by Diederich and co-workers (Table 2, entry 6; $\delta = 161.6$ and 161.3 ppm).[3a]

For comparison, the all equivalent sp carbon atoms of hexaphenyl-*carbo*-benzene **15** resonate out of this range, at $\delta = 118.5$ ppm (Table 2, entry 8), and are thus quite far from the corresponding resonance (ca. $\delta = 148$ ppm) of acyclic dialkynylbutatriene hydrocarbons such as **2** and **21** (Table 2, entries 2 and 3). This is clearly due to the partial dialkynylbutatriene Lewis character of the edges of the C_{18} macrocycle, which is mesomerically hybridized with a dialkenylacetylene character. The pure latter character is found in acyclic diphenyl dienynes, for which the central sp-carbon atoms resonate at approximately 95 ppm ($\delta = 96.3$ ppm for **14a** and $\delta = 94.6$ ppm for **18**). The average chemical shift of the central sp carbon atoms of diphenyldienynes and diphenyldialkynylbutatrienes is thus equal to $1/2(95+148) \approx 121.5$ ppm, which is very close to the value observed for hexaphenyl-*carbo*-benzene **15**. This is a quantifiable consequence (and confirmation) of the 50:50 contributions of the two Kekule forms of the aromatic *carbo*-benzene macrocycle.

Table 2. ^{13}C NMR chemical shifts of the central sp carbon atoms (ppm, in $CDCl_3$), and maximum absorption wavelengths [nm, in $CHCl_3$ unless otherwise noted] of symmetrical 1,4-dialkynylbutatrienes (E−C≡C)RC=*C*=*C*=CR(C≡C−E).

Entry (Compd)	R	E	δ(=*C*=***C***=)	λ_{max} (λ')	Reference
1 (**1**)	Ph	H	n.d.	426	this work
2 (**6**)	Ph	Me	148.4	437	this work
3 (**21**)	Ph	C≡C−Ph	148.0, 148.2	499	this work
4 (**2**)	Ph	Si(*i*Pr)$_3$	149.0	453	this work
5 (**24**)	CF_3	Si(*i*Pr)$_3$	158.5	373	this work
6	H	Si(*i*Pr)$_3$	161.6, 161.3	356[a]	[3b]
7	C≡C−Si(*i*Pr)$_3$	Si(*i*Pr)$_3$	150.6	424[b]	[3a]
8 (**15**)	Ph	(C(Ph)C$_2$)$_{3\infty}$	118.5	472 (515)	[11]

[a] Recorded in CH_2Cl_2. [b] Recorded in hexane.

Absorption spectroscopy: The UV/Vis absorption spectra in chloroform of the five dialkynylbutatrienes **1**, **2**, **6**, **21**, and **24**, display the same general profile, with an intense maximum absorption band and two shoulders at shorter wave-

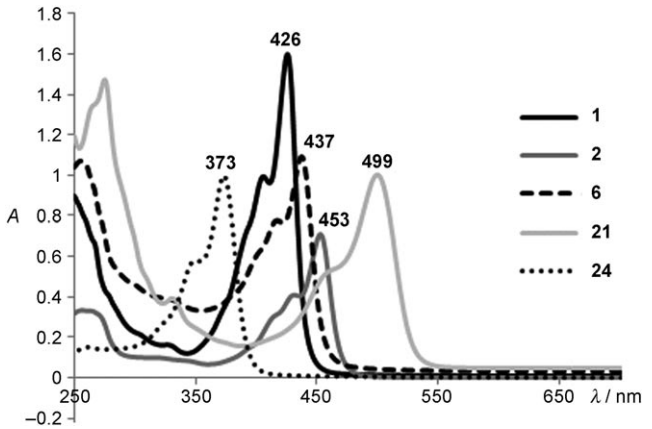


Figure 6. Absorption UV/Vis spectra of the four dialkynylbutatrienes **1**, **2**, **6**, **21**, and **24** ($CHCl_3$). See also Table 2.

length (Figure 6, Table 2). The absorption coefficients of **2**, **21**, and **24** (which are stable in the solid state) are equal to 53440, 7000, and 40250 $mol\,L^{-1}\,cm^{-1}$, respectively. The phenyl-substituted dialkynylbutatrienes **1**, **2**, and **6**, with the same extent of π conjugation, exhibit similar λ_{max} values (between 426 and 453 nm), indicating that the alkyl, silyl, or H caps have a weak influence on the electronic transitions. Increasing the extent of conjugation through the phenylethynyl caps of **21** induces a bathochromic shift of 45 nm from λ_{max} (**2**) = 453 nm to λ_{max} (**21**) = 499 nm. By comparison, hexaphenyl-*carbo*-benzene **15** exhibits a similar pattern at λ_{max} (**15**) = 472 nm, with a secondary absorption band at an even higher wavelength of λ′(**15**) = 515 nm (Table 2).[11b] Conversely, reducing the extent of π-conjugation of **2** by replacement of the phenyl substituents with trisopropylsilylethynyl substituents (Table 2, entry 7), induces a moderate hypsochromic shift (from 453 nm in $CHCl_3$ for **2**, to 424 nm in hexane for Diederich's TIPS-capped tetraethynylbutatriene).[3a] Complete interruption of cross-conjugation by the introduction of trifluoromethyl substituents at the butatriene vertices of **24**, induces a dramatic hypsochromic shift of 80 nm (from 453 for **2** to 373 nm for **24**). Nevertheless, the hypsochromic effect of CF_3 remains lower by approximately 20 nm than that observed for the corresponding hydrogen-substituted compound (Table 2, entry 6).[3b]

Voltammetry: The electrochemical properties of *cis*/*trans* mixtures of the dialkynylbutatrienes **1**, **2**, **6**, **21**, and **24** were investigated by square-wave voltammetry (SWV) and cyclic voltammetry (CV) in dichloromethane solution (10^{-3} M), with $[n\mathrm{Bu_4N}][PF_6]$ as a supporting electrolyte (0.1 M). The potentials listed in Table 3 are given versus the ferricinium/ferrocene couple (Fc^+/Fc) as internal standard. According to SWV, all the dialkynylbutatrienes **1**, **2**, **6**, **21**, and **24** undergo two to four reduction processes, and at most one oxidation step that occurs between 0.75 and 0.97 V. CV experiments at 0.1 $V\,s^{-1}$ indicated that only the first reduction couples between −1.17 and −1.73 V are reversible.

The three phenylated butatrienes **1**, **2**, and **6** (R = Ph) possess the same degree of π conjugation (over 20 sp or sp^2 carbon centers, limited by saturated caps E = H, Me, TIPS), and behave similarly, with a single reversible couple be-

Table 3. SWV and CV electrochemical data of dialkynylbutatrienes in CH_2Cl_2 with $[n\mathrm{Bu_4N}][PF_6]$ as a supporting electrolyte (0.1 M). Potentials are given versus the Fc^+/Fc couple as internal standard. CV: scan rate = 100 $mV\,s^{-1}$.

Compd	R	E	CV					SWV	
			E_p^{ox} [V][a]	$E_{1/2}^{0\,red}$ [V][b]	ΔE^{red} [mV][c]	RI_p[d]	E_p^{red} [V][e]	$E_{1/2}^{ox}$ [V][f]	$E_{1/2}^{red}$ [V][g]
1	Ph	H	1.0	−1.52	68	1.12	−2.01	0.97	−1.52
									−1.97
									−2.20
									−2.47
2	Ph	$Si(iPr)_3$	0.90[h]	−1.57	83	0.99	−2.14	0.90	−1.57
									−2.02
									−2.10
									−230
6	Ph	Me	0.78	−1.73	98	1.13	−2.27	0.75	−1.73
									−2.14
							−2.41		−2.29
									−2.42
21	Ph	C≡C-Ph	0.88	−1.27	53	1.17	−1.66	0.88	−1.29
									−1.66
				−1.66	63	1.21			
24	CF_3	$Si(iPr)_3$	–	−1.17	107	1.00	–	–	−1.17
									−1.64
									−2.20
29[i]	C≡C-Ar	$Si(iPr)_3$	1.03	−1.28	80	–	−1.78	–	–

[a] First oxidation peak potential determined by CV. [b] Half-wave potential of the first reversible reduction process determined by CV, $E_{1/2} = [E_{pc} + E_{pa}]/2$, the arithmetic mean of the corresponding anodic and cathodic peak potentials. [c] CV peak-to-peak separations $E_{p(backward)} - E_{p(forward)} = E_{pa} - E_{pb}$, for the first reversible reduction process. [d] Absolute current ratio $|I_{p(backward)}/I_{p(forward)}| = |I_{pa}/I_{pc}|$ for the first reversible reduction process measured by CV. [e] Reduction peak potential determined by CV for other reduction processes. [f] Half-wave potential of the first oxidation process determined by SWV. [g] Half-wave potentials of all reduction processes determined by SWV. [h] The oxidation process becomes reversible at scan rate of 1 $V\,s^{-1}$. [i] CV data for the tetraalkynylbutatriene hydrocarbon with Ar = 3,5-$(t\mathrm{Bu})_2C_6H_4$ (Scheme 14).[3b]

tween −1.52 V and −1.73 V, and three irreversible processes in the range −1.97/−2.47 V. Reduction of **6** is, however, more difficult because of the pure σ-inductive effect of the methyl cap (the σ-inductive effect of the TIPS caps of **2** is stronger, but is balanced by the silicon α-effect stabilizing the reduced form -C⁻=C⁻−Si). The uncapped diethynylbutatriene **1** exhibits the smallest absolute first reduction potential, but the reversibility of this step is a further illustration of its chemical stability (see Figure 7 and section on the synthesis above). Extending the π conjugation to 36 carbon centers through the phenylethynyl caps of **21** results in an easier reversible reduction at −1.27 V, and in the replacement of the three irreversible reductions of **1**, **2**, and **6** with a second reversible process at −1.66 V.

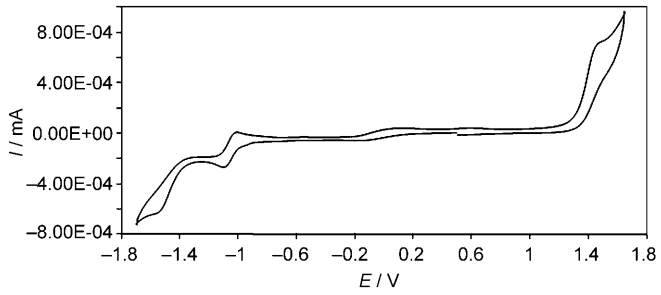
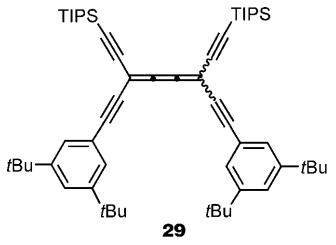


Figure 7. Cyclic voltammogram of the uncapped diethynylbutatriene **1** (10^{-3} mol L^{-1}) in CH_2Cl_2 + 0.1 mol L^{-1} [nBu$_4$N][PF_6] on Pt microdisk (r = 0.25 mm) at room temperature. Scan rate: 0.1 V s^{-1}. Potentials were measured versus SCE.

The first reduction potentials of the diphenyl-dialkynylbutatrienes **1**, **2**, and **6** are consistently lower than those of aryl- and silyl-capped tetraethynylbutatrienes reported by Diederich and co-workers (in the range −1.28/−1.41 V).[3b] This can be explained by the difference in the extent of π conjugation through the phenyl substituent (6 C) and ethynylaryl substituents (8 C). Nevertheless, the behavior and the first peak reduction potential values of **21** (with a 36-carbon π-conjugation extent) are almost identical to those of the tetraalkynylbutatriene hydrocarbon **29** ($E_{1/2}$ = −1.28, −1.78 V), with a π-conjugation extent over 24 carbon centers only (Scheme 14). This illustrates the specific stabilizing effect of silyl caps and/or the tetraethynylbutatriene core on the anions.



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Scheme 14. Known tetraalkynylbutatriene hydrocarbon with an extended 24-carbon π-conjugation system (see electrochemical data in Table 3).[3b]

With respect to the phenylated analogue **2**, two opposite effects of the CF_3 substituents of **24** on the corresponding anions could be expected: 1) a destabilization by a reduction in the extent of π-conjugation (from 20 to 8 carbon centers), and 2) a stabilization by the σ-withdrawing effect of the electronegative fluorine atoms. Evidence that the latter effect overcomes the former was obtained by observing a cathodic shift of 0.4 V (−1.57 V for **2**, −1.17 V for **24**). According to SWV, the second (irreversible) reduction potential is shifted by the same amount (from −2.02 V for **2** to −1.64 V for **24**).

Conclusion

Six 1,4-dialkynylbutatrienes substituted with phenyl or trifluoromethyl groups at the sp^2 vertices have been synthesized and characterized. Whereas 1,4-diphenyl-1,4-diethynylbutatriene **1** is the first uncapped diethynylbutatriene that has been characterized to date (including by voltammetry), the five other products can be considered to be functionally capped 1,4-diethynylbutatrienes at the sp termini. Their accessibility and chemical stability open up new prospects for their use in the scaffolding of phenylacetylene building-blocks, especially in the synthesis of phenyl-substituted *carbo*-benzene rings. The dynamics of *cis*/*trans* equilibria might even be useful for the thermodynamic control of the scaffolding under dilute conditions. Systematic studies are currently focused on the reactivity of 1,4-diphenyl-1,4-propynylbutatriene **6** and diphenyltetrabromodienyne **14a** in alkyne metathesis and vinylidene coupling reactions, respectively.

Experimental Section

General: THF and diethyl ether were dried and distilled over sodium/benzophenone; pentane and dichloromethane over P_2O_5. All other reagents were used as commercially available. In particular, commercial 2.5 M solutions of nBuLi in hexane, and 0.5 M solutions of ethynylmagnesium bromide in THF were used. Previously described procedures were used for the preparation of **8**,[12] **10**, **12**, and **13**.[13,14] Experimental details for compounds **3**, **4**, **16**, **17**, **18**, **19**, **26**, and **27** are available in the Supporting Information. All reactions were carried out under nitrogen or Argon using Schlenk and vacuum line techniques. Column chromatography was carried out with silica gel (60 P, 70–200 mm). Silica gel thin-layer chromatography plates (60F254; 0.25 mm) were developed by treatment with an ethanolic solution of phosphomolybdic acid (20%) or an aqueous potassium permanganate solution for fluorinated derivatives.

Bruker ARX 250, DPX 300, Avance 300, or Avance 400 spectrometers were used; all NMR spectra were recorded as $CDCl_3$ solutions. NMR chemical shifts (δ) are given in ppm, with positive values to high frequency relative to the tetramethylsilane reference for ^{1}H and ^{13}C spectra, and CCl_3F for ^{19}F spectra; coupling constants (J) are given in Hz. Mass spectra were recorded with a Quadrupolar Nermag R10–10H spectrometer. UV spectra were recorded with a Perkin–Elmer UV/Vis Win-Lab Lambda 35 spectrometer. HPLC were recorded with Semi-preparative Waters Deltaprep chains, coupled with a UV 486 Waters detector and a Gibson 201 fraction collector (column: Sunfire Si 150 × 19 mm; elution with petroleum ether/chloroform, 95:5; 15 mL min^{-1}). Voltammetric measurements were carried out with a potentiostat Autolab PGSTAT100

instrument controlled by GPES 4.09 software. Experiments were performed at RT in a homemade, airtight, three-electrode cell connected to a vacuum/argon line. The reference electrode consisted of a saturated calomel electrode (SCE) separated from the solution by a bridge compartment. The counter electrode was a platinum wire of ca. 1 cm^2 apparent surface area. The working electrode was either a Pt microdisk (0.5 mm diameter) or a glassy carbon microdisk (1 mm diameter). The supporting electrolyte [nBu$_4$N][PF$_6$] (Fluka, 99% electrochemical grade) was used as received and simply degassed under argon. Dichloromethane was freshly distilled prior to use. The solutions used during the electrochemical studies were typically 10^{-3} M in butatriene and 0.1 M in supporting electrolyte. Before each measurement, the solutions were degassed by bubbling Ar, and the working electrode was polished with a polishing machine (Presi P230). Typical instrumental parameters for recorded square-wave voltammograms were: SW frequency $f=20$ Hz, SW amplitude $E_{sw}=20$ mV, and scan increment $\Delta E=0.5$ mV. All reported potentials are referenced to the formal potential of the ferrocenium/ferrocene (Fc^+/Fc) couple measured in the same electrolyte (ca. (0.45 ± 0.02) V vs. SCE).

Synthesis of 1: TBAF (0.500 mL, 0.50 mmol) was added at −78 °C to a solution of **3** (0.100 g, 0.18 mmol) in THF (5 mL). The resulting mixture was stirred for 30 min at the same temperature, then treated with water. After extraction of the aqueous layer with diethyl ether, the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was partially evaporated to give a 5 mL solution, which was rapidly purified by silica-gel chromatography (pentane). $CDCl_3$ was added before removal of most of the pentane under controlled vacuum to give a yellow solution of **1** that was analyzed spectroscopically. ^{1}H NMR ($CDCl_3$): $\delta=3.69$, 3.75 (2×s, 2H; ≡C-H), 7.36–7.46 (m, 6H; *m*- and *p*-C$_6H_5$), 7.84–7.87 (m, 4H; *o*-C$_6H_5$). UV/Vis: $\lambda_{max}=426$ nm.

Synthesis of 2 from 5a: nBuLi (180 μL, 0.45 mmol) was added to a solution of **5a** (0.200 g, 0.45 mmol) in anhydrous THF (10 mL) under stirring at −100 °C. After stirring the resulting solution for 1 h at −100 °C, a solution of CuI·PBu$_3$ (0.091 g, 0.23 mmol) in anhydrous THF (5 mL) was added. This mixture was slowly warmed to RT and stirring was maintained overnight. The solution was filtered through 5 cm of silica gel, eluting with diethyl ether, and, after evaporation to dryness, the residue was purified by silica gel chromatography (pentane) to give **2** as a yellow solid in 65% yield.

Synthesis of 2 from 5b: nBuLi (225 μL, 0.56 mmol) was added to a solution of **5b** (0.200 g, 0.56 mmol) in anhydrous THF (10 mL) under stirring at −90 °C. After stirring the resulting solution for 1 h at −90 °C, a suspension of CuCN (0.025 g, 0.283 mmol) or a solution of CuI·PBu$_3$ (0.114 g, 0.23 mmol) in anhydrous THF (5 mL) was added at −100 °C. This mixture was slowly warmed to RT and stirring was maintained overnight. The solution was filtered through 5 cm of silica gel, eluting with diethyl ether, and, after evaporation to dryness, the residue was purified by silica gel chromatography (pentane) to give **2** as a yellow solid (50–91% with CuCN and 94% with CuI·PBu$_3$). ^{1}H NMR ($CDCl_3$): $\delta=1.21$ (m, 42H; C*H*-C*H*$_3$), 7.30–7.50 (m, 6H; *m*-C$_6H_5$ and *p*-C$_6H_5$), 7.85–7.87 ppm (m, 4H; *o*-C$_6H_5$); ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta=11.4$ (s, Si-*C*H-CH$_3$), 18.7 (s, Si-CH-*C*H$_3$), 102.0 and 102.3 (2×s, Si-*C*≡), 104.1 (s, Ph-*C*), 104.5 and 104.9 (2×s, Si-C≡*C*), 127.2 and 127.4 (2×s, *o*-C$_6H_5$), 128.5 and 128.6 (2×s, *m*-C$_6H_5$), 128.8 (s, *p*-C$_6H_5$), 136.3 and 136.9 (2×s, *i*-C$_6H_5$), 149.1 ppm (s, -C=*C*=*C*=C-); FTIR: $\tilde{\nu}=2941$–2864 (C$_{sp3}$-H), 2127 (C≡C), 1548, 1488, 1461, 1383, 1265 cm^{-1} (C-Si); UV/Vis: λ_{max} (ε) = 453 nm (53 440 mol L^{-1} cm^{-1}); MS (DCI/NH$_3$): m/z: 565.3 $[M+H]^+$; HRMS (DCI/CH$_4$): m/z calcd for C$_{38}$H$_{53}$Si$_2$: 565.3686 $[M+H]^+$; found: 565.3698.

Synthesis of 5a: A solution of triisopropylphosphite (1.2 mL, 4.87 mmol) in CH_2Cl_2 (5 mL) was added at 0 °C to a mixture of ketone **3** (0.465 g, 1.62 mmol) and CBr_4 (0.810 g, 2.43 mmol) in CH_2Cl_2 (10 mL). After stirring for 1.5 h, the solution was treated with saturated aqueous $NaHCO_3$. The aqueous layer was extracted with diethyl ether, and the combined organic layers were washed with brine, dried over $MgSO_4$ and evaporated to dryness. The residue was purified by silica gel chromatography (pentane) to give **5a** as a white solid in 89% yield. ^{1}H NMR ($CDCl_3$): $\delta=1.12$ (s, 21H; Si-C*H*-C*H*$_3$), 7.37–7.40 (m, 3H; *m*- and *p*-C$_6H_5$), 7.49–7.53 ppm (m, 2H; *o*-C$_6H_5$); ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta=11.2$ (s, Si-*C*H-CH$_3$), 18.6 (s, Si-CH-*C*H$_3$), 99.6 (s, Si-*C*≡*C*-), 101.2 (s, *C*Br$_2$), 105.2 (s, Si-*C*≡C), 128.2 (s, *o*- or *m*-C$_6H_5$), 128.5 (s, *p*-C$_6H_5$), 128.7 (s, *o*- or *m*-C$_6H_5$), 131.2 (s, *i*-C$_6H_5$), 138.0 ppm (s, *C*=CBr$_2$); FTIR: $\tilde{\nu}=2942$–2864 (C$_{sp3}$-H), 2137 (C≡C), 1462, 1443 cm^{-1} (C=C); MS (DCI/NH$_3$): m/z: 441.8 $[M+H]^-$; HRMS (DCI/CH$_4$): m/z calcd for C$_{19}$H$_{26}$SiBr$_2$: 440.0171 $[M]^+$; found: 440.0178.

Synthesis of 5b: PPh$_3$ (2.490 g, 9.49 mmol) and CCl_4 (0.46 mL, 4.75 mmol) were added to a solution of **3** (0.680 g, 2.37 mmol) in anhydrous CH_3CN (40 mL) at 0 °C. After stirring for 2 h at RT, the orange solution was diluted with diethyl ether, washed with water and with brine, dried over $MgSO_4$, and evaporated to dryness. After purification by silica gel chromatography (AcOEt/pentane, 5:95), the dichlorovinylidene derivative **5b** was isolated as a colorless oil in 88% yield. ^{1}H NMR ($CDCl_3$): $\delta=1.64$ (s, 21H; *i*Pr), 7.40–7.43 (m, 3H; *m*-C$_6H_5$ and *p*-C$_6H_5$), 7.57 ppm (m, 2H; *o*-C$_6H_5$); ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta=11.3$ (s, Si-*C*H-CH$_3$), 18.7 (s, Si-CH-*C*H$_3$), 101.1 (s, ≡C-Si), 103.4 (s, *C*≡C-Si), 124.0 and 128.1 (2 s, *C*=*C*Cl$_2$), 128.2 (s, *o*-C$_6H_5$ or *m*-C$_6H_5$), 128.5 (s, *p*-C$_6H_5$), 128.9 (s, *o*-C$_6H_5$ or *m*-C$_6H_5$), 135.8 ppm (s, *i*-C$_6H_5$); MS (DCI/NH$_3$): m/z: 352.1 $[M-H]^+$, 370.1 $[M+NH_4]^+$.

Synthesis of 6: $SnCl_2$ (10 equiv., 1.66 g, 8.77 mmol) was added to a solution of **7** (0.300 g, 0.877 mmol) in anhydrous CH_2Cl_2 (50 mL) at −30 °C. After stirring for 10 min at the same temperature, HCl·OEt$_2$ (20 equiv., 2 M in Et$_2$O, 8.77 mL, 17.54 mmol) was added. The resulting mixture was stirred until complete disappearance of **7** was observed (reaction monitored by TLC; ca. 2 h), then the reaction was neutralized by addition of aqueous 1 N NaOH solution. The intense yellow organic layer was washed three times with water and dried over $MgSO_4$. The resulting solution was filtered through silica gel (CH_2Cl_2) and concentrated under vacuum to approximately 20 mL (this compound must be kept in solution and at low temperature). Slow evaporation of a CH_2Cl_2 concentrated solution of **6** gave crystals of its *trans* isomer. The same reaction was performed in an NMR tube using $CDCl_3$ as solvent and DCl in D_2O as reagent to characterize the compound. ^{1}H NMR ($CDCl_3$): $\delta=2.25$ (2 s, 6H; ≡C-C*H*$_3$), 7.31–7.44 (m, 6H; *m*- and *p*-C$_6H_5$), 7.82–7.86 ppm (m, 4H; *o*-C$_6H_5$); ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta=5.2$, 5.3 (2 s; ≡C-*C*H$_3$), 77.2, 78.0 (2 s; C≡*C*-CH$_3$), 95.8, 96.0 (2 s; *C*≡C-CH$_3$), 103.8, 104.3 (2 s; *C*-Ph), 127.2, 127.4 (2 s; *o*-C$_6H_5$), 128.5 (s; *p*-C$_6H_5$), 128.4, 128.5 (2 s; *m*-C$_6H_5$), 137.0, 137.4 (2 s; *i*-C$_6H_5$), 148.4 ppm (s; C=*C*=*C*=C). UV/Vis: $\lambda_{max}=437$ nm.

Synthesis of 7: nBuLi (4.45 mL, 11.13 mmol) was added to a solution of **9** (1.59 g, 5.06 mmol) in anhydrous THF (40 mL) under stirring at −78 °C. The resulting mixture was stirred for 50 min at −78 °C, then MeI (0.95 mL, 15.18 mmol) was added and stirring was continued for 30 min at −78 °C and for 75 min at RT. The mixture was diluted with diethyl ether and treated with saturated aqueous NH_4Cl. The aqueous layer was extracted two times with diethyl ether, and the combined organic layers were washed with brine, dried over $MgSO_4$, and evaporated under reduced pressure. The residue was purified by silica gel chromatography (AcOEt/pentane, 1:9) to give **7** as a crude sticky oil in 95% yield. A sample of pure *meso* isomer was obtained by selective crystallization in pentane from the mixture of diastereoisomers. ^{1}H NMR ($CDCl_3$): $\delta=1.98$ (s, 6H; ≡C-CH$_3$), 3.53 (s, 6H; OCH$_3$), 7.37–7.40 (m, 6H; *m*- and *p*-C$_6H_5$), 7.77–7.81 ppm (m, 4H; *o*-C$_6H_5$); ^{13}C{^{1}H} NMR ($CDCl_3$; mixture *meso*/*dl*): $\delta=3.81$ (s; ≡C-*C*H$_3$), 53.07 (s; OCH$_3$), 72.01 (s; *C*-OCH$_3$), 76.95 and 76.97 (2×s; ≡*C*-CH$_3$), 83.71 and 83.72, 84.51 and 84.53 (4×s; ≡*C*-C-OCH$_3$), 126.61 and 126.62 (2×s; *o*-C$_6H_5$), 128.36 (s; *m*-C$_6H_5$), 128.69 (s; *p*-C$_6H_5$), 140.84 and 140.86 ppm (2×s; *i*-C$_6H_5$); ^{13}C{^{1}H} NMR ($CDCl_3$; pure *meso*): $\delta=3.8$ (s; ≡C-*C*H$_3$), 53.0 (s; OCH$_3$), 72.0 (s; *C*-OCH$_3$), 76.9 (s; ≡*C*-CH$_3$), 83.6 and 84.4 (2 s; ≡*C*-C-OCH$_3$), 126.6 (s; *o*-C$_6H_5$), 128.3 (s; *m*-C$_6H_5$), 128.6 (s; *p*-C$_6H_5$), 140.7 ppm (s; *i*-C$_6H_5$); FTIR: $\tilde{\nu}=2922$ (C$_{sp3}$-H), 2822 (OC$_{sp3}$-H), 2239 (C≡C), 1599, 1489, 1449 (C=C), 1062 cm^{-1} (C-O); MS (DCI/CH$_4$): m/z: 311.1 $[M-OMe]^+$, 296.1 $[M-OMe-Me]^+$; HRMS (DCI/CH$_4$): m/z calcd for C$_{23}$H$_{19}$O: 311.1436 $[M-OCH_3]^+$; found: 311.1441.

Synthesis of 14a: A solution of P(O*i*Pr)$_3$ (1.26 mL, 5.12 mmol) in CH_2Cl_2 (2 mL) was added at 0 °C to a solution of **8** (0.200 g, 0.85 mmol) and CBr_4 (0.850 g, 2.56 mmol) in CH_2Cl_2 (6 mL). The reaction mixture, which became instantaneously red, was stirred for 1 h at 0 °C and then for 1 h at RT. After treatment with aqueous saturated $NaHCO_3$ and extraction with diethyl ether, the combined organic layers were washed with brine, dried over $MgSO_4$, and evaporated under reduced pressure. The obtained

white crystals were washed with ethanol and dried to give **14a** in 70% yield. M.p. 154°C; ^{1}H NMR ($CDCl_3$): $\delta = 7.37$–7.42 (m, 6H; *m*- and *p*-C_6H_5), 7.47–7.51 ppm (m, 4H; *o*-C_6H_5); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 96.3$ (*C*≡*C*), 100.4 (CBr_2), 128.4, 128.7, 128.7 (*o*-, *m*-, *p*-C_6H_5), 130.7 (*i*-C_6H_5), 137.2 ppm (*C*=CBr_2); MS (DCI/NH_3): *m*/*z*: 564 $[M+NH_4]^+$, 546 $[M+H]^+$; HRMS (DCI/CH_4): *m*/*z* calcd for $C_{18}H_{10}Br_4$: 541.7516 $[M]^+$; found: 541.7505.

Synthesis of 21: A solution of *n*BuLi (0.750 mL, 1.83 mmol) was added at −105°C to a solution of **14a** (0.500 g, 0.92 mmol) in THF (175 mL). After stirring for 1 h at this temperature, either a suspension of CuCN (0.082 g, 0.92 mmol) in THF (10 mL) or a solution of CuI·PBu_3 (0.361 g, 0.92 mmol) in THF (10 mL), was added at −90°C. The temperature was allowed to warm slowly to RT and stirring was maintained overnight. After treatment with saturated aqueous NH_4Cl and extraction with diethyl ether, the combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated under vacuum. After pre-purification by silica gel chromatography (pentane/chloroform, 98:2 then 9:1), the orange fraction was finally purified by semi-preparative HPLC (petroleum ether/chloroform, 95:5) to give **21** as an orange oil (ca. 2%). ^{1}H NMR ($CDCl_3$): $\delta = 7.38$–7.49 (m, 12H; *m*- and *p*-C_6H_5), 7.60 and 7.62 (2×d, ^3J(H,H) = 6.8 Hz, 4H; *o*-C_6H_5-C≡), 7.85 and 7.87 (2×d, ^3J(H,H) = 7.5 Hz, 4H; *o*-C_6H_5-C=); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 74.5$, 74.6, 80.0, 80.1, 84.1, 84.5 (=C-*C*≡*C*-*C*≡), 86.9, 87.1 (C_6H_5-*C*≡), 104.5, 104.9 (*C*=C=C=*C*), 121.57, 121.60 (*i*-C_6H_5-C≡), 127.4, 127.5 (*o*-C_6H_5-C=), 128.5, 128.6, 128.76, 128.81 (*m*-C_6H_5), 129.3, 129.4, 129.6, 129.7 (*p*-C_6H_5), 132.6 (*o*-C_6H_5-C≡), 135.9, 136.4 (*i*-C_6H_5-C=), 148.0, 148.2 ppm (C=*C*=*C*=C); UV/Vis: λ_{max} (ε) = 499.2 nm (7000 mol L^{-1} cm^{-1}); MS (DCI/NH_3): *m*/*z*: 451.9 $[M]^-$.

Characterization of 22: Yield: 5%. ^{1}H NMR ($CDCl_3$): $\delta = 7.18$ (s, 1H; =C*H*Br), 7.37–7.50 (m, 12H; *m*- and *p*-C_6H_5), 7.58–7.63 (m, 2H; *o*-C_6H_5-C≡), 7.68–7.71 (m, 2H; *o*-C_6H_5-C=CHBr), 7.85–7.89 and 7.97–8.01 ppm (2×m, 4H; *o*-C_6H_5-C≡); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 74.5$, 74.7, 80.0, 84.0, 86.5, 86.8 (*C*≡*C*−*C*≡*C*), 96.2, 97.2 (=C−*C*≡*C*−C=), 103.9, 105.6 (*C*=C=C=*C*), 114.7, 114.8 (=CHBr), 121.6 (*i*-C_6H_5-C≡), 126.35, 126.39 (*o*- or *m*-C_6H_5-C=CHBr), 127.4, 127.5, 127.6, 127.8 (*o*-C_6H_5-C=C=C=), 128.5, 128.6, 128.65, 128.70, 128.73, 128.79, 128.83, 128.9 (*o*- or *m*-C_6H_5-C=CHBr and *m*-C_6H_5-C=C=C=), 129.2, 129.3, 129.4, 129.59, 129.64 (*p*-C_6H_5), 130.3, 130.4 (*i*-C_6H_5-C=CHBr), 132.6 (*o*-C_6H_5-C≡), 135.7, 135.8, 136.21, 136.24, 136.3, 136.6 (*i*-C_6H_5-C=C=C= and *C*=CHBr), 147.4, 148.4 ppm (C=*C*=*C*=C); MS (Maldi, DCTB): *m*/*z*: 532 $[M]^+$.

Synthesis of 24: Dibromo olefin precursor **28** (0.300 g, 0.690 mmol), freshly activated zinc (0.045 g, 0.690 mmol; washed with diluted HCl) and distilled DMF (2 mL) were sonicated for 1.5 h. The resulting orange-brown solution was cooled under stirring at −78°C and freshly purified CuBr (0.050 g, 0.350 mmol) was added. The temperature was slowly warmed to RT and stirring was maintained overnight. After treatment with water, the crude mixture was filtered through Celite and the latter was washed with diethyl ether. After separation of the two layers, the aqueous layer was extracted with diethyl ether, and the combined organic layers were dried over $MgSO_4$ and evaporated to dryness. The residue was purified by silica gel chromatography (pentane) to give **24** as a yellow oil in 22% yield. ^{1}H NMR ($CDCl_3$): $\delta = 1.087$–1.150 ppm (m; Si-C*H*-C*H*$_3$); ^{19}F NMR ($CDCl_3$): $\delta = -64.13$ and −64.31 ppm (2×s; C*F*$_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 11.13$ (s; Si-*C*H-CH$_3$), 18.44 (s; Si-CH-*C*H$_3$), 98.20 and 98.24 (2×s; ≡*C*-Si), 101.22 (q, ^2J(C,F) = 49 Hz; *C*-CF_3), 110.03 and 110.50 (2×s; *C*≡C-Si), 119.67 and 119.86 (2×q, ^1J(C,F) = 275 Hz; CF_3), 158.54 ppm (s; C=*C*=*C*=C); FTIR: $\tilde{\nu}$ = 2946–2894 (C_{sp^3}-H), 1614, 1464 (C=C), 1385, 1368, 1278, 1261, 1192 ppm (CF_3); UV/Vis: λ_{max} (ε) = 373 nm (40250 mol L^{-1} cm^{-1}); MS (DCI/NH_3): *m*/*z*: 548.1 $[M]^-$; HRMS (DCI/CH_4): *m*/*z* calcd for $C_{28}H_{42}F_5Si_2$: 529.2745 $[M-F]^+$; found: 529.2755.

Synthesis of 25: *n*BuLi (1.97 mL, 4.93 mmol) was added to a solution of **27** (0.750 g, 2.46 mmol) in THF (20 mL) at −78°C. The resulting mixture was stirred for 20 min at −78°C and for 20 min at RT, then a solution of **26** (0.686 g, 2.46 mmol) in THF (10 mL) was added at −78°C. The mixture was slowly warmed to RT and stirred overnight. After treatment with saturated aqueous NH_4Cl, the aqueous layer was extracted with diethyl ether, and the combined organic layers were washed with brine, dried over $MgSO_4$, and evaporated to dryness. The residue was purified by silica gel chromatography (acetone/pentane, 5:95) to give **25** in 71% yield as a colorless oil, from which the *d*/*l* isomer progressively crystallized at RT. ^{1}H NMR ($CDCl_3$): $\delta = 1.11$ ppm (s, 42H; Si-C*H*-C*H*$_3$);

Table 4. X-ray crystallographic data and structural refinement parameters for **2**, **6**, **7**, **18**, and **25**.

	2	**6**	**7**	**18**	**25**
formula	$C_{38}H_{52}Si_2$	$C_{22}H_{16}$	$C_{24}H_{22}O_2$	$C_{18}H_{12}Br_2$	$C_{28}H_{44}F_6O_2Si_2$
M [g mol^{-1}]	565.00	280.35	342.42	388.10	582.82
crystal system	triclinic	monoclinic	monoclinic	orthorhombic	tetragonal
space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$	*Pbca*	$P4_2/n$
a [Å]	9.1361(3)	5.7944(3)	8.0280(4)	15.7508(11)	20.7861(12)
b [Å]	9.9084(3)	7.7835(4)	12.1192(5)	5.8226(4)	20.7861(12)
c [Å]	10.2409(4)	17.4735(10)	9.6318(5)	16.2345(12)	15.7939(13)
α [°]	93.308(2)	90	90	90	90
β [°]	108.6820(10)	94.335(5)	92.342(4)	90	90
γ [°]	98.8660(10)	90	90	90	90
V [Å^3]	862.01(5)	785.81(7)	936.32(8)	1488.88(18)	6823.9(8)
Z	1	2	2	4	8
ρ_{calcd}	1.088	1.185	1.215	1.731	1.135
μ [mm^{-1}]	0.126	0.067	0.076	5.431	0.1575
$2\theta_{max}$ [°]	70.86	52.74	64.22	68.40	56.20
crystal size [mm]	0.15×0.20×0.25	0.05×0.12×0.20	0.12×0.25×0.35	0.08×0.25×0.30	0.15×0.25×0.25
T [K]	180	180	180	180	180
measured refkns	25264	5920	10000	35046	67894
unique reflns	7112	1607	3279	2305	8193
R_{int}	0.023	0.029	0.027	0.034	0.111
reflns [$I > n\sigma(I)$]	5602 (n=3)	1156 (n=2)	3110 (n=2)	1326 (n=3)	3438 (n=2.2)
refinement	F	F^2	F^2	F	F
parameters	181	101	120	91	319
R [$I > n\sigma(I)$]	0.0367	0.0404	0.0515	0.0242	0.0699
R_w [$I > n\sigma(I)$]	0.0423	0.1152	0.1383	0.0265	0.0812
residual electron density [eÅ^{-3}]	−0.17/0.44	−0.15/0.18	−0.19/0.38	−0.38/0.55	−0.56/0.70

^{19}F NMR ($CDCl_3$): $\delta = -81.46$, -81.48 ppm ($2\times$s; CF_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 10.9$ (s; Si-*C*H-CH_3), 18.3 (s; Si-CH-*C*H_3), 64.3 (q, $^2J(C,F) = 37$ Hz; *C*-CF_3), 78.8 (s; C-*C*≡*C*-C), 91.2 (s; Si-C≡*C*), 97.3 (s; Si-*C*≡C), 121.6 ppm (q, $^1J(C,F) = 285$ Hz; *C*F_3); MS (DCI/NH_3): *m*/*z*: 600.2 $[M+NH_4]^+$.

Synthesis of 28: PPh_3 (1.743 g, 6.64 mmol) was added to a solution of CBr_4 (1.072 g, 3.23 mmol) in CH_2Cl_2 (40 mL). After stirring at RT for 15 min, this orange mixture was added to a solution of **26** (0.500 g, 1.80 mmol) in CH_2Cl_2 (20 mL) at -78°C. The mixture was warmed slowly to RT and stirred overnight. After evaporation of the solvent under vacuum, the residue was extracted three times with CH_2Cl_2/pentane (1:5). The product was finally purified by silica gel chromatography (pentane) to finally give **28** as a white solid in 82% yield. ^{1}H NMR ($CDCl_3$): $\delta = 1.27$ ppm (m, 21H; Si-C*H*-CH_3); ^{19}F NMR ($CDCl_3$): $\delta = -60.09$ ppm (CF_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 11.0$ (s; Si-*C*H-CH_3), 18.5 (s; Si-CH-*C*H_3), 98.9 (s; ≡C-Si), 106.4 (s; *C*≡C-Si), 108.5 (s; CBr_2), 120.5 (q, $^1J(C,F) = 276$ Hz; *C*F_3), 122.8 ppm (q, $^2J(C,F) = 36$ Hz; *C*=CBr_2); MS (DCI/NH_3): *m*/*z*: 433.9 $[M+H]^-$. HRMS (DCI/CH_4): *m*/*z* calcd for $C_{14}H_{21}SiBr_2F_2$: 412.9771 $[M-F]^+$; found: 412.9747.

X-ray crystallographic structure determination of 2, 6, 7, 18, and 25: Data collection and refinement parameters are given in Table 4. Intensity data were collected with an Oxford Diffraction Xcalibur or a Bruker Apex2 instrument equipped with an Oxford Cryosystems Cryostream Cooler Device, using a graphite-monochromated $Mo_{K\alpha}$ radiation source ($\lambda = 0.71073$ Å). Structures were solved by direct methods using SIR92 or SIR2004, and refined by full-matrix least-squares procedures using the PC version of CRYSTALS or WINGX software. Scan modes Φ and Ω were used; absorption corrections were obtained in a multiscan mode. Atomic scattering factors were taken from the International Tables for X-ray Crystallography. All non-hydrogen atoms were refined anisotropically. For compound **25**, because the crystal was weakly diffracting, the data were of poor quality and some constraints were applied. Hydrogen atoms were located in a difference map and repositioned geometrically, then refined using a riding model. CCDC-793457 (**18**), 793458 (**2**), 793459 (**25**), 793460 (**7**), and 793461 (**6**), contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

The authors wish to thank the Centre National de la Recherche Scientifique and the Ministère de l'Education Nationale, de la Recherche et de la Technologie for financial support. Thanks are due to the Paul Sabatier University and the French Ministery of Research for the Ph.D. fellowship of L.L.

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[32] Preparation of **24** was also envisioned using *n*BuLi and a copper salt ($CuI{\cdot}PBu_3$) as previously described for the synthesis of **2**. In one case, the butatriene **24** could then be detected by NMR analysis as a minor product. However, in spite of many attempts, this result could not be reproduced. In most cases, the dibromo precursor **28** was recovered, indicating that the intermediate lithium derivative was not formed.

Received: September 27, 2010
Revised: January 12, 2011
Published online: March 22, 2011

