

From allenes to tetracenes: Syntheses, structures, and reactivity of the intermediates*

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Abstract: Each step of the conversion of a series of 9-alkynyl-9*H*-fluorenes into the corresponding fluorenylidene-allenes that dimerize and proceed sequentially via head-to-tail and tail-to-tail dialkylidene-cyclobutanes, en route to electroluminescent tetracenes, has been characterized X-ray crystallographically. Allenes possessing substituents of very different electronic and steric character, such as aryl, halogeno, silyl, phosphino, and ferrocenyl, exhibit novel and unexpected reactivity patterns. The silyl-allenes dimerize to yield 1,2-bis(fluorenylidene)cyclobutanes of intrinsic *C*₂ symmetry as a result of the overlapping fluorenylidenes with their large wingspans. Thermal rearrangement of a bis(fluorenyl)-bis(trimethylsilyl)-diallene generates the tetrabenzocyclopentadiene, C₆₀H₃₆, which represents 60 % of the C₆₀ framework. An attempt to isolate a “push–pull” allene, whose central carbon possesses carbene character, was made by incorporating a cation-stabilizing substituent (ferrocenyl) and an aromatic anionic moiety (fluorenide) at the termini. However, the allene underwent facile dimerization to the very heavily congested 3,4-di(spirofluorenyl)-1,2-bis(ferrocenyl-chloromethylene)cyclobutane that exhibits a very long (1.65 Å) C(3)–C(4) bond. Extension of this chemistry to dibenzosuberenyldene-allenes led to a straightforward route to the hitherto difficultly available dibenz[c,d,h]azulene system. Moreover, the reaction of 5-phenylethynyl-5*H*-dibenzo[a,d]cyclohepten-5-ol with dicobalt octacarbonyl yielded, surprisingly, the first isolated example of a (μ -alkyne)Co₂(CO)₅(η^2 -alkene)complex, the long-sought first intermediate in the proposed mechanism of the Pauson–Khand reaction (PKR).

Keywords: allene dimers; bis(fluorenylidene)cyclobutanes; silyl-allenes; ferrocenyl-allenes; propargyl-allenes; X-ray crystallography.

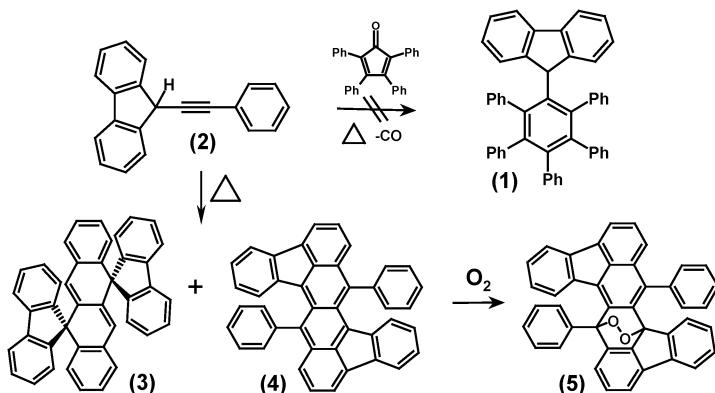
INTRODUCTION

As with many scientific projects, our venture into the chemistry of allenes and their derivatives arose somewhat serendipitously. In continuation of our long-term study of sterically very hindered organometallic or organic molecules that might function as molecular propellers or gears, we had prepared [(η^6 -C₆E₆)Cr(CO)(CS)NO]⁺ [1], (η^5 -C₅Ph₅)Fe(CO)(HC=O)PMe₂Ph [2], ferrocenyl-penta-naphthylbenzene [3], [C₇Ph₇]⁺ [4], 9-tritycyl-indenyl dimer [5], and numerous others.

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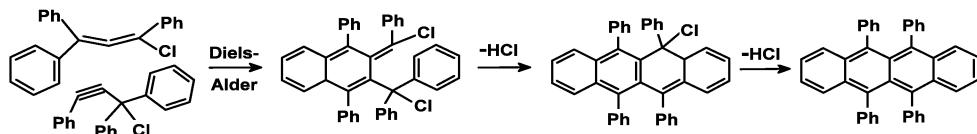
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Subsequently, we wished to prepare (9-fluorenyl)pentaphenylbenzene, **1**, with the goal of using reversible $\eta^6 \rightleftharpoons \eta^5$ haptotropic shifts of an organometallic moiety as the moving component of a molecular brake; such a system requires the juxtaposition of a bulky rotating moiety and a polycyclic fragment over which the controlled migrations could occur [6]. We shall return to this theme in the final section of this report. The conventional Diels–Alder route to highly substituted arenes involves the thermolysis at 180–200 °C of a suitably substituted cyclopentadienone with the appropriate alkyne: in this case, 9-phenylethynylfluorene, **2**, with tetracyclone. Unexpectedly, however, the only isolated products were the dispiro-tetracene, **3**, the di-indenotetracene, **4**, and its corresponding peroxide, **5**, as shown in Scheme 1 [7,8].



Scheme 1 The attempted Diels–Alder reaction of 9-phenylethynyl-9H-fluorene with tetracyclone instead yields the tetracenes **3**, **4**, and **5**.

In recent years, tetracenes have attracted much attention because of their important photophysical properties, in particular, their use as organic light-emitting diodes (OLEDs) in electroluminescent devices [9], and also in organic field-effect transistors [10]. It had been known for more than 80 years that cyclization of the chloride derived from the acetylenic carbinol, $\text{Ph}_2\text{C}(\text{OH})\text{C}\equiv\text{CPh}$, furnished 5,6,11,12-tetraphenyltetracene (rubrene) [11]; however, it was only in 1963 that a mechanism was proposed which involved initial rearrangement to the chloroallene, with subsequent Diels–Alder addition and elimination of HCl , as depicted in Scheme 2 [12].



Scheme 2 Original (1963) mechanistic proposal for the formation of rubrene.

However, since allenes are known to dimerize to give multiple products, such as head-to-tail, tail-to-tail, and head-to-head di-alkylenecyclobutanes [13], it prompted us to investigate the mechanism of the formation of **3** and **4**, little anticipating the stereochemical complexity of the process.

ALLENE DIMERIZATIONS

Under the assumption that 9-(phenylethynyl)fluorene, **2**, underwent facile isomerization to 3,3-(biphenyl-2,2'-diyl)-1-phenyllallene, **6**, the alkyne was treated with triethylamine at 0 °C and furnished the yellow head-to-tail dimer, **7**. Gentle thermolysis of **7** in tetrahydrofuran at 40 °C led to the red tail-to-tail isomer, *trans*-3,4-diphenyl-1,2-bis(fluorenylidene)cyclobutane, **8**, in which the adjacent fluorenylidenes, with their large (8.7 Å) wingspans, overlapped such that their helical sense paralleled that of the *trans*-phenyls. However, at 80 °C, **8** isomerized cleanly into *cis*-3,4-diphenyl-1,2-bis(fluorenylidene)cyclobutane, **9**, before rearranging again, this time at 110 °C, into orange **10**, a diastereomer of **8**, in which the helicity of the overlapping fluorenylidenes now opposed to that of the *trans*-phenyls. This subtle difference in stereochemistry is clearly illustrated in the space-filling representations shown in Figs. 1a and 1b. Finally, thermolysis of the initially formed dimer, **7**, at 180 °C yielded the previously observed tetracenes **3** and **4** [8].

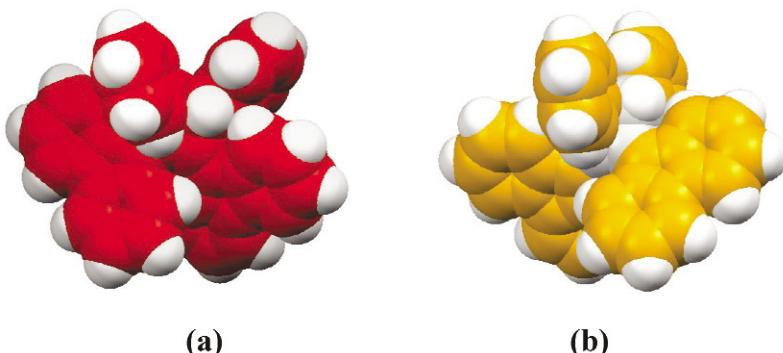
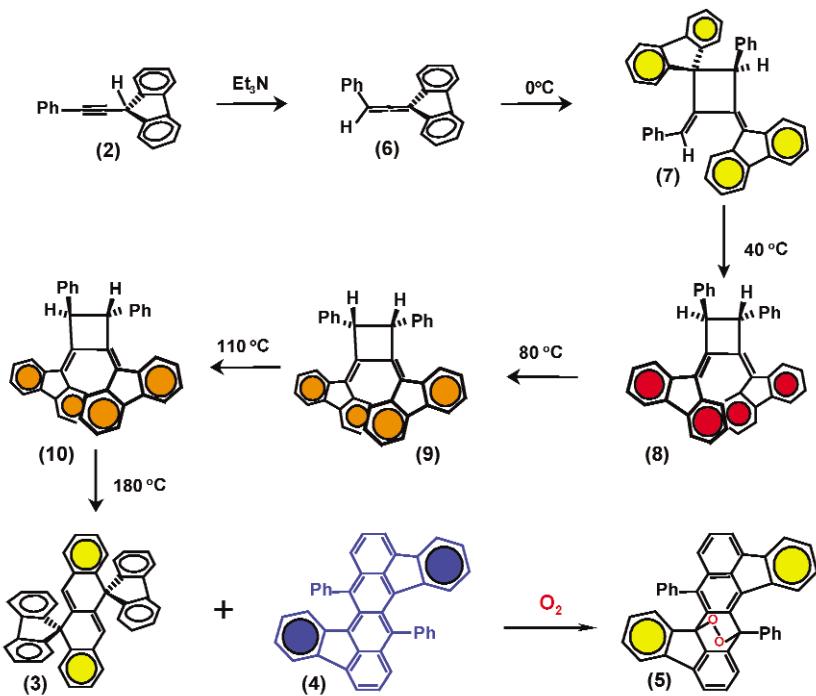
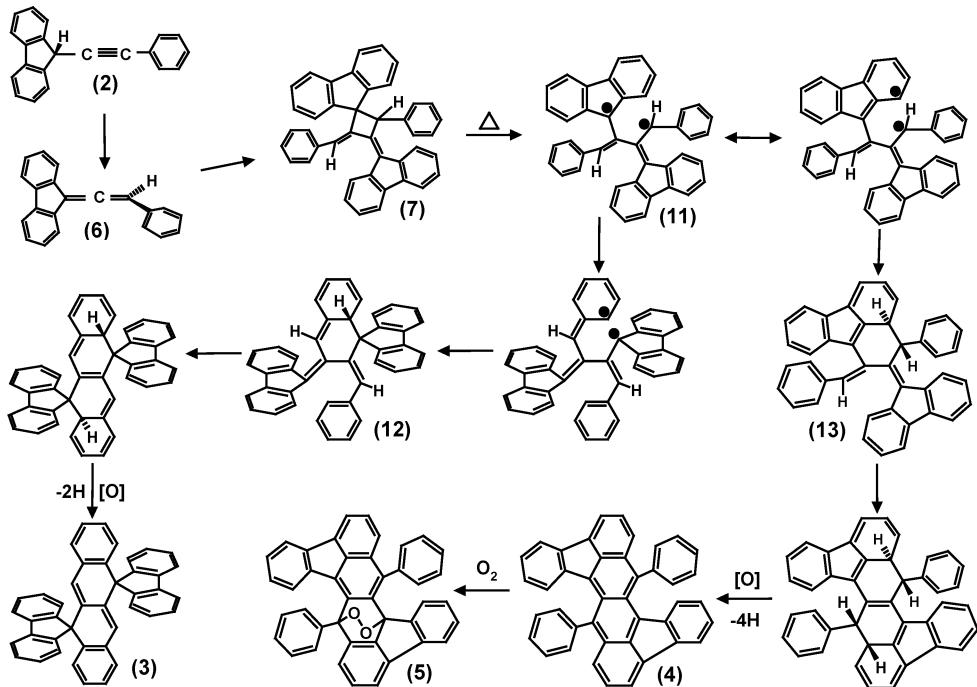


Fig. 1 (a) In the red isomer (**8**) the helicity of the overlapping fluorenylidenes parallels that of the *trans*-disposed phenyls; (b) in the thermodynamically favored orange isomer (**10**), the helical sense of the fluorenylidenes is reversed from that of the *trans*-phenyls.

This entire sequence of intermediates, as depicted in Scheme 3, was definitively elucidated by means of NMR spectroscopy and X-ray crystallography. Gratifyingly, the dramatically changing colors of these materials facilitated the chromatographic separations. Thus, the complete three-dimensional structure has been determined for each molecule in the progression: fluorenyl-alkyne **2** → fluorenyl-allene **6** → yellow head-to-tail dimer **7** → red *trans* tail-to-tail dimer **8** → orange *cis* tail-to-tail dimer **9** → orange *trans* tail-to-tail dimer **10** → yellow dispirotetracene **3** and blue di-indenotetracene **4** → peroxide **5** [8].

One can perhaps relate the colors of the diastereomers, **8** and **10**, each of which possesses *trans*-disposed phenyls, to the different degrees of conjugation between the two fluorenylidene moieties. In the red isomer, **8**, the dihedral angle between these substituents is 41°, but this opens up to 60° in **10**. Assuming that a greater deviation from coplanarity brings about an increase in the highest occupied molecular orbital/lowest unoccupied molecular orbital (HOMO/LUMO) gap, one would anticipate absorption at higher energy in the orange product, **10**, and this is indeed the case (457 nm for red **8**; 431 nm for orange **10**) [8].

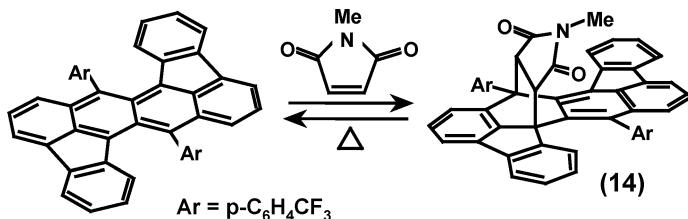
As noted above, prolonged thermolysis of the yellow allene dimer, **7**, yields the dispiro-dihydro-tetracene, **3**, and the di-indenotetracene, **4**. It is relevant to note the important studies by Capdeville and Rigaudy [14], and also by Christl and co-workers [15], who demonstrated the intermediacy of bi-allyl diradicals that can be delocalized onto the *ortho*-positions of neighboring aromatic rings, thus allowing the formation of six-membered rings. In Scheme 4, we show how these ideas can account for the generation of the observed products **3**, **4**, and **5**.

**Scheme 3** Sequential formation of allene dimers.**Scheme 4** Proposed mechanism of formation of tetracenes **3** and **4** from an allene dimer.

Cleavage of the long (1.606 Å) C(3)–C(4) bond of the initially formed [2+2] dimer, **7**, leads ultimately to diradical **11**. Two routes can now be envisaged: coupling between an *ortho*-phenyl site and C(9) position of a neighboring fluorenyl ring leads to **12**, whereas coupling between an *ortho*-fluorenyl position and the benzylic site gives **13**. Subsequent disrotatory electrocyclization of the 6π systems in **12** and **13** generates the required molecular frameworks. Finally, aerial oxidation yields the observed products **3** and **4** and, eventually, **5**.

Having developed a simple one-pot synthesis of tetracenes via dimerization of allenes derived from readily available alkynyl-fluorenes, we decided to investigate the chemistry of allenes possessing a range of organic and organometallic substituents. The initial work on 3,3-(biphenyl-2,2'-diyl)-1-phenyllallene, $C_{13}H_8=C=C(\text{Ph})H$, **6**, was rapidly extended into a series of compounds of the general type $C_{13}H_8=C=C(\text{R})X$ where R = *p*-C₆H₄Me, *p*-C₆H₄OMe, *p*-C₆H₄CF₃, SiMe₃, PPh₂, or ferrocenyl, and X = H, Cl or Br, each of which exhibited fascinating, and occasionally completely unexpected, behavior.

A number of the aryl allenes, $C_{13}H_8=C=C(C_6H_5X)\text{Br}$, where X = Me, OMe, or CF₃, had been previously reported [16], but their reactivity had scarcely been studied. Lithiation and hydrolysis to form the corresponding $C_{13}H_8=C=C(\text{Ar})\text{H}$ systems led to the expected head-to-tail dimers, which then proceeded through the previously established tail-to-tail *trans* → *cis* → *trans* pathway depicted in Scheme 3 en route to the corresponding tetracenes; several of these dimeric intermediates were also characterized by X-ray crystallography [17]. The di-indenotetracenes undergo ready oxidation in air to the peroxides, typified by **5**; however, they may be conveniently stored (and then thermally regenerated) as their Diels–Alder adduct with *N*-methylmaleimide, as in Scheme 5. The X-ray crystal structure of the *p*-trifluoromethyl-phenyl derivative, **14** (Fig. 2), revealed the product to be the *endo*-isomer on a central ring.



Scheme 5 Reversible Diels–Alder addition of *N*-methylmaleimide to a tetracene.

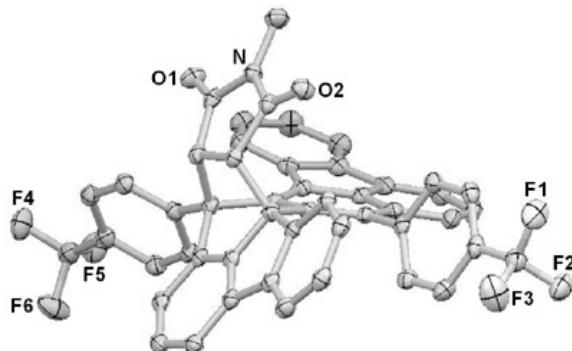
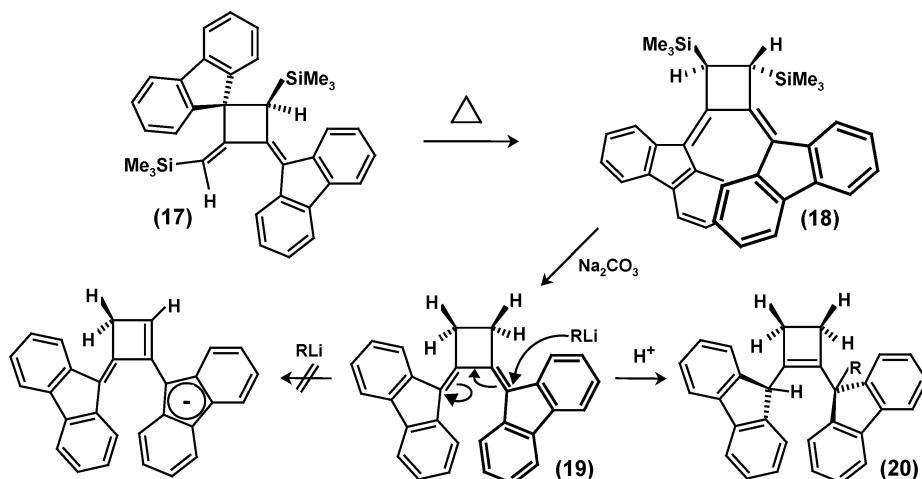


Fig. 2 X-ray crystal structure of the Diels–Alder adduct **14**.

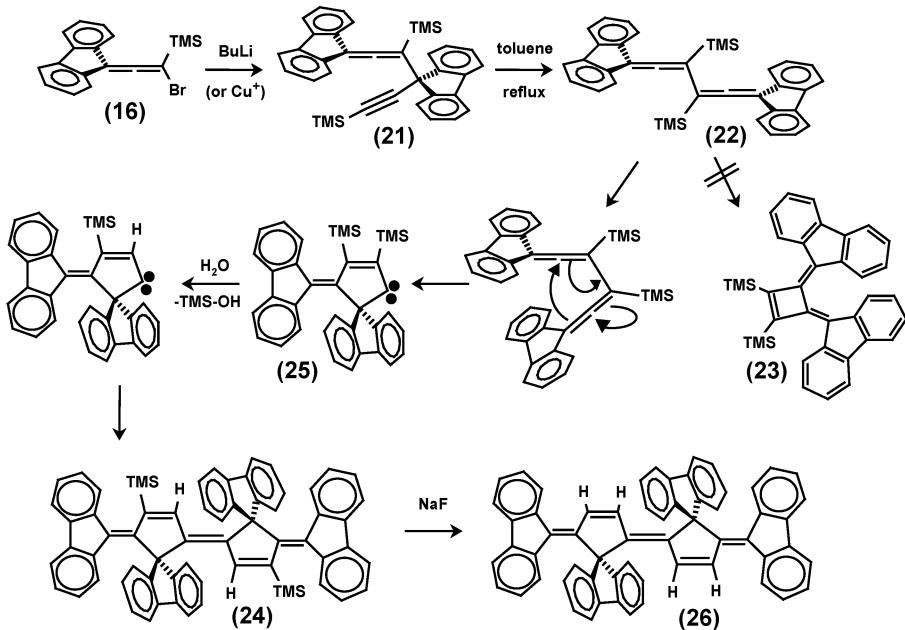
SILYL ALLENES

The fluorenylidene-silyl-allenes, $C_{13}H_8=C=C(SiMe_3)H$, **15**, and $C_{13}H_8=C=C(SiMe_3)Br$, **16**, exhibited particularly interesting reactivity [17]. The former slowly dimerized to give the anticipated head-to-tail 1,2-dialkylidene cyclobutane, **17**, in which the steric bulk of the trimethylsilyl groups brought about a marked lengthening (to 1.62 Å) of the C(3)–C(4) linkage. As depicted in Scheme 6, subsequent thermolysis yielded the thermodynamically favored *trans*-isomer, **18**, in which the helicities of the overlapping fluorenylidenes and the TMS groups were opposed; finally, desilylation furnished the “parent” 1,2-bis-(fluorenylidene)cyclobutane, **19**, whose C_2 symmetry arises solely as a consequence of the large wingspans of the $C_{13}H_8$ fragments [17]. One might take advantage of this structural feature to generate C_2 -symmetric diphosphine complexes analogous to Noyori’s *binap* systems that are very widely used in asymmetric catalysis [18]. Surprisingly, attempted deprotonation of a methylene group in **19** with *t*-butyl-lithium, that would be expected to generate an aromatic fluorenide anion, instead proceeded with 1,4 addition to the exocyclic diene to give **20** [19].



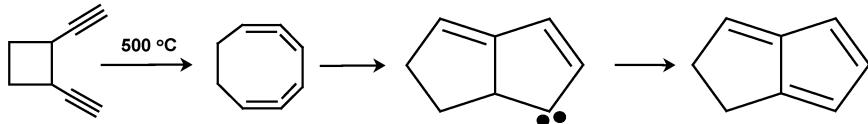
Scheme 6 Reactions of head-to-tail and tail-to-tail dimers of $C_{13}H_8=C=C(SiMe_3)H$, **15**.

The bromo-allene, **16**, underwent copper-mediated debromination to yield the propargyl-allene, **21**, the product of head-to-tail coupling, that, when thermolyzed, yielded the disilyl-diallene, **22**. However, attempted electrocyclization to the 3,4-bis(fluorenylidene)cyclobutene, **23**, led instead to the novel dihydrotetrabenzo-*quater*cyclopentadiene, **24** [20]. In terms of a mechanistic hypothesis, one can visualize rotation about the central bond of the diallene, **22**, and cyclization to form a cyclopentenylidene ring, **25**, whereby the carbene is initially sterically protected by its very bulky trimethylsilyl and spiro-bonded fluorenyl neighbors. As indicated in Scheme 7, subsequent desilylation, possibly as trimethylsilanol and mediated by traces of water, would allow formation of the observed carbene dimer, **24**.



Scheme 7 Proposed mechanism for the formation of C₆₀H₃₆, **26**.

In seeking a literature precedent for such a cyclization to form a cyclopentylidene carbene, we note Hopf's report of the thermolytic formation of dihydropentalene from *cis*-1,2-diethynylcyclobutane, via cycloocta-1,2,4,5-tetraene (Scheme 8) [21].



Scheme 8 Cyclization of a diallene to form a carbene.

Even more fascinating was the observation [20] that treatment of the disilyl-diallene, **22**, with sodium fluoride yields directly the "parent" molecule C₆₀H₃₆, **26**, whose X-ray crystal structure appears as Fig. 3. We note that the octacyclic C₃₆ unit in **26** can be mapped directly onto the C₆₀ framework, and indeed represents 60 % of the fullerene skeleton. It is tempting to visualize the rearrangement of such a molecule with its central C₃₆ moiety, and two spiro-bonded fluorenyl C₁₂ fragments, as a potential precursor to a C₆₀H₃₆ fullerene, and further investigations are ongoing.

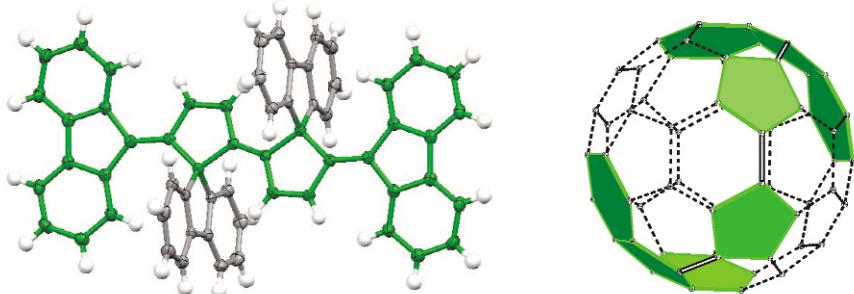
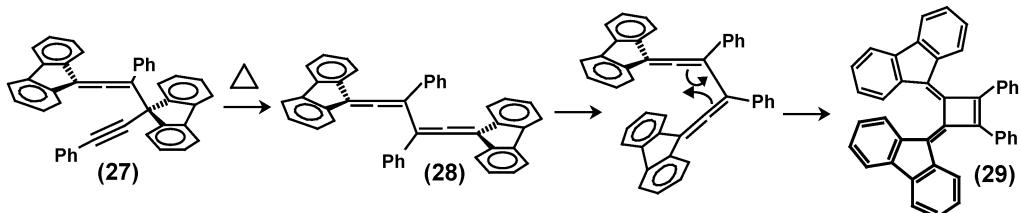


Fig. 3 X-ray crystal structure of $C_{60}H_{36}$, **26**, and its mapping onto the C_{60} framework.

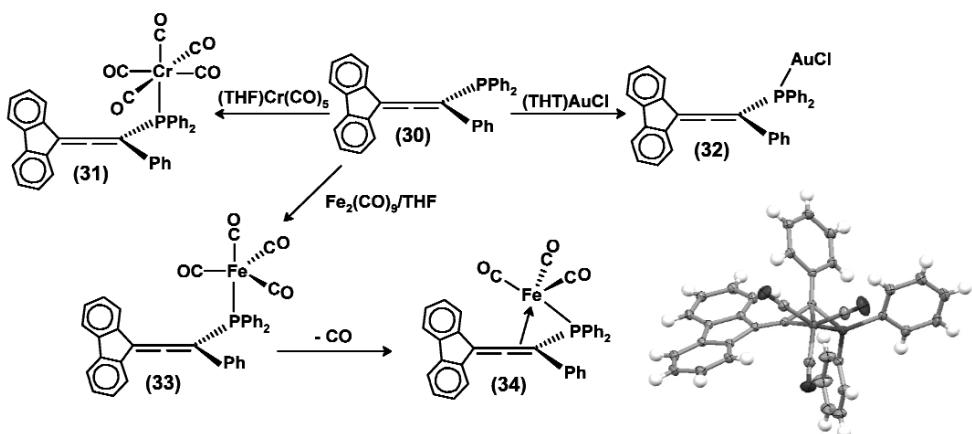
Interestingly, as shown in Scheme 9, thermolysis of the analogous diphenyl-substituted propargyl-allene, **27**, results in rearrangement to the corresponding diphenyl-diallene, **28**; however, this latter species could not be isolated and spontaneously electrocycliclyzed to the 3,4-bis(fluorenylidene)-1,2-diphenylcyclobutene, **29** [22].



Scheme 9 Electrocyclic ring closure of a diallene to a cyclobutene.

METAL COMPLEXES OF ALLENYLPHOSPHINES

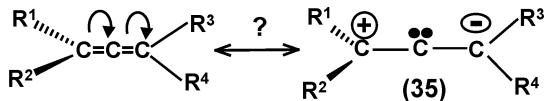
Lithiation of the fluorenylidene-bromoallene, $C_{13}H_8=C=C(\text{Ph})\text{Br}$, and treatment with Ph_2PCl yielded the allenylphosphine, **30**, which offers multiple sites for metal coordination. Reaction with (tetrahydrofuran)chromiumpentacarbonyl and with (tetrahydrothiophene)Au(I) chloride afforded the expected (allenylphosphine) $\text{Cr}(\text{CO})_5$ and (allenylphosphine) AuCl complexes, **31** and **32**, respectively (Scheme 10). In contrast, diiron nonacarbonyl and **30** react initially to yield the (allenylphosphine) $\text{Fe}(\text{CO})_4$, **33**, whereby the iron adopts trigonal bipyramidal geometry. However, this complex readily loses a carbonyl ligand, even at room temperature, and the vacant coordination site is now occupied by the adjacent allene double bond such that the iron is now in a pseudo-octahedral environment in **34**. Interestingly, although the $\text{Fe}(\text{CO})_4$ complex is highly fluxional and exhibits only a single ^{13}CO NMR resonance, the barrier to rotation of the $\text{Fe}(\text{CO})_3$ fragment in **34** is ~ 13 kcal mol $^{-1}$, indicating strong linkages to the phosphorus and the allene double bond [23].



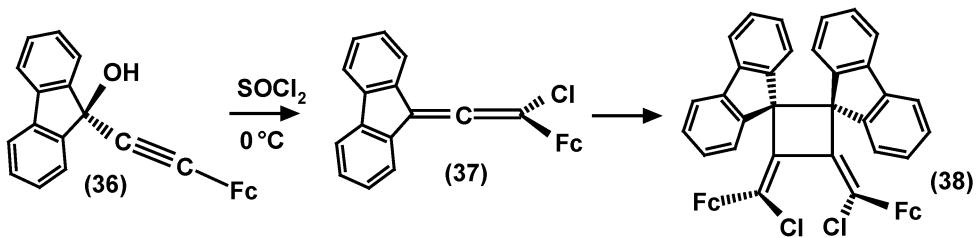
Scheme 10 Metal complexes of an allenylphosphine.

FERROCENYL-ALLENES

In 1972, Salisbury postulated that an extreme resonance form of an allene would place opposite charges at the terminal positions, thus engendering carbene character at the central carbon [24], as in **35**. Such a scenario might be enhanced by incorporating electron-donating and -withdrawing substituents at the termini, and “push–pull” allenes of this type have been comprehensively reviewed by Saalfrank [25]. However, thus far there is no compelling evidence that the carbene-like structure is a predominant resonance contributor.



It is well established that organometallic moieties, such as ferrocenyl [26,27], or tetrahedral alkynyl-dimetalloc clusters, $(RC\equiv C)(ML_n)_2$ where $ML_n = Co(CO)_3$ or $Mo(CO)_2(C_5H_5)$ [28], are well able to alleviate positive charge, while cyclopentadienide, ester, or nitrile substituents can play the opposite role. We therefore chose to develop synthetic routes to such potentially zwitterionic systems with the goal of probing the carbenic character of the central carbon. It has long been known that propargyl alcohols react with thionyl chloride to form chlorosulfites that subsequently eliminate SO_2 and yield chloroallenes [12]. To this end, 9-(ferrocenylethynyl)-9*H*-fluoren-9-ol, **36**, was allowed to react with $SOCl_2$ at 0 °C, and the initially generated allene, **37**, was characterized spectroscopically at low temperature (Scheme 11). The product exhibited infrared absorption at 1940 cm⁻¹, and a ¹³C NMR resonance for the central *sp*-hybridized carbon at 198 ppm, more typical of an allene than a carbene environment. However, the chloroallene, **37**, could not be isolated because of the facile formation of the head-to-head dimer, **38**, whose X-ray crystal structure (Fig. 4) revealed that the four-membered ring adopts a marked butterfly (pseudo- C_2) conformation in response to the pronounced twisting of the double bonds that minimizes the steric crowding of the two vinylic chlorines. The dihedral angle $C\ell(Fc)C=C_{(1)}-C_{(2)}=C(Fc)C\ell$ between the two (ferrocenyl)chloromethylidene moieties is 45°, and the ferrocenyl fragments are oriented almost orthogonally to each other. However, the most striking feature of the structure is the very long (1.65 Å) bond [29] connecting the spiro positions of the fluorenyl groups, which are themselves severely arced away from each other. Nevertheless, the fluorenyl moieties



Scheme 11 Dimerization of a ferrocenyl-chloroallene.

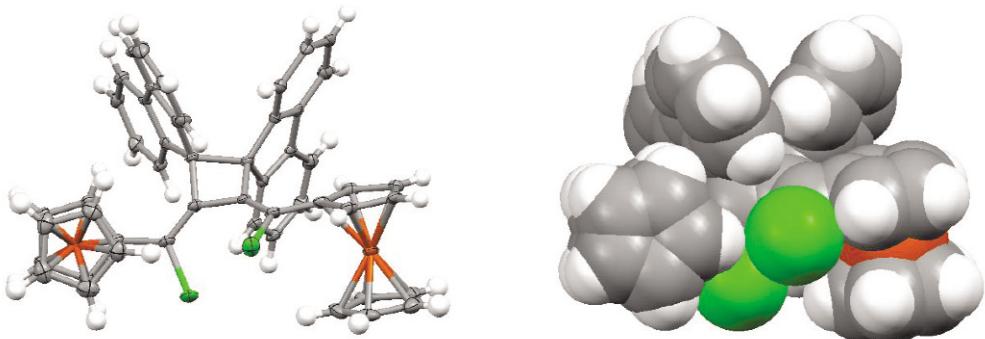
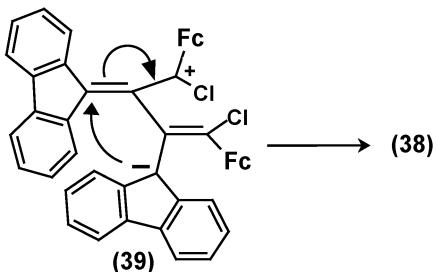


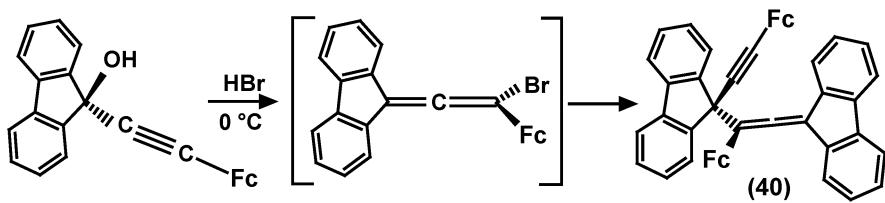
Fig. 4 X-ray crystal structure, and space-filling view of head-to-head chloroallene dimer (38).

gave rise to only four proton NMR resonances in solution, thus indicating time-averaged C_{2v} symmetry despite the evident steric crowding in the molecule [30].

Although the ferrocenyl-chloroallene, **37**, could not be isolated in crystalline form, and its ^{13}C NMR spectrum did not indicate marked carbene character for the central carbon, its ease of dimerization might imply the intermediacy of a dimeric zwitterion, **39**, prior to head-to-head ring closure.



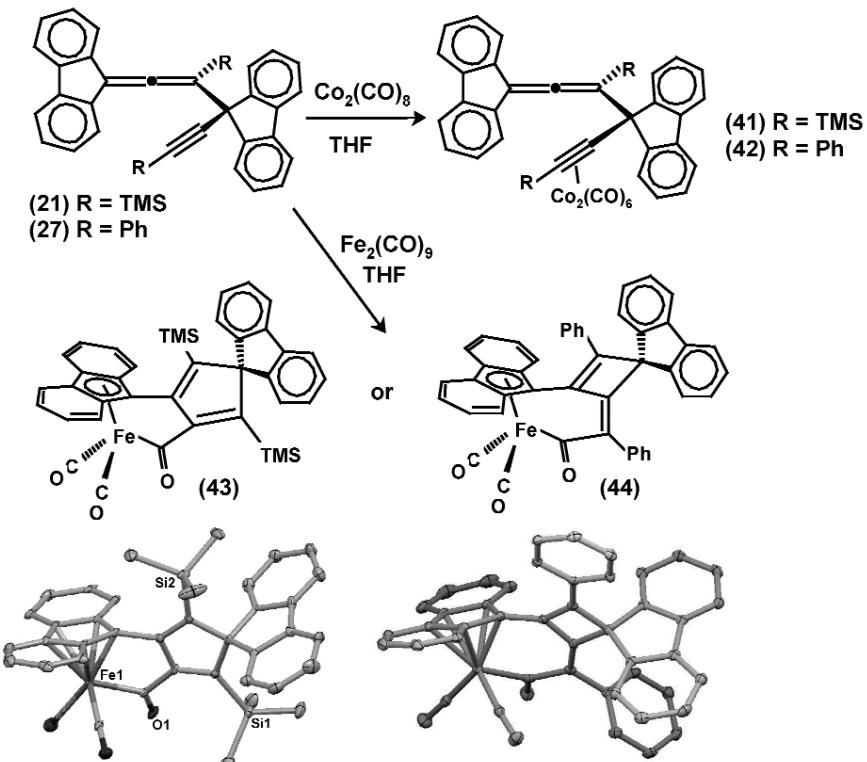
A second attempt to produce a “push–pull” allene involved the reaction of 9-(ferrocenylethynyl)-9*H*-fluoren-9-ol with cold, dilute HBr, a method known to lead to bromoallenenes [16,17]. However, the only isolated product was the diferrocnetyl-propargyl-allene, **40**, shown in Scheme 12, possibly via homolytic cleavage of the presumed bromoallene intermediate [30]. In light of the unanticipated reactivity patterns of the bis(trimethylsilyl)-propargyl-allene, **21**, discussed above, it is evident that the ferrocenyl analog, **40**, merits further investigation, and such a study is planned.



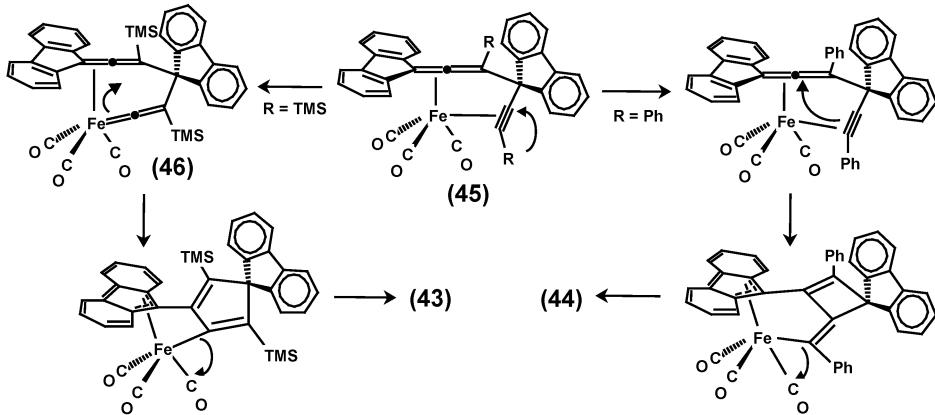
Scheme 12 Formation of a diferrocenyl-propargyl-allene.

ORGANOMETALLIC DERIVATIVES OF PROPARGYL-ALLENES

The disilyl- and diphenyl-propargyl-allenes, **21** and **27**, respectively, react readily with dicobalt octacarbonyl to form tetrahedral alkyne-dicobalt hexacarbonyl clusters, **41** and **42**, respectively. However, their reactions with diiron nonacarbonyl are strikingly different. As shown in Scheme 13, the silyl system yields a novel complex, **43**, 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 [20]. In contrast, the reaction of diphenyl-propargyl-allene and Fe₂(CO)₉ yielded **44**, that also contained an (η^5 -fluorenyl)Fe(CO)₂ moiety, but now linked directly, and via a =C(Ph)-C=O bridge, to a cyclobutene ring bearing a phenyl and a spiro-bonded fluorenyl unit [22]. A mechanistic rationale is presented in Scheme 14, whereby initial coordination of an Fe(CO)₃ fragment was followed either (a) by rearrangement of the (propargyl-allene)Fe(CO)₃, **45**, into a silyl-vinylidene complex, **46**, that underwent cyclization to **43**, or (b) in the phenyl case by direct rearrangement to the cyclobutene, **44**.

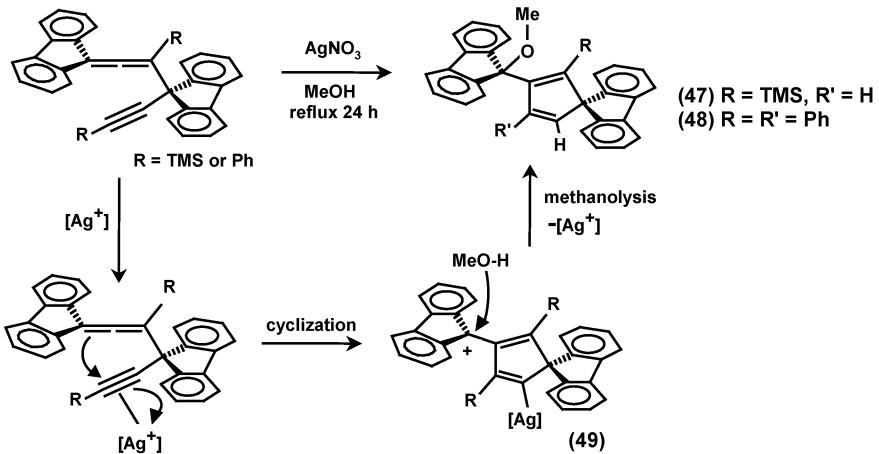


Scheme 13 Reactions of propargyl-allenes with cobalt and iron carbonyls.



Scheme 14 Mechanisms of reactions of propargyl-allenes with iron carbonyl.

When treated with silver nitrate in methanol, the propargyl-allenes **21** and **27** underwent cyclization of the allene onto the alkyne to furnish the cyclopentadienes **47** and **48**, respectively, each spiro-linked to a fluorenyl unit, and also possessing a 9-methoxy-9H-fluorenyl substituent [22]. Mechanistically, one can envisage initial coordination of Ag^+ to the alkyne, cyclization to form the cationic five-membered ring system, **49**, and finally nucleophilic attack by methanol, as in Scheme 15. Related Ag-promoted cyclizations of hydroxylated 1,5-allenynes have been very recently reported in an elegant study by Malacria [31].



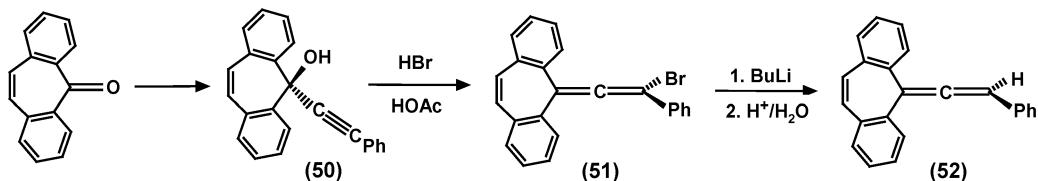
Scheme 15 Ag^+ -mediated cyclizations of propargylallenes.

ALKYNYL AND ALLENYL DERIVATIVES OF 5H-DIBENZO[a,d]CYCLOHEPTENE

Having explored the chemistry of allenes containing one or more fluorenylidene moieties, we decided to investigate the corresponding dibenzosuberenyldiene systems. There were two principal reasons to study such molecules: firstly, the tricyclic dibenzo[a,d]cycloheptenyl ring system would stabilize *cations* (whereas the fluorenyl *anion* is a 14π Hückel system), and secondly, we wished to prepare analogs of the previously described C_2 -symmetric bis-(fluorenylidene)cyclobutanes, whereby the overlap between the dibenzosuberenyldienes with their even larger wingspans (9.5 vs. 8.7 Å) would be more

severe, thus modifying the geometry, and thereby controlling the bite between *trans*-phosphorus ligands positioned at C(3) and C(4) in the cyclobutane ring.

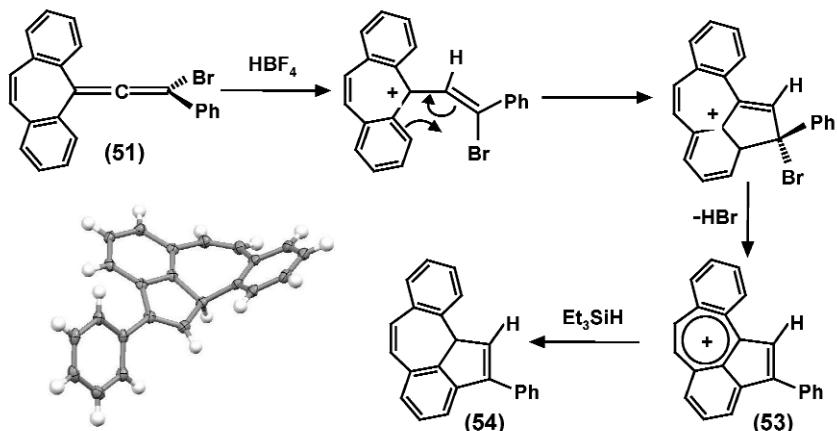
To this end, as depicted in Scheme 16, dibenzosuberenone was converted to the alkynol, **50**, then to the corresponding bromoallene, **51**, and finally to the “parent” allene, **52**, all of which have been characterized X-ray crystallographically [32]. Somewhat to our surprise, the hydrocarbon, **52**, unlike its fluorenylidene analog, **6**, shows no tendency to dimerize at room temperature. Interestingly, the diphenyl analog of **6**, i.e., $\text{Ph}_2\text{C}=\text{C}=\text{CHPh}$, is also thermally stable, and indeed has been characterized by X-ray crystallography [33]. One may surmise that dimerization is favored when the terminal substituents on the allene can stabilize opposite charges, as was particularly noticeable in the ferrocenyl-chloroallene, **37**. Preliminary attempts to facilitate dimerization of the suberenylidene allene have involved the incorporation of strongly electron-withdrawing groups (CF_3 or CN) in the phenyl substituent [32]; such systems may give rise to an *umpolung* effect, whereby the positive charge resides on the suberenyl group and the negative charge is delocalized onto the substituted aryl ring. However, this is still a work in progress.



Scheme 16 Syntheses of dibenzosuberenyldene-allenes.

2-Phenyl-12*H*-dibenz[*c,d,h*]azulene

The ready availability of the dibenzosuberenyldene-bromoallene, **51**, raised the possibility of developing a simple route to the benz[*c,d*]azulene skeleton, a hitherto relatively inaccessible ring system [34–36]. As shown in Scheme 17, protonation of **51** with HBF_4 at 0 °C occurs at the central allene carbon, resulting in Nazarov cyclization, elimination of HBr , and generation of the tropylium-type cation, **53**; subsequent reduction with triethylsilane delivers the dibenz[*c,d,h*]azulene, **54**, the X-ray crystal structure of which reveals a non-planar geometry [32]. A molecular orbital study suggests that the central carbon, which is common to the five-, six-, and seven-membered rings, may be electronically iso-

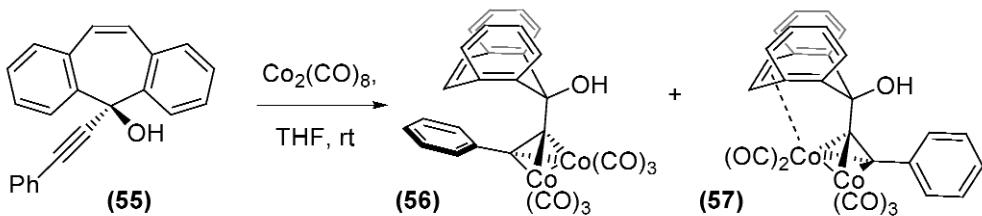


Scheme 17 Synthesis of 2-phenyl-12*H*-dibenz[*c,d,h*]azulene, **54**.

lated from the molecular periphery, and an NMR study on the cation, **53**, and the corresponding anion, will provide data on the aromatic (or antiaromatic) character of those ions.

(5-Phenylethynyl-5*H*-dibenz[*a,d*]cyclohepten-5-ol) $\text{Co}_2(\text{CO})_n$, $n = 6$ or 5

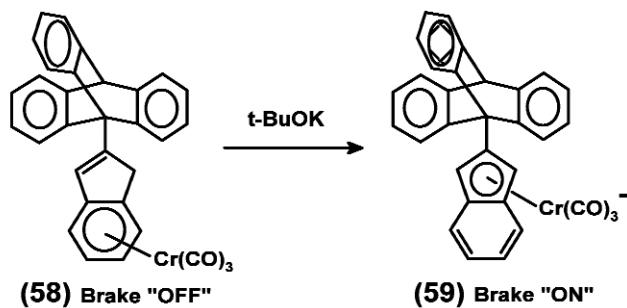
The potential for the dibenzosuberenyl moiety to form an aromatic 14π cation prompted us to investigate its ability to compete with an adjacent (μ -alkynyl) $\text{Co}_2(\text{CO})_6$ moiety to stabilize a positive charge [28,37,38]. Thus, the alkynyl-suberenol, **55**, was treated with dicobalt octacarbonyl in the expectation of obtaining the corresponding (alkyne) $\text{Co}_2(\text{CO})_6$ cluster, **56**. As depicted in Scheme 18, this cobalt complex was indeed formed, but in addition a second product was isolated and characterized by X-ray crystallography [39] as the novel (μ -alkyne) $\text{Co}_2(\text{CO})_5(\eta^2\text{-alkene})$ cluster, **57**, whereby the vacant site on the $\text{Co}(\text{CO})_2$ vertex was now coordinated by the $\text{C}(10)=\text{C}(11)$ double bond in the seven-membered ring. The significance of this observation was that it represented the first step of Magnus's proposed mechanism [40] for the Pauson–Khand reaction (PKR), widely used for the syntheses of cyclopentenones from an alkyne, an alkene, and a source of carbon monoxide [41]. This mechanism has attracted the attention of numerous theoreticians who have calculated the structures and energetics of this process [42,43]; it is only now that experimental data are available, and, gratifyingly, these are in excellent accord with the theoretical predictions.



Scheme 18 Formation of the first (μ -alkyne) $\text{Co}_2(\text{CO})_5(\eta^2\text{-alkene})$ cluster, **57**.

AN ORGANOMETALLIC MOLECULAR BRAKE

Coming full circle, and as noted in the introduction to this report, one of our original goals was the construction of a molecular brake based on reversible $\eta^6 \rightleftharpoons \eta^5$ haptotropic shifts of an organometallic moiety adjacent to a bulky rotating moiety. This has now been accomplished by linking a 2-indenyl moiety to a 9-tritycyl unit that functions as a three-bladed paddlewheel. Incorporation of an $\eta^6\text{-Cr}(\text{CO})_3$ tripod on the benzo ring of the indenyl, as in **58**, still allows the triptycyl to rotate freely. However, deprotonation engenders negative charge on the indenyl fragment and causes the organometallic tripod to migrate onto the five-membered ring, as in **59**, thus blocking rotation of the paddlewheel and rendering one of the blades inequivalent to the other two. The system has been characterized in both its η^6 "OFF" and η^5 "ON" forms by NMR spectroscopy and by X-ray crystallography [44].



CONCLUDING REMARKS

The chemistry of allenes continues to provide surprises. The range of geometric, diastereomeric, and enantiomeric structures exhibited by their dimers, and other larger molecular assemblies, poses fascinating spectroscopic and mechanistic questions. The present work has elucidated some aspects of this area, but much remains to be done. Synthetic routes to allenes, allene dimers, and tetracenes possessing a range of electronically and sterically very disparate substituents have been developed, but their photophysics has yet to be fully investigated. The concept of using overlapping fluorenylidene or dibenzosuberenyldenes, with their very large wingspans, to impose axial symmetry on the systems is being extended so as to generate ligands for applications in asymmetric catalysis. Furthermore, the isolation and complete characterization of the first proposed intermediate in the PKR has prompted us to synthesize molecules with slightly diminished steric strain that may allow the process to continue and so yield a stable example of a subsequent step in the PKR mechanism. In closing, it is evident that the synthetic chemistry of allenes, and the wide range of dimers derived from them will continue to attract the attention of synthetic, structural, catalytic, and computational chemists for many years to come.

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