676 *Organometallics* **2010,** *29,* 676–686
DOI: 10.1021/om9009872

ORGANOMETALLICS
Article

Different Reactivity Patterns of Trimethylsilyl- and Phenyl-Substituted Propargylallenes: $Fe_2(CO)_9$- and $[Ag]^+$-Promoted Cyclizations

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Received November 12, 2009

Thermolytic rearrangement of the diphenyl-propargylallene [3,3-(biphenyl-2,2′-diyl)-1-phenyl-1-{9-[(phenylethynyl]-9*H*-fluorenyl}allene], **9**, yields the bis-fluorenyliden-bis-allene **10**, which undergoes electrocyclization to form 3,4-di(fluorenyliden)-1,2-diphenylcyclobutene, **12**, in which the overlapping fluorenylidenes give rise to C_2 symmetry. The propargylallene **9** reacts with iron carbonyls to form **15**, in which an (η^5-fluorenyl)$Fe(CO)_2$ moiety is linked both directly and via a bridging $=C(Ph)-C(=O)-$ linkage to a cyclobutene ring possessing a phenyl group and a spiro-bonded fluorenyl substituent. The diphenyl-propargylallene **9** and its bis(trimethylsilyl)propargylallene analogue, **2**, each react with $Co_2(CO)_8$ to furnish the corresponding alkyne-$Co_2(CO)_6$ complexes **14** and **13**, respectively. Treatment of the diphenyl-propargylallene **9** or the mono(trimethylsilyl)propargylallene **25** with silver nitrate in methanol or water effects cyclization of the allene onto the alkyne to furnish a cyclopentadiene that bears a 9-methoxy- or 9-hydroxy-fluorenyl substituent and is also spiro-bonded to a second fluorenyl moiety. The reaction of 3,3-(biphenyl-2,2′-diyl)-1-bromo-1-phenylallene with $Fe_2(CO)_9$ yields the novel bicyclo-[3.2.0]heptadienone **21**, which possesses two phenyl groups and is also spiro-linked to two fluorenyl fragments. All new compounds were characterized by NMR spectroscopy and X-ray crystallography.

Introduction

The number of conceivable isomers of C_6H_6 is 218! Of course, the chemistry of benzene—and even of its Dewar, prismane, and benzvalene isomers—has been comprehensively investigated.[1] However, the majority of this enormous number of potential molecules will never be capable of existence under normal conditions because of the intrinsic strain imposed by the presence of triple bonds or allene units in small rings or of bridgehead double bonds that would violate Bredt's rule.

There are only 15 acyclic isomers of C_6H_6; these include diynes, dienynes, and tetraenes, and their existence owes much to the pioneering investigations of Hopf and his colleagues.[2] Most importantly, we note his synthesis of hexa-1,2-dien-5-yne (C_6H_6), the parent propargylallene.[3] Nevertheless, the chemistry of propargylallenes, in particular their organometallic chemistry, remains underexploited. We here focus on the syntheses, structures, and reactivity of several propargylallenes, their organic and organometallic derivatives, and their rearrangement behavior.

In continuation of our studies on the organic and organometallic chemistry of fluorenylidene-containing allenes and their dimers,[4] we here describe the syntheses, structures, and reactivity of propargylallenes bearing trimethylsilyl or phenyl substituents. Our initial investigations[5] on the conversion of fluorenylidene-allenes, via a series of isomeric 1,2-dialkylidenecyclobutanes, to electroluminescent tetracenes prompted us to pursue the chemistry of other allenes, including those bearing ferrocenyl,[6] phosphino,[7] or silyl[8] substituents, each of which led to unexpected results.

Thus, treatment of the trimethylsilyl-bromoallene, **1**, with half an equivalent of butyllithium furnished the propargylallene **2**, the product of head-to-tail coupling, which, when thermolyzed, yielded the disilyl-diallene **3**. However, attempted electrocyclization to the 3,4-bis(fluorenyliden)-cyclobutene **4** led instead to the novel dihydrotetrabenzoquatercyclopentadiene **5**.[9] Moreover, removal of the bulky trimethylsilyl groups in **3** also did not result in cyclization; instead the molecule underwent isomerization to form the hexa-1,5-dien-3-yne **6**, which had previously been prepared via a different multistep route.[10]

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Treatment of either the bis(trimethylsilyl)propargylallene **2** or the disilyl-diallene **3** with di-iron nonacarbonyl led initially to the cyclized product **7**, whereby the (η^5-fluorenyl)Fe(CO)$_2$ moiety is linked both directly and via a bridging carbonyl to a cyclopentadiene ring bearing two trimethylsilyl substituents and a spiro-bonded fluorenyl fragment. This observation suggests the existence of an equilibrium between the propargylallene, **2**, and the bis-allene, **3**. Furthermore, when the complex **7** was allowed to stand in chloroform at room temperature, it gradually decomposed with loss of metal to yield the lactone **8**, a previously unknown bicyclo[3.3.0]oxa-octadienone system.[9]

Results and Discussion

Syntheses and Reactivity of Propargylallenes. In light of the results gained with the bis(trimethylsilyl)propargylallene **2** and the bis(trimethylsilyl)diallene **3**, it was decided to prepare and study the reactivity of the corresponding diphenyl systems **9** and **10**, respectively. Incorporation of a planar aryl group in place of a bulky three-dimensional trimethylsilyl substituent would be expected to reduce the steric hindrance in **9** relative to **2**. However, the available literature on these molecules is rather confusing, and we describe here our attempt to clarify the situation. In 1965, Kuhn and Rewicki reported that when 9-phenylethynylfluoren-9-ol was treated with TiCl$_3$−EtOH and trisodium citrate at 70−80 °C, a colorless, light-sensitive hydrocarbon, C$_{42}$H$_{26}$, *"presumably 3,4-diphenyl-1,6-bis(biphenylene)-1,2,4,5-hexatetraene"*, **10**, mp 268−270 °C, turning brown-red from 180 °C, was isolated in 20% yield. Interestingly, this product absorbed only 3 molar equiv of H$_2$.[11] Subsequently, in 1975, Toda and Takehira claimed that the CuCl-mediated coupling of the phenyl-bromoallene **11** in DMF at room temperature furnished **10**, mp 173.5−174 °C.[12] Since melting points are sometimes the only viable historical link to assignments made prior to the ready availability of modern spectroscopic or X-ray diffraction techniques,[13] we wished to correlate our observations with the original data.

In our hands, treatment of the phenylbromoallene **11** with half an equivalent of butyllithium delivered the diphenylpropargylallene **9** as pale yellow crystals, mp 284−286 °C, in 43% yield. When **9** was heated at reflux in toluene for 5 h, an orange product, mp 266−268 °C, was unambiguously identified as 3,4-di(9-fluorenyliden)-1,2-diphenylcyclobutene, **12**. One might surmise that the product reported by Toda was in fact the diallene **10** (mp 174 °C), as was the molecule described by Kuhn as *turning brown-red from 180 °C*; however, the melting point of Kuhn's ultimate product indicates that electrocyclization must have occurred to form the cyclobutene **12**. The X-ray crystal structures of the diphenylpropargylallene **9** and the cyclobutene **12** are shown in Figures 1 and 2, respectively. In **9**, the carbon−carbon distances in the allenyl and alkynyl units are within the normal ranges (C(9)−C(10) 1.315(2) Å, C(10)−C(11) 1.303(2) Å, C(13)−C(14) 1.198(2) Å), and the angle C(9)−C(10)−C(11) is 176.3°. In **12**, the bond distances around the cyclobutene ring are C(9)−C(10) 1.360(3), C(10)−C(10′) 1.496(4), C(10)−C(11) 1.476(3), and C(11)−C(11′) 1.392(4) Å.

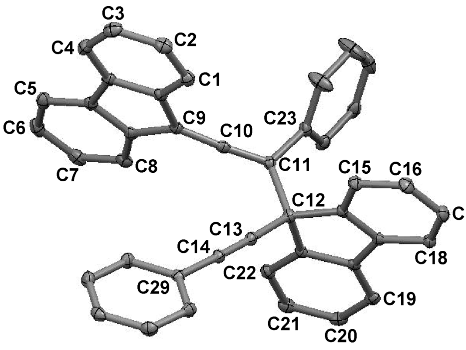

Figure 1. Molecular structure of the diphenyl propargylallene **9**. Thermal ellipsoids are at 30%.

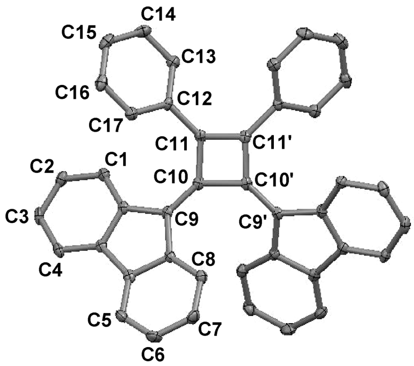

Figure 2. Structure of the difluorenylidene-cyclobutene **12**. Thermal ellipsoids are at 50%.

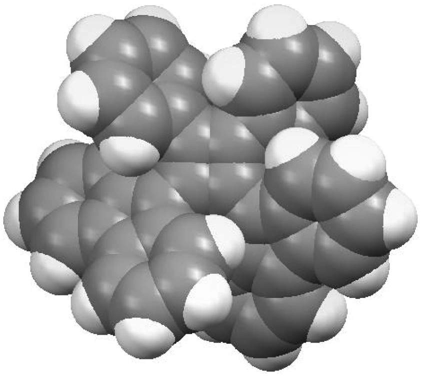

Figure 3. Space-filling representation of **12**, emphasizing the overlap of the fluorenylidenes.

As with the 1,2-difluorenylidene-cyclobutanes reported previously,[4,5,8] their large wingspans (~8.8 Å) cause severe overlap of the fluorenylidenes in the cyclobutene **12**, such that the molecule adopts C_2 symmetry with a dihedral angle of 51.3° between the fluorenylidene planes. The phenyls and fluorenylidenes are twisted out of the cyclobutene plane by 32° and 35°, respectively, as depicted in the space-filling representation in Figure 3. It is also noteworthy that the direction of helicity of the fluorenylidenes is opposed to that of the phenyls. This matches the thermodynamically favored orientation found in the corresponding 1,2-difluorenyliden-3,4-diphenylcyclobutanes.[4]

Reactions with Cobalt and Iron Carbonyls. The Pauson−Khand reaction of an alkyne, an alkene, and a source of CO (commonly Co$_2$(CO)$_8$) to form a cyclopentenone continues to attract attention, not merely as a powerful and versatile

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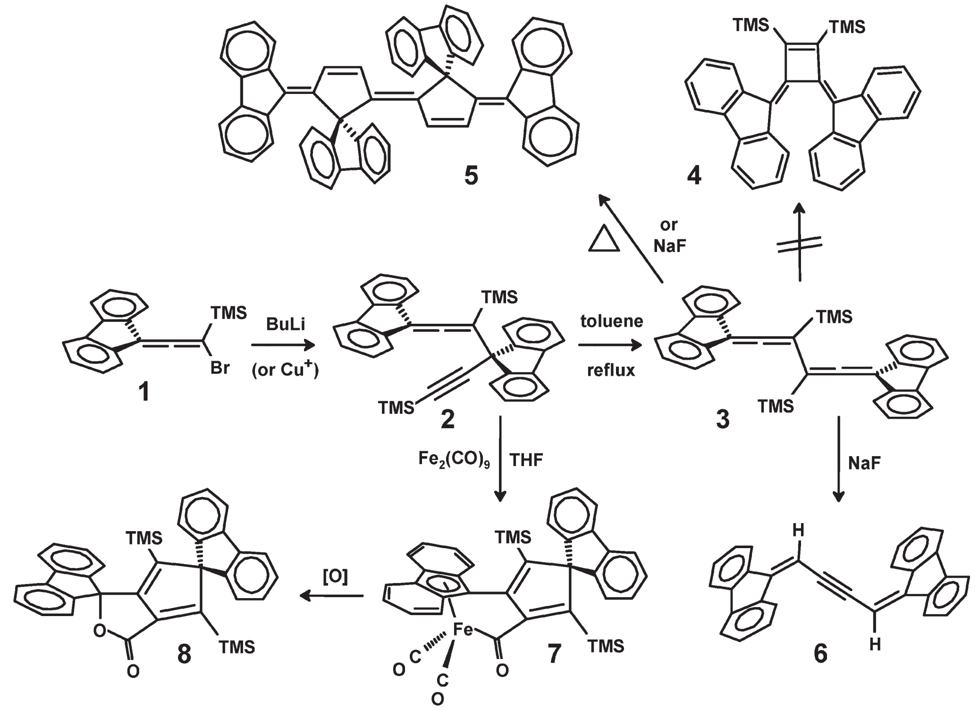
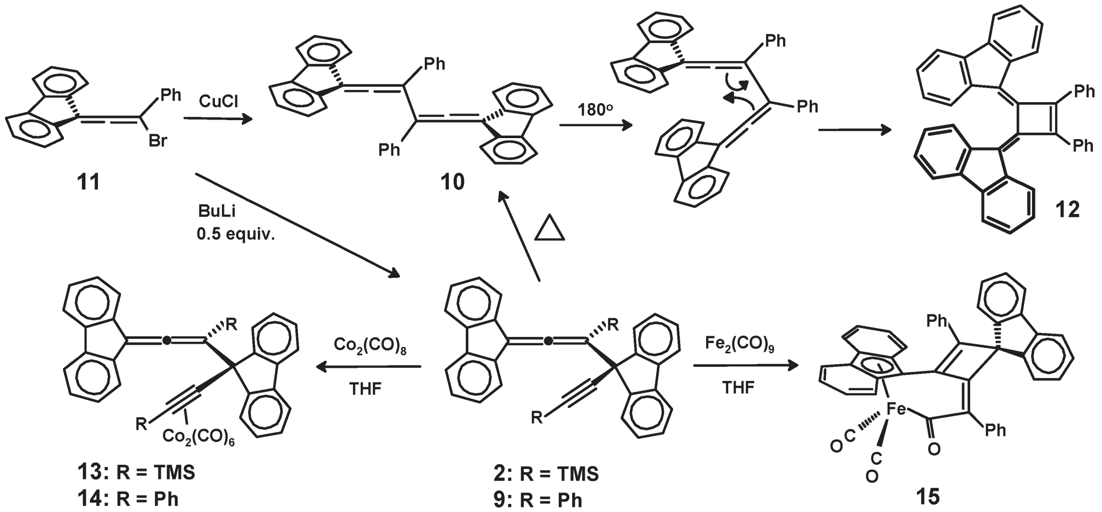
Scheme 1. Reactions of the Bis(trimethylsilyl)propargylallene 2 and of the Bis(trimethylsilyl)diallene 3



Scheme 2. Reactions of Propargylallenes with Cobalt and Iron Carbonyls



synthetic approach,[14] but also to clarify the mechanistic details.[15] Thus, we recently reported the first structurally characterized example of a (μ-alkyne)(η^2-alkene)pentacarbonyldicobalt complex,[16] the first intermediate in the proposed mechanism of the PKR.[17] Although intramolecular Pauson–Khand reactions of allenynes connected through aromatic rings have been described,[18] we are unaware of any corresponding reports on propargylallenes.

As shown in Scheme 2, the disilyl- and diphenylpropargylallenes **2** and **9**, respectively, react readily with dicobalt octacarbonyl to form the tetrahedral alkyne-dicobalt hexacarbonyl clusters **13** and **14**, respectively, and their structures are shown in Figures 4 and 5. In both cases, the bulkiness of the alkynyl-$Co_2(CO)_6$ cluster causes a bending of the allene moiety away from linearity (167.3° in **13**, 171.6° in **14**), but

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(14) For reviews of the Pauson–Khand reaction see: (a) Jeong, N. *Comprehensive Organometallic Chemistry III*; Crabtree, R. H.; Mingos, D. M. P. Eds.; Elsevier: Oxford, U.K., 2006; Vol. *11*, pp 335–366, and references therein. (b) Laschat, S.; Becheanu, A.; Bell, T.; Baro, A. *Synlett* **2005**, 2547–2570. (c) Gibson, S. E.; Mainolfi, N. *Angew. Chem., Int. Ed.* **2005**, *44*, 3022–3037. (d) Boñaga, L. V. R.; Krafft, M. E. *Tetrahedron* **2004**, *60*, 9795–9833.

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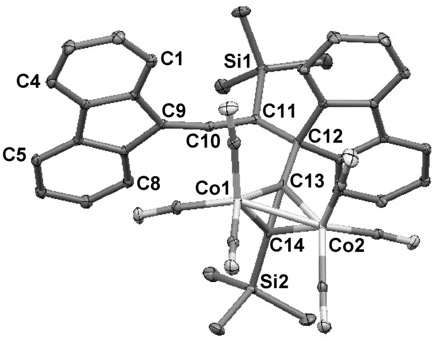

Figure 4. X-ray structure of dicobalt cluster **13**. Thermal ellipsoids are at 50%. Selected bond lengths (Å): C(9)−C(10) 1.324(2), C(10)−C(11) 1.299(2), C(11)−C(12) 1.531(2), C(12)−C(13) 1.520(2), C(13)−C(14) 1.333(2), Co(1)−Co(2) 2.4465(4), Co(1)−C(14) 2.005(2), Co(1)−C(13) 1.988(2), Co(2)−C(14) 1.988(2), Co(2)−C(13) 1.996(2).

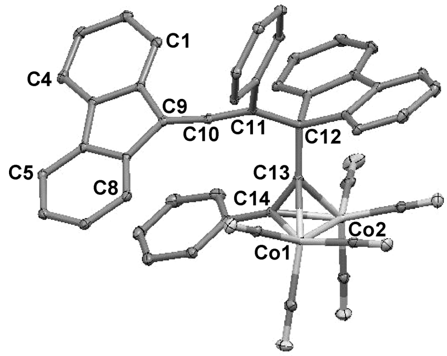

Figure 5. Structure of dicobalt cluster **14**. Thermal ellipsoids are at 50%. Selected bond lengths (Å): C(9)−C(10) 1.320(2), C(10)−C(11) 1.309(2), C(11)−C(12) 1.548(2), C(12)−C(13) 1.520(2), C(13)−C(14) 1.342(2), Co(1)−Co(2) 2.4530(3), Co(1)−C(14) 1.990(2), Co(1)−C(13) 1.955(2), Co(2)−C(14) 1.953(2), Co(2)−C(13) 1.970(2).

there is no evidence of loss of a carbonyl ligand, even when heated at reflux in toluene. In the free diphenylpropargylallene **9** (Figure 1) the two fluorenyl fragments are close to parallel (dihedral angle of 7.7°), but when complexed to $Co_2(CO)_6$ in **14** this opens up to 34.6°; in contrast, in the disilyl-dicobalt propargylallene **13**, these planes maintain their relative orientation (dihedral angle of 4.6°).

Although **2** and **9** react with dicobalt octacarbonyl in identical fashion, their reactions with diiron nonacarbonyl are strikingly different. As noted already in Scheme 1, the silyl system **2** yields a novel complex, **7**, in which an (η^5-fluorenyl)$Fe(CO)_2$ moiety is linked both directly and via a bridging carbonyl to a cyclopentadiene ring possessing two trimethylsilyl groups and a spiro-bonded fluorenyl substituent.[9] The product, **15**, from the reaction of the diphenyl propargylallene **9** with $Fe_2(CO)_9$ (or better with $Fe(CO)_5$ and morpholine *N*-oxide) likewise exhibited ^1H and ^{13}C NMR spectra indicating the presence of two different fluorenyl groups and two nonequivalent phenyl substituents, as well as terminal and bridging Fe−^{13}CO NMR resonances at 212.8 and 249.3 ppm, respectively. In the infrared spectrum, ν_{CO} absorptions were found at 2017, 1961, and 1604 cm^{-1}. In comparison, complex **7** derived from the disilyl-propargylallene **2** and iron carbonyl exhibited ν_{CO} absorptions at 2017, 1965, and 1649 cm^{-1}. This difference could indicate that the organic carbonyl function in **15** is part of a more extended π-system.

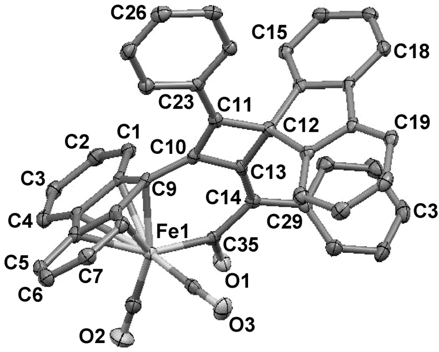

Figure 6. Structure of the (η^5-fluorenyl)iron complex **15**. Thermal ellipsoids are at 50%. Selected bond lengths (Å): Fe(1)−C(9) 2.070(3), Fe(1)−C(9a) 2.143(3), Fe(1)−C(4a) 2.202(3), Fe(1)−C(4b) 2.244(3), Fe(1)−C(8a) 2.207(3), C(9)−C(10) 1.455(4), C(10)−C(11) 1.360(4), C(11)−C(12) 1.542(4), C(12)−C(13) 1.556(4), C(13)−C(14) 1.338(4).

The structure of **15** was unambiguously determined by X-ray crystallography and revealed that, as in **7**, it possesses an (η^5-fluorenyl)iron-dicarbonyl moiety and also a second fluorenyl substituent but now spiro-bonded to a cyclobutene. This four-membered ring is bonded directly to C(9) of the complexed fluorenyl system and is also attached to the iron atom via a =C(Ph)−C(=O)− linkage. The iron atom in **15** is not symmetrically bonded to the central ring of the fluorenyl ligand, with distances ranging from 2.070(3) Å, for Fe(1)−C(9), to 2.244(3) Å for Fe(1)−C(4b). The fluorenyl ligand is not planar, but rather is slightly arced such that the interplanar angle between the six-membered rings is 7°. The iron-to-acyl-carbon distance, Fe(1)−C(35), is slightly longer (2.008(3) Å) than the corresponding distance (1.997(5) Å) in **7**. Although **15** is not actually mirror-symmetric in the solid state, NMR data indicate time-averaged C_s symmetry in solution. To the best of our knowledge, apart from **7**, there is only one previous report of a crystallographically characterized molecule possessing an (η^5-fluorenyl) unit coordinated to iron;[19] thus, **15** is only the third example of this type.

A mechanistic rationale is presented in Scheme 3, whereby initial coordination of an $Fe(CO)_3$ fragment was followed either (i) by rearrangement of the (propargyl-allene)Fe-$(CO)_3$, **16a** (R = TMS), into a silyl-vinylidene complex, **17**, that underwent cyclization to **18** and then to **7** or (ii) in the phenyl case, **16b**, by direct rearrangement to the cyclobutene **19**; subsequent migration onto a terminal carbonyl group yields the observed product, **15**. Evidently, the formation of the cyclopentadiene or cyclobutene ring depends on whether the alkynyl substituent can migrate to form the vinylidene intermediate, **17**, as is known for trimethylsilylalkyne complexes of Ru, Rh, and Ir.[20]

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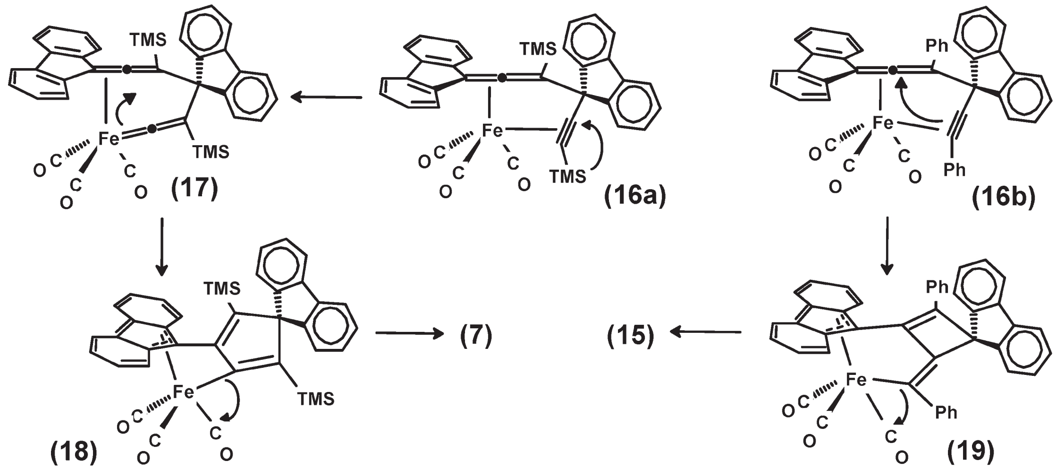
Scheme 3. Mechanisms of Reactions of Propargylallenes with Iron Carbonyl



Reaction of $Fe_2(CO)_9$ with the Phenylbromoallene 11. Since bromoallenes are known to dimerize in the presence of metal salts such as Cu(I),[12] and allyl bromides undergo coupling reactions with iron carbonyls,[21] we decided to investigate the reaction of the phenylbromoallene **11** with di-iron nonacarbonyl to see whether allenyl coupling or any other processes could be elucidated. Moreover, diallenes can cyclize and undergo carbonyl insertions to form highly fluorescent 2,5-dialkylidene-3-cyclopentenones in the presence of iron or cobalt carbonyls.[22] By analogy, we had anticipated the formation of mirror-symmetric 2,5-di(fluorenylidene)-3-cyclopentenone, **20**, and indeed one of the several products did have the molecular formula $C_{43}H_{26}O$ and fluoresced strongly. Moreover, the presence in its ^1H and ^{13}C NMR spectra of eight fluorenyl CH units, two phenyl rings, and a $^{13}C{=}O$ resonance at 203 ppm, together with an infrared absorption at 1704 cm^{-1}, indicated **20** to be a possible product whereby the "inner" and "outer" benzo rings would each exhibit two doublets and two triplets. However, X-ray crystallography (Figure 7) revealed the true answer! The molecule does indeed possess a molecular mirror plane, but not the one anticipated. The product is the bicyclo[3.2.0]heptadienone **21**, in which two nonequivalent spiro-bonded fluorenyls are positioned orthogonal to the planar bicyclic system, and so each exhibits only four CH environments. The angles at the three unsaturated carbons in the cyclobutene ring are C(5)−C(4)−C(3) 92°, C(4)−C(3)−C(6) 94.9°, and C(3)−C(6)−C(5) 90.9°, but the angle containing the spirofluorenyl moiety, C(4)−C(5)−C(6), is only 82.2°. The sequence C(4)−C(3)−C(6)−C(7) is a 1,3-butadiene fragment, and the relevant bond distances are C(4)−C(3) 1.361(2) Å, C(3)−C(6) 1.418(2) Å, and C(6)−C(7) 1.356(2) Å; thus, the central bond that is common to both rings is markedly shorter than the value of ~1.48 Å, which is more typical of a butadiene fragment.

The major product of the reaction of the bromoallene **11** and $Fe_2(CO)_9$ is the diphenylpropargylallene **9**, formally derivable by the head-to-tail coupling of 9-(phenylethynyl)fluorenyl radicals. However, complex **15**, the above-mentioned product of reaction of **9** with iron carbonyl, was not detectable. While any proposed mechanism for the formation of the bicycloheptadienone **21** must remain speculative, it could conceivably arise simply by reductive elimination from **15**, as in Scheme 4. However, the observed long-term thermal stability of **15** at room temperature may militate against such a process.

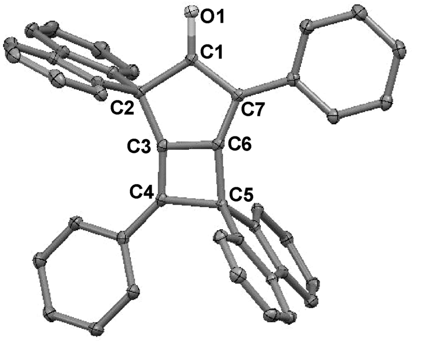
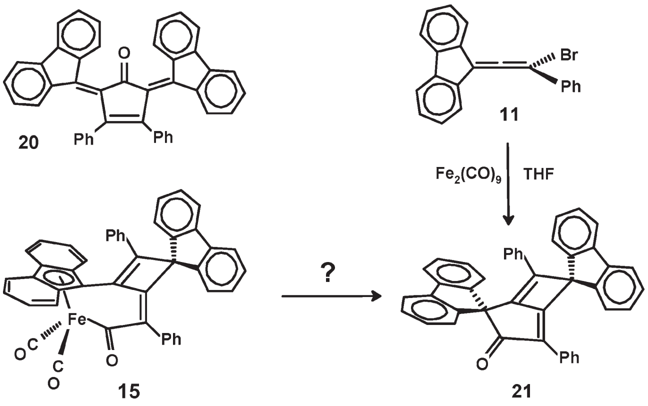


Figure 7. Structure of the bicyclo[3.2.0]heptadienone **21**. Thermal ellipsoids are at 30%.

Scheme 4. Possible Route to 21 via a Reductive Elimination



The bicyclic system in **21** has been reported only very rarely, and we are unaware of any structural studies: pyrolysis of [perchloro-3,4-di(methylene)cyclobutene]$Fe(CO)_3$, **22**, is reported to yield a ketone formulated as either **23a** or **23b** only on the basis of its UV spectrum.[23] Moreover, the

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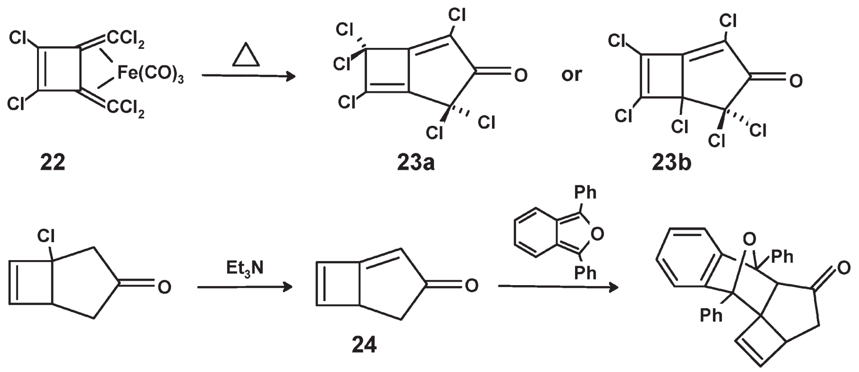
Scheme 5. Previously Reported Bicyclo[3.2.0]heptadienones



molecule **24**, an isomer of tropone, C_7H_6O, and formally the "parent" compound of **23b**, has been characterized in solution by NMR and can be trapped as a Diels−Alder adduct with diphenylisobenzofuran (Scheme 5).[24]

Reactions of Propargylallenes with Silver Nitrate. The use of coinage metals to promote inter- and intramolecular coupling processes is a burgeoning area in organic/organometallic chemistry. Indeed, an entire recent issue of *Chemical Reviews* was devoted to this important theme.[25] In particular, cyclizations of alkynyl-allenes have been effected by treatment with gold or platinum salts, notably by Malacria's group[26−29] and more recently by others.[30] Within the past few years, the intramolecular coupling of alkene and alkyne units has provided direct one-step routes to vinylcyclopentenols,[26] aryl steroids,[31] and methylene-cyclopentenones,[32] as well as a range of small-ring heterocycles.[33] We here describe the reactions of propargylallenes with $AgNO_3$ in the presence of methanol or water.

When the disilylpropargylallene **2** was treated with silver nitrate in methanol at ambient temperature overnight, the terminal trimethylsilyl substituent was eliminated, thus forming the monosilylated propargylallene **25**, whose structure is shown in Figure 8. The carbon−carbon distances in the allenyl and alkynyl units are C(9)−C(10) 1.325(3) Å, C(10)−C(11) 1.298(3) Å, and C(13)−C(14) 1.161(4) Å, and the angle C(9)−C(10)−C(11) is 173.1°.

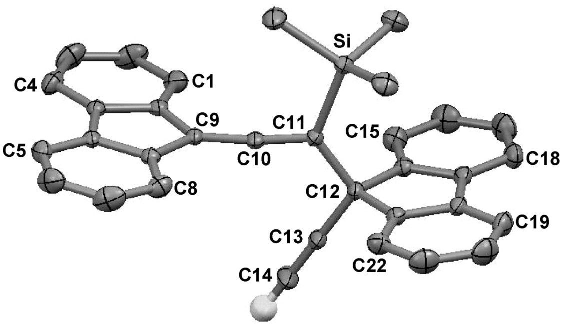


Figure 8. Molecular structure of propargylallene **25**. Thermal ellipsoids are at 20%.

As depicted in Scheme 6, when the monosilyl- and diphenylpropargylallenes **25** and **9** were heated at ~50 °C for 24 h in methanol together with silver nitrate, they underwent cyclization of the allene onto the alkyne to furnish the cyclopentadienes **26** and **27**, respectively, each spiro-linked to a fluorenyl and also possessing a 9-methoxy-[9*H*]-fluorenyl substituent (see Figure 9). In **27**, the phenyls at C(11) and C(14) adopt torsional angles of 78.9° and 85.3°, respectively, with the cyclopentadiene ring. Mechanistically, one can envisage initial coordination of Ag^+ to the alkyne, cyclization to form the cationic five-membered ring system, **28**, and finally nucleophilic attack by methanol.

The ^1H NMR spectrum of **27** reveals that, although the fluorenyl resonances between 7.6 and 7.1 ppm are clearly resolved, the ortho and meta positions of both phenyl rings are markedly broadened at ambient temperature (see Figure 10); evidently the phenyls are in sterically encumbered sites and exhibit slowed rotation on the NMR time-scale. This severe steric hindrance (see Figure 11) may account for the fact that the incoming nucleophile attacks the diphenyl cation **28b** at the fluorenyl C(9) position when one might have assumed that positive charge would be better localized at the benzylic center rather than forming an antiaromatic fluorenyl cation.

The reactions of **25** and **9** with $AgNO_3$ in aqueous acetone, to give **29** and **30**, respectively, proceed analogously in that the products contain a 9-hydroxy-9*H*-fluorenyl group bonded to a cyclopentadiene bearing a spiro-bonded fluorene. However, in the diphenyl system, quenching of the intermediate cation, **28b**, with water, rather than methanol, yields the alcohol **30** (Figure 12a) only as a minor product; the major product (Figure 12b) is the (dispirofluorenyl)-dihydrobenzpentalene **31**, resulting from Friedel−Crafts alkylation of the adjacent phenyl ring.

To conclude, the proximity of the allenyl and alkynyl moieties in the trimethylsilyl- or phenyl-substituted propargylallenes **2**, **25**, and **9** facilitates metal-mediated interactions

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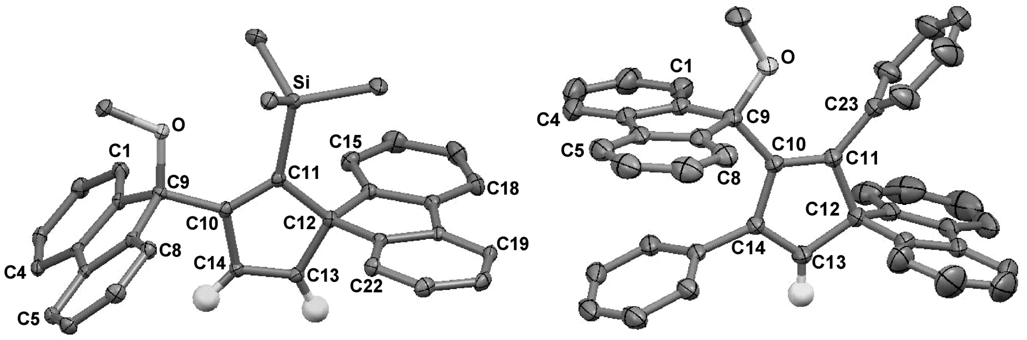


Figure 9. Molecular structures of the 9-(methoxyfluorenyl)(trimethylsilyl)cyclopentadiene **26** and the 9-(methoxyfluorenyl)diphenylcyclopentadiene **27**. Thermal ellipsoids are shown at 50%. Selected bond lengths (Å) for **26**: C(9)−C(10) 1.506(3), C(10)−C(11) 1.353(3), C(11)−C(12) 1.535(3), C(12)−C(13) 1.510(3), C(13)−C(14) 1.321(3) C(14)−C(10) 1.474(3); for **27**: C(9)−C(10) 1.508(3), C(10)−C(11) 1.341(3), C(11)−C(12) 1.529(3), C(12)−C(13) 1.489(3), C(13)−C(14) 1.328(3) C(14)−C(10) 1.488(3), C(11)−C(23) 1.485 (3).

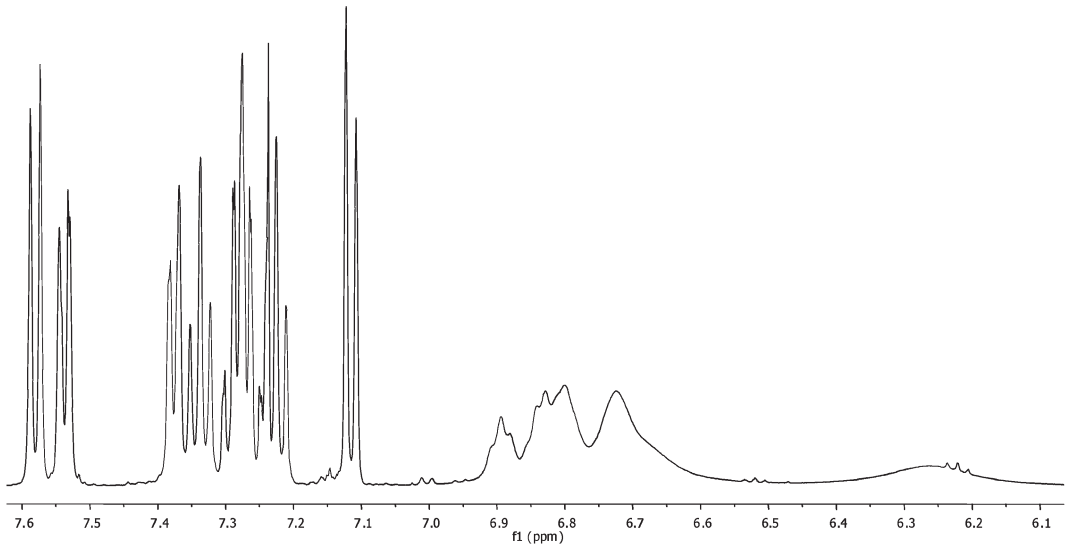
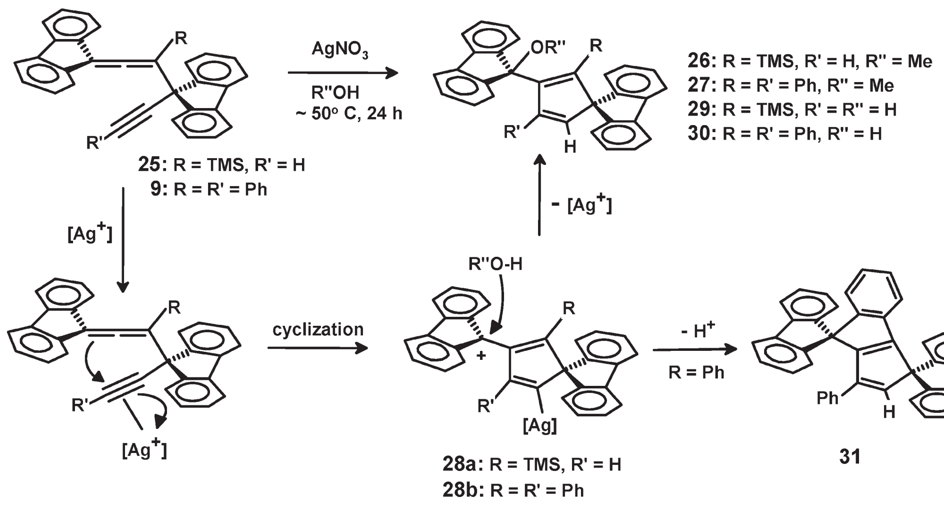


Figure 10. Aromatic region of the 500 MHz ^{1}H NMR spectrum of the 9-(methoxyfluorenyl)diphenylcyclopentadiene **27**, illustrating the clearly resolved fluorenyl peaks from 7.6 to 7.1 ppm and the very broad phenyl resonances between 7.0 and 6.0 ppm.

Scheme 6. Silver-Promoted Cyclization of Propargylallenes



between these functional groups. Iron carbonyl-promoted cyclizations to form the cyclopentadiene or cyclobutene complex **7** or **15** are controlled by the character of the alkynyl substituent in the initial Fe(CO)$_3$ complex, **16**, whereby the trimethylsilyl, but not the phenyl, undergoes rearrangement to form a vinylidene complex. Current work is focused on trapping the propargylallene metal complex prior to cyclization. Propargylallenes react with silver(I) to yield cyclopentadienes and also a dihydrobenzpentalene; extension of this to other polyalkynyl allenes is under investigation. The preliminary study of the organometallic chemistry of bromoallenes demonstrates the potential for novel cyclization processes to be uncovered and will be the subject of a future report.

Experimental Section

General Methods. All reactions were carried under a nitrogen atmosphere, and solvents were dried by standard procedures. ^{1}H and ^{13}C NMR spectra were recorded on Varian 300, 400, 500, or 600 MHz spectrometers. Assignments were based on standard two-dimensional NMR techniques (^{1}H−^{1}H COSY, ^{1}H−^{13}C HSQC, and HMBC, NOESY). Electrospray mass spectrometry was performed on a Micromass Quattro microinstrument. Infrared spectra were recorded on a Perkin-Elmer Paragon 1000 FT-IR spectrometer and were calibrated with polystyrene. Merck silica gel 60 (230−400 mesh) or alumina was used for flash chromatography. Melting points were determined on an Electrothermal ENG instrument and are uncorrected. Elemental analyses were carried out by the Microanalytical Laboratory at University College Dublin. 3,3-(Biphenyl-2,2′-diyl)-1-trimethylsilyl-1-{9-[(trimethylsilyl)ethynyl]-9*H*-fluorenyl}allene, **2**, and 3,3-(biphenyl-2,2′-diyl)-1-bromo-1-phenylallene, **11**, were prepared as previously described.[8,9]

Preparation of 3,3-(Biphenyl-2,2′-diyl)-1-phenyl-1-{9-[(phenylethynyl]-9*H*-fluorenyl}allene (9). 3,3-(Biphenyl-2,2′-diyl)-1-bromo-1-phenylallene (**11**) (2.6 g, 7.5 mmol) was dissolved in dry THF (50 mL) and then added dropwise to a solution of BuLi (2.2 mL, 1.7 M in hexane, 3.75 mmol) in dry THF (10 mL) at −78 °C. This solution was stirred overnight, after which time a solution of saturated NH_4Cl was added, the THF was removed, and the residue was washed with water. The organic layer was extracted using ethyl acetate, washed with brine, and dried over $MgSO_4$, and the solvent removed in vacuo. The residual solid was purified by chromatography on a silica column using dichloromethane/pentane. The yellow-orange powder was washed once with a dichloromethane/pentane mixture, then three times with pure pentane to give the desired product, **9** (850 mg, 1.58 mmol; 42%), as a white-yellow powder, mp 284−286 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.82 (pseudo t, $J = 7.5$ Hz, 2H, H_1, H_8), 7.81 (pseudo t, $J = 7.5$ Hz, 2H, H_{15}, H_{22}), 7.79 (d, $J = 7.5$ Hz, 2H, H_4, H_5), 7.71 (d, $J = 7.5$ Hz, 2H, H_{18}, H_{19}), 7.42−7.35 (m, 8H, H_2, H_3, H_6, H_7, H_{16}, H_{17}, H_{20}, H_{21}), 7.06 (t, $J = 7.5$ Hz, 1H, H_{32}), 7.03 (t, $J = 7.5$ Hz, 1H, H_{26}), 6.97 (t, $J = 7.5$ Hz, 2H, H_{25}, H_{27}), 6.96 (t, $J = 7.5$ Hz, 2H, H_{31}, H_{33}), 6.90 (d, $J = 8.0$ Hz, 2H, H_{24}, H_{28}), 6.83 (d, $J = 8.0$ Hz, 2H, H_{30}, H_{34}). ^{13}C NMR (151 MHz, $CDCl_3$): δ 204.2 (C_{10}), 146.9 (C_{18a}, C_{18b}), 140.5 (C_{12a}, C_{22a}), 139.1 (C_{4a}, C_{4b}), 138.1 (C_{8a}, C_{9a}), 133.9 (C_{23}), 131.7 (C_{30}, C_{34}), 128.7, 128.3, 128.2, 127.4 (C_2, C_3, C_6, C_7, C_{16}, C_{17}, C_{20}, C_{21}), 128.5 (C_{24}, C_{28}), 127.9, 127.89 (C_{25}, C_{27}, C_{31}, C_{33}), 127.8, 127.7 (C_{26}, C_{32}), 125.5 (C_{15}, C_{22}), 123.2 (C_{29}), 123.1 (C_1, C_8), 120.4 (C_{18}, C_{19}), 120.3 (C_4, C_5), 118.4, 109.4 (C_9, C_{11}), 89.4 (C_{13}), 83.00 (C_{14}), 54.6 (C_{12}). HRMS: calcd for $C_{42}H_{27}$ [M + H$^+$], 531.2090; found, 531.2113. A sample for an X-ray crystal structure determination was obtained by crystallization from dichloromethane/pentane.

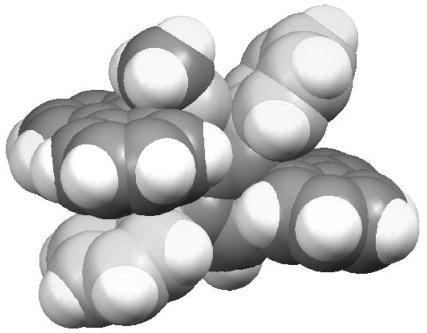


Figure 11. Space-filling representation of the 9-(methoxyfluorenyl)diphenylcyclopentadiene **27**, emphasizing the sterically crowded phenyl environments.

Preparation of 3,4-Di(fluorenyliden)-1,2-diphenylcyclobutene (12). 3,3-(Biphenyl-2,2′-diyl)-1-phenyl-1-(9-phenylethynyl)-9*H*-fluorenylallene (**9**) (250 mg, 0.471 mmol) was dissolved in toluene (10 mL) and heated for 5 h at reflux. The solvent was removed in vacuo and the residual solid purified by chromatography on a silica column using dichloromethane/pentane to yield **12** (50 mg, 0.094 mmol; 20%) as an orange powder, mp 266−268 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.76 (d, $J = 7.5$ Hz, 2H, H_4), 7.70 (d, $J = 7.5$ Hz, 2H, H_5), 7.57 (d, $J = 7.8$ Hz, 2H, H_8), 7.37 (t, $J = 7.5$ Hz, 2H, H_{15}), 7.31 (t, $J = 7.5$ Hz, 4H, H_{14}, H_{16}), 7.28 (t, $J = 7.5$ Hz, 2H, H_3), 7.27 (d, $J = 7.5$ Hz, 4H, H_{13}, H_{17}), 7.15 (t, $J = 7.5$ Hz, 2H, H_6), 6.88 (t, $J = 7.5$ Hz, 2H, H_2), 6.85 (d, $J = 7.5$ Hz, 2H, H_1), 6.81 (t, $J = 7.5$ Hz, 2H, H_7). ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.6 (C_{11}), 145.0 (C_{10}), 140.0 (C_{4b}), 140.4 (C_{4a}), 137.9 (C_{8a}), 137.2 (C_{9a}), 133.0 (C_{12}), 128.7 (C_8), 128.6 (C_{13}, C_{17}), 128.1 (C_{14}, C_{16}), 127.7 (C_{15}), 127.6 (C_1), 127.6 (C_9), 127.2 (C_3), 127.1 (C_6), 126.4 (C_7), 125.6 (C_2), 119.3 (C_4), 119.1 (C_5). HRMS: calcd for $C_{42}H_{27}$ [M + H$^+$], 531.2121; found, 531.2113. A sample for an X-ray crystal structure determination was obtained by crystallization from dichloromethane/pentane.

Preparation of [3,3-(Biphenyl-2,2′-diyl)-1-trimethylsilyl-1-{9-[(trimethylsilylethynyl]-9*H*-fluorenyl}allene]$Co_2(CO)_6$ (13). $Co_2(CO)_8$ (183 mg, 0.535 mmol) was added to a solution of bis(trimethylsilyl)propargylallene **2** (280 mg, 0.535 mmol) in degassed pentane (50 mL). The brown-yellow solution was stirred

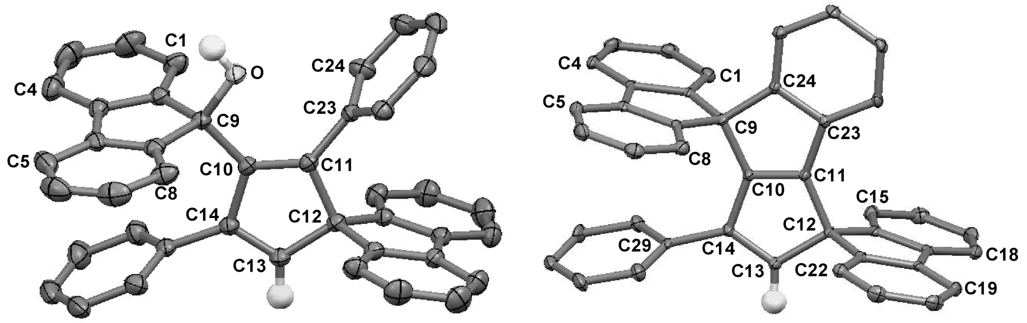


Figure 12. Molecular structures of (a) the cyclopentadiene **30** and (b) the dihydrobenzpentalene **31**. Thermal ellipsoids are shown at 20% and 50%, respectively. Selected bond lengths (Å) for **30**: C(9)−C(10) 1.515(2), C(10)−C(11) 1.343(2), C(11)−C(12) 1.533(2), C(12)−C(13) 1.497(2), C(13)−C(14) 1.329(2), C(14)−C10 1.493(2), C(11)−C(23) 1.487(2); for **31**: C(9)−C(10) 1.515(3), C(10)−C(11) 1.333(3), C(11)−C(12) 1.514(3), C(12)−C(13) 1.528(3), C(13)−C(14) 1.349(3), C(14)−C10 1.465(3), C(9)−C(24) 1.520(4), C(23)−C(24) 1.415(3), C(11)−C(23) 1.456(3).

for 15 min and turned dark red. The crude was purified by chromatography on a silica column using ether/pentane to yield **13** (410 mg, 0.51 mmol; 95%) as a dark red powder. ^{1}H NMR (400 MHz, C_6D_6): δ 8.06 (d, J = 7.4 Hz, 4H), 7.66 (d, J = 7.5 Hz, 2H), 7.44 (d, J = 7.2 Hz, 2H), 7.38 (t, J = 7.2 Hz, 2H), 7.26 (t, J = 7.9 Hz, 2H), 7.25 (t, J = 7.4 Hz, 2H), 7.20 (td, J = 7.4, 1.0 Hz, 2H), 0.12 (s, 9H, TMS), −0.42 (s, 9H, TMS). ^{13}C NMR (101 MHz, C_6D_6): δ 201.7 (C_{10}), 200.3 (brd, Co-CO), 152.3, 141.2, 139.1, 138.8 (fluorenyl *C*), 129.4, 128.3, 127.9, 127.0, 126.5, 123.6, 120.9, 120.7 (fluorenyl *C*H), 117.7, 110.6, 108.8, 82.4 (C_9, C_{11}, C_{13}, C_{14}), 62.1 (C_{12}), 1.8 ($Si(CH_3)_3$), 0.6 ($Si(CH_3)_3$). Anal. Calcd for $C_{42}H_{34}Co_2O_6Si_2$: C, 62.37; H, 4.24; Co, 14.57. Found: C, 62.20; H, 4.48; Co, 14.30. A sample for an X-ray crystal structure determination was obtained by crystallization from ether/pentane.

Preparation of [3,3-(Biphenyl-2,2′-diyl)-1-phenyl-1-{9-[(phenylethynyl]-9*H*-fluorenyl}allene]$Co_2(CO)_6$ (14). $Co_2(CO)_8$ (900 mg, 2.6 mmol) was added to a solution of diphenyl propargylallene **9** (480 mg, 0.905 mmol) in dry degassed THF (20 mL). The black solution was stirred overnight. The solvent was removed in vacuo and the residual solid purified by chromatography on a silica column using dichloromethane/pentane to yield **14** (335 mg, 0.41 mmol; 45%) as a dark red powder. ^{1}H NMR (500 MHz, C_6D_6): δ 7.97 (d, J = 6.3 Hz, 2H), 7.88 (d, J = 6.0 Hz, 2H), 7.51 (d, J = 6.5 Hz, 2H), 7.46 (d, J = 6.0 Hz, 2H), 7.42 (d, J = 6.4 Hz, 2H), 7.22−7.07 (m, 8H), 6.98 (d, J = 4.6 Hz, 2H), 6.88−6.76 (m, 3H), 6.68−6.55 (m, 3H). ^{13}C NMR (101 MHz, C_6D_6): δ 203.2 (C_{10}), 197.4 (Co-CO), 149.9, 138.7, 137.7, 136.6 (fluorenyl *C*), 137.4, 135.8 (C_{23}, C_{29}), 127.9, 127.1, 126.7, 126.3, 126.1, 126.0, 125.8, 125.6, 125.2, 124.9, 121.9, 118.7, 118.4 (aromatic *C*H), 117.6, 109.3, 103.8, 96.7 (C_9, C_{11}, C_{13}, C_{14}), 61.7 (C_{12}). Anal. Calcd for $C_{48}H_{26}Co_2O_6$: C, 70.60; H, 3.21; Co, 14.43. Found: C, 70.40; H, 3.46; Co, 14.20. A sample for an X-ray crystal structure determination was obtained by crystallization from dichloromethane/pentane.

Reaction of 9 with Iron Carbonyl. To a solution of 3,3-(biphenyl-2,2′-diyl)-1-phenyl-1-(9-phenylethynyl)-9*H*-fluorenyl-allene (**9**) (0.30 g, 0.57 mmol) dissolved in dry THF (16 mL) was added $Fe(CO)_5$ (0.08 mL, 0.62 mmol). The solution was cooled to −20 °C, and morpholine *N*-oxide (72.9 mg, 0.622 mmol) dissolved in dry THF (14 mL) was added dropwise. The solution was stirred for 1 h at −20 °C and a further 2.5 h at room temperature. The solvent was removed in vacuo and the residual solid purified by chromatography on a silica column using dichloromethane/pentane to yield **15** (49 mg, 0.073 mmol; 12%) as an orange powder. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.13 (d, J = 8.4 Hz, 2H, H_4, H_5), 7.75 (d, J = 8.5 Hz, 2H, H_1, H_8), 7.68 (d, J = 8.4 Hz, 4H, H_{15}, H_{18}, H_{19}, H_{22}), 7.51 (t, J = 7.7 Hz, 2H, H_2, H_7), 7.46 (t, J = 7.7 Hz, 2H, H_3, H_6), 7.37, 7.28 (2 td, J = 7.4, 1.0 Hz, 4H, H_{16}, H_{17}, H_{20}, H_{21}), 7.20 (t, J = 7.1 Hz, 1H, H_{26}), 7.12 (t, J = 7.7 Hz, 2H, H_{25}, H_{27}), 7.09 (dd, J = 8.4, 1.3 Hz, 2H, H_{24}, H_{28}), 6.75 (t, J = 7.4 Hz, 1H, H_{32}), 6.63 (t, J = 7.7 Hz, 2H, H_{31}, H_{33}), 6.24 (dd, J = 8.2, 1.1 Hz, 2H, H_{30}, H_{34}). ^{13}C NMR (126 MHz, $CDCl_3$): δ 249.3 (Fe μ-CO), 212.8 (Fe-CO), 162.3 (C_{10}), 154.1 (C_{11}), 145.1, 141.2 (C_{12a}, C_{18a}, C_{18b}, C_{22a}), 135.8 (C_{13}), 134.4 (C_{29}), 133.8 (C_{14}), 131.6 (C_{23}), 129.8 (C_{26}), 129.5 (C_2, C_7), 129.1 (C_{25}, C_{27}), 128.6 (C_{30}, C_{34}), 128.4, 127.7 (C_{16}, C_{17}, C_{20}, C_{21}), 127.7 (C_{24}, C_{28}), 126.9 (C_{31}, C_{33}), 126.5 (C_3, C_6), 126.3 (C_{32}), 124.2 (C_1, C_8), 124.1 (C_4, C_5), 123.6, 120.3 (C_{15}, C_{18}, C_{19}, C_{22}), 108.8 (C_{8a}, C_{9a}), 98.2 (C_{4a}, C_{4b}), 67.0 (C_{12}), 60.0 (C_9). IR (liquid, CH_2Cl_2): ν 2017, 1961 cm^{-1} (terminal C=O), 1604 cm^{-1} (bridging C=O). HRMS: calcd for $C_{42}H_{27}Fe(CO)_3$ [M + H$^+$], 671.1332; found, 671.1310. A sample for an X-ray crystal structure determination was obtained by crystallization from dichloromethane.

Preparation of Bicyclo[3.2.0]heptadienone (21). Diiron-nonacarbonyl (1.93 g, 5.30 mmol) and 3,3-(biphenyl-2,2′-diyl)-1-bromo-1-phenylallene (**11**) (300 mg, 0.87 mmol) were dissolved in dry THF (20 mL) and stirred for 3 days at room temperature. The solvent was removed in vacuo and the residual solid purified by chromatography on a silica column using dichloromethane/pentane to yield **21** (34 mg, 0.06 mmol; 7%) as a bright yellow powder. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.00 (d, J = 7.6 Hz, 2H, fluorenyl-A), 7.95 (d, J = 7.6 Hz, 2H, fluorenyl-B), 7.63 (d, J = 7.5 Hz, 2H, fluorenyl-A), 7.53 (t, J = 7.6 Hz, 2H, fluorenyl-A), 7.50 (t, J = 7.6 Hz, 2H, fluorenyl-B), 7.49 (d, J = 7.6 Hz, 2H, fluorenyl-B), 7.38 (t, J = 7.6 Hz, 2H, fluorenyl-B), 7.36 (t, J = 7.6 Hz, 2H, fluorenyl-A), 7.24 (dd, J = 7.5, 1.9 Hz, 2H, phenyl-B o-*H*), 7.07 − 7.00 (m, 3H, phenyl-B m/p-*H*), 6.97 (t, J = 7.4 Hz, 1H, phenyl-A p-*H*), 6.85 (t, J = 7.7 Hz, 2H, phenyl-A m-*H*), 6.24 (d, J = 7.6 Hz, 2H, phenyl-A o-*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ 203.3 (C=O), 180.2, 153.0 (C_3, C_6), 146.4 (phenyl-A ipso-*C*), 143.5, 142.9, 142.4, 141.0 (fluorenyl *C*), 130.9, 130.7 (C_4, C_7), 129.5 (fluorenyl-A *C*H), 129.3 (phenyl-A p-*C*), 128.8 (fluorenyl-B *C*H), 128.7 (phenyl-A m-*C*), 128.5 (phenyl-B m-*C*), 128.3 (fluorenyl-A *C*H), 128.2 (fluorenyl-B *C*H), 127.8 (phenyl-B p-*C*), 127.5 (phenyl-B o-*C*), 127.2 (phenyl-A o-*C*), 124.5 (fluorenyl-A *C*H), 123.6 (fluorenyl-B *C*H), 121.6 (phenyl-B ipso-*C*), 121.0 (fluorenyl-B *C*H), 120.9 (fluorenyl-A *C*H), 68.69, 65.09 (C_2, C_5). IR (liquid, CH_2Cl_2): 1704 cm^{-1} (C=O). Anal. Calcd for $C_{43}H_{26}O\cdot 0.9CH_2Cl_2$: C, 83.02; H, 4.41. Found: C, 83.28; H, 4.71. A sample for an X-ray crystal structure determination was obtained by crystallization from dichloromethane/pentane.

Preparation of 3,3-(Biphenyl-2,2′-diyl)-1-trimethylsilyl-1-{9-[(ethynyl]-9*H*-fluorenyl}allene (25). To a solution of bis(trimethylsilyl)propargylallene (**2**) (500 mg, 0.96 mmol) in degassed ether/methanol/water (32 mL/18 mL/4 mL) was added silver nitrate (120 mg, 0.70 mmol) as a powder at once. After stirring overnight in the dark, water was added and the mixture was extracted with ether. The organic layers were combined, washed with water and brine, dried over $MgSO_4$, filtered, and concentrated to give a slightly yellow powder. The powder was washed with a small amount of ether to give **25** (350 mg, 0.77 mmol; 81%) as a white powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86−7.76 (m, 8H), 7.50−7.45 (m, 4H), 7.44−7.38 (m, 4H), 2.05 (s, 1H, C≡C*H*), −0.44 (s, 9H, TMS). ^{13}C NMR (125 MHz, $CDCl_3$): δ 204.7 (C_{10}), 147.2, 140.3, 138.7, 138.0 (fluorenyl *C*), 128.8, 128.3, 127.1, 126.9, 125.5, 122.3, 120.3, 120.2 (fluorenyl *C*H), 110.7, 105.4 (C_9, C_{11}), 89.4, 84.1 (C_{13}, C_{14}), 70.3 (C_{12}), −0.1 ($Si(CH_3)_3$). IR (liquid, CH_2Cl_2): 3300 cm^{-1} (C≡C), 1920 cm^{-1} (C=C=C). ESMS: calcd for $C_{33}H_{26}Si$ [M + H$^+$], 451.19; found, 451.21. A sample for X-ray crystal structure determination was obtained by crystallization from dichloromethane/pentane.

Preparation of 9-(2-Trimethylsilylspiro[cyclopenta[2,4]diene-1,9′-[9*H*]fluorene]-3-yl)-9-methoxy-9*H*-fluorene (26). $AgNO_3$ (220 mg, 1.30 mmol) was added to a solution of bis(trimethylsilyl)propargylallene, **2** (500 mg, 0.956 mmol), in degassed methanol (20 mL); the mixture was heated at 55 °C for 24 h. After evaporation of the methanol, the residual solid was dissolved in ether, washed with water and brine, dried over $MgSO_4$, and concentrated to give **26** (300 mg, 0.62 mmol; 65%) as a yellow powder. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.76 (d, J = 8.0 Hz, 2H, H_4, H_5), 7.74 (d, J = 8.0 Hz, 2H, H_{18}, H_{19}), 7.55 (dd, J = 7.2, 0.6 Hz, 2H, H_1, H_8), 7.47 (td, J = 7.4, 1.4 Hz, 2H, H_3, H_6), 7.43 (td, J = 7.3, 1.1 Hz, 2H, H_2, H_7), 7.34 (td, J = 7.5, 0.8 Hz, 2H, H_{17}, H_{20}), 7.23 (t, J = 7.5 Hz, 2H, H_{16}, H_{21}), 7.04 (d, J = 7.5 Hz, 2H, H_{15}, H_{22}), 5.81 (d, J = 5.0 Hz, 1H, H_{13}), 5.36 (d, J = 5.0 Hz, 1H, H_{14}), 2.86 (s, 3H, OC*H*$_3$), −0.17 (s, 9H, TMS). ^{13}C NMR (126 MHz, $CDCl_3$): δ 159.4 (C_{10}), 145.6 (C_{8a}, C_{9a}), 145.3 (C_{13}), 144.2 (C_{12a}, C_{22a}), 142.5 (C_{18a}, C_{18b}), 141.8 (C_{11}), 141.4 (C_{4a}, C_{4b}), 131.5 (C_{14}), 129.5 (C_3, C_6), 128.6 (C_2, C_7), 127.4 (C_{17}, C_{20}), 127.3 (C_{16}, C_{21}), 125.3 (C_1, C_8), 123.0 (C_{15}, C_{22}), 120.4 (C_{18}, C_{19}), 120.2 (C_4, C_5), 89.6 (C_9), 76.5 (C_{12}), 50.0 (OCH_3), 1.9 ($Si(CH_3)_3$). ESMS: calcd for $C_{34}H_{30}OSi$ [M − OCH_3^-], 451.20; found, 451.25. Anal. Calcd for $C_{34}H_{30}OSi\cdot 0.5MeOH$: C, 83.09; H, 6.47. Found: C, 82.72; H, 6.19. A sample suitable for an X-ray crystal structure determination was obtained by crystallization from ether/dichloromethane.

Table 1. Crystallographic Data for 9, 12, 13, 14, and 15

	9	12	13	14	15
formula	$C_{42}H_{26}$	$C_{42}H_{26}\cdot CH_2Cl_2$	$C_{42}H_{34}Si_2Co_2O_6$	$C_{48}H_{26}Co_2O_6$	$(C_{45}H_{27}FeO_3)_2\cdot CH_2Cl_2\cdot (H_2O)_{0.3}$
M	530.63	615.55	808.73	816.55	1430.45
cryst syst	triclinic	orthorhombic	monoclinic	triclinic	monoclinic
space group	$P\bar{1}$ (#2)	$P2_12_12_1$ (#18)	$P2_1/n$ (#14)	$P\bar{1}$ (#2)	$P2_1/c$ (#14)
a [Å]	8.8808(10)	14.220(2)	9.2714(17)	9.8101(4)	25.699(2)
b [Å]	8.9416(10)	8.4832(12)	20.869(4)	18.4399(8)	13.8982 (13)
c [Å]	19.076(2)	12.4919(18)	20.063(4)	20.9994(9)	19.1186(17)
α [deg]	87.529(2)	90	90	103.436(1)	90
β [deg]	78.066(2)	90	95.647(4)	93.299((1)	99.035(3)
γ [deg]	72.726(2)	90	90	92.751(1)	90
V [Å^3]	1419.9(3)	1507.0(4)	3862.9(12)	3681.3(3)	6736.1(11)
Z	2	2	4	4	4
ρ_{calcd} [g cm^{-3}]	1.245	1.357	1.391	1.473	1.410
T [K]	100(2)	100(2)	100(2)	100(2)	100(2)
μ [mm^{-1}]	0.071	0.248	0.967	0.954	0.571
F(000)	556	640	1664	1664	2946
θ range for data collection [deg]	2.18 to 25.00	1.63 to 26.42	1.41 to 28.30	1.14 to 30.50	1.61 to 22.08
index ranges	$-10 \le h \le 10$	$-17 \le h \le 17$	$-12 \le h \le 12$	$-13 \le h \le 13$	$-27 \le h \le 27$
	$-10 \le k \le 10$	$-10 \le k \le 10$	$-27 \le k \le 27$	$-26 \le k \le 26$	$-14 \le k \le 14$
	$-22 \le l \le 22$	$-15 \le l \le 15$	$-26 \le l \le 26$	$-29 \le l \le 29$	$-20 \le l \le 20$
reflns measd	22 612	13 075	38 946	86 123	40 546
indep reflns	4992	3098	9585	22 081	8285
R_{int}	0.0311	0.0436	0.0360	0.0333	0.0549
data/restraints/params	4992/0/483	3098/0/204	9585/0/605	22 081/0/1217	8285/377/920
final R values [$I > 2\theta(I)$]:					
R1	0.0381	0.0431	0.0355	0.0363	0.0375
wR2	0.0907	0.0884	0.0868	0.0886	0.0853
R values (all data):					
R1	0.0448	0.0513	0.0439	0.0451	0.0471
wR2	0.0950	0.0912	0.0915	0.0929	0.0902
GOF on F^2	1.043	1.068	1.049	1.048	1.023

Preparation of 9-(2,4-Diphenylspiro[cyclopenta[2,4]diene-1,9′-[9*H*]-fluorene]-3-yl)-9-methoxy-9*H*-fluorene (27). $AgNO_3$ (170 mg, 1.00 mmol) was added to a solution of diphenylpropargylallene **9** (330 mg, 0.565 mmol) in degassed methanol (20 mL); the mixture was heated at 45 °C for 24 h. After evaporation of the methanol, the residual solid was dissolved in ether, washed with water and brine, dried over $MgSO_4$, concentrated, and recrystallized from ether/dichloromethane to give **27** (125 mg, 0.22 mmol; 39%) as yellow crystals. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.58 (d, J = 7.4 Hz, 2H, H_1, H_8), 7.54 (d, J = 7.4 Hz, 2H, H_{18}, H_{19}), 7.38 (d, J = 7.4 Hz, 2H, H_{15}, H_{22}), 7.34 (t, J = 7.3 Hz, 2H, H_2, H_7), 7.29 (td, J = 7.3, 1.3 Hz, 2H, H_{16}, H_{21}), 7.26 (td, J = 7.3, 1.3 Hz, 2H, H_{17}, H_{20}), 7.22 (t, J = 7.3 Hz, 2H, H_3, H_6), 7.11 (d, J = 7.4 Hz, 2H, H_4, H_5), 6.94−6.58 (m, 8H, phenyl *H*), 6.38−6.13 (m, 2H, phenyl *H*), 5.84 (s, 1H, H_{13}), 2.22 (s, 3H, OCH_3). ^{13}C NMR (126 MHz, $CDCl_3$): δ 149.5, 147.7 (C_{10}, C_{11}), 145.4 (C_{8a}, C_{9a}), 142.9 (C_{12a}, C_{22a}), 142.6 (C_{18a}, C_{18b}), 142.3 (C_{14}), 142.0 (C_{4a}, C_{4b}), 137.2 (C_{13}), 129.0 (C_3, C_6), 128.9 (4C, phenyl o/m-*C*), 127.9 (C_2, C_7), 127.6 (C_{17}, C_{20}), 127.2 (C_{16}, C_{21}), 126.4 (2C, phenyl o/m-*C*), 125.9 (2C, phenyl o/m-*C*), 125.5 (1C, phenyl p-*C*), 125.4 (1C, phenyl p-*C*), 125.3 (C_1, C_8), 123.7 (C_{15}, C_{22}), 120.3 (C_{18}, C_{19}), 119.9 (C_4, C_5), 88.3 (C_9), 72.9 (C_{12}), 49.5 (OCH_3). ESMS: calcd for $C_{43}H_{30}O$ [$M - OCH_3^-$], 531.21; found, 531.27. HRMS: calcd for $C_{43}H_{30}O$ [$M + H^+$], 563.2375; found, 563.2387. A sample suitable for an X-ray crystal structure determination was obtained by crystallization from ether/dichloromethane.

Preparation of 9-(2-Trimethylsilylspiro[cyclopenta[2,4]diene-1,9′-[9*H*]fluorene]-3-yl)-9*H*-fluoren-9-ol (29). $AgNO_3$ (40 mg, 0.235 mmol) was added to a solution of bis(trimethylsilyl)-propargylallene **9** (330 mg, 0.565 mmol) in a degassed water/acetone/THF (5 mL/20 mL/2 mL) solution; the mixture was heated at 55 °C for 24 h in the dark. After evaporation of the solvent, the residual solid was dissolved in ether, washed with water and brine, dried over $MgSO_4$, and concentrated. The residual solid was purified by chromatography on a silica column using dichloromethane/pentane to yield **29** (60 mg, 0.13 mmol; 34%) as a yellow powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, J = 7.0 Hz, 2H, H_{18}, H_{19}), 7.71 (d, J = 7.0 Hz, 2H, H_1, H_8), 7.60 (dd, J = 7.0, 0.9 Hz, 2H, H_4, H_5), 7.44 (td, J = 7.4, 1.2 Hz, 2H, H_2, H_7), 7.41 (td, J = 7.4, 1.2 Hz, 2H, H_3, H_6), 7.33 (td, J = 7.5, 1.0 Hz, 2H, H_{17}, H_{20}), 7.22 (td, J = 7.5, 1.0 Hz, 2H, H_{16}, H_{21}), 7.04 (d, J = 7.5 Hz, 2H, H_{15}, H_{22}), 5.81 (d, J = 5.0 Hz, 1H, H_{13}), 5.35 (d, J = 4.9 Hz, 2H, H_{14}), 2.29 (s, 1H, O*H*), −0.16 (s, 9H, TMS). ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.7 (C_{10}), 149.2 (C_{8a}, C_{9a}), 145.5 (C_{13}), 144.0 (C_{18a}, C_{18b}), 142.5 (C_{12a}, C_{22a}), 142.1 (C_{11}), 140.0 (C_{4a}, C_{4b}), 131.7 (C_{14}), 129.5 (C_2, C_7), 128.9 (C_3, C_6), 127.5 (C_{17}, C_{20}), 127.3 (C_{16}, C_{21}), 124.7 (C_4, C_5), 123.0 (C_{15}, C_{22}), 120.4 (C_{18}, C_{19}), 84.3 (C_9), 76.7 (C_{12}), 2.0 ($Si(CH_3)_3$). ESMS: calcd for $C_{33}H_{28}OSi$ [$M - OH^-$], 451.19; found, 451.23.

Preparation of 9-(2,4-Diphenylspiro[cyclopenta[2,4]diene-1,9′-[9*H*]fluorene]-3-yl)-9*H*-fluoren-9-ol (30) and Its Corresponding Dihydrobenzpentalene (31). $AgNO_3$ (40 mg, 0.235 mmol) was added to a solution of the diphenylpropargylallene **9** (200 mg, 0.383 mmol) in a degassed water/acetone/THF (5 mL/20 mL/2 mL) solution; the mixture was heated at 55 °C for 24 h in the dark. After evaporation of the solvent, the residual solid was dissolved in ether, washed with water and brine, dried over $MgSO_4$, and concentrated. The residual solid was purified by chromatography on a silica column using dichloromethane/pentane to yield **30** (20 mg, 0.036 mmol; 10%) as a yellow powder and its corresponding dihydrobenzpentalene, **31** (150 mg, 0.283 mmol; 74%), as a yellow powder. Data for **30**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, J = 7.4 Hz, 2H, H_1, H_8), 7.57 (dd, J = 7.0, 1.4 Hz, 2H, H_{18}, H_{19}), 7.43 (d, J = 7.0 Hz, 2H, H_{15}, H_{22}), 7.36 (t, J = 7.2 Hz, 2H, H_2, H_7), 7.35 (t, J = 7.0 Hz, 2H, H_{16}, H_{21}), 7.31 (td, J = 7.3, 1.4 Hz, 2H, H_{17}, H_{20}), 7.25 (t, J = 7.4 Hz, 2H, H_3, H_6), 7.14 (d, J = 7.5 Hz, 2H, H_4, H_5), 7.02−6.94 (m, 3H, 1 phenyl p-*H*, 2 phenyl o/m-*H*), 6.94−6.83 (m, 3H, 1 phenyl p-*H*, 2 phenyl o/m-*H*), 6.68 (t, J = 6.9 Hz, 2H, phenyl o/m-*H*), 6.20−6.10 (m, 2H, phenyl o/m-*H*), 5.90 (s, 1H, H_{13}), 2.21 (s, 1H, O*H*). ^{13}C NMR (101 MHz, $CDCl_3$): δ 149.4 (C_{10} or C_{11}), 148.5 (C_{8a}, C_{9a}), 147.3 (C_{10} or C_{11}), 143.1 (C_{14}), 142.7 (C_{18a}, C_{18b}), 142.3 (C_{12a}, C_{22a}), 140.9 (C_{4a}, C_{4b}), 137.2 (C_{13}), 136.0 (phenyl ipso-*C*), 129.2 (phenyl o/m-*C*), 129.0 (C_3, C_6), 128.9 (phenyl o/m-*C*), 128.1 (C_2, C_7), 127.9 (C_{17}, C_{20}), 127.4

Table 2. Crystallographic Data for 21, 25, 26, 27, 30, and 31

	21	**25**	**26**	**27**	**30**	**31**
formula	$C_{44}H_{26}O \cdot CH_2Cl_2$	$C_{33}H_{26}Si$	$C_{34}H_{30}SiO$	$C_{43}H_{30}O$	$(C_{42}H_{28}O)_2 \cdot CH_3OH$	$C_{42}H_{26}$
M	643.56	450.63	482.67	562.67	1129.33	530.63
cryst syst	monoclinic	orthorhombic	triclinic	monoclinic	triclinic	monoclinic
space group	$P2_1/n$ (#14)	*Pnma* (#62)	$P\bar{1}$ (#2)	$P2_1/n$ (#14)	$P\bar{1}$ (#2)	$P2_1/c$ (#14)
a [Å]	10.8528(8)	19.0833(15)	12.1774(13)	8.4024(12)	9.0716(7)	22.645(4)
b [Å]	21.7590(15)	16.0230(12)	15.1205(16)	23.421(3)	13.6689(10)	17.311(3)
c [Å]	13.7075(10)	8.2882(6)	16.2574(17)	15.892(2)	14.0514 (11)	14.296(2)
α [deg]	90	90	104.410(2)	90	65.498(2)	90
β [deg]	90.513(2)	90	90.132(2)	91.641(4)	72.612(2)	90.186(4)
γ [deg]	90	90	112.246(2)	90	86.536(2)	90
V [Å^3]	3236.8(4)	2534.3(3)	2667.9(5)	3126.2(8)	1508.9(2)	5604.3(16)
Z	4	4	4	4	1	8
ρ_{calcd} [g cm^{-3}]	1.321	1.181	1.202	1.195	1.243	1.258
T [K]	100(2)	293(2)	100(2)	293(2)	293(2)	100(2)
μ [mm^{-1}]	0.236	0.111	0.113	0.070	0.074	0.071
$F(000)$	1336	952	1024	1184	594	2224
θ range for data collection [deg]	1.76 to 26.44	2.13 to 24.10	1.51 to 23.29	1.55 to 20.86	1.67 to 22.01	0.90 to 24.59
index ranges	$-13 \le h \le 13$	$-21 \le h \le 18$	$-13 \le h \le 13$	$-8 \le h \le 8$	$-9 \le h \le 9$	$-26 \le h \le 26$
	$-27 \le k \le 27$	$-18 \le k \le 17$	$-16 \le k \le 16$	$-23 \le k \le 23$	$-14 \le k \le 14$	$-19 \le k \le 20$
	$-16 \le l \le 17$	$-9 \le l \le 9$	$-18 \le l \le 18$	$-15 \le l \le 15$	$-14 \le l \le 14$	$-16 \le l \le 16$
reflns measd	28 596	12 349	18 239	16 631	18 707	41 155
indep reflns	6635	2090	7653	3291	3690	9131
R_{int}	0.0317	0.0259	0.0328	0.0242	0.0218	0.0521
data/restraints/params	6635/0/397	2090/0/168	7653/0/657	3291/131/398[a]	3690/131/409[a]	9131/0/758
final R values [$I > 2\theta(I)$]:						
R1	0.0437	0.0427	0.0432	0.0397	0.0363	0.0524
wR2	0.1052	0.1140	0.0978	0.0920	0.0916	0.1361
R values (all data):						
R1	0.0524	0.0496	0.0589	0.0496	0.0412	0.0613
wR2	0.1087	0.1194	0.1047	0.0976	0.0948	0.1450
GOF on F^2	1.062	1.027	1.017	1.044	1.052	1.026

[a] DELU restraints were applied to all thermal displacement parameters.

(phenyl o/m-*C*), 127.3 (C_{16}, C_{21}), 127.1 (phenyl p-*C*), 126.5 (phenyl o/m-*C*), 125.7 (phenyl p-*C*), 124.1 (C_1, C_8), 123.6 (C_{15}, C_{22}), 120.5 (C_{18}, C_{19}), 120.4 (C_4, C_5), 83.7 (C_9), 73.0 (C_{12}). ESMS: calcd for $C_{42}H_{28}O$ [M$-$OH$^-$], 531.21; found, 531.31. Data for **31**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, J = 7.6 Hz, 2H, H_{18}, H_{19}), 7.81 (d, J = 7.6 Hz, 2H, H_4, H_5), 7.46$-$7.39 (m, 2H, H_{17}, H_{20}), 7.35 (td, J = 7.5, 0.8 Hz, 2H, H_3, H_6), 7.29$-$7.21 (m, 4H, H_{15}, H_{16}, H_{21}, H_{22}), 7.17 (td, J = 7.4, 0.8 Hz, 2H, H_2, H_7), 7.07 (d, J = 7.5 Hz, 2H, H_1, H_8), 6.94 (t, J = 7.3 Hz, 1H, H_{32}), 6.85 (t, J = 7.6 Hz, 2H, H_{31}, H_{33}), 6.81 (td, J = 7.5, 1.0 Hz, 1H, H_{27}), 6.74 (td, J = 7.5, 1.1 Hz, 1H, H_{26}), 6.72 (d, J = 7.6 Hz, 2H, H_{30}, H_{34}), 6.48 (d, J = 7.6 Hz, 1H, H_{25}), 6.46 (s, 1H, H_{13}), 6.24 (d, J = 7.2 Hz, 1H, H_{28}). ^{13}C NMR (101 MHz, $CDCl_3$): δ 157.5, 155.5 (C_{10}, C_{11}), 153.5 (C_{24}), 145.6 (C_{8a}, C_{9a}), 144.8 (C_{14}), 143.1 (C_{12a}, C_{22a}), 142.5 (C_{4a}, C_{4b}), 142.2 (C_{18a}, C_{18b}), 138.2 (C_{13}), 138.0 (C_{23}), 134.2 (C_{29}), 128.1 (C_3, C_6, C_{17}, C_{20}), 128.0 (C_2, C_7), 127.9 (C_{16}, C_{21}, C_{31}, C_{33}), 127.3 (C_{32}), 127.2 (C_{27}), 126.7 (C_{30}, C_{34}), 125.5 (C_{26}), 123.8 (C_{15}, C_{22}), 123.6 (C_1, C_8), 122.8 (C_{25}), 120.7 (C_{18}, C_{19}), 120.4 (C_4, C_5), 118.5 (C_{28}), 64.6 (C_{12}), 64.3 (C_9). HRMS: calcd for $C_{42}H_{26}$ [M + H$^+$], 531.2113; found, 531.2120. Anal. Calcd for $C_{42}H_{26} \cdot 0.5MeOH$: C, 93.37; H, 5.16. Found: C, 92.87; H, 5.11. A sample suitable for an X-ray crystal structure determination was obtained by recrystallization from ether/dichloromethane for both **30** and **31**.

X-ray Crystallography. X-ray crystallographic data for **9**, **12**$-$**15**, **21**, **25**, **26**, **27**, **30**, and **31** were collected using a Bruker SMART APEX CCD area detector diffractometer and are listed in Tables 1 and 2. A hemisphere of reciprocal space for **25** and a full sphere of reciprocal space for all the others were scanned by phi-omega scans. Pseudoempirical absorption correction based on redundant reflections was performed by the program SADABS.[34] The structures were solved by direct methods using SHELXS-97[35] and refined by full matrix least-squares on F^2 for all data using SHELXL-97.[35] The treatment of the hydrogen atoms varies from compound to compound, depending on the data quality. All hydrogen atoms in **9** and **14** were located in the difference Fourier map and allowed to refine freely with isotropic thermal displacement parameters. All other hydrogen atoms were added at calculated positions and refined using a riding model. Their isotropic temperature factors were fixed to 1.2 times (1.5 times for methyl groups) the equivalent isotropic displacement parameters of the carbon atom the H-atom is attached to. Anisotropic thermal displacement parameters were used for all non-hydrogen atoms. In **21** the solvent dichloromethane could not be located in the unit cell. The Platon SQUEEZE procedure was used to compensate for the electron density spread. In **15** the hydrogen atoms of the water molecule could not be detected. The structure of **31** was refined as a pseudo-orthorhombic twin. Refinement in the other possible space group, *Pbca*, did not lead to a satisfactory result. All structures are shown as Mercury[36] representations.

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications nos. CCDC 752575 (**9**), 752577 (**12**), 752580 (**13**), 752579 (**14**), 752576 (**15**), 752585 (**21**), 752583 (**25**), 752578 (**26**), 752584 (**27**), 752581 (**30**), and 752582 (**31**).

Acknowledgment. We are grateful to Science Foundation Ireland and University College Dublin for generous financial support. L.A. (University of Hamburg) and R.B. (Ecole Nationale Supérieure de Chimie, Paris) thank the Erasmus Programme for Exchange Fellowships.

Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

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(36) *Mercury 1.4.2*, available from http://www.ccdc.cam.ac.uk/mercury/.