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The Intricate Assembling of *gem*-Diphenylpropargylic Units

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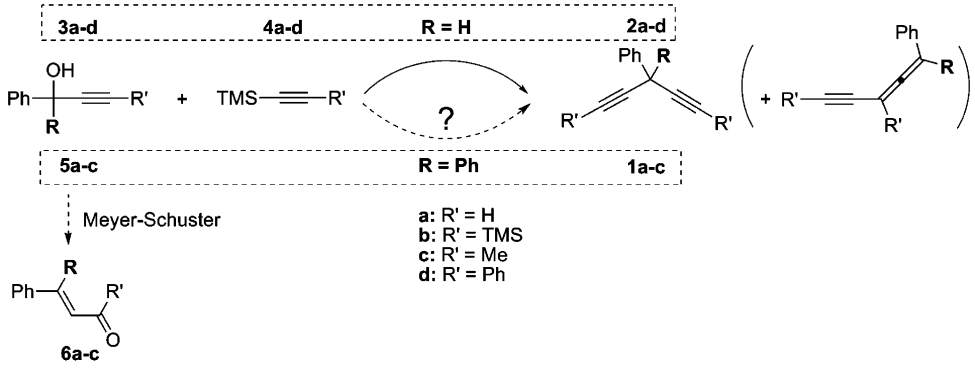
While optimized procedures for selective propargylic – versus allenic – attack (in particular by alkynylsilanes) have proven to be compatible with many substitution patterns at the propargylic center, the case of diarylpropargyl electrophiles has remained problematic. The intrinsic reactivity of 1,1-diphenylpropargylic alcohols [R–C≡C–C(Ph_2)OH (R = TMS, H, Me)] in the presence of various acids (and in the absence of additional nucleophile) has thus been systematically investigated. Whereas the monophenyl analogues [R–C≡C–CH(Ph)OH] afford the expected bis(phenylpropargyl) ethers, the diphenyl versions undergo complex but quite selective processes to afford various structural types: depending on the acid used, a diallene, an allenyne, an indenylallene, an indanone or a condensed tetra- and pentacycles were obtained. When the reactions were conducted in the presence of an alkynylsilane capable of playing the role of a competing nucleophile, the expected propargylic substitution products – dialkynyldiphenylmethanes or their isomers – were never observed. The hitherto unknown simple hydrocarbons diethynyl- and dipropynyl-diphenylmethane could, however, be obtained in low yields through a four-step sequence involving allenylidene- and alkynylruthenium intermediates.

Introduction

Despite the increasing wealth of acetylene chemistry,[1] a number of simple acetylenic molecules remain unknown. As recently emphasized, no example of a dialkynylamine has ever been described in the literature.[2] Even more paradoxical is the paucity of references on a certain class of quaternary dialkynylmethane hydrocarbons ($R'–C≡C)_2$-CR_2 – to the best of our knowledge, while examples have been provided for R = alkyl[3] or alkynyl,[4] the case of R = aryl has not been observed. In particular, the diphenyl derivative **1a**, a "trivial" $C_{17}H_{12}$ hydrocarbon, has not been reported. The simplest retrosynthetic pathway to **1a** is based on a propargylic substitution of a diphenylpropargyl alcohol derivative by an acetylide equivalent. While unsubstituted –C≡C–CH_2–X propargylic centers may undergo selective S_N2 attack (vs. $S_N'2$) by alkynyl metals (in particular copper acetylides), substituted –C≡C–$CR^1(R^2)$–X propargylic centers require S_N1 processes, and thus the use of Lewis acid additives.[5] Despite the remaining propargylic/allenic ambivalence ($S_N1/S_N'1$) revealing the versatile charge delocalization in the alkynylcarbenium intermediate,[6] procedures favoring propargylic attack have been



Scheme 1. Propargylic substitution of phenylpropargylic alcohols by alkynylsilanes: one known result (**2d**) in the monophenyl series (*top*), and challenges in the diphenyl series (*bottom*).

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claimed to be efficient, especially with allyl or aryl nucleophiles.[7] With the goal of controlling the regioselectivity, many efforts have also been based on precomplexation of the triple bond[8] or propargylic substituents[9] to transition metal fragments. Nevertheless, the intrinsic "organic" behavior of propargylic cations still deserves investigation.

Very recently, Kuninobu and Takai reported that use of the specific Lewis acid $[ReBr(CO)_3(THF)]_2$ allows for the efficient preparation of **2d** from the monophenyl propargylic alcohol **3d** and trimethylsilylphenylacetylene **4d** (Scheme 1).[10] In our efforts to synthesize quaternary 1,4-diynes, application of the Kuninobu–Takai method to the *di*phenyl propargylic substrate **5c** with trimethylsilylpropyne **4c** failed to produce diphenyldipropynylmethane (**1c**), but afforded enone **6c**, resulting from a Meyer–Schuster rearrangement of **5c**.[11] With bis(trimethylsilyl)acetylene (**4b**) as a more nucleophilic alkyne, the same substrate **5c** afforded a mixture of unidentified products.

In the light of these results, the versatile reaction behavior of the diphenylpropargylic alcohols **5a**–**c** in the presence of various Lewis acids was systematically investigated, and compared with that of the corresponding monophenylpropargylic alcohols **3a**–**c**. The full results are reported and discussed here.

1. Results

1.1. Reactivity of Mono- and Diphenylpropargylic Alcohols in the Presence of Brønsted Acids

Simple organic acids such as *p*-toluenesulfonic acid (PTSA) were recently found to catalyze the substitution of the hydroxy groups of propargylic alcohols by heteroatom- and carbon-centered nucleophiles (allyltrimethylsilane, electron-rich aromatics or heteroaromatics).[7c] This was studied, however, only with secondary *mono*arylpropargylic substrates. Application of this method to electrophile **3b** with bis(trimethylsilyl)acetylene (**4b**) as nucleophile led almost quantitatively to the bispropargylic ether **7b**, as a mixture of diastereoisomers. The same result could be obtained in the absence of **4b** (Scheme 2). Treatment of **7b** with K_2CO_3/MeOH quantitatively gave the corresponding silyl-free ether **7a** as a mixture of diastereoisomers (Scheme 2). Very recently, a preparation of **7a** from the propargylic alcohol **3a** through the use of a catalytic ruthenium complex was reported to occur in moderate yield.[12] The method proved to be quite general, affording various bispropargylic ethers, symmetrical or not, from the corresponding primary or secondary propargylic alcohols. Such self-condensation processes had previously been observed, albeit as side reactions in the etherification of terminal propargylic alcohols with various other alcohols.[7a]

When treated under similar conditions (catalytic PTSA in acetonitrile at reflux for 1 h), the diphenylpropargylic tertiary alcohol **5b** reacted in a completely different manner, leading to the allenyne **8** and indanone **9** in 20 and 51% yields, respectively (Scheme 3).

When carried out at room temperature, the reaction became more selective in the formation of the indanone **9** (62% isolated yield), while only small amounts of **8** were obtained. The allenyne structure of **8** could, however, be

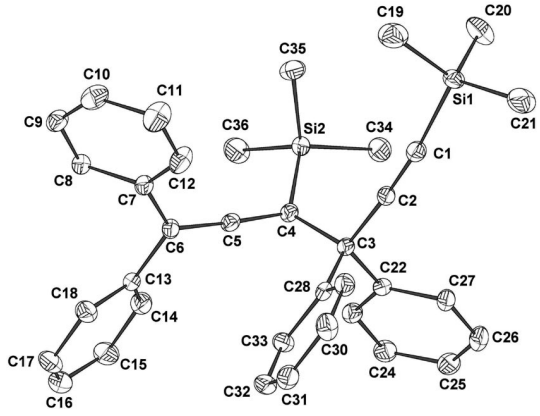
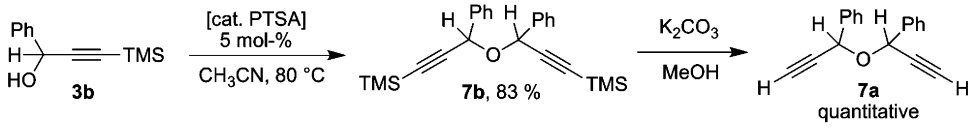
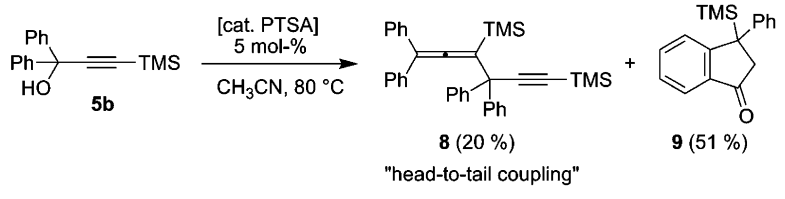


Figure 1. ORTEP diagram of the X-ray crystal structure of the head-to-tail allenyne coupling product **8** ($R = 0.061$). Selected bond lengths (in Å): Si(1)–C(1) 1.838(3), C(1)–C(2) 1.212(4), C(2)–C(3) 1.472(4), C(3)–C(4) 1.550(4), C(4)–C(5) 1.312(4), C(5)–C(6) 1.319(4), C(4)–Si(2) 1.900(3), C(6)–C(7) 1.480(5), C(6)–C(13) 1.498(4). Selected bond angles (in degrees): Si(1)–C(1)–C(2) 173.5(3), C(1)–C(2)–C(3) 176.2(3), C(2)–C(3)–C(4) 105.7(2), C(3)–C(4)–C(5) 121.6(3), C(4)–C(5)–C(6) 176.7(3).



Scheme 2. High-yield synthesis of the bispropargylic ethers **7b** and **7a**.

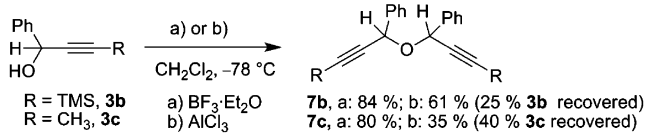


Scheme 3. Reactivity of diphenylpropargylic alcohol **5b** with a Brønsted acid.

confirmed by an X-ray diffraction analysis of monocrystals deposited from a diluted ethyl acetate/heptane solution (Figure 1).

1.2. Reactivity of Mono- and Diphenylpropargylic Alcohols in the Presence of Group 13 Lewis Acids (BF_3, $AlCl_3$)

The monoarylpropargylic alcohols **3b** and **3c** were first treated with stoichiometric amounts of two group 13 Lewis acids: as previously observed with PTSA, the bis-propargylic ethers **7b** and **7c** were formed (Scheme 4). The yields were generally higher with $BF_3{\cdot}Et_2O$ than with $AlCl_3$, in the presence of which the unreacted propargylic alcohols **3b** and **3c** were retrieved from the reaction mixture.



Scheme 4. Reactivity of the secondary propargylic alcohols **3b**–**c** with group 13 Lewis acids.

The coupling products were obtained as mixtures of diastereoisomers, but in the case of **7c** bearing two terminal methyl groups, their resolution could be achieved by simple chromatography on silica gel.

The behavior of diphenylpropargylic alcohols **5a**–**c** in the presence of the same Lewis acids was found to be much more varied. Compound **5a** was studied first, but gave only polymeric materials. In the case of **5b**, two different original products were obtained with the two Lewis acids. The use of $BF_3{\cdot}Et_2O$ mainly afforded the conjugated diallene **10**, the result of a tail-to-tail reductive dimerization of **5b**. Several attempts to resolve the X-ray diffraction structure of **10** failed to give satisfactory results. In contrast, and unexpectedly, the use of $AlCl_3$ led to the chlorinated bicyclic indene derivative **11** (Scheme 5).

The structure of **11** was confirmed by X-ray diffraction analysis (Figure 2). In the sterically congested chloroindenylallene structure of **11** the allene axis is orthogonal to the indenyl plane with a quite long indenyl–allene bond (ca. 1.49 Å) and the TMS groups in *anti* position.

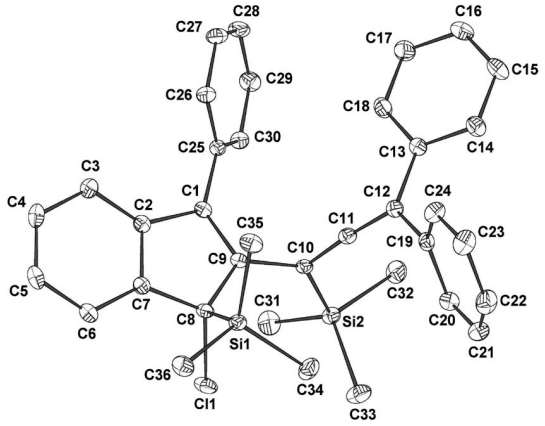
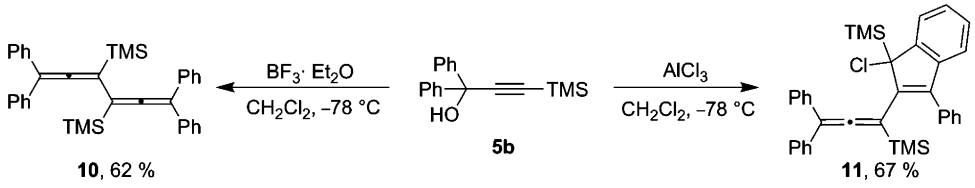
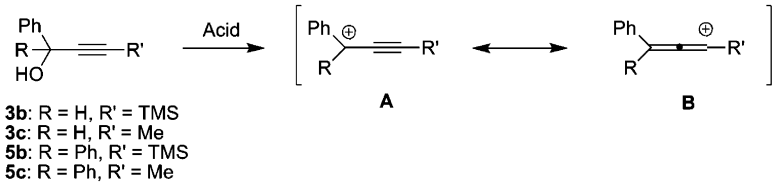


Figure 2. ORTEP diagram of the X-ray crystal structure of chloroindenylallene **11** (R = 0.031). Selected bond lengths (in Å): C(1)–C(2) 1.472(3), C(2)–C(7) 1.394(3), C(7)–C(8) 1.494(3), C(8)–C(9) 1.513(3), C(1)–C(9) 1.350(3), C(9)–C(10) 1.492(3), C(10)–C(11) 1.304(3), C(11)–C(12) 1.323(3), C(10)–Si(2) 1.909(2), C(8)–Cl(1) 1.8144(19), C(8)–Si(1) 1.930(2). Selected bond angles (in degrees): C(1)–C(2)–C(3) 131.38(18), C(1)–C(2)–C(7) 108.39(17), C(2)–C(7)–C(8) 108.59(16), C(1)–C(9)–C(8) 109.57(17), C(1)–C(9)–C(10) 127.39(17), C(9)–C(10)–C(11) 121.55(17), C(10)–C(11)–C(12) 174.9(2).

These results require detailed mechanistic interpretation (see Section 2.1), but one may assume a priori that they rely on the reactivity of the carbocations of **3b** and **3c** and **5b** and **5c** (Scheme 6). While the formation of ethers **7b** and **7c** reveals the contribution of the propargylic form **A** for the *mono*phenyl substrates **3b** and **3c**, the formation of **10**–**11** reveals the contribution of the allenyl form **B** for the *di*-phenyl substrates **5b** and **5c**.

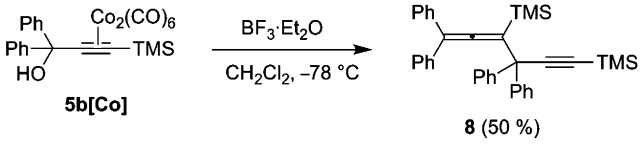


Scheme 5. Original reactivity of **5b** in the presence of Lewis acids.



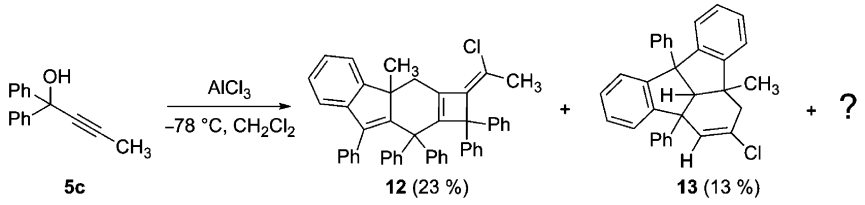
Scheme 6. Canonical structures of propargylic cations generated from mono- and diphenylpropargylic alcohols **3b** and **3c** and **5b** and **5c**.

In an attempt to "stabilize" the mesomeric form **A** of the cation of **5b**, and thus preserve the triple bond in a Nicholas cation,[8] the cobalt complex **5b[Co]** was prepared before treatment with $BF_3{\cdot}Et_2O$. The main product, however, was the allenyne **8** previously obtained by direct treatment of **5b** with Brønsted acids (Section 1.1, Scheme 3). The formation of the Ph_2C–C(TMS) bond thus suggests that partial decomplexation occurred before reductive head-to-tail coupling (Scheme 7).



Scheme 7. Reaction of the cobalt complex **5b[Co]** in the presence of boron trifluoride.

The case of the propynyl-diphenyl derivative **5c** was then studied. In the presence of $AlCl_3$, the chloroindenylallene derivative equivalent to **11** was not observed in the NMR spectrum of the crude material. Purification of this crude material proved to be awkward, but preliminary chromatography afforded a fraction containing three main products, corresponding to a weighted yield of approximately 70% with respect to **5c**. Two of the components – **12** and **13** – could be separated by successive crystallizations, while the third remained unidentified (Scheme 8). The first selective crystallization from dichloromethane thus afforded monocrystals of **12** (23% yield), and X-ray diffraction analysis allowed for the assignment of its condensed tetracyclic structure (Figure 3). Evaporation of the mother liquor and subsequent crystallization from diethyl ether afforded a 13% yield of **13**, a monocrystal of which allowed for the assignment of its condensed pentacyclic structure by X-ray diffraction analysis (Figure 3). Products **12** and **13** thus each contain a chlorine atom (abstracted from $AlCl_3$), and correspond to trimeric and dimeric derivatives of **5c**, respectively. It is noteworthy that they were both formed as single diastereoisomers (out of two for **12** and eight for **13**). Their fascinating structures also indicate that one or two phenyl *o*-carbon atoms and one propynyl methyl group of **5c** have



Scheme 8. Reaction of **5c** with $AlCl_3$.

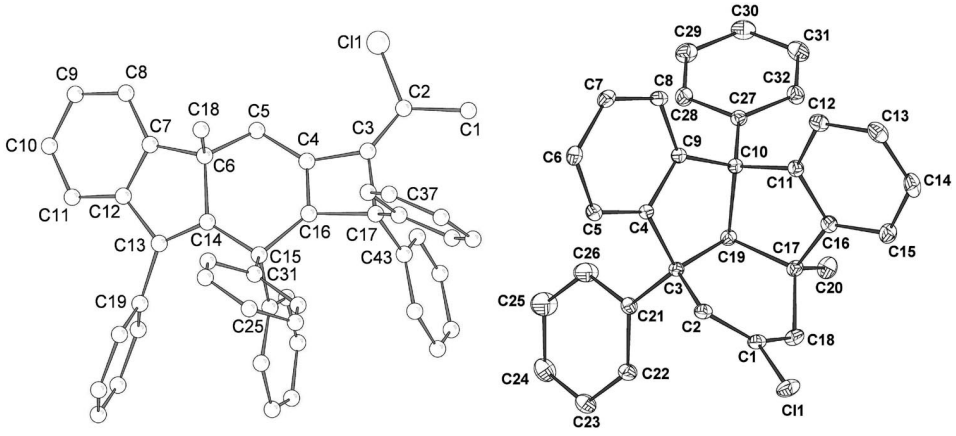


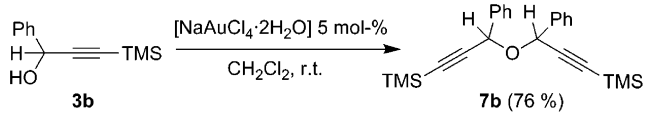
Figure 3. ORTEP diagram of the X-ray crystal structures of the polycyclic derivatives **12** (*left*, R = 0.052) and **13** (*right*, R = 0.042). Selected bond lengths of **12** (in Å): C(1)–C(2) 1.538(7), C(2)–Cl(1) 1.735(5), C(2)–C(3) 1.460(7), C(4)–C(5) 1.477(7), C(4)–C(16) 1.321(7), C(3)–C(17) 1.560(7), C(16)–C(17) 1.580(7), C(5)–C(6) 1.535(7), C(6)–C(7) 1.503(7), C(7)–C(12) 1.384(7), C(12)–C(13) 1.471(7), C(13)–C(14) 1.355(7), C(14)–C(15) 1.519(7), C(15)–C(16) 1.522(7), C(6)–C(14) 1.539(7), C(6)–C(18) 1.531(7). Selected bond angles (in degrees): C(1)–C(2)–C(3) 126.2(5), C(2)–C(3)–C(4) 137.6(5), C(4)–C(3)–C(17) 89.8(4), C(3)–C(4)–C(16) 94.5(5), C(3)–C(17)–C(16) 81.3(4), C(5)–C(4)–C(16) 127.7(5), C(4)–C(16)–C(15) 126.5(5), C(4)–C(5)–C(6) 106.7(4), C(14)–C(15)–C(16) 105.5(4), C(5)–C(6)–C(14) 110.7(4), C(5)–C(6)–C(7) 113.1(5), C(13)–C(14)–C(15) 128.0(5), C(6)–C(7)–C(12) 110.3(5), C(7)–C(12)–C(13) 108.1(5), C(12)–C(13)–C(14) 110.0(4), C(6)–C(7)–C(8) 118.9(6), C(11)–C(12)–C(13) 130.7(5). Selected bond lengths of **13** (in Å): Cl(1)–C(1) 1.7442(13), C(1)–C(2) 1.3199(19), C(2)–C(3) 1.5174(17), C(3)–C(4) 1.5232(17), C(4)–C(9) 1.3870(17), C(9)–C(10) 1.5105(17), C(10)–C(11) 1.5211(17), C(11)–C(16) 1.3895(18), C(16)–C(17) 1.5143(18), C(17)–C(18) 1.5323(19), C(18)–C(1) 1.492(2), C(3)–C(19) 1.5844(18), C(10)–C(19) 1.5793(17), C(17)–C(19) 1.5620(18). Selected bond angles of **13** (in degrees): Cl(1)–C(1)–C(2) 120.78(11), C(1)–C(2)–C(3) 121.61(12), C(2)–C(3)–C(4) 107.16(10), C(3)–C(4)–C(9) 112.42(11), C(4)–C(9)–C(10) 111.91(11), C(9)–C(10)–C(11) 112.15(10), C(10)–C(11)–C(16) 111.22(11), C(11)–C(16)–C(17) 112.63(11), C(16)–C(17)–C(18) 111.45(11), C(17)–C(18)–C(1) 110.51(10), C(18)–C(1)–C(2) 122.35(12), C(2)–C(3)–C(19) 113.00(10), C(4)–C(3)–C(19) 103.23(9), C(9)–C(10)–C(19) 104.19(10), C(11)–C(10)–C(19) 102.17(9), C(16)–C(17)–C(19) 102.45(10), C(18)–C(17)–C(19) 113.23(11), C(3)–C(19)–C(10) 106.30(9), C(3)–C(19)–C(17) 116.23(10).

been activated in five-membered and six-membered ring closures, respectively. It is worth mentioning that related transformations of 1-chloro-1,1,3-triphenylpropyne into rubrene polycyclic derivatives were reported at the beginning of the last century.[13] Mechanistic issues are discussed in Section 2.1.

1.3. Reactivity of Mono- and Diphenylpropargylic Alcohols in the Presence of a Gold Complex ($NaAuCl_4 \cdot 2H_2O$)

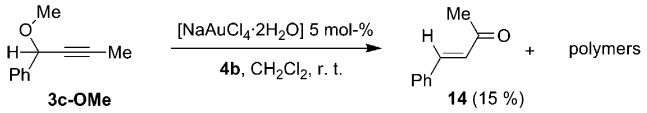
A few examples of propargylic substitution catalyzed by transition metal complexes have been reported in the recent literature, especially with ruthenium[12] and gold[7a] complexes. These complexes are reported to be versatile reagents, giving substitution products from secondary propargylic alcohols, and Meyer–Schuster rearrangement products from tertiary homologues.[14]

The *mono*phenyl propargylic alcohol **3b** was first treated in dichloromethane solution with a catalytic amount (5 mol-%) of the commercially available $NaAuCl_4 \cdot 2H_2O$ in the presence of bis(trimethylsilyl)acetylene (**4b**). Only the previously described dipropargyl ether **7b** was obtained: once again, the acetylenic nucleophile does not intervene in the reaction, and the same product was obtained in the absence of **4b** (Scheme 9).



Scheme 9. Synthesis of the bis-propargylic ether **7b** in the presence of a catalytic amount of a gold complex.

All conditions tested with secondary propargylic alcohols **3b** and **3c** afforded the corresponding bis-propargylic ethers **7b** and **7c**. In order to prevent the formation of **7b** and to force the reaction with **4b** to take place at the propargylic position, substrates with ether-locked oxy groups were investigated. Reactions of **3c-OMe** in the presence of either $NaAuCl_4 \cdot 2H_2O$ or $BF_3 \cdot Et_2O$ gave undetermined polymeric products. With the gold complex, however, the Meyer–Schuster-type product **14** was obtained in ca. 15% yield, along with a ca. 30% yield of unreacted **3c-OMe**, which was recovered by chromatography (Scheme 10).



Scheme 10. Reactivity of propargylic ether **3c-OMe** in the presence of $NaAuCl_4 \cdot 2H_2O$ and bis(trimethylsilyl)acetylene (**4b**).

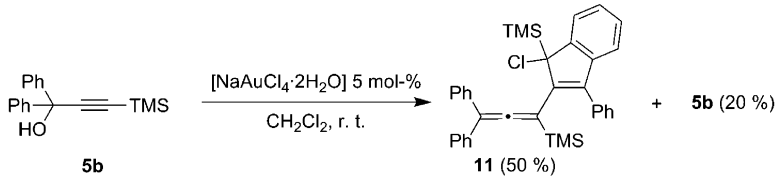
Under the same conditions, the *diphenyl*propargylic alcohol **5b** gave the indenylallene derivative **11** described above in moderate yield (Scheme 11). It is worth noting here that the synthesis of indene derivatives from phenylpropargylic acetates has previously been reported to be promoted by cationic gold complexes, via an intramolecular hydroarylation process.[15] A very recent review dealing with gold-catalyzed syntheses of hetero- and carbocycles from alkynes, allenes, and alkenes emphasized the general propensity of gold salts to promote cyclization reactions.[16] Such cycloisomerizations were reported, however, only with *mono*phenyl propargylic substrates: the case of *diphenyl* derivatives such as **5b** is unprecedented.

2. Discussion

The remarkable specificity, selectivity, and complexity of acid-catalyzed iso-/di-/trimerization processes of diphenylpropargylic alcohols require mechanistic interpretation. Under all the acidic conditions tested in the presence of bis(trimethylsilyl)acetylene, however, the initially targeted dialkynyldiphenylmethanes escaped observation: in order to rule out any intrinsic instability of the hitherto unknown targets, and thus to provide further support for the proposed mechanisms, the existence of dialkynyl- and dipropynyldiphenylmethanes needs to be verified by their preparation under alternative conditions.

2.1. Mechanisms

The described reactions can be classified into two main categories: i) isohypsic reactions (leading to enones **6a**–**c** and **14**, ethers **7a**–**c**, indanone **9**, allenylindene **11**, condensed polycycles **12** and **13**), and ii) reductive homocoupling reactions (leading to allenyne **8** and diallene **10**). In the



Scheme 11. Gold-catalyzed synthesis of indenylallene **11** from a *diphenyl*propargylic substrate.

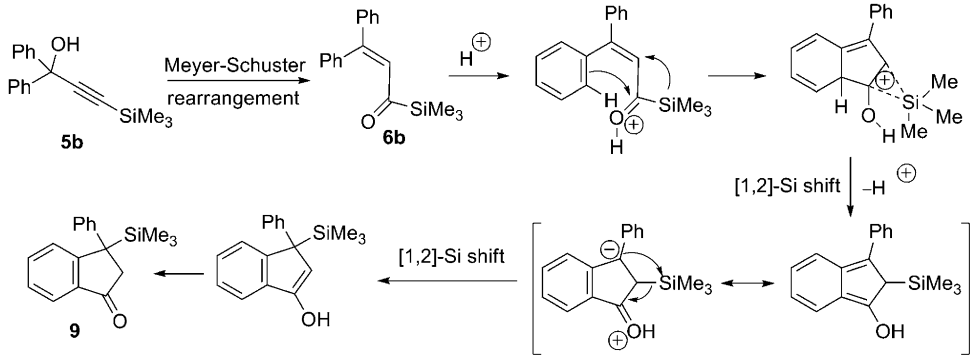
monophenylpropargylic series, the ethers **7a**–**c** were the sole products resulting from a trivial intermolecular dehydration. In the diphenylpropargylic series, the absence of ether products analogous to **7b** can be simply explained by the higher steric demand of the diphenylpropargylic center and by a lower reactivity of the corresponding carbocation. Several alternative evolutions were observed.

The formation of indanone **9** involves an unusual migration of the silyl group (Scheme 12). In 2005, the synthesis of indanones from propargylic alcohols through rhodium-catalyzed processes under basic conditions was reported simultaneously by Iwasawa[17] and Hayashi.[18] This method was limited, however, to the case of secondary propargylic alcohols, and was implicitly predicted not to be applicable to the tertiary version **5b**. Indeed, according to the proposed mechanism,[19] the basic conditions would lead to an intermediate rhodium alkoxide that would undergo a β-H elimination to afford an alkynyl ketone complex [–C≡C–CH(Ar)–O–Rh→–C≡C–C(Ar)=O→Rh–H]. The acidic conditions and the absence of a propargylic hydrogen in **5b** here call for a different mechanistic scheme. The first step would thus consist of the isomerization of **5b** to the α,β-unsaturated acylsilane **6b**.[14] The propensity of tertiary propargylic alcohols to undergo analogous Meyer–Schuster rearrangements under PTSA catalytic conditions has indeed recently been emphasized.[20] After protonation of the carbonyl group, the five-membered ring would be formed by an intramolecular S_EAr reaction. Finally, instead of a direct 1,3-shift of the TMS group to afford the silylindanone **9**, the possibility of two successive 1,2-shifts is supported by literature data.[21]

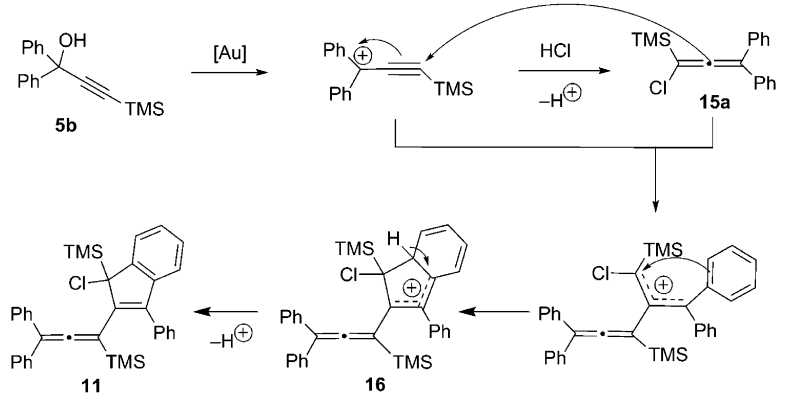
When the same substrate **5b** was treated with $NaAuCl_4 \cdot 2H_2O$, the indenylallene **11** consisting of two units of **5b** was obtained as the major product. The dimerization process can be explained by the mechanism described in Scheme 13. After formation of the carbocation (likely coordinated to gold) and partial chlorination to afford the allenic intermediate **15a**, subsequent C–C coupling would lead to an allylic cation, which would readily give the bicyclic intermediate **16** by an intramolecular S_EAr reaction. Deprotonation would finally give the isolated indenylallene **11**.

The formation of the condensed tetracyclic trimerization derivative **12** observed when **5c** was treated with $AlCl_3$ can be explained in terms of tandem [2+2] and [4+2] cycloadditions, followed by intramolecular hydroarylation of the terminal *exo* double bond of the putative intermediate **18** (Scheme 14).

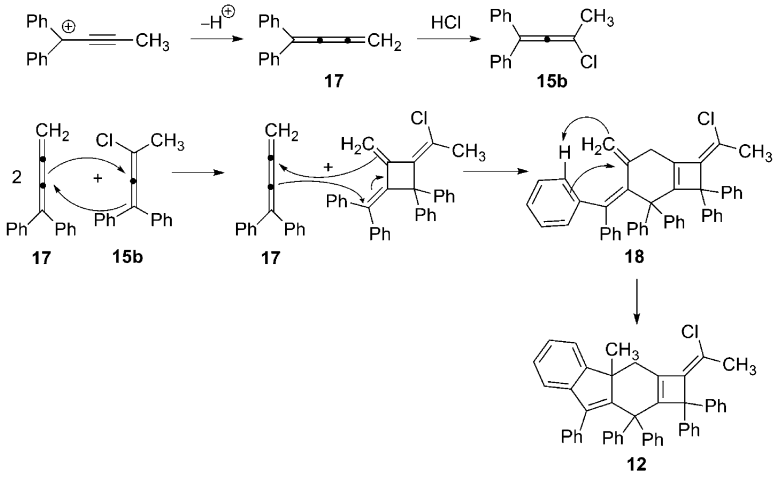
The fused pentacyclic dimerization derivative **13**, isolated from the same reaction mixture starting from **5c** and $AlCl_3$, is presumably formed by a different mechanism. In a possible sequence (Scheme 15), after addition of the triple bond of **5c** onto the corresponding propargylic carbocation, an intramolecular Friedel–Crafts attack of a neighboring



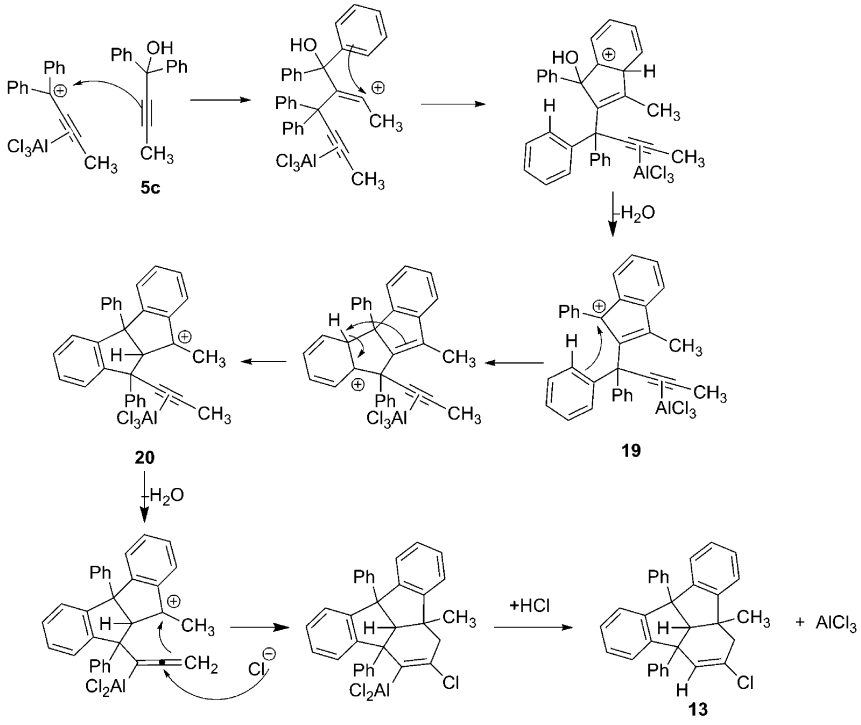
Scheme 12. Proposed mechanism for the formation of the silylindanone **9** from **5b** in the presence of PTSA.



Scheme 13. Proposed mechanism for the formation of the indenylallene **11** in the presence of $NaAuCl_4 \cdot 2H_2O$.



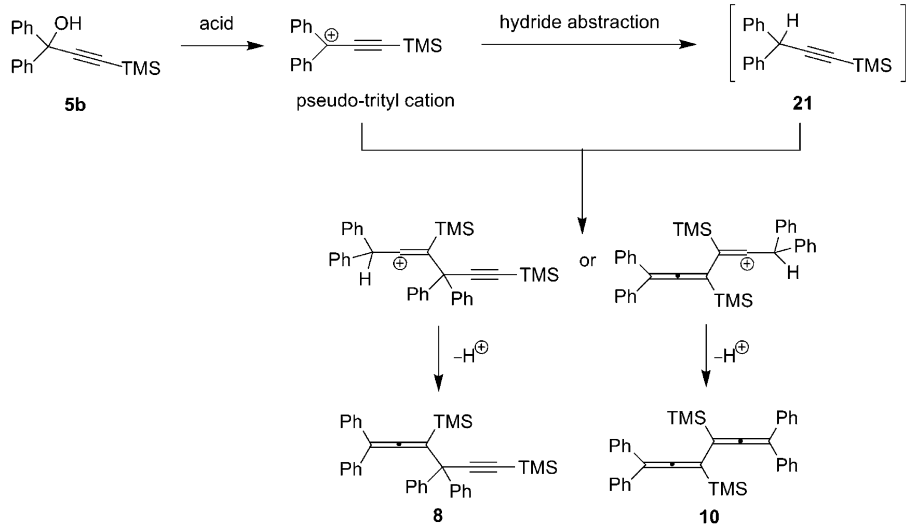
Scheme 14. Proposed mechanism for the formation of the trimeric tetracycle **12** in the presence of $AlCl_3$.



Scheme 15. One possible mechanistic sequence for the formation of the condensed pentacycle **13**. The transformation [propynyl·$AlCl_3$]→[allenyldichloroaluminium] is arbitrarily depicted as occurring at the sixth step (from **20**), but may of course take place at any stage.

phenyl ring, followed by a dehydration, would lead to the indenyl cation **19**. Subsequent intramolecular hydroarylation of **19** should then afford the indanyl cation **20**. At any stage, the aluminium-propynyl complex (hitherto assumed to be present) is equivalent to an allenyl dichloroaluminium moiety after HCl elimination. Internal attack of the allene by a chloride ion could finally trigger the closure of the last ring to give the pentacycle **13** after hydrochloric acidolysis of the C–Al bond.

Reductive homocoupling was observed solely from the silylated diphenylpropargylic alcohol **5b**, but under various sets of conditions [PTSA/CH_3CN, $Et_2O{\cdot}BF_3/CH_2Cl_2$, with or without preliminary η^2 complexation to $Co_2(CO)_6$]. Coupling of propargylic alcohols or acetates to allenynes has previously been reported to be induced by stoichiometric amounts of low-valent titanium complexes, likely through a radical mechanism.[22] In the absence of any metal additive, the reducing agent allowing for the formation of allenyne **8** and diallene **10** here is "concealed" in the reaction medium, and is likely activated by the hydride abstractor character of the "pseudo-trityl" diaryl(silylethynyl) carbocation of **5b**. Although the actual hydride donor could not be determined,[23] a generic mechanistic scheme can be based on the nucleophilic attack of the cation of **5b**



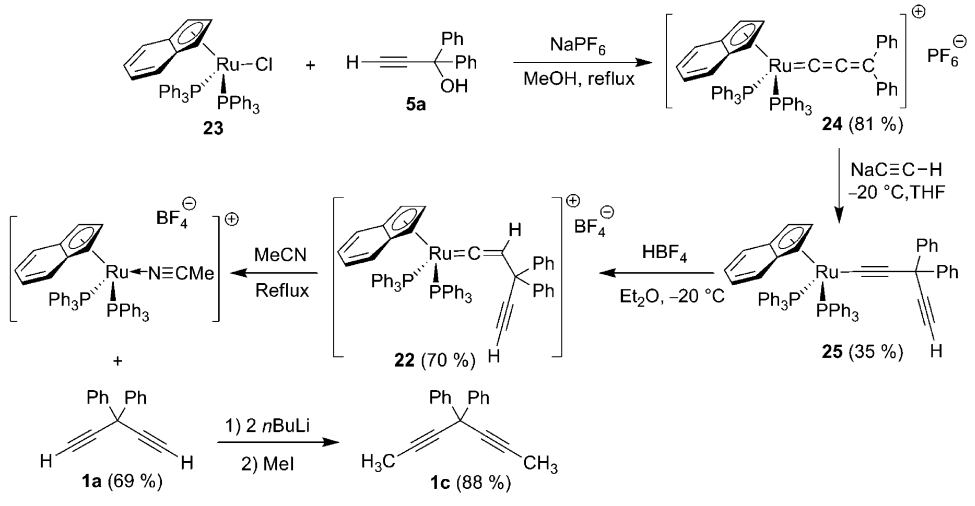
Scheme 16. Proposed mechanistic principle for the reductive coupling of two units of **5b** to allenyne **8** and diallene **10** in the presence of Brønsted (PTSA) or Lewis (BF_3) acids.

to its reduced known derivative 3,3-diphenyl-1-trimethylsilylpropyne **21** (Scheme 16).[24] The formation of allenyne **8** or diallene **10** depends on the regioselectivity of the attack, itself depending on the conditions revealing either reacting form **A** or **B** of the cation (Scheme 6).

2.2. Existence of the Target Molecule – Organometallic Route to Diphenyl Dialkynylmethanes

In the 1990s, Gimeno et al. published a series of articles on the synthesis and reactivity of indenyl-ruthenium(II)-allenylidene complexes obtained by treatment of propargylic alcohols with chloro-ruthenium precursors.[25] These allenylidene complexes were shown to react with various nucleophiles, including alkynylmetals, thus giving the corresponding alkynyl-ruthenium derivatives. A two-step procedure for the release of free alkyne ligands was also described and illustrated with a few examples. The allenylidene precursor of the targeted diethynyl-diphenylmethane **1a** was reported, but its decomplexation was not. In order to check the availability of **1a**, the procedure was first resumed from **5a** to the ruthenium complex **22** (Scheme 17).

Commercially available chloro-ruthenium complex **23** was thus treated with diphenylpropargyl alcohol **5a** in the presence of $NaPF_6$ in methanol at reflux. The cationic allenylidene-ruthenium complex **24** was isolated in 81% yield, and was then converted into the neutral alkynyl-ruthenium complex **25** in 35% yield by regioselective addition of sodium acetylide. Subsequent protonation of **25** with tetrafluoroboric acid in diethyl ether at –20 °C afforded the known vinylidene complex **22** in 70% yield.[24] Heating of complex **22** in acetonitrile gave a mixture of a ruthenium-acetonitrile complex and diethynyldiphenylmethane **1a** [δ(≡C*H*) = 2.76 ppm]. The latter could be purified by silica gel chromatography and finally isolated as a stable oil in 69% yield. The dialkynyl-diphenylmethane series was fur-



Scheme 17. Achievement of Gimeno's organometallic route to diethynyl-diphenylmethane.

ther completed with dipropynyldiphenylmethane [**1c**; $\delta(CH_3)$ = 2.00 ppm], obtained by double methylation of **1a** with iodomethane in 88% yield.

Beyond their academic interest and potential for future developments, the dialkynyldiphenylmethane structure can be regarded as the basic motif of unknown ring *carbo*-mers.[26] In particular, the dipropynyl version **1c** could serve as key unit for a rapid synthesis of the challenging perphenyl-[*n*]pericyclynes[27] by cyclizing sequential metathesis.[28] The limited preparative value of the disclosed method, however, calls for a search for alternative routes. Efforts in this area are in progress.

Conclusions

Quaternary carbon atoms bearing two aromatic and two acetylenic substituents have been described for the first time. The lack of previous examples in the literature is explained by the peculiar reactivity of 1,1-diarylpropargylic carbocations, which can be considered the natural precursors. The intrinsic chemical behavior of the cations has been analyzed in detail under various sets of conditions. Beyond classical Meyer–Schuster-type rearrangements, di- and trimerization-based processes prevail. Despite moderate selectivity, such processes could be synthetically valuable for the easy one-step generation of complex molecules. On the basis of mechanistic issues, the versatile reactivity of 1,1-diarylpropargylic cations can be ascribed to the unique combined effects of i) steric hindrance, ii) balanced propargylic/allenic resonance, and iii) trityl-like reactivity. Generalization of these results to other 1,1-diarylpropargylic alcohols **5** by variation of the terminal substituent R′ (Scheme 1) would be a cheap source of novel original structures.

Experimental Section

General: THF and diethyl ether were dried and distilled from sodium/benzophenone, pentane and dichloromethane over P_2O_5. All other reagents were used as commercially available. In particular, commercial solutions of propynylmagnesium bromide were 0.5 M in THF, those of *n*BuLi were 2.5 M in hexane. Previously described procedures were used for the preparation of **24**,[25b] **25**,[25c] and **22**.[25c] Compounds **3a**, **3b**, **5a**, and **5c** are commercially available but were prepared as described below. Although compounds **3c**,[29] **3c-OMe**,[30] **5b**,[6b] **5b-TMS**,[31] and **5c-OMe**[32] are known, their preparation is also reported below. All reactions were carried out under nitrogen or argon with use of Schlenk and vacuum line techniques. Column chromatography was carried out on silica gel (60 P, 70–200 mm). Silica gel thin-layer chromatography plates (60F254, 0.25 mm) were developed by treatment with ethanolic phosphomolybdic acid (20%). Preparative thin-layer chromatography was performed with 60F254, 2 mm plates. The following analytical instruments were used. ^{1}H and ^{13}C NMR: Bruker ARX 250, DPX 300, or Avance 500 spectrometers. Mass spectrometry: Quadrupolar Nermag R10-10H spectrometer. All NMR spectra were recorded in $CDCl_3$ solutions. NMR chemical shifts (δ) are in ppm, with positive values to high frequency relative to the tetramethylsilane reference; coupling constants (J) are in Hz. When not specified, the numbering of H and C atoms for NMR assignment is the one used in the X-ray diffraction diagrams.

1-Phenyl-3-(trimethylsilyl)prop-2-yn-1-ol (3b): Butyllithium in hexane (9.4 mL, 23.3 mmol) was added at –78 °C to a stirred solution of (trimethylsilyl)acetylene (3.3 mL, 23.3 mmol) in THF (30 mL). The resulting mixture was stirred for 20 min at –78 °C, and then for 20 min at room temperature. After the system had been cooled once more to –78 °C, a solution of benzaldehyde (2 mL, 19.7 mmol) in THF (20 mL) was added, and this mixture was allowed to warm to room temperature overnight whilst stirring. Saturated aqueous NH_4Cl was added, and the mixture was extracted with Et_2O. The organic layer was washed with brine, dried with $MgSO_4$, and concentrated under reduced pressure to give **3b** as a colorless oil (3.90 g, 97%). ^{1}H NMR ($CDCl_3$): δ = 0.24 [s, 9 H, Si(CH_3)$_3$], 2.35 (br. s, 1 H, O*H*), 5.48 (s, 1 H, C*H*–OH), 7.38–7.41 (m, 3 H, *m*-C*H* and *p*-C*H*); 7.56–7.59 (d, 2 H, ^3J = 7.2 Hz, *o*-C*H*) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$): δ = –0.07 [s, Si(CH_3)$_3$], 64.85 (s, *C*H-OH), 91.44 (s, C-*C*≡), 105.34 (s, ≡*C*–Si), 126.84 (s, *o*-C), 128.35 (s, *p*-C), 128.61 (s, *m*-C), 140.43 (s, *i*-C) ppm.

1-Phenylprop-2-yn-1-ol (3a): A solution of **3b** (750 mg, 3.67 mmol) in methanol (20 mL) was treated with K_2CO_3 (2.536 g, 18.35 mmol) for 3 h at room temperature. The mixture was filtered, and the resulting solution was concentrated under reduced pressure and then diluted with Et_2O. After treatment with saturated aqueous NH_4Cl and extraction with Et_2O, the organic layers were combined, washed with brine, and dried with $MgSO_4$, and the solvents were evaporated to dryness. Purification by column chromatography on silica gel (diethyl ether/pentane, 1:9) gave **3a** as a colorless oil (460 mg, 95%). ^{1}H NMR ($CDCl_3$): δ = 2.68 (d, ^4J = 2.2 Hz, 1 H, ≡C*H*), 2.80 (br. s, 1 H, O*H*), 5.46 (d, ^4J = 2.2 Hz, 1 H, O–C*H*), 7.32–7.44 (m, 3 H, *m*-C*H* and *p*-C*H*), 7.55–7.58 (m, 2 H, *o*-C*H*) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 64.22 (s, *C*H–OH), 74.83 (s, ≡*C*–H), 83.76 (s, *C*≡C–H), 126.72 (s, *o*-C), 128.48 (s, *p*-C), 128.67 (s, *m*-C), 140.21 (s, *i*-C) ppm.

1-Phenylbut-3-yn-1-ol (3c): Propynylmagnesium bromide (24.5 mL, 12.29 mmol) was added at 0 °C to a stirred solution of benzaldehyde (1 mL, 9.83 mmol) in dry diethyl ether (15 mL). The resulting solution was allowed to warm slowly to room temperature and was kept overnight whilst stirring at the same temperature. After treatment with saturated aqueous NH_4Cl and extraction with Et_2O, the organic layers were combined, washed with brine, and dried with $MgSO_4$, and the solvents were evaporated to dryness. Filtration through a small pad of silica gel (diethyl ether/pentane, 1:9) gave **3c** as a yellow oil (1.35 g, 94%). ^{1}H NMR ($CDCl_3$): δ = 1.91 (s, 3 H, CH_3), 2.80 (br. s, 1 H, O*H*), 5.43 (s, 1 H, O–C*H*), 7.28–7.42 (m, 3 H, *m*-C*H* and *p*-C*H*), 7.42–7.57 (m, 2 H, *o*-C*H*) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 3.71 (s, ≡C–*C*H$_3$), 64.61 (s, *C*H–OH), 79.44 (s, ≡*C*–Me), 82.83 (s, HO-C-*C*≡), 126.61 (s, C*o*), 128.11 (s, *p*-C), 128.51 (s, *m*-C), 141.44 (s, *i*-C) ppm.

1-Phenyl-1-methoxybut-2-yne (3c-OMe): PTSA (0.026 g, 0.14 mmol) was added to a solution of 1-phenylbutyn-1-ol (**3c**, 0.400 g, 2.74 mmol) and methanol (0.44 mL, 10.89 mmol) in acetonitrile (15 mL). The resulting mixture was heated at reflux whilst stirring for 2 h. The solvent was then removed under vacuum, and the residue was purified by silica gel chromatography, with elution first with pure pentane and then with a pentane/diethyl ether (99:1) mixture. The ether **3c-OMe** was isolated as a yellow oil in 80% yield. ^{1}H NMR ($CDCl_3$): δ = 1.97 (d, ^5J = 2.2 Hz, 3 H, ≡C–*C*H$_3$), 3.46 (d, ^3J = 3.9 Hz, 3 H, O–CH_3), 5.09 (s, 1 H, C*H*–O), 7.35–7.45 (m, 3 H, *m*-C*H* and *p*-C*H*), 7.54–7.56 (m, 2 H, *o*-C*H*) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 3.73 (s, ≡C–*C*H$_3$), 55.75 (s, O–*C*H$_3$), 73.30 (s, *C*H–O), 77.01 (s, ≡*C*–CH$_3$), 83.98 (s, *C*≡C–Me), 127.38 (s, *o*-C),

128.28 (s, *p*-C), 128.45 (s, *m*-C), 139.14 (s, *i*-C) ppm. MS (DCI/CH_4): *m*/*z* = 160.1 $[M]^+$.

1,1-Diphenyl-3-(trimethylsilyl)prop-2-yn-1-ol (5b): Butyllithium in hexane (5.3 mL, 13.25 mmol) was added at –78 °C to a stirred solution of (trimethylsilyl)acetylene (1.86 mL, 13.16 mmol) in THF (20 mL). The resulting mixture was stirred for 20 min at –78 °C, and then for 20 min at room temperature. After the system had been cooled once more to –78 °C, a solution of benzophenone (2.00 g, 10.98 mmol) in THF (20 mL) was added, and the resulting mixture was allowed to warm slowly to room temperature whilst stirring overnight. After treatment with saturated aqueous NH_4Cl and extraction with Et_2O, the organic layers were combined, washed with brine, and dried with $MgSO_4$, and the solvents were evaporated to dryness, thus giving **5b** as a colorless oil (3.042 g, 99%). ^1H NMR ($CDCl_3$): δ = 0.25 [s, 9 H, Si(CH_3)$_3$], 3.80 (br. s, 1 H, O*H*), 7.26–7.37 (m, 6 H, *m*-C*H* and *p*-C*H*), 7.63–7.67 (m, 4 H, *o*-C*H*); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = –0.03 [s, Si(*C*H$_3$)$_3$], 74.60 (s, C–OH), 91.77 (s, *C*≡C–Si), 107.17 (s, ≡C–Si), 126.08 (s, *o*-C), 127.64 (s, *p*-C), 128.25 (s, *m*-C), 145.05 (s, *i*-C) ppm. MS (DCI/CH_4): *m*/*z* = 203.09 $[M - C_6H_5]^+$, 263.13 $[M - Cl]^+$, 445.17 $[M]^+$.

1,1-Diphenylprop-2-yn-1-ol (5a): Potassium carbonate (2.96 g, 21.40 mmol) was added to a solution of **5b** (0.300 g, 1.070 mmol) in methanol (15 mL). After stirring for 2 h at room temperature, the mixture was filtered, and the resulting solution was concentrated under reduced pressure and then diluted with Et_2O. After treatment with saturated aqueous NH_4Cl and extraction with Et_2O, the organic layers were combined, washed with brine, and dried with $MgSO_4$, and the solvents were evaporated to dryness, thus giving **5a** as a white solid (0.222 g, 99%). ^1H NMR ($CDCl_3$): δ = 2.90 (s, 1 H, ≡C–*H*), 3.10 (br. s, 1 H, O*H*), 7.27–7.41 (m, 6 H, *m*-C*H* and *p*-C*H*), 7.64–7.68 (m, 4 H, *o*-C*H*) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 74.25 (s, *C*–OH), 75.50 (s, ≡C–H), 86.52 (s, C–*C*≡), 126.04 (s, *o*-C), 127.84 (s, *p*-C), 128.31 (s, *m*-C), 144.56 (s, *i*-C) ppm. MS (DCI/CH_4): *m*/*z* = 131.05 $[M - C_6H_5]^+$, 183.08 $[M - C_2H]^+$, 191.09 $[M - OH]^+$, 208.09 $[M]^+$.

1,1-Diphenylbut-3-yn-1-ol (5c): A propynylmagnesium bromide solution (13.2 mL, 6.58 mmol) was added at 0 °C to a stirred solution of benzophenone (1.00 g, 5.49 mmol) in THF (10 mL). The resulting mixture was allowed to warm to room temperature and stirred overnight. After treatment with saturated aqueous NH_4Cl and extraction with Et_2O, the organic layers were combined, washed with brine, and dried with $MgSO_4$, and the solvents were evaporated to dryness, thus giving **5c** as a yellow oil (1.215 g, quantitative). ^1H NMR ($CDCl_3$): δ = 1.99 (s, 3 H, CH_3), 3.80 (br. s, 1 H, O*H*), 7.26–7.37 (m, 6 H, *m*-C*H* and *p*-C*H*), 7.63–7.66 (m, 4 H, *o*-C*H*) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 3.92 (s, *C*H$_3$), 74.52 (s, *C*–OH), 82.38 (s, ≡*C*–Me), 83.78 (s, *C*≡C–Me), 126.15 (s, *o*-C), 127.59 (s, *p*-C), 128.24 (s, *m*-C), 145.60 (s, *i*-C) ppm. MS (DCI/CH_4): *m*/*z* = 145.07 $[M - C_6H_5]^+$, 205.10 $[M - OH]^+$, 222.11 $[M]^+$.

1,1-Diphenyl-3-(trimethylsilyl)-1-(trimethylsilyloxy)prop-2-yne (5b-TMS): Butyllithium in hexane (1.9 mL, 4.75 mmol) was added at –78 °C to a solution of **5b** (1.00 g, 3.57 mmol) in THF (20 mL). After the system had been stirred for 30 min, chlorotrimethylsilane (0.61 mL, 4.75 mmol) was added, and the mixture was allowed to warm to room temperature slowly over 2 h. After treatment with saturated aqueous NH_4Cl and extraction with Et_2O, the organic layers were combined, washed with brine, and dried with $MgSO_4$, and the solvents were evaporated to dryness, thus giving **5b-TMS** as a colorless oil (1.152 g, quantitative). ^1H NMR ($CDCl_3$): δ = 0.16 [s, 9 H, O–Si(CH_3)$_3$], 0.28 [s, 9 H, C–Si(CH_3)$_3$], 7.23–7.34 (m, 6 H, *m*-C*H* and *p*-C*H*), 7.58–7.62 (m, 4 H, *o*-C*H*) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = –0.25 [s, ≡C–Si(*C*H$_3$)$_3$], 1.61 [s, O–Si(*C*H$_3$)$_3$], 75.79 (s, *C*–OSi), 92.95 (s, *C*≡C–Si), 108.08 (s, ≡*C*–Si), 125.96 (s, *o*-C), 127.07 (s, *p*-C), 127.92 (s, *m*-C), 146.57 (s, *i*-C) ppm.

1,1-Diphenyl-1-methoxybut-2-yne (5c-OMe): Butyllithium in hexane (1.5 mL, 3.75 mmol) was added at –78 °C to a stirred solution of **5a** (0.300 g, 1.44 mmol) in THF (15 mL). The resulting mixture was stirred for 20 min at –78 °C, and then for 20 min at room temperature. After the system had been cooled once more to –78 °C, iodomethane (1.80 mL, 28.80 mmol) and dry DMSO (0.266 mL, 3.75 mmol) were added. The mixture was allowed to warm slowly to room temperature and stirred overnight. After treatment with saturated aqueous NH_4Cl and extraction with Et_2O, the organic layers were combined, washed with brine, and dried with $MgSO_4$, and the solvents were evaporated to dryness, thus giving **5c-OMe** as a yellow oil (0.335 g, 98%). ^1H NMR ($CDCl_3$): δ = 2.08 (s, 3 H, ≡C–CH_3), 3.41 (s, 3 H, O–CH_3), 7.27–7.41 (m, 6 H, *m*-C*H* and *p*-C*H*), 7.61–7.65 (m, 4 H, *o*-C*H*) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 3.87 (s, ≡C–*C*H$_3$), 52.26 (s, O–*C*H$_3$), 78.76 (s, ≡*C*–Me), 80.94 (s, *C*–OMe), 85.82 (s, *C*≡C–Me), 126.71 (s, *o*-C), 127.46 (s, *p*-C), 128.23 (s, *m*-C), 143.99 (s, *i*-C) ppm.

General Procedures for the Reactions of Propargylic Alcohols 3b–c and 5b–c with Acids

Procedure A: With PTSA (in the presence or absence of 2 equiv. of (trimethylsilyl)acetylene·PTSA (5 mol-%) was added to a solution of **3b–c** or **5b–c** (ca. 1 mmol) in acetonitrile (5 mL). The resulting mixture was heated at reflux for 1 h whilst stirring. The solvent was removed under reduced pressure, and the residue was purified by silica gel chromatography.

Procedure B: With $NaAuCl_4{\cdot}2H_2O$ [in the presence or absence of 2 equiv. of bis(trimethylsilyl)acetylene]·$NaAuCl_4{\cdot}2H_2O$ (5 mol-%) was added to a solution of **3b** or **3c** (ca. 1 mmol) in dry dichloromethane (5 mL). After the system had been stirred for 2 h at room temperature, the solvent was removed under vacuum, and the residue was purified by silica gel chromatography.

Procedure C: With $BF_3{\cdot}Et_2O$ [in the presence or absence of 2 equiv. of bis(trimethylsilyl)acetylene]·$BF_3{\cdot}Et_2O$ (1 equiv.) was added at –78 °C to a solution of **3b** or **3c** (ca. 1 mmol) in dry dichloromethane (5 mL). After stirring for 1 h, the mixture was treated with saturated aqueous NH_4Cl and extracted with diethyl ether. The combined organic layers were washed with brine, dried with $MgSO_4$, and concentrated under reduced pressure. The residue was purified by silica gel chromatography.

Procedure D: With $[Re(CO)_3(THF)]_2$ [in the presence or absence of 2 equiv. of bis(trimethylsilyl)acetylene]. The rhenium complex (2.5 mol-%) was added to a solution of **3b** or **3c** (ca. 1 mmol) in dry dichloromethane (5 mL). After the system had been stirred for 3 h, the solvent was removed under vacuum and the residue was purified by silica gel chromatography.

Procedure E: With $AlCl_3$ [in the presence or absence of 2 equiv. of bis(trimethylsilyl)acetylene]·$AlCl_3$ (1 equiv.) was added at –78 °C to a stirred solution of **3b** or **3c** (ca. 1 mmol) in dry dichloromethane (5 mL). After 2 h, the mixture was treated with saturated aqueous $NaHCO_3$ and extracted with diethyl ether. The combined organic layers were washed with brine, dried with $MgSO_4$, and concentrated under reduced pressure. The residue was purified by silica gel chromatography.

1,1′-Diphenyl-3,3′-bis(trimethylsilyl)-1,1′-dipropynyl Ether (7b): Silica gel chromatography (elution with ethyl acetate/heptane, 1:9) gave **7b** as a slightly brown, viscous oil. Yields: *Procedure A*, 83%, *Procedure B*, 76%; *Procedure C*, 84%; *Procedure D*, 87%; *Procedure E*, 61%. ^1H NMR ($CDCl_3$): δ = 0.24 and 0.29 [2 s, 18 H,

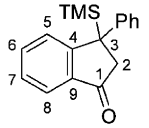
C– and O–Si(CH_3)$_3$], 5.30 and 5.69 (2 s, 2 H, O–C*H*), 7.30–7.63 (m, 10 H, *o*-, *m*-, *p*-C*H*) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 0.00 and 0.06 [2 s, C– and O–Si(*C*H$_3$)$_3$], 69.39 and 70.26 (2 s, O–*C*H), 92.82 and 93.11 (2 s, O-C-*C*≡), 102.90 and 103.03 (2 s, ≡*C*–SiMe$_3$), 127.89 and 128.12 (2 s, *o*-C), 128.41 (s, *p*-C), 128.55 and 128.62 (2 s, *m*-C), 138.08 and 138.19 (2 s, *i*-C) ppm. MS (DCI/NH_3): *m*/*z* = 391.4 [M + H]$^+$, 408.4 [M + NH_4]$^+$, 425.4 [M + N_2H_7]$^+$.

1,1′-Diphenyl-1,1′-dipropynyl Ether (7a): Potassium carbonate (0.425 g, 3.07 mmol) was added to a solution of **7b** (0.120 g, 0.31 mmol) in methanol (10 mL), and the resulting mixture was stirred for 2 h at room temperature. The mixture was filtered, and the resulting solution was concentrated under reduced pressure and was then diluted with Et_2O. After treatment with saturated aqueous NH_4Cl and extraction with Et_2O, the organic layers were combined, washed with brine, and dried with $MgSO_4$, and the solvents were evaporated to dryness, thus giving **7a** as a orange, viscous oil (0.075 g, quantitative). ^{1}H NMR ($CDCl_3$): δ = 2.70 and 2.75 (2 d, ^4J = 2.2 Hz, 1 H each, ≡C*H*), 5.30 and 5.71 (2 d, ^4J = 2.2 Hz, 1 H each, O–C*H*), 7.35–7.38 (m, 2 H, *p*-C*H*), 7.38–7.44 (m, 4 H, *m*-C*H*), 7.55–7.57 and 7.61–7.63 (2 dd, ^3J = 7.7, ^4J = 1.1 Hz, 4 H, *o*-C*H*) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 68.92 and 69.43 (2 s, O–C), 75.98 and 76.32 (2 s, ≡C–H), 81.08 and 81.48 (2 s, C–*C*≡), 127.60 and 127.81 (2 s, *o*-C), 128.51 and 128.69 (2 s, *m*-C), 128.58 and 128.87 (2 s, *p*-C), 137.55 and 137.78 (2 s, *i*-C) ppm. MS (DCI/NH_3): *m*/*z* = 264.2 [M + NH_4]$^+$, 281.2 [M + N_2H_7]$^+$.

1,1′-Diphenyl-1,1′-dibutynyl Ether (7c): Silica gel chromatography (elution with diethyl ether/pentane, 5:95) allowed for the separation of the two diastereoisomers of **7c** as orange oils. Yields: *Procedure C*, 60%; *Procedure D*, 94%; *Procedure E*, 50%. *Diastereoisomer I:* ^{1}H NMR ($CDCl_3$): δ = 1.93 (d, ^5J = 2.1 Hz, 6 H, CH_3), 5.22 (q, ^5J = 2.1 Hz, 2 H, C*H*–O), 7.29–7.54 (m, 10 H, *o*-, *m*-, *p*-C*H*) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 3.93 (s, CH_3), 69.11 (s, O–*C*), 77.34 (s, ≡*C*–CH_3), 84.03 (s, O-C-*C*≡), 127.80 (s, *o*-C), 128.40 (s, *p*-C), 128.49 (s, *m*-C), 138.90 (s, *i*-C) ppm. *Diastereoisomer II:* ^{1}H NMR ($CDCl_3$): δ = 1.98 (d, ^5J = 2.1 Hz, 6 H, CH_3), 5.62 (q, ^5J = 2.1 Hz, 2 H, C*H*–O), 7.34–7.63 (m, 10 H, *o*-, *m*-, *p*-C*H*) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 3.88 (s, *C*H$_3$), 69.44 (s, O–*C*), 77.05 (s, ≡*C*–CH_3), 84.12 (s, O-C-*C*≡), 127.54 (s, *o*-C), 128.12 (s, *p*-C), 128.35 (s, *m*-C), 139.33 (s, *i*-C) ppm. MS (DCI/NH_3): *m*/*z* = 275.2 [M + H]$^+$, 292.3 [M + NH_4]$^+$, 309.3 [M + N_2H_7]$^+$.

1,1,4,4-Tetraphenyl-3,6-bis(trimethylsilyl)hex-1,2-dien-5-yne (8): Silica gel chromatography (elution with diethyl ether/pentane, 2:98) afforded **8** as pale yellow–brown crystals (m.p. 86 °C). Yields: *Procedure A*, 25%; *Procedure A from* **5b-TMS**, 18%; *Procedure C from* **5b-[Co]** *and a 15 h reaction time*, 51%. ^{1}H NMR ($CDCl_3$): δ = 0.14 [s, 9 H, (CH_3)$_3$Si–C=], 0.28 [s, 9 H, (CH_3)$_3$Si–C≡], 7.03–7.46 (m, 20 H, ar-H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 0.01 and 0.62 [2 s, (*C*H$_3$)$_3$Si–C-1 and (*C*H$_3$)$_3$Si–C-4], 54.78 (s, *C*-3), 90.80 (s, *C*-2), 108.54, 109.36, 110.00 (3 s, *C*-1, *C*-4 and *C*-6), 126.56 and 126.65 (2 s, *p*-C), 127.70, 127.93, 128.19, 128.40 (4 s, *o*-C and *p*-C), 136.77 and 143.93 (2 s, *i*-C), 207.84 (s, *C*-5) ppm. MS (DCI/NH_3): *m*/*z* = 544.4 [M + NH_4]$^+$.

3–Phenyl-3-trimethylsilylindan-1-one (9): Silica gel chromatography (elution with diethyl ether/pentane, 2:98) gave **9** as an orange oil. Yields: *Procedure A*, 50%; *Procedure A at room temperature for 24 h*, 62%; *Procedure A from* **5b-TMS**, 51%. ^{1}H NMR ($CDCl_3$): δ = 0.0 [s, 9 H, (CH_3)$_3$Si], 3.03 (d, ^1J = 19.6 Hz, 1 H, 2-*H*), 3.27 (d, ^1J = 19.6 Hz, 1 H, 2-*H*), 7.20 (tt, ^3J = 7.2, ^4J = 1.2 Hz, 1 H, *p*-C*H*), 7.32 (dd, ^3J = 8.3 Hz, 2 H, *m*-C*H*), 7.37 (dd, ^3J = 7.2, ^4J = 1.2 Hz, 2 H, *o*-C*H*), 7.42 (ddd, ^3J = 6.1, ^4J = 2.0 Hz, 1 H, 6-*H*), 7.70 (dd, ^3J = 6.1, ^4J = 2.0 Hz, 1 H, 5-*H*), 7.70 (ddd, ^3J = 6.1, ^4J = 2.0 Hz, 1 H, 7-H), 7.83 (dd, ^3J = 6.1, ^4J = 2.0 Hz, 1 H, 8-*H*) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 42.99 (s, *C*-3), 49.83 (s, *C*-2), 124.19 (s, *C*-8), 125.58 (s, *p*-C), 126.70 (s, *C*-6), 126.87 (s, C*o*), 127.69 (s, *C*-5), 128.44 (s, *m*-C), 134.26 (s, C-7), 136.59 (s, *C*-4), 144.59 (s, *i*-C), 159.11 (s, *C*-9), 205.57 (s, *C*-1) ppm. MS (DCI/NH_3): *m*/*z* = 280.3 [M]$^+$, 281.3 [M + H]$^+$, 298.3 [M + NH_4]$^+$, 315.3 [M + N_2H_7]$^+$.



1,1,6,6-Tetraphenyl-3,4-bis(trimethylsilyl)hex-1,2,4,5-tetraene (10): Silica gel chromatography (elution with diethyl ether/pentane, 1:99) afforded crude crystals of **10** (m.p. 122 °C). Yields: *Procedure C*, 62%.^{1}H NMR ($CDCl_3$): δ = 0.13 [s, 18 H, (CH_3)$_3$Si], 7.29–7.40 (m, 20 H, ar-H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = –0.65 [s, Si(*C*H$_3$)$_3$], 98.17 [s, =*C*–Si(*C*H$_3$)$_3$], 105.88 (s, Ph–*C*=), 126.67 (s, *p*-C), 128.19 (s, *o*-C), 128.39 (s, *m*-C), 136.89 (s, *i*-C), 208.36 (s, C=*C*=C) ppm. MS (DCI/NH_3): *m*/*z* = 527.5 [M + H]$^+$, 544.5 [M + NH_4]$^+$.

Indenylallene (11): Silica gel chromatography (elution with diethyl ether/pentane, 1:99) afforded **11** as crude crystals (m.p. 136 °C). Yields: *Procedure B*, 50%; *Procedure E*, 67%. ^{1}H NMR ($CDCl_3$): δ = –0.08 [s, 9 H, C-8–Si(CH_3)$_3$], 0.18 [s, 9 H, C-10–Si(CH_3)$_3$], 6.75–6.78 (dd, ^3J = 8.1, ^4J = 1.5 Hz, 2 H, *o*-C*H*–C-12), 7.11–7.49 (m, 17 H, ar-CH) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = –2.98 [s, *C*-8–Si(*C*H$_3$)$_3$], 0.60 [s, C-10–Si(*C*H$_3$)$_3$], 67.83 (s, *C*-8), 98.35 (s, *C*-10), 104.53 (s, C-12), 120.11 (s, *C*-3), 123.87 (s, *C*-6), 124.72 (s, *C*-4), 126.14 (s, *p*-C), 127.03 (s, *p*-C), 127.10 (s, *C*-5), 127.67 (s, *o*-C or *m*-C), 127.77 (s, *p*-C), 128.19 (s, *o*-C or *m*-C), 128.32 (s, *o*-C or *m*-C), 128.66 (s, *o*-C or *m*-C), 129.58 (s, *o*-C or *m*-C), 129.90 (s, *o*-C or *m*-C), 135.23 (s, *i*-C–*C*-1), 136.15 (s, *i*-C–C-12), 136.82 (s, *i*-C–C-12), 138.85 (s, *C*-9), 142.76 (s, *C*-2 or C-7), 142.85 (s, C-7 or *C*-2), 146.68 (s, *C*-1), 206.29 (s, *C*-11) ppm. MS (DCI/NH_3): *m*/*z* = 527.4 [M – Cl + H]$^+$, 544.4 [M – Cl + NH_4]$^+$.

Fused Tetracycle 12: Silica gel chromatography (elution with diethyl ether/pentane, 5:95) gave a mixture from which **12** precipitated as white crystals from dichloromethane (m.p. 217 °C). Yield: *Procedure E*, 23%. ^{1}H NMR ($CDCl_3$): δ = 1.68 (s, 3 H, 1-H_3), 1.72 (s, 3 H, 18-H_3), 2.70, 3.48 (2 d, ^2J = 16.8 Hz, 2H, 5-H_2), 5.80–7.70 (m, 29 H, ar-CH) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 22.33 (s, C-1), 26.76 (s, C-18), 35.59 (s, C-5), 51.22 (s, C-6), 58.15 (s, C-15), 68.01 (s, C-17), 115.46 (s, C-2), 120.74 (s, C-11), 120.91 (s, C-8), 124.95 (s, C_{Ph}), 125.49 (s, C-9), 125.51 (s, C_{Ph}), 126.04 (s, C_{Ph}), 126.24 (s, C_{Ph}), 126.56 (s, C_{Ph}), 126.75 (s, C_{Ph}), 126.84 (s, C-10), 126.88 (s, C_{Ph}), 127.23 (s, C_{Ph}), 127.40 (s, C_{Ph}), 127.50 (s, C_{Ph}), 128.56 (s, C_{Ph}), 128.59 (s, C_{Ph}), 128.92 (s, C_{Ph}), 129.51 (s, C_{Ph}), 130.52 (s, C_{Ph}), 135.53 (s, C_{Ph}), 138.27 (s, C_{Ph}), 138.90 (s, C_{Ph}), 141.46 (s, C_{Ph}), 141.60 (s, C-13), 141.63 (s, C_{Ph}), 141.99 (s, C-3), 144.84 (s, C-12), 146.60 (s, C-4 or C-16), 151.68 (s, C-7), 151.81 (s, C-14), 156.84 (s, C-4 or C-16) ppm. MS (DCI/CH_4): *m*/*z* = 571.21 [M – C_6H_5]$^+$, 613.28 [M – Cl]$^+$, 649.26 [M]$^+$.

Fused Pentacycle 13: Silica gel chromatography (elution with diethyl ether/pentane, 5:95) afforded a mixture, from which **13** precipitated as white crystals from diethyl ether (m.p. 206 °C). Yield: *Procedure E*, 13%. ^{1}H NMR ($CDCl_3$): δ = 1.22 (s, 3 H, 20-H_3), 2.68 (d, ^2J = 15.9 Hz, 1 H, 18-H_2), 2.74 (dd, ^2J = 15.9, ^4J = 2.0 Hz, 1 H, 18-H_2), 3.29 (s, 1 H, 19-H), 6.05 (d, ^4J = 2.0 Hz, 1 H, 2-H), 6.97–7.34 (m, 18 H, ar-CH) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 30.72 (s, C-20), 42.99 (s, C-18), 49.73 (s, *C*-17), 59.60 (s, C-3), 68.82 (s, C-10), 75.96 (s, C-19), 121.86 (s, C-15), 124.64 (s, C-8), 124.98 (s, C-5), 125.64 (s, C-12), 126.19 (s, C-30), 126.35 (s, C-24), 127.23 (s, C-22 and C-26), 127.61 (s, C-13), 127.95 (s, C-14, C-29 and C-

Table 1. Crystal data for compounds **8**, **11**, **12**, and **13**.

	8	**11**	**12**	**13**
Chemical formula	$C_{36}H_{38}Si_2$	$C_{36}H_{37}ClSi_2$	$C_{48}H_{37}Cl$	$C_{32}H_2Cl$
M [g·mol^{-1}]	526.87	561.31	649.27	445.00
Crystal system	triclinic	triclinic	orthorhombic	orthorhombic
Space group	$P\bar{1}$	$P\bar{1}$	*Pbca*	*Pbca*
a [Å]	9.3695(10)	10.4281(5)	22.0214(14)	8.8289(4)
b [Å]	9.4830(10)	16.6893(9)	9.1390(6)	16.7184(8)
c [Å]	19.053(2)	18.8076(8)	33.868(3)	31.1687(16)
α [°]	97.869(14)	73.341(4)	90	90
β [°]	91.205(14)	85.926(3)	90	90
γ [°]	111.937(12)	82.247(4)	90	90
V [Å^3]	1550.7(3)	3105.4(3)	6816.1(9)	4600.7(4)
Z	2	4	8	8
$\rho_{calcd.}$	1.128	1.201	1.265	1.285
μ [mm]$^{-1}$	0.136	0.223	0.147	0.185
$2\theta_{max}$ [°]	51.95	58.18	58.24	62.80
Crystal size [mm]	$0.20\times0.25\times0.30$	$0.20\times0.20\times0.25$	$0.15\times0.15\times0.20$	$0.20\times0.22\times0.35$
λ (Mo-K_α) [Å]	0.71073	0.71073	0.71073	0.71073
Scan mode	Φ scans	Φ and Ω scans	Φ and Ω scans	Φ and Ω scans
T [K]	180	180	180	180
Reflections measured	15397	29755	61583	81187
Reflections unique	5664	16356	9073	7553
R_{int}	0.124	0.033	0.118	0.038
Reflections with $I > n\sigma(I)$	3360 (n = 1)	7621 (n = 3)	1982 (n = 2.8)	4382 (n = 3)
Number of parameters	343	703	196	298
R	0.0615	0.0307	0.0521	0.0423
Rw	0.0698	0.0341	0.0561	0.0474
Absorption corrections	multiscan	multiscan	multiscan	multiscan
Min./max. transmission	0.88/0.97	0.86/0.96	0.94/0.98	0.93/0.97
Residual electron density [e Å^{-3}])	0.40/0.25	–0.22/0.32	–0.83/0.58	–0.24/0.56

31), 128.11 (s, C-6), 128.15 (s, C-7), 128.31 (s, C-28 and C-32), 128.55 (s, C-23 and C-25), 131.48 (s, C-2), 131.50 (s, C-1), 145.72 (s, C-11), 148.74 (s, C-4), 148.77 (s, C-21), 148.95 (s, C-27), 149.06 (s, C-9), 149.28 (s, C-16) ppm. MS (DCI/CH_4): m/z = 367.12 [M – C_6H_5]$^+$, 409.19 [M – Cl]$^+$, 445.17 [M]$^+$.

Diphenyldiethynylmethane (1a): A solution of the vinylidene ruthenium complex **22** (0.275 g, 0.264 mmol) in acetonitrile (20 mL) was stirred for 2 h at 80 °C. The mixture was then cooled, and the solvents were evaporated to dryness. Silica gel chromatography (elution first with pentane, then with diethyl ether/pentane, 1:9) afforded a fraction containing **1a** in admixture with triphenylphosphane. Purification was achieved on a preparative TLC plate with elution with diethyl ether/pentane (1:9). Pure **1a** was obtained as a colorless oil (40 mg, 69%). ^{1}H NMR ($CDCl_3$): δ = 2.76 (s, 2 H, ≡C*H*); 7.27–7.41 (m, 6 H, *m*-CH and *p*-CH), 7.41–7.69 (m, 4 H, *o*-CH) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 44.50 (s, *C*–C≡CH), 73.46 (s, ≡CH), 84.36 (s, *C*≡CH), 126.74 (s, *o*-C), 127.52 (s, *p*-C), 128.51 (s, *m*-C), 142.32 (s, *i*-C) ppm. MS (DCI/NH_3): m/z = 139.05 [M – C_6H_5]$^+$, 217.10 [M + H]$^+$. HRMS (DCI/NH_3) calcd. for $C_{17}H_{13}$: 217.1017, found 217.0999.

Diphenyldipropynylmethane (1c): Butyllithium in hexane (100 μL, 0.25 mmol) was added at –78 °C to a stirred solution of **1a** (0.020 g, 0.092 mmol) in THF (3 mL). The mixture was stirred for 20 min at –78 °C, and then for 20 min at room temperature. Iodomethane (60 μL, 0.925 mmol) was added at –78 °C, and the mixture was allowed to warm slowly to room temperature whilst stirring overnight. After treatment with saturated aqueous NH_4Cl and extraction with Et_2O, the organic layers were combined, washed with brine, and dried with $MgSO_4$, and the solvents were evaporated to dryness. The crude product was purified by silica gel chromatography (elution with pentane), giving **1c** as a colorless oil (0.019 mg, 88% yield). ^{1}H NMR ($CDCl_3$): δ = 2.00 (s, 6 H, C*H*$_3$), 7.23–7.36 (m, 6 H, *m*-C*H* and *p*-C*H*), 7.62–7.66 (m, 4 H, *o*-C*H*) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 3.99 (s, *C*H$_3$), 45.00 (s, *C*–C≡C–Me), 72.50 (s, ≡*C*–Me), 80.53 (s, C–*C*≡C–Me), 126.91 (s, *o*-C), 127.20 (s, *p*-C), 128.19 (s, *m*-C), 144.50 (s, *i*-C) ppm. MS (DCI/NH_3): m/z = 167.08 [M – C_6H_5]$^+$, 205.10 [M – C_2CH_3]$^+$, 245.13 [M + H]$^+$. HRMS (DCI/NH_3): calcd. for $C_{19}H_{17}$: 245.1330; found 245.1306.

X-ray Crystallographic Data for Compounds 8, 11, 12, and 13: X-ray intensity data were collected on an Oxford Diffraction Xcalibur, Bruker Apex2, or Stoe IPDS diffractometer equipped with an Oxford Cryosystems Cryostream Cooler Device, with use of a graphite-monochromated Mo-K_α radiation source (Table 1). Structures were solved by direct methods with SIR92, and refined by full-matrix, least-squares procedures on F with use of the programs of the PC version of CRYSTALS. Atomic scattering factors were taken from the International Tables for X-ray Crystallography. For compounds **8**, **11**, and **13** all non-hydrogen atoms were refined anisotropically. For compound **12** (weakly diffracting crystal), atoms were refined isotropically. Hydrogen atoms were located in a difference map and repositioned geometrically, then refined with a riding model.

CCDC-690479, -690480, -690481, and -690482 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.

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