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The Rubrenic Synthesis: The Delicate Equilibrium between Tetracene and Cyclobutene

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Herein we describe the synthesis of new substituted tetraaryltetracenes, obtained by the dimerization of triarylchloroallenes, prepared from propargyl alcohols. The propargyl alcohols were prepared by two different synthetic strategies and then the alcohols were treated to obtain the corresponding acenes. In addition to the expected tetracene derivatives, we observed the formation of bis(alkylidene)cyclobutenes. When strong electron-donating substituents were present, the main product was the cyclobutene. We discuss a reaction mechanism that accounts for the formation of the cyclobutenes.

Introduction

Rubrene (5,6,11,12-tetraphenyltetracene; Figure 1, **a**) has been known since the first half of the 20th century.[1] Its chemi- and electrochemiluminescence properties were thoroughly studied in the 1960s[2] and later it found application in organic light-emitting devices (OLEDs).[3] Recently the interest in rubrene has increased enormously thanks to the outstanding charge mobilities (up to 40 $cm^2 V^{-1} s^{-1}$) observed in single crystals.[4] These high charge mobilities are observed in single crystals obtained from highly pure materials by accurate purification. Nowadays rubrene is one of the most studied molecular organic semiconductors in single-crystal transistors due to the ease of crystal growth and a higher stability against oxidation in comparison with unsubstituted acenes. In addition to oxidation products, commercially available rubrene is contaminated by impurities, namely 3,4-bis(diphenylmethylidene)-1,2-diphenylcyclobutene (Figure 1, **b**) and 4b,8b-diphenyl-4b,8b-dihydrodiindeno[1,2,3-*fg*:1′,2′,3′-*op*]tetracene (Figure 1, **c**).[5]

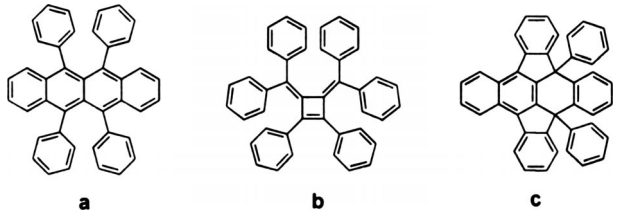

Figure 1. Rubrene and its main impurities found during the growth of single crystals.

The formation of the dihydrotetracene **c** is attributed to oxidation processes occurring during crystal growth whereas the origin of the cyclobutene **b** has never been explained.[5a] Concerning rubrene, methods of preparation are relatively scarce and, in spite of its great potential in materials science, few substituted tetracenes or analogues of rubrene are known.[6] Commercial rubrene is prepared from 1,1,3-triphenylpropargyl alcohol following a well-established, one-pot protocol (Scheme 1). This protocol appears to be very general and applicable to the synthesis of a number of centrosymmetric tetraaryltetracenes, analogues of rubrene, because, in principle, it can tolerate the presence of substituents of different nature (electron-donating or -withdrawing) on all phenyl groups and also heteroaromatic rings, making accessible various derivatives of tetracene with tailored electronic properties.

The aim of this work was to prepare new analogues of rubrene as new potential organic semiconductors and to test the robustness of the reaction. Herein we report the synthesis of new propargyl alcohols and their transformation into the corresponding substituted tetraaryltetracenes.

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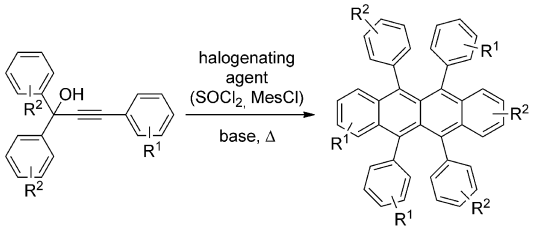


Scheme 1. General scheme for the synthesis of rubrene derivatives from triarylpropargyl alcohol.

Table 1. Synthesis of propargyl alcohols.

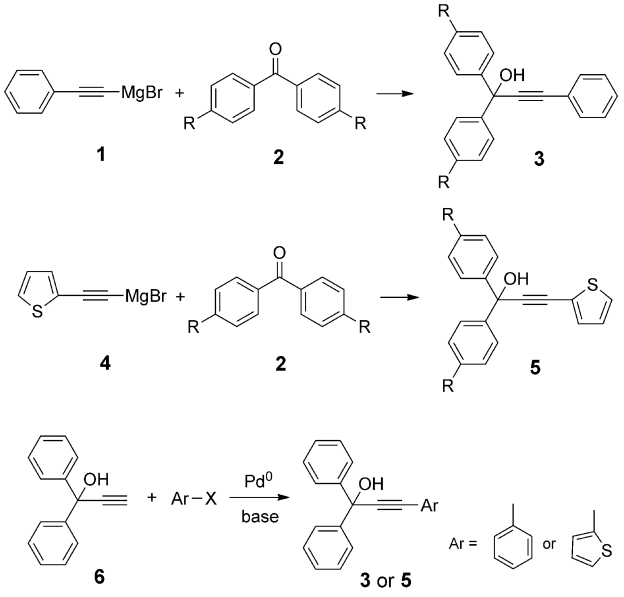
	Ar[a]	Substituents[b]	Method[c]	% Yield
3a	phenyl	H	B	80
3b		F	A	86
3c		NEt_2	A	80
5a	thienyl	H	A	64
5a		H	B	75
5b		F	A	45
5c		NEt_2	A	88

[a] Aromatic ring bound to C-3. [b] Substituent present at the *para* position of the phenyl ring bound to C-1. [c] Method A: organometallic (Grignard) route. Method B: Sonogashira reaction.

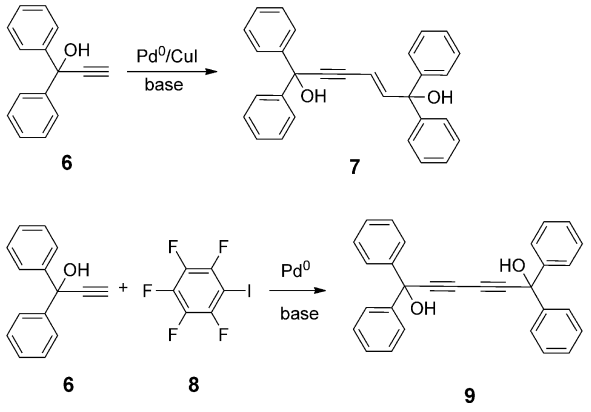
Results and Discussion

Synthesis of Propargyl Alcohols

We planned the synthesis of a series of substituted tetraaryltetracenes bearing diethylamino, fluoro and thienyl groups starting from suitable propargyl alcohols. The propargyl alcohols were synthesized by following two different strategies: 1) the classic organometallic method, that is, by addition of magnesium arylacetylide (or lithium acetylide) to diaryl ketones following a procedure reported in the literature[7] and 2) Sonogashira reaction between 1,1-diphenylpropargyl alcohol and bromo- or iodoarenes and heteroarenes. Based on the first synthetic strategy, propargyl alcohols bearing diethylamino- and fluorine-substituted phenyl (**3b** and **3c**) or thiophene rings (**5a**–**c**) were prepared in satisfactory-to-good yields by addition of the corresponding magnesium acetylide (**1** or **4**) to the corresponding benzophenones **2a**–**c** (Table 1 and Scheme 2). The propargyl derivatives were prepared from phenylacetylene and 2-ethynylthiophene. This latter was readily synthesized from commercially available thiophene-2-carbaldehyde in a two-step Corey–Fuchs sequence via the dibromoalkene.[8] We prepared propargyl alcohols **3a** and **5a** in a one-pot reaction starting from iodobenzene and 2-bromo- and 2-iodothiophene and 1,1-diphenylpropargyl alcohol (**6**) by a copper-free Sonogashira reaction.[9] The synthesis of propargyl alcohols by Sonogashira reaction required the development of a copper-free protocol. The presence of copper salts (CuI normally used in standard Sonogashira reaction) produced the dehydrodimerization product [1,1,6,6-tetraphenyl-4-hexen-2-yne-1,6-diol (**7**); Scheme 3] of 1,1-diphenylpropargyl alcohol as the main product. X-ray diffraction of a single crystal allowed the crystal structure to be determined, thereby confirming the structure of this compound, which has a *trans* geometry of the C=C bond (see Figure B in the Supporting Information). The dehydro dimer was formed without the involvement of bromothiophene. In fact, this dehydro dimer was formed as the single reaction product when the reaction was carried out in the absence of 2-bromothiophene. The dimerization of the propargyl alcohol is reported in the literature to occur with ruthenium catalysts,[10] but so far no reaction involving the use of a palladium catalyst has been reported.



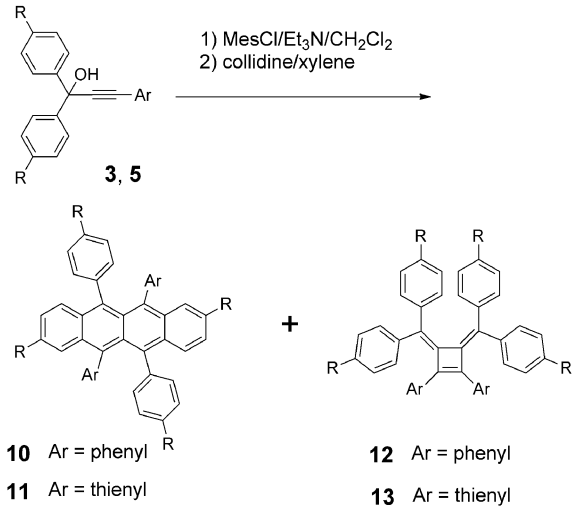
Scheme 2. Propargyl alcohol derivatives prepared by the classic organometallic and Sonogashira methods. R = H (**2a, 3a**, **5a**), F (**2b, 3b**, **5b**), NEt_2 (**2c, 3c**), X = Br or I.



Scheme 3. Unexpected dimerization product of 1,1-diphenylpropargyl alcohol (**6**) under classic and copper-free Sonogashira reaction conditions.

The organometallic approach proved to be quite robust. On the other hand, the limits of applicability of the copper-free Sonogashira protocol are less predictable. Some preliminary experiments showed that this protocol is not compati-

ble with labile hydrogen atoms such as amino groups (of *p*-bromoaniline). An unexpected reaction occurred with pentafluoro(iodo)benzene. In this latter case, we did not obtain the desired propargyl derivative; the main product was the dimer **9** (obtained in 80% yield) of the starting 1,1-diphenylpropargyl alcohol (**6**; Scheme 3). This result was also unexpected because it has been reported that pentafluoro(iodo)benzene reacts with (trimethylsilyl)acetylene under standard Sonogashira conditions to afford the expected (trimethylsilyl)(pentafluorophenyl)acetylene.[11] At the moment we do not have any reasonable hypothesis to explain the formation of this dimer but it is plausible that iodopropargyl alcohol is involved and the pentafluoro(iodo)benzene could behave as a source of iodine, in line with what it is reported in the literature for similar dimerizations under standard Sonogashira conditions in the presence of iodine.[12]



Scheme 4. Synthesis of tetraaryltetracenes from propargyl alcohols **3** and **5**. Depending on the substituents, tetracenes **10** and **11** or cyclobutenes **12** and **13** were obtained.

Synthesis of Rubrene

We used two different approaches for the synthesis of rubrene derivatives, namely the classic one-pot approach and an approach based on chloroallene isolation. In the first case (one-pot protocol), at first we treated the appropriate propargyl alcohol with mesyl chloride (MesCl) and then heated the mixture at reflux in xylene. In the second case we isolated the chloroallene, produced by treatment of the propargyl alcohol with MesCl and then heated it in xylene. The chloroallenes were synthesized in CH_2Cl_2 instead of in diethyl ether as solvent because triethylammonium chloride is soluble in this solvent and provides a higher chloride ion concentration. The alcohol was completely consumed with 3 equiv. of MesCl. At first we synthesized the rubrene **10a** following the one-pot protocol[1] by treating 1,1,3-triphenylpropargyl alcohol with mesyl chloride in the presence of triethylamine in CH_2Cl_2 at 0 °C. Then we replaced CH_2Cl_2 with xylene, added collidine and heated the mixture for 4 h at reflux, obtaining the desired product **10a**. This protocol was then applied to the other synthesized propargyl alcohols (Scheme 4 and Table 2).

Table 2. Synthesis of rubrene derivatives.

	Ar[a]	R[b]	Method[c]	% Yield of tetracene (**10**/**11**)	% Yield of cyclobutene (**12**/**13**)
3a	phenyl	H	A	40	–
		H	B	60	–
3b		F	A	70	–
3c		NEt_2	A	–	69
5a	thienyl	H	A	25	8
5b		F	A	68	3
5c		NEt_2	A	–	46

[a] Aromatic ring bound to C-3. [b] Substituent present at the *para* position of the phenyl ring bound to C-1. [c] Method A: one-pot method. Method B: reaction carried out with purified chloroallene.

Suitable single crystals of **10b** were grown and the crystal structure was determined by X ray diffraction (Figure 2). The molecular structure of **10b** is closely related to that of unsubstituted rubrene,[13] showing similar intramolecular distortions due to the steric crowding of the four phenyl substituents. Thus, for each pair of phenyl rings lying on the same side of the naphthacene core, the torsion angle defined by the *ipso* carbon atoms is 28.7° in **10b** and 25.0° in rubrene. The non-bonding distance between the same pair of *ipso* carbon atoms is 2.83 Å for both **10b** and rubrene, whereas the four phenyls rings in **10b** do not show any significant bending to relax the crowding as occurs in rubrene.[13] For more clean and controlled reaction conditions, we also investigated a second approach based on the synthesis and isolation of chloroallene derivatives and their transformation into rubrene. Even though it is commonly accepted that chloro-triphenylallene is responsible for the formation of rubrene and cyclobutene derivatives, contrasting information on its stability and on its transformation into rubrene has been reported.[14] To clarify this point we prepared 1-chloro-1,3,3-triphenylallene as described before. No other byproducts were observed, the only impurity being the starting propargyl alcohol. The chloroallene was then purified by column chromatography and was definitively stable. ^{1}H NMR and IR spectroscopy confirmed its structure. The IR spectrum clearly shows that the signals of the OH and triple bond stretches are no longer present and the appearance of a band at 1922 cm^{-1} corresponding to stretching of the cumulenic C=C. Thermolysis of neat 1-chloro-1,1,3-triphenylallene or at reflux in xylene afforded the desired rubrene. High-performance liquid chromatography (HPLC) with a CCD detector (see the Supporting Information) was used to analyse the reaction products. The HPLC chromatograms of commercial rubrene and the reaction product are similar. The only contaminants present in rubrene **10a** are the same impurities, if any, as are present in the starting chloroallene, this reaction being very clean. We did not detect any cyclobutene, which is probably eliminated during the crystallization from EtOH. Thus, in con-

clusion, we can claim that 1) the chloro-triphenylallene is definitively stable and can be isolated and 2) for allenes derived from alcohol **3a**, its transformation into rubrene is very clean.

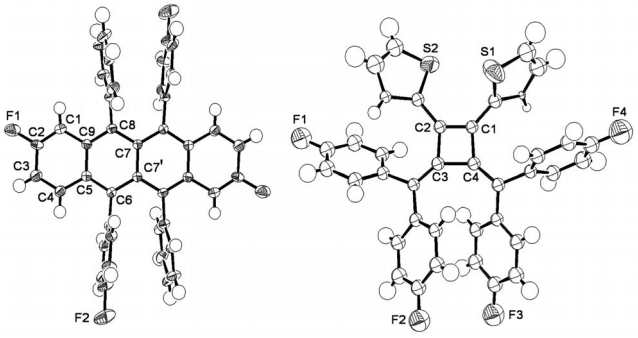


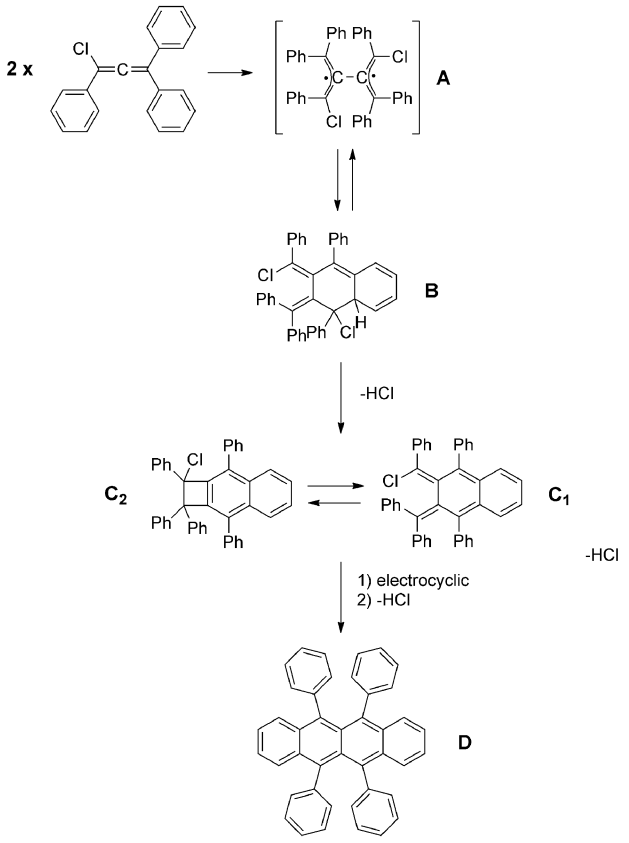
Figure 2. Left: molecular structure of tetraaryltetracene **10b**. Thermal ellipsoids are drawn at the 30% probability level. Primed atoms are related to unprimed atoms by the symmetry operator (–*x*, –*y*, 1 – *z*). Right: molecular structure of cyclobutene **13b**. Thermal ellipsoids are drawn at the 30% probability level.

Although this approach seemed robust and general, when the reaction was run with **5b**, after purification of the crude product by column chromatography, we obtained a mixture of two products. We wish to highlight that the separation of cyclobutene from the rubrene derivative by standard column chromatography is not trivial because they have similar polarities and similar interactions with the commonly used stationary phases. These two products were separated by repeated crystallization from hexane (in which cyclobutane is less soluble) and further purified by medium-pressure liquid chromatography. On the basis of the NMR and HRMS analyses, we confirmed the structure of the desired tetracene derivative as the product with *m*/*z* = 616 and assigned the structure of the bis(methylidene)cyclobutene as the product with *m*/*z* = 618. Note that combustion analyses were not suitable to determine the degree of purity of these acenes because the molecular weights of the acene and cyclobutene, produced together during the reaction, differ by only 2 amu (two hydrogen atoms) and the differences in their combustion analyses are below the acceptance limits of this technique. During the purification and crystallization of rubrene **11b** we were able to grow single crystals of **13b** (Figure 2) and XRD analysis confirmed our assessment. The pattern of the C–C bond lengths of **13b** closely resembles that of 1,2-diphenyl-3,4-bis(diphenylmethylidene)cyclobutene[5a] with one short intracyclic C=C bond (1.366 and 1.348 Å, respectively) and two short exocyclic C=C bonds of around 1.34 Å. The other C–C bond lengths are compatible with strained single bonds (Figure 2). Also, when we allowed the alcohol **5a** to react we obtained a mixture of tetracene **11a** and the corresponding cyclobutene **13a**, which were separated by successive crystallization from hexane followed by purification by medium-pressure liquid chromatography. On the other hand, the reactions of chloroallene derivatives obtained from propargyl alcohols **3c** and **5c** provided only the cyclobutenes **12c** and **13c**. These findings clearly show that the nature of the substituents is a key factor driving the transformation of propargyl alcohols towards the rubrene or cyclobutene derivatives. In fact, when electron-donating groups were present, the formation of cyclobutene was competitive with the formation of rubrene or even favoured by strong electron-donating groups.

Mechanistic Considerations

In spite of the apparent simplicity of the synthesis, the mechanism of this reaction has been discussed over several decades. Various mechanisms have been proposed to explain the formation of rubrene, which is a formal dimerization of two units of propargyl alcohols, as demonstrated by Dufraisse and co-workers in their pioneering work on rubrene.[1] Since the beginning it has been suggested that an allenic intermediate is formed during the formation of rubrene,[15] formed by anionotropy on treatment of a propargyl alcohol with a chlorinating agent. Carbocationic or purely radical reactions were discarded early on.[16] Indeed, triphenylallenyl carbocations are not formed under the reaction conditions but for instance by photolysis of chlorotriarylallenes[7] or solvolysis.[8] The solvolysis (at room temp.) of chloro-triphenylallene occurs by the formation of a carbocation, which is stabilized by resonance and affords either the enone or the starting propargyl alcohol,[18] but the formation of cyclobutenes or acenes has never been reported under solvolytic conditions. A clearer picture of the mechanism was available only after the reactions of chloro- and polyphenylallenes had been thoroughly studied. The first reliable mechanism, explaining the formation of rubrene, was proposed by Rigaudy and Capdevielle[14a] in the 1970s (Scheme 5). The first step of the reaction is the formal [2+2] dimerization of two molecules of chlorotriphenylallene, which affords a bis(allenic) diradical (compound **A**, Scheme 5) that collapses into bis(methylidene)cyclobutane. The possible formation of 2,2′-bis(allyl) diradicals in allene thermal dimerization was first suggested by Roberts and Sharts in 1962[19] and then confirmed and thoroughly studied by Gajewski and Shih.[20] All these studies underline that the formation of the diradical intermediate is an irreversible process and, once formed, it collapses to bis(methylidene)cyclobutane isomers, depending on the substituents present on the allene. An equilibrium between these cyclobutane isomers is established through the bis(allenic) diradical, regenerated by thermal cyclobutane ring-opening. Both the dimerization process (affording cyclobutane derivatives) and the thermal cyclobutane ring-opening depend on the steric crowding. Indeed, although tetraphenylallene does not dimerize, the thermal isomerization of the cyclobutane derivatives obtained from the dimerization of 1,3-diphenylallene was not observed.[11] Triphenylallenes show an intermediate behaviour, easily affording the corresponding cyclobutane and being able to undergo thermal isomerization by opening of the cyclobutane ring. In the specific cases of triphenylallene[6b,6e] and chlorotriphenylallene a dihydronaphthalenic derivative (compound **B**) may be produced. This latter is formed by the possibility of delo-

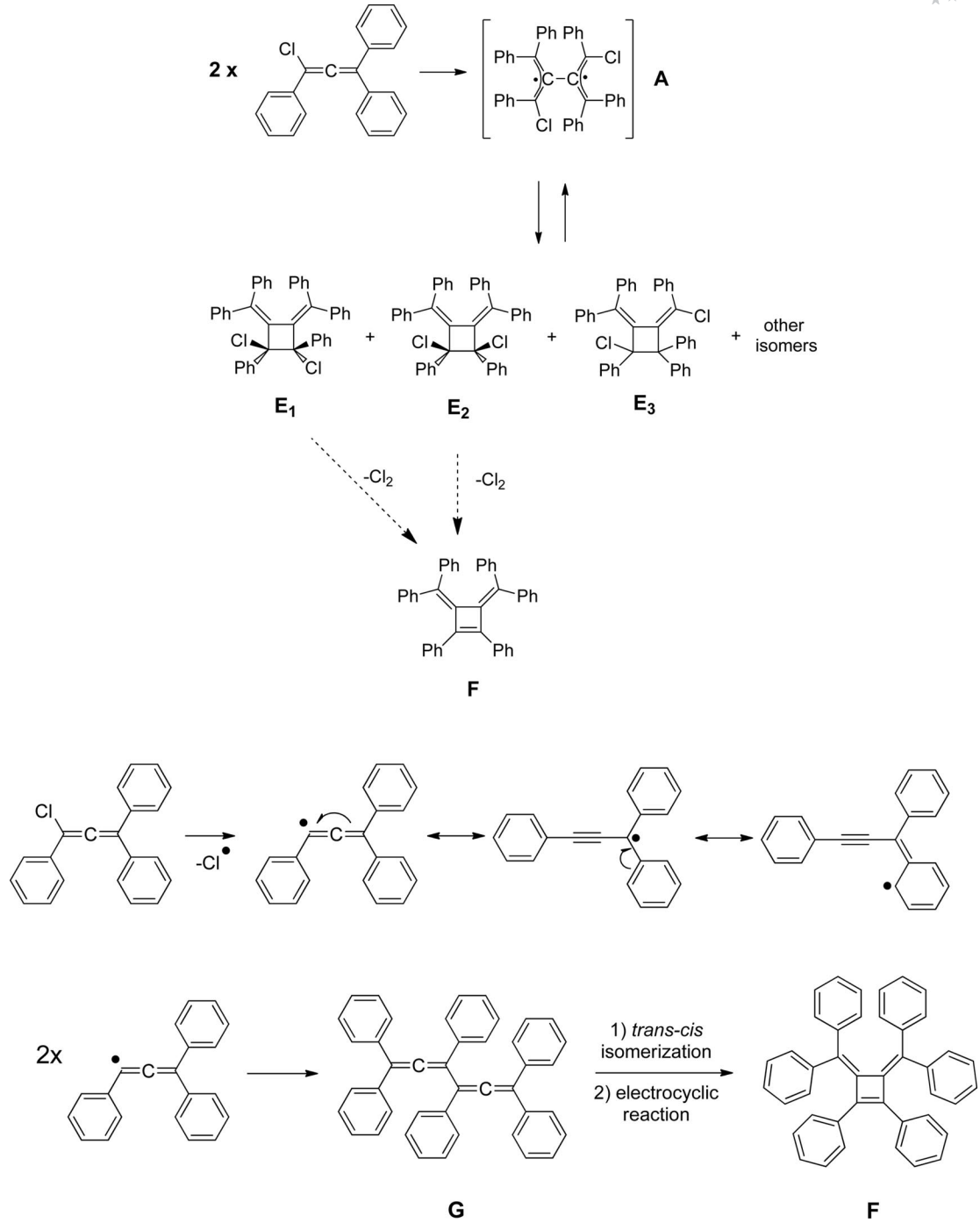
calizing the radical onto the *ortho* position of the phenyl ring, as already demonstrated by Christl et al.[17] Compound **B** is then irreversibly transformed into naphthocyclobutene (compounds $\mathbf{C_1/C_2}$), which is finally converted into rubrene (compound **D**) through a double dehydrohalogenation and an electrocyclic reaction. The driving force for the formation of naphthocyclobutene is the rearomatization of a dehydronaphthalene by loss of HCl. This process may proceed by a carbocationic mechanism without the assistance of a base because rubrene is formed from chloroallene also in the absence of a base, as we have shown. The detailed mechanism presented by Rigaudy and Capdevielle[14a] still remains the most plausible for rubrene formation, however, they did not observe any trace of either dialkylidenecyclobutane or of dialkylidenecyclobutene when they transformed this chlorotriphenylallene into rubrene. On the contrary, it is well known that dialkylidenecyclobutene is a typical impurity of commercial rubrene **10a**[5a] and we demonstrated that, depending on the substituents present on the propargyl alcohol, the presence of dialkylidenecyclobutene could become more important or even the main product.



Scheme 5. Mechanism of Rigaudy and Capdevielle for the formation of tetraaryltetracene (rubrene) from chlorotriphenylallene.

Starting from our findings and an overview of the data presented in the literature, we propose two possible explanations for the formation of bis(alkylidene)cyclobutenes and for the observed ratio between tetraaryltetracenes and bis(alkylidene)cyclobutenes. Within the framework of Rigaudy and Capdevielle's mechanism,[14a] cyclobutene **F** can originate from cyclobutanes **E1/E2** by the formal elimination of a Cl_2 molecule (Scheme 6, top). Cyclobutenes **E** can be produced by thermal treatment of phenylchloroallenes even though in the work of Rigaudy and Capdevielle[14] no dialkylidenecyclobutane was observed after the thermal treatment of chloro-triphenylallene under the conditions that usually afford rubrene. On the other hand, bis(alkylidene)cyclobutene **F** can be easily formed by electrocyclization of a diallene **G** (see Scheme 6, bottom). The formation of diallenes from bromoallenes has already been observed,[21] but the reactivity of these allenes and the experimental conditions used for their dimerization are different to those reported herein. Herein we will detail both hypotheses on the basis of our findings and of the literature data.

Within the framework of the first hypothesis (loss of Cl_2 from **E**), it is not trivial to ascertain a possible mechanism that is responsible for the formal elimination of Cl_2. The formation of **F** should occur by a monomolecular elimination (E1) mechanism via a carbocation or by the formation of a radical. The formation of such species may be promoted by the presence of strong donating groups, such as diethylamino; both carbocationic and radical mechanisms are reasonable as both a carbocation and a radical would be stabilized for the same reasons, the cation and radical being both benzylic and allylic in nature and due to the presence of electron-donating groups (such as Et_2N) on the aromatic rings. Under the experimental conditions used for the rubrene synthesis, before the elimination of HCl from **B** or of Cl_2 from $\mathbf{E_1/E_2}$, these species should be in equilibrium through the diradical species **A**, so what should control the final **D/F** ratio should be the ratio between the elimination rates of HCl (k_{HCl} from **B**) and Cl_2 (k_{Cl2} from $\mathbf{E_1/E_2}$), as these two latter steps are irreversible because both HCl and Cl_2 are eliminated as gases from the reaction mixture or trapped by bases (if present) in the case of HCl. Therefore the ratio between k_{HCl} and K_{Cl2} should control the ratio between rubrene and cyclobutene. From our findings, it is evident that the presence of electron-donating groups, which are able to stabilize carbocationic or radical species, should favour the formation of **F** against the formation of **D**. Looking at the nature of the intermediate formed during the elimination of Cl_2 from **E**, the positive charge or the radical is delocalized at both the benzylic and allylic positions. In addition, the phenyls bonded to the *exo* double bonds can be involved in the delocalization of the positive charge or the radical. The stabilization effect is strongly improved when electron-releasing groups, such as phenyls bearing a diethylamino, are present. Also thiophene, as an electron-rich aromatic ring, can contribute to stabilizing this intermediate. The donor effect of substituents does not play a role in the formation of rubrene because the driving force for HCl elimination, which affords the naphthocyclobutene **C**, is the rearomatization of the naphthocyclobutene **B** and therefore the donor effect of substituents does not affect significantly the elimination rate of HCl, which remains more or less constant or only temperature-dependent. On the other hand, electron-donat-



Scheme 6. Top: mechanism for the formation of the cyclobutene based on formal loss of Cl_2 from bis(alkylidene)cyclobutanes. Bottom: mechanism for the formation of the cyclobutene based on the dimerization of allenes followed by electrocyclic ring closure of a diallene to a cyclobutene.

ing groups could increase the Cl_2 elimination rate from $\mathbf{E}_1$/$\mathbf{E}_2$, driving the reaction towards the preferential formation of the cyclobutene **F**, as observed.

An alternative explanation for the formation of **F** is offered by the reactivity of diallenes (**G**; Scheme 6, bottom). The formation of bis(alkylidene)cyclobutenes by the electrocyclization of *cis*-diallenes, propargylallenes and bis(alkynes) is a well known process and should occur easily under our experimental conditions.[15d,22] McGlinchey and coworkers reported that the thermolysis of propargylallenes resulted in the formation of bis(fluorenylidene)diphenylcyclobutenes, the structures of which are very similar to the structures of our cyclobutenes, through a rearrangement to a diallene.[23] Note that this diallene was not isolated due to its high reactivity. The thermal conversion of diallenes was also found to occur in the solid state.[24] Similar behaviour has been observed for cumulenic derivatives, giving tetrakis(methylidene)cyclobutanes and other radialenes.[25] Ther-

mal rearrangements of heteroatom-bridged diallenes have also been reported.[26] Although diallenes can be easily and even quantitatively transformed into bis(alkylidene)cyclobutenes, the formation of diallenes is harder to explain. Within this framework, the problem of the formation of **F** is shifted to a possible reaction pathway able to explain the formation of a diallene. Diallenes can be prepared by isomerization of a propargylallene[27] or by dimerization of bromoallenes.[23] Examples of the dimerization of allenes catalysed by copper,[28] iron or other Lewis and Brønsted acid catalysts[29] or by a strong base such as BuLi have been reported in the literature.[23] Various mechanisms have been invoked to explain these dimerizations. Acid-catalysed dimerization of 1,3-diarylpropargyls to afford diallenes has been reported.[30] Also, radical and carbenoid mechanisms have been invoked to explain the formation of propargylallenes from bromoallenes.[27,28] In our case the formation of **F** occurs without any catalysis and a pure radical mechanism (already proposed by McGlinchey and co-workers for the formation of some dimers of bromoallene) can be envisaged. The first step is the formation of an allenic/propargyl radical. The reactivity of the unsubstituted propargyl radical has already been studied, both theoretically and experimentally, but mainly under pyrolytic conditions.[31] Unsubstituted propargyl radicals under pyrolytic conditions undergo a complex series of simultaneous and consecutive reactions, also affording 3,4-bis(methylidene)cyclobutene.[31] In our case, the formation of two propargyl (allenic) radicals can be promoted by the presence of electron-donating groups, which are able to delocalize the radical (as already explained within the framework of the previous hypothesis), and can therefore occur under mild conditions. The presence of radical species during the dimerization of a bromoallene has already been invoked.[27] The photolytic formation of the allylic radical from chloroallene has also been reported.[7]

Little data concerning the reactivity of chloroallenes with electron-donating substituents have been reported and at the present moment we cannot exclude either of the two mechanisms. As we did not isolate any dichlorocyclobutane or any diallenes, we cannot exclude either of these two hypotheses. Further studies are in progress to elucidate the mechanism responsible for the formation of these cyclobutenes.

Conclusions

In this report we have presented the synthesis of new tetraaryltetracenes starting from propargyl alcohols. At first we analysed two simple and versatile approaches to propargyl alcohols, which allowed the easy preparation of these alcohols in high yields. We demonstrated that chloro-triphenylallenes are definitively stable and that, under heating, they dimerize leading to the formation of rubrene analogues or bis(alkylidene)cyclobutenes depending upon the substituents present on the chloroallene. Through an analysis of the data present in the literature and on the basis of our findings, we have discussed two possible mechanisms responsible for the formation of cyclobutenes and the effect of substituents (in this case electron-donating groups) on the ratio of tetraaryltetracenes and cyclobutenes.

Experimental Section

General: Solvents of analytical grade were used without further purification. Reagents were purchased from Sigma–Aldrich and used without further purification. IR spectra were obtained with a Perkin–Elmer Spectrum 100 FT-IR spectrometer. NMR spectra were recorded with a Varian Mercury 400 Spectrometer. Molecular structures and purity were analysed by GC–MS (GCD 1800C; Hewlett–Packard) with a 50 m DB-5MS column (J & W Scientific, Folsom, California). Silica gel (230–400 mesh) was used for column chromatography.

General Procedure for the Synthesis of Substituted Triarylpropargyl Alcohol via Grignard Reagents

Method A. Synthesis of the Grignard Reagent: 2-Bromopropane (1 equiv.) was added dropwise over a 60 min period to magnesium turnings (0.9 equiv.) in anhydrous THF under argon. The reaction temperature was kept at 40 °C and after the addition was complete the mixture was stirred for another 60 min. Then phenyl- or thienylacetylene (0.9 equiv.) dissolved in THF was added. The mixture was stirred at room temp. for 3 h to produce the Grignard reagent. Br/Mg exchange was completed after 3 h.

Method B. Reaction of the Grignard Reagent with Benzophenone: The appropriate Grignard reagent (1.1 equiv.) was added dropwise to a solution of the appropriate benzophenone (1 equiv.) in dry THF at 0 °C. After being warmed to room temp. the mixture was heated at reflux for 2 h, cooled to RT, then quenched with water and extracted with AcOEt. The combined extracts were washed with saturated aq. NH_4Cl and dried with anhydrous $MgSO_4$. After evaporation of the solvents under vacuum, the residue was purified by column chromatography (silica gel, petroleum ether/AcOEt) to give the desired 1,1,3-trisubstituted arylpropargyl alcohols.

1,1-Bis(4-fluorophenyl)-3-phenylprop-2-yn-1-ol (3b): 4,4′-Difluorobenzophenone (6.0 g, 27.5 mmol) dissolved in anhydrous THF (50 mL) was treated with phenylethynylmagnesium bromide, derived from 2-phenylacetylene (3.0 g, 29 mmol), dissolved in THF (150 mL) to afford after column chromatography (SiO_2, petroleum ether/diethyl ether, 17:3) the desired product (7.5 g, 86% yield), white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.85 (s, 1 H), 7.05–7.70 (m) ppm. GC–MS: *m*/*z* (%) = 320 $[M]^+$ (t_r = 10.98 min).

1,1-Bis(4-ethylaminophenyl)-3-phenylprop-2-yn-1-ol (3c): 4,4′-Bis(diethylamino)benzophenone (4.0 g, 12 mmol) dissolved in THF (60 mL) was treated with phenylethynylmagnesium bromide, derived from phenylacetylene (1.5 g, 15 mmol), dissolved in THF (120 mL) to afford after column chromatography (SiO_2, CH_2Cl_2/MeOH, 17:3) the desired product (4.1 g, 80% yield), yellow solid. ^{1}H NMR (400 MHz, DMSO): δ = 1.2 (t, 3 H), 3.4 (q, 2 H), 6.17 (s, 1 H), 6.25 (dd, J = 8 Hz, 3 H), 6.55 (dd, J = 8 Hz, 1 H), 7.3 (dd, J = 8 Hz, 3 H), 7.4–7.5 (m, 5 H), 7.54 (dd, J = 8 Hz, 1 H) ppm. GC–MS: *m*/*z* (%) = $[M]^+$ 426.4 (5), 309.3 (100), 147.2 (50), 132.0 (30) (t_r = 17.73 min).

1,1-Diphenyl-3-(thiophen-2-yl)prop-2-yn-1-ol (5a): Benzophenone (1.0 g, 9.0 mmol) was dissolved in THF (50 mL) and treated with (2-thienylethynyl)magnesium bromide, derived from 2-ethynylthiophene (1.0 g, 9.25 mmol), in THF (100 mL) to afford after column chromatography (SiO_2, petroleum ether/AcOEt, 19:1) the desired

product (1.7 g, 64% yield), white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.01 (dd, J = 3.59, 5.1 Hz, 1 H), 7.26–7.80 m (5 H, phenyl, 2 H, thiophene) ppm. GC–MS: m/z (%) = 290.01 (20) $[M]^+$, 205.96 (100), 104.88 (90), 76.88 (80) (99% purity, t_r = 11.71 min).

1,1-Bis(4-fluorophenyl)-3-(thiophen-2-yl)prop-2-yn-1-ol (5b): 4,4′-Difluorobenzophenone (8.2 g, 38 mmol) was dissolved in THF (150 mL) and treated with (2-thienylethynyl)magnesium bromide, derived from 2-ethynylthiophene (4.1 g, 38 mmol), dissolved in THF (50 mL) to afford after column chromatography with petroleum ether/diethyl ether (17:3) the desired product (5.0 g, 45% yield), white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.16 (dd, J = 3.59, 5.1 Hz), 7.45 (dd, J = 3.8, 1.13 Hz), 7.7 (dd 5.1, J = 1.1 Hz), 8.0–8.2 (m, phenyl) ppm. GC–MS: m/z (%) = $[M]^+$ 326.07 (98% purity, t_r = 11.52 min).

1,1-Bis(4-diethylaminophenyl)-3-(thiophen-2-yl)prop-2-yn-1-ol (5c): 4,4′-Bis(diethylamino)benzophenone (3.4 g, 10.5 mmol) was dissolved in THF (30 mL) and treated with (2-thienylethynyl)magnesium bromide, derived from 2-ethynylthiophene (3.4 g, 30 mmol), dissolved in THF (150 mL) to afford after column chromatography (CH_2Cl_2/MeOH, 17:3) the desired product (4.0 g, 88% yield), yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.2 (br.), 3.3 (br.), 6.3–7.8 (br., phenyl) ppm. GC–MS: m/z (%) = 432 (5) $[M]^+$, 309, 324 (t_r = 17.83 min).

General Procedure for the Synthesis of Substituted Triarylpropargyl Alcohol by the Copper-Free Sonogashira Protocol: $Pd(AcO)_2$ (5% molar ratio, see the Supporting Information for further details) and triphenylphosphane (2 equiv.) were dissolved in anhydrous CH_3CN [1 mL for every 2.5 mg of $Pd(AcO)_2$]. The yellow solution was stirred at room temp. under N_2. After 4–6 h the formation of the catalyst was complete and the solution turned bright red. Under N_2, finely ground K_3PO_4 (1.2 equiv.), triethylamine (3 equiv.) and the appropriate diphenylpropargyl alcohol were added. After 30 min, the appropriate haloarene (iodo-/bromobenzene or thiophene; 1,2 equiv.) was added. The solution was kept at room temp. whilst stirring for 12 h. Then the solvent was removed under reduced pressure and the crude product was purified by column chromatography (toluene, SiO_2).

To accelerate the formation of the catalyst an ultrasound bath (at room temp.) may be used. Indeed, the slow formation of the catalyst is mainly due to the poor solubility of $Pd(AcO)_2$ in CH_3CN and it occurs in a liquid/solid heterogeneous system. With this method we were able to prepare the catalyst in 1 h 30 min, instead of the 4–6 h required without ultrasound.

1,1,3-Triphenylprop-2-yn-1-ol (3a): 1,1-Diphenylpropargyl alcohol (114 mg (0.547 mmol) and iodobenzene (135 mg, 0.662 mmol) were added to the catalyst (3.4 mg, 0.015 mmol, 2.5% molar ratio) dissolved in anhydrous CH_3CN (1.5 mL). We obtained after column chromatography the desired product in a yield of 83%, white solid; m.p. 83 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.87 (s, 1 H), 7.27–7.68 (m) ppm. MS (EI): m/z (%) = 284 (100) $[M]^+$, 321 (29). IR (Nujol): $\tilde{\nu}$ = 3554 (OH), 3055 (aromatic C–H), 2222 (triple bond CC), 1596 (aromatic C–C) cm^{-1}.

1,1-Diphenyl-3-(thiophen-2-yl)prop-2-yn-1-ol (5a): 1,1-Diphenylpropargyl alcohol (120 mg, 0.577 mmol) and 2-bromothiophene (113 mg, 0.692 mmol) were added to the catalyst (14 mg, 0.06 mmol, 10% molar ratio) dissolved in anhydrous CH_3CN (5 mL). We obtained after column chromatography the desired product in a yield of 40%. The same product was obtained in a yield of 75% when using 2-iodothiophene with 2.5% of catalyst.

1,1,6,6-Tetraphenyl-2-hexen-4-yne-1,6-diol (7): White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.280 (s, 1 H), 2.77 (s, 1 H), 6.00–5.96 (d, J = 16 Hz, 1 H), 6.84–6.79 (d, J = 18 Hz, 1 H), 7.30–7.24 (m, 20 H) ppm. MS (EI): m/z (%) = 398 (100) $[M]^+$, 321 (29).

1,1,6,6-Tetraphenyl-2,4-hexadiyne-1,6-diol (9): White solid; m.p. 147 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.82 (s, 1 H), 7.56 (d, 1 H), 7.59–7.28 (m, 2 H), 7.59–7.28 (m, 2 H) ppm. IR (Nujol): $\tilde{\nu}$ = 3550 (OH), 3068 (aromatic C–H), 2149 (C≡C), 1596 (aromatic C–C).

General Procedure for the Synthesis of Substituted Tetraaryltetracenes. One-Pot Method: Under nitrogen the propargyl alcohol was dissolved in anhydrous CH_2Cl_2 and the solution was cooled to 0 °C. Anhydrous triethylamine and methanesulfonyl chloride were added to this solution and the mixture was stirred for 1 h at 0 °C and then warmed to room temperature. The reaction was then heated at reflux to distil off CH_2Cl_2, which was gradually replaced with xylene. Then the solution was heated; when the temperature reached 80 °C, collidine was added dropwise. The reaction temperature was raised to 95 °C and held at this temperature for 7 h. Then the reaction was allowed to cool to RT and the precipitate was collected by filtration.

5,6,11,12-Tetraphenyltetracene (Rubrene, 10a): We applied the general procedure using 1,1,3-triphenylprop-2-yn-1-ol (**3a**; 2.0 g, 7.0 mmol) dissolved in anhydrous CH_2Cl_2 (15 mL) with triethylamine (1.1 mL, 7.9 mmol), methanesulfonyl chloride (1.2 mL, 16 mmol) and 1 mL of collidine. The red solid was recrystallized from ethanol to afford the desired product (0.76 g, 40% yield). The identity of the compound was confirmed by comparison with a sample of commercial rubrene.

2,8-Difluoro-5,11-bis(4-fluorophenyl)-6,12-diphenyltetracene (10b): We applied the general procedure using 1,1-bis(4-fluorophenyl)-3-phenyl-2-propyn-1-ol (**3b**; 3.5 g, 11 mmol), triethylamine (2.0 mL, 14 mmol), methanesulfonyl chloride (1.5 mL, 19 mmol) and collidine (1 mL). The crude was first purified by column chromatography (SiO_2, petroleum ether/diethyl ether, 8:2). The product was further purified by crystallization from petroleum ether and by medium-pressure chromatography (petroleum ether/CH_2Cl_2, 8:2) to afford the product (0.92 g, 70% yield), red solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36 (d, J = 6 Hz, 1 H), 7.33 (d, J = 6 Hz, 1 H), 7.19 (d, J = 7 Hz, 1 H), 7.15 (d, J = 7 Hz, 2 H, phenyl), 6.93 (br., 1 H, phenyl), 6.85 (d, J = 7 Hz, 2 H, phenyl), 6.79 (d, J = 7 Hz, 2 H, fluorophenyl), 6.76 (d, J = 7 Hz, 2 H, fluorophenyl) ppm. HRMS (ESI): calcd. for $C_{42}H_{24}F_4$ $[M]^+$ 604.1814; found 604.1800. Single crystals of **10b** were grown from solution by dissolving **10b** (5 mg) in toluene (20 mL). The solution was filtered (size of the pores 0.2 μm), placed on the surface of water and kept in air during solvent evaporation. Crystals grew as needles. A single crystal suitable for X-ray diffraction was selected under crossed polarizations using an optical polarizing microscope Olympus SZX12.

3,4-Bis{bis[4-(diethylamino)phenyl]methylidene}-1,2-diphenylcyclobutene (12c): We applied the general procedure using 1,1-bis(4-diethylaminophenyl)-3-phenyl-2-propyn-1-ol (**3c**; 3.0 g, 6.9 mmol), triethylamine (1 mL, 7.4 mmol) and methanesulfonyl chloride (1.0 mL, 13 mmol) to afford after column chromatography (SiO_2, petroleum ether/diethyl, 8:2) the desired product (2.0 g, 69% yield), green solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86 (d, J = 8 Hz, 2 H, Ph-NEt_2), 7.75 (d, J = 9 Hz, 2 H, Ph-NEt_2), 7.32 (d, J = 8 Hz, 2 H, Ph-NEt_2), 7.08 (d, J = 9 Hz, 2 H, Ph-NEt_2), 6.85 (br., 1 H, phenyl), 6.63 (t, J = 9 Hz, 2 H, phenyl), 6.50 (d, J = 9 Hz, 2 H, phenyl), 3.41 (q, J = 7 Hz, 4 H, NCH_2CH_3), 3.33 (q, J = 8 Hz, 4 H, NCH_2CH_3), 1.19 (t, J = 7 Hz, 6 H, NCH_2CH_3), 1.13 (t, J = 7 Hz, 6 H, NCH_2CH_3) ppm. HRMS (ESI): calcd. for $C_{58}H_{66}N_4$ $[M]^+$ 818.5287; found 818.5310.

6,12-Diphenyl-5,11-dithienyltetracene (11a) and 3,4-Bis(diphenylmethylidene)-1,2-dithienyl-cyclobutene (13a): We applied the general procedure using 1,1-diphenyl-3-(thiophen-2-yl)prop-2-yn-1-ol (**5a**; 1.5 g, 5.1 mmol), triethylamine (1 mL, 7.5 mmol) and methanesulfonyl chloride (1.0 mL, 13 mmol) to afford after column chromatography (SiO_2, petroleum ether/diethyl ether, 8:2) a mixture of **11a** and **13a**, which were separated by repeated crystallization from petroleum ether (in which **13a** is less soluble) and then further purified by medium-pressure chromatography (petroleum ether/CH_2Cl_2, 8:2) to afford pure samples of **11a** and **13a** (25 and 8% yields).

11a: Red solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57 (d, J = 9 Hz, 1 H), 7.40 (d, J = 9 Hz, 1 H), 7.20–7.12 (br., 2 H), 7.06 (d, J = 7 Hz, 1 H, phenyl), 6.95 (d, J = 8 Hz, 2 H, phenyl), 6.74 (t, J = 7 Hz, 2 H, phenyl), 6.80 (d, J = 5 Hz, 1 H, thienyl), 6.60 (t, J = 4 Hz, 1 H, thienyl), 6.01 (d, J = 4 Hz, 1 H, thienyl) ppm. HRMS (ESI): calcd. for 544.1295 $[M]^+$. $C_{38}H_{24}S_2$ requires 544.1320.

13a: Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40 (dd, J_1 = 8, J_2 = 2 Hz, 2 H), 7.36 (dd, J_1 = 8, J_2 = 2 Hz, 2 H), 7.04 (br., 1 H), 6.95 (br., 1 H), 6.81 (t, J = 7 Hz, 2 H), 6.74 (t, J = 7 Hz, 2 H), 6.63 (d, J = 5 Hz, 1 H, thienyl), 6.60 (d, J = 5 Hz, 1 H, thienyl), 6.01 (d, J = 5 Hz, 1 H, thienyl) ppm. HRMS (ESI): calcd. for $C_{38}H_{26}S_2$ $[M]^+$ 546.1476; found 546.1474.

2,8-Difluoro-5,11-bis(4-fluorophenyl)-6,12-dithienyltetracene (11b) and 3,4-Bis[bis(4-fluorophenyl)methylidene]-1,2-dithienylcyclobutene (13b): We applied the general procedure using 1,1-bis(4-fluorophenyl)-3-thienylprop-2-yn-1-ol (**5b**; 2.7 g, 8.2 mmol) with triethylamine (1.8 mL, 13 mmol) and methanesulfonyl chloride (1.3 mL, 17 mmol). The crude was first purified by column chromatography (petroleum ether/diethyl ether, 8:2) to afford 1.78 g of a mixture of **11b** and **13b**, which were separated by repeated crystallization from petroleum ether (in which **13b** is less soluble) and then further purified by medium-pressure chromatography (petroleum ether/CH_2Cl_2, 8:2) to afford pure samples of **11b** and **13b** (68 and 3% yields). Single crystals of **13b** were grown by using the horizontal physical vapour transport growth technique. The source, containing the powder, was heated to 220 °C in a furnace under a stream of argon. Single crystals of **13b** nucleated on the wall of the glass tube in the colder zone of the furnace and grew as elongated flat red needles.

11b: Red solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63 (d, J = 8 Hz, 1 H), 7.39 (br., 2 H), 7.13 (d, J = 9 Hz, 2 H), 7.02 (d, J = 9 Hz, 1 H), 6.90 (d, J = 9 Hz, 1 H), 6.75 (d, J = 6 Hz, 1 H, thienyl), 6.73 (d, J = 5 Hz, 1 H, thienyl), 6.46 (br., 1 H, thienyl) ppm. HRMS (ESI): calcd. for $C_{38}H_{20}S_2F_4$ $[M]^+$ 616.0943; found 616.0968.

13b: Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.14 (d, J = 5 Hz, 1 H, thienyl), 7.00 (dd, J_1 = 7, J_2 = 3 Hz, 2 H), 6.89 (dd, J_1 = 8, J_2 = 3 Hz, 2 H), 6.76 (t, J = 9 Hz, 2 H), 6.68 (d, J = 4 Hz, 1 H, thienyl), 6.51 (t, J = 9 Hz, 2 H), 6.11 (d, J = 5 Hz, 1 H, thienyl) ppm. HRMS (ESI): calcd. for $C_{38}H_{22}S_2F_4$ $[M]^+$ 618.1099; found 618.1107.

3,4-Bis{bis[4-(diethylamino)phenyl]methylidene}-1,2-dithienylcyclobutene (13c): We applied the general procedure using 1,1-bis[4-(diethylamino)phenyl]-3-thienylprop-2-yn-1-ol (**5c**; 3.0 g, 6.9 mmol), triethylamine (1.5 mL, 11 mmol) and methanesulfonyl chloride (1.2 mL, 15 mmol) to obtain after column chromatography (SiO_2, acetone/methanol, 17:3) the desired product (1.33 g, 46% yield), dark-green solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (d, J = 9 Hz, 2 H), 7.62 (d, J = 9 Hz, 2 H), 6.65 (d, J = 10 Hz, 2 H), 6.60 (d, J = 10 Hz, 2 H), 6.28 (d, J = 6 Hz, 1 H, thienyl), 6.22 (d, J = 6 Hz, 1 H, thienyl), 6.00 (d, J = 6 Hz, 1 H, thienyl) ppm. HRMS (ESI): calcd. for $C_{54}H_{62}N_2S_2$ $[M]^+$ 830.4416; found 830.4408.

General Procedure for the Synthesis of Substituted Tetraaryltetracenes. The Chloroallene Method

Method A. Synthesis of Chloroallene: Under nitrogen, 1,1,3-triphenylprop-2-yn-1-ol (**3a**; 0.76 g, 2.6 mmol) was dissolved in anhydrous CH_2Cl_2 (20 mL) and the solution was cooled to 0 °C. Triethylamine (0.4 mL) and methanesulfonyl chloride (0.21 mL) were added to this solution and the mixture was stirred for 1 h in 0 °C and then warmed to room temperature. Then the solution was washed with water and the dichloromethane was removed under vacuum at room temp. to avoid any degradation of the product. The crude product was subjected to silica gel column chromatography (petroleum ether/diethyl ether, 9:1) to give 1-chloro-1,1,3-triphenylallene (0.34 g, 42% yield, m.p. 70–71 °C).

Method B. Transformation of Chloroallene into Tetraaryltetracene: Under nitrogen, 1-chloro-1,1,3-triphenylallene (1.2 g) was dissolved in xylene (15 mL) and then heated for 1 h at 150 °C. Then the xylene was removed under vacuum. The red solid was recrystallized from ethanol to afford the desired product (1.27 g, 60% yield). High-performance liquid chromatography (HPLC)/diode array detector was used to check the purity of the recrystallized product. The HPLC chromatogram of commercial rubrene (Aldrich, 98%) shows a peak at around 26 min corresponding to rubrene and a small peak at 27 min corresponding to a degradation product. The HPLC of the synthesized rubrene shows one peak at 26 min and an impurity at 10 min (see the Supporting Information).

X-ray Measurements for 7, 10b and 13b: The crystal dimensions, crystal system, space group, unit cell dimensions, volume, $\rho_{calcd.}$, $2\theta_{max}$, radiation, wavelength, scan mode, temperature of measurement, numbers of measured and independent reflections, number of reflections included in the refinement, σ limits, whether and how Lorentzian polarization and absorption corrections were performed (μ, min./max. transmission), method of structure solution and program, method of refinement and program, number of parameters, treatment of H atoms, R, wR, whether refined against $|F|$ or $|F^2|$, residual electron density are reported elsewhere.

CCDC-812726 (for **10b**), -812727 (for **7**) and -812728 (for **13b**) 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.

Supporting Information (see footnote on the first page of this article): Optimization of the Sonogashira coupling, HPLC data for compound **1**, resonance structures of the radical and carbocation formed during the loss of Cl_2 from **E** to form **F**.

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