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Unexpected Dimerization of a Bis(fluorenyl)-bis(trimethylsilyl)-diallene to a Dihydroquatercyclopentadiene, an Octacyclic C_{36} Fragment Corresponding to 60% of C_{60}: Reaction of the Diallene with $Fe_2(CO)_9$

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The propargylallene 3,3′-biphenylene-1-trimethylsilyl-1-(9-trimethylsilylethynyl)-9*H*-fluorenylallene, **12**, undergoes thermal rearrangement in refluxing THF to the corresponding *s-trans*-bis(fluorenylidene)bis(trimethylsilyl)diallene, **13**. In contrast, when thermolyzed in refluxing toluene, **12** cyclizes to form a cyclopentenylidene carbene that dimerizes to furnish the tetrabenzodihydroquatercyclopentadiene **15**. Moreover, treatment of **13** with NaF yields $C_{60}H_{36}$, **17** (the "parent" analogue of **15**), whose C_{36} backbone can be mapped onto C_{60} and which represents 60% of the fullerene framework. The ligands **12** and **13** both react with di-iron nonacarbonyl to produce the novel complex **21**, in which an (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. The proposed mechanism involves rearrangement of a coordinated trimethylsilylalkyne unit into a vinylidene complex prior to formation of the cyclopentadiene ring. However, the complex **21** is relatively unstable and undergoes oxidative decomposition with loss of iron and formation of a bicyclic lactone, **27**, possessing two spiro-bonded fluorenyl groups. The X-ray crystal structures of **13**, **15**, **17**, **21**, and **27**, as well as that of 1,4-bis(fluorenylidene)-2-butyne, **20**, are reported.

Introduction

The intramolecular proximity of an alkyne and an allene, or of two allene moieties, can lead to the formation of a wide range of novel polycyclic aromatics.[1] Typically, as depicted in Scheme 1, the Schmittel cyclization[2] of an *in situ* generated benzoenyne-allene, **1**, furnished the nonacyclic system **2**, which represents a major portion of the C_{60} skeletal framework.[3] Moreover, the iron- or cobalt-carbonyl-promoted conversion of diallenes into 2,5-bis(alkylidene)cyclopent-3-enones, **3**, is a well-established process.[4,5] Alkynyl-allenes are also capable of undergoing Pauson−Khand reactions to yield cyclopentenones possessing an exocyclic methylene moiety.[6]

More recently, the detailed mechanism of the stepwise dimerization of fluorenylidene-allenes, via a series of head-to-tail and tail-to-tail 1,2-bis(alkylidene)cyclobutanes into tetracenes, has been fully elucidated (Scheme 2).[7,8]

Furthermore, in a series of elegant studies by Toda, the cyclization of *s-trans* diallenes into 3,4-dimethylenecyclobutenes, e.g., **4** → **5**, and of diallenylbenzenes **6** into benzocyclobutanes **7**, with extraordinarily long (~1.7 Å) carbon−carbon single bonds, have been reported (Scheme 3).[9] We note also that the particularly fascinating rearrangement of the propargyl-allene **8** into the furo-furan **10** is thought to proceed via the diallene **9**. This reaction occurs in the crystalline state and exhibits photochromism.[10]

We here describe the synthesis, structure, and unanticipated dimerization of a bis(fluorenylidene)-bis(trimethylsilyl)-diallene and also its reaction with di-iron nonacarbonyl, which leads to a novel molecular rearrangement.

Results and Discussion

In continuation of our earlier studies[7,8] on the conversion of fluorenylidene-allenes into tetracenes, we had prepared 3,3′-biphenylene-1-bromo-1-trimethylsilylallene, **11**, and had shown that the dropwise addition of butyllithium led to formation of 3,3′-biphenylene-1-trimethylsilyl-1-(9-trimethylsilylethynyl)-9*H*-fluorenylallene, **12**.[11] We are aware of only a single prior report on the preparation and reactivity of the silyl-bromoallene **11**,

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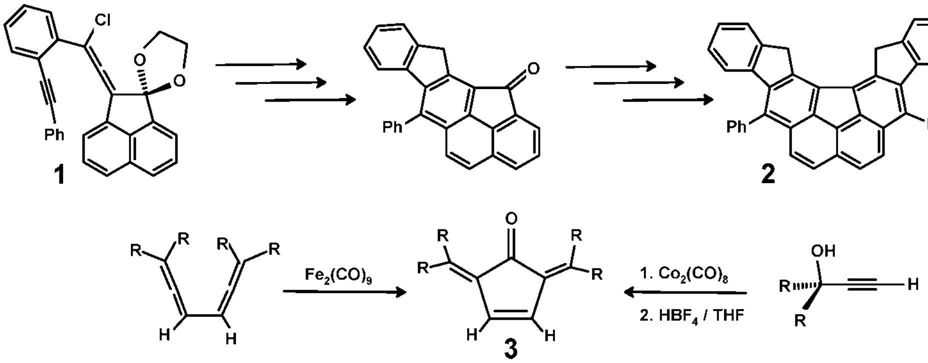
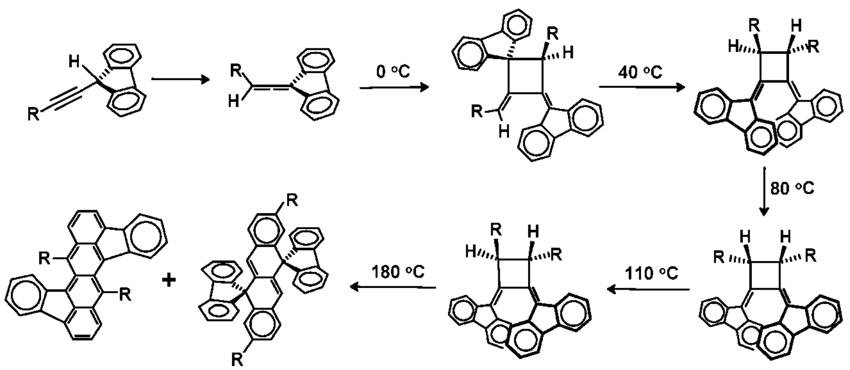
[11] Full crystallographic data for **12** (CCDC 622239) are reported elsewhere: Banide, E. V.; Molloy, B. C.; Ortin, Y.; Müller-Bunz, H.; McGlinchey, M. J. *Eur. J. Org. Chem.* **2007**, 2611–2622.

10.1021/om8005855 CCC: $40.75

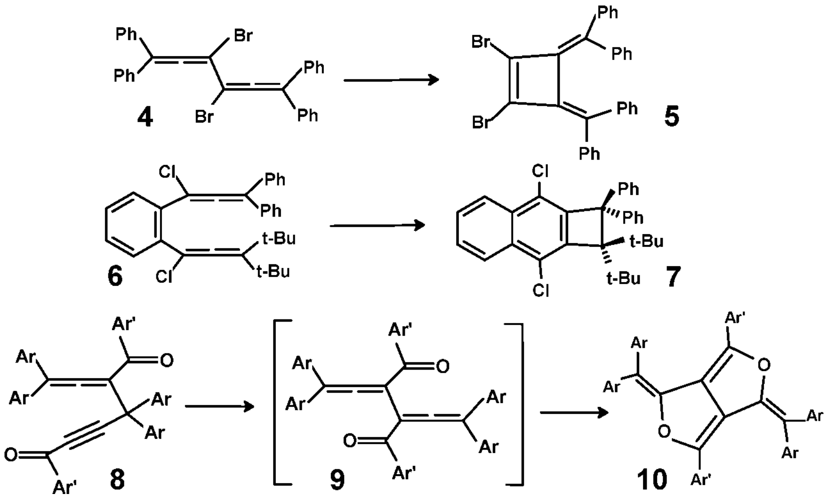
Scheme 1. Synthetic Transformations of Diallenes



Scheme 2. Sequential Conversion of Fluorenylidene-Allenes into Tetracenes



Scheme 3. Cyclizations of Diallenes



whereby it was found to yield **12** when treated with a thiolate anion.[12] However, a series of analogous hexa-1,2-dien-5-ynes **8** have been prepared via the copper-mediated coupling of 1-aroyl-3,3-biphenylene-1-chloro-allenes.[13] As noted above,[10] it is known that propargyl-allenes **8** can undergo a 1,3-shift to yield diallenes **9**. Consequently, the silyl-alkynyl-allene **12** was heated at reflux in toluene for 48 h. and furnished the diallene **13**, which was identified initially by the strong IR band at 1919 cm^{-1} and the ^{13}C NMR chemical shift of the allenic central carbon atom at 204.7 ppm. This transformation also occurs in the solid state; an attempted melting point of the propargyl-allene **12** revealed clear changes at 177−179 °C and became deep red at 271−274 °C. Subsequently, it was shown that **12** is converted cleanly into **13** when heated in the solid state at 170 °C for 15 min. The simplicity of the NMR spectra of **13** implied the formation of a system with 2-fold and/or inversion symmetry. As shown in Figure 1, in the crystalline state, the diallene **13** adopted the *s-trans* conformation, analogous to the structure of **4**. The C(9)=C(10) bond (1.318(2) Å) is significantly longer than the C(10)=C(11) bond (1.306(2) Å); moreover, while the Si(1)−methyl bond lengths are normal (average of the six values is 1.860 Å), the silicon−carbon C(11)−Si(1) distance is slightly longer, 1.9107(13) Å. These values are similar to those previously observed in Me$_2$C=C=C(TMS)−C(TMS)=C=CMe$_2$.[15]

With the expectation of effecting an electrocyclization of the allene double bonds in **13** to form 1,2-bis(trimethylsilyl)-3,4-bis(fluorenylidene)cyclobutene, **14**, the diallene precursor was

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[12] Toda, T.; Kuwana, M.; Ohhashi, Y.; Yoshida, M. *Chem. Lett.* **1997**, 21–22.

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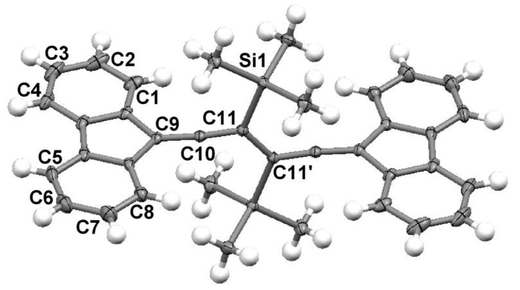


Figure 1. *Mercury*[14] representation of the molecular structure of *s-trans* diallene **13** (30% thermal ellipsoids). Selected bond lengths (Å) and angles (deg): C(9)−C(10) 1.318(2), C(10)−C(11) 1.306(2), C(11)-C(11′) 1.496(2), C(11)−Si(1) 1.911(2), C(9)−C(10)−C(11) 174.0(1).

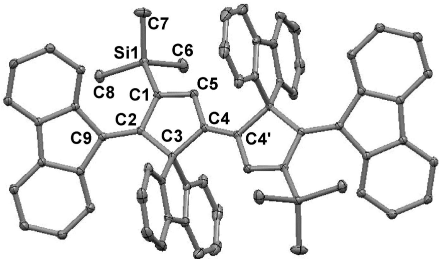


Figure 2. *Mercury* representation of the molecular structure of the dihydro-quatercyclopentadiene **15** (30% thermal ellipsoids). Hydrogens have been removed for clarity. Selected bond lengths (Å) and angles (deg): C(1)−C(2) 1.458(2), C(2)−C(3) 1.546(2), C(3)−C(4) 1.553(2), C(4)−C(5) 1.435(2), C(5)−C(1) 1.368(2), C(4)-C(4′) 1.360(3), C(2)−C(9) 1.370(2), C(1)−Si(1) 1.890(2), C(3)−C(4)−C(5) 106.4(1).

heated at reflux in toluene for 5 days. Subsequent chromatographic separation revealed a multicolored plethora of products, of which the major one was a blue-violet material, **15**, which yielded green crystals, which were characterized by X-ray crystallography.

Figure 2 illustrates the molecular structure of **15** and reveals it to be a dimer of **13** that has suffered desilylation at the positions adjacent to the central double bond, the length of which is 1.36 Å. The molecule is centrosymmetric, but not completely planar; each half of the structure contains two fluorenylidene moieties, one of which is spiro-bonded. The resulting molecule is a tetrabenzo-dihydro-quatercyclopentadiene; previous attempts to obtain quatercyclopentadienes by successive attachment of Cp rings to fulvalene complexes have been described by Vollhardt.[16]

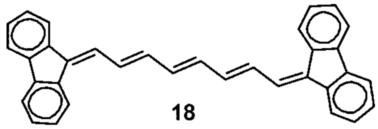
Apparently, formation of the anticipated cyclobutene ring, as in **14**, is thwarted by extreme steric congestion. In terms of a mechanistic hypothesis, one can visualize rotation about the central bond of the diallene **13** and cyclization to form a cyclopentenylidene ring, **16**, whereby the carbene is initially sterically protected by its very bulky trimethylsilyl and spiro-bonded fluorenyl neighbors. As indicated in Scheme 4, subsequent desilylation, possibly as trimethylsilanol and mediated by traces of water, would allow formation of the observed carbene dimer **15**.[17]

However, the reaction proceeds only at high temperatures and is somewhat capricious, and yields of **15** are variable. In contrast, treatment of the diallene **13** with sodium fluoride in THF (containing a minimum quantity of water to dissolve the NaF) at room temperature rapidly brings about the development of a blood-red coloration; subsequent chromatographic separation and recrystallization yielded a purple product, **17**, of X-ray diffraction quality. The structure of **17**, depicted in Figure 3, reveals it to be the "parent" tetrabenzo-dihydro-quatercyclopentadiene, whereby both trimethylsilyl substituents in **15** have been removed. The ^{1}H NMR spectrum of **17**, shown in Figure 4, is consistent with a molecule of effective C_{2h} symmetry and clearly reveals the presence of two different fluorenyl environments: one that straddles the molecular mirror plane and the other lying in the plane thereby rendering its benzo rings inequivalent. The two adjacent protons in the central five-membered rings give rise to 5.7 Hz doublets at δ 7.70 and 6.41, reflecting their very different surroundings. The more shielded proton, H(2), is sited directly above the spiro-bonded fluorenyl substituent, whereas H(3) lies in the deshielding zone of a benzo ring of the in-plane fluorenylidene. These assignments were confirmed by NOE measurements.

Interestingly, the octacyclic C_{36} framework of **17** represents 60% of C_{60} and, as illustrated in Figure 5, can be mapped directly onto the parent fullerene.

Precedent for cyclization of a diallene to a five-membered ring carbene is provided by Hopf's report of the thermolytic formation of dihydropentalene from *cis*-1,2-diethynylcyclobutane, via cycloocta-1,2,4,5-tetraene (Scheme 5).[18]

The tetrabenzo-dihydro-quatercyclopentadiene **17** absorbs strongly in the green, at 504 nm, and consequently appears red-violet. The most closely analogous system of which we are aware is *trans*,*trans*,*trans*-1,1,10,10-bis(3,3′-biphenylene)deca-1,3,5,7,9-pentaene, **18**, which absorbs at 507 nm and is also intensely purple.[19] Surprisingly, perhaps, in the disilyl system **15** the absorption maximum is found at 560 nm, and the role of the silicon substituents merits further investigation.



18

Molecule 18

Whether cyclization of diallene **13**, and dimerization to give **15** or **17**, occurs at the disilylated or monosilylated stage is unclear. However, it is less likely to involve the nonsilylated diallene **19** since another minor product 1,4-bis(fluorenylidene)-2-butyne, **20**, presumably derived from **19**, was also observed.[20] The structure of **20** is shown in Figure 6 and represents the product of two prototropic shifts, thus generating a central alkyne linkage, as in Scheme 6. This hexa-1,5-dien-3-yne had been synthesized previously by treatment of biphenyleneacrolein with the dilithio salt of 9-ethynylfluoren-9-ol, reduction of the resulting hydroxyl substituents to yield a hexa-1,2,3,5-tetraene, and finally base-promoted isomerization to **20**.[19]

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[15] Jones, P. G.; Bubenitschek, P.; Hopf, H.; Stamm, R. *Acta Crystallogr.* **2003**, *E5*, 90119−0120.

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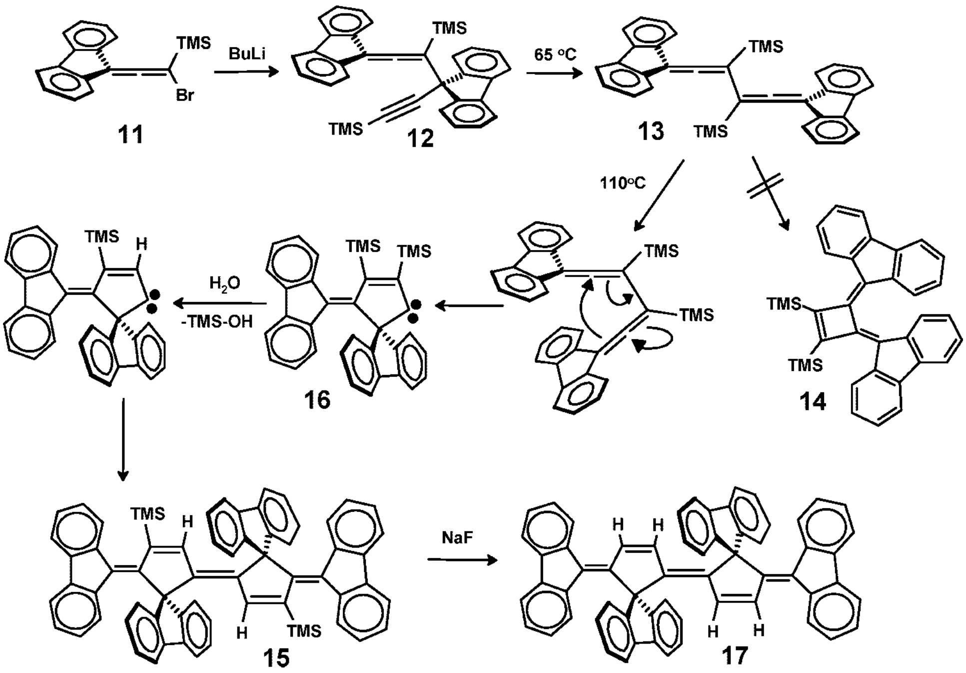
[17] Coupling of silylated polyalkynes, possibly via cobalt-carbene intermediates, has been extensively studied:(a) Fritch, J. R.; Vollhardt, K. P. C.; Thompson, M. R.; Day, V. W. *J. Am. Chem. Soc.* **1979**, *101*, 2768–2770. (b) Fritch, J. R.; Vollhardt, K. P. C. *Organometallics* **1982**, *1*, 590–602.

[18] (a) Eisenhuth, L.; Hopf, H. *J. Am. Chem. Soc.* **1974**, *96*, 5667–5668. (b) Eisenhuth, L.; Hopf, H. *Chem. Ber.* **1975**, *108*, 2635–2648.

[19] Fischer, H.; Fischer, H. *Tetrahedron* **1965**, *25*, 955–958.

[20] A detailed vibrational study of the parent diallenyl, $CH_2{=}C{=}CH{-}CH{=}C{=}CH_2$, has been reported: Powell, D. L.; Klaboe, P.; Christensen, D. H.; Hopf, H. *Spectrochim. Acta* **1973**, *29A*, 7–16.

Scheme 4. Proposed Mechanism for the Dimerization of Diallene 13



The apparent ability of the diallene **13** to adopt the *s-cis* conformation prompted us to attempt to trap this rotamer, possibly as a cyclopentadienone-tricarbonyliron complex.[21] However, when a THF solution of **13** was stirred at room temperature for 36 h with $Fe_2(CO)_9$, the product isolated after chromatographic separation exhibited ^1H and ^{13}C NMR spectra indicating the presence of two different fluorenyl groups and two nonequivalent trimethylsilyl substituents, as well as terminal and bridging Fe−^{13}CO NMR resonances at 213.7 and 249.8 ppm, respectively. In the infrared spectrum, ν_{CO} absorptions were found at 2017, 1965, and 1649 cm^{-1}. The simplicity of the spectra suggested a molecule possessing mirror symmetry, but it was only finally characterized by X-ray crystallographically (Figure 7) as the novel system **21**, 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. To the best of our knowledge, there has been only one, very recent, previous report of a crystallographically characterized molecule possessing an (η^5-fluorenyl)Fe moiety,[22] although η^5-fluorenyl complexes of other metals, such as Ti,[23] Mn,[24] Zr,[25] and Ru,[26] have been unequivocally identified.

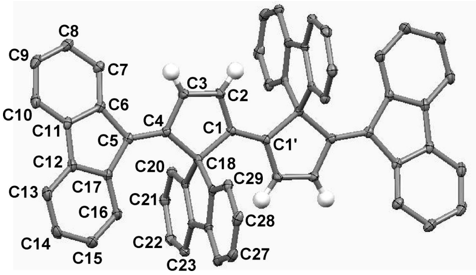


Figure 3. *Mercury* representation of the molecular structure of the "parent" dihydro-quatercyclopentadiene **17** (30% thermal ellipsoids). Aromatic hydrogens have been removed for clarity. Selected bond lengths (Å) and angles (deg): C(1)−C(2) 1.421(2), C(2)−C(3) 1.346(2), C(3)−C(4) 1.433(2), C(4)−C(18) 1.564(2), C(18)−C(1) 1.558(2), C(1)−C(1′) 1.358(3), C(4)−C(5) 1.372(2), C(18)−C(1)−C(2) 111.9(1); interplanar fold angle: C(2)−C(3)−C(4)−C(18)/C(2)−C(1)−C(18)−C(1′) 9.5.

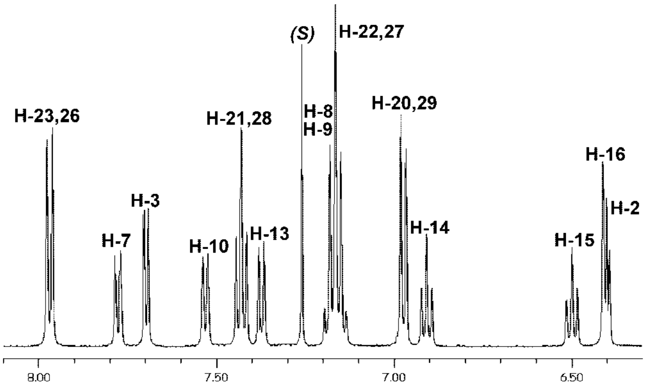


Figure 4. 500 MHz ^1H NMR spectrum of **17**, recorded in $CDCl_3$ (***S***).

The iron in **21** is not completely symmetrically bonded to the central ring of the fluorenyl ligand; the distances to C(13) [2.061(5) Å] and to C(1) and C(12) [2.180(5) and 2.146(5) Å,

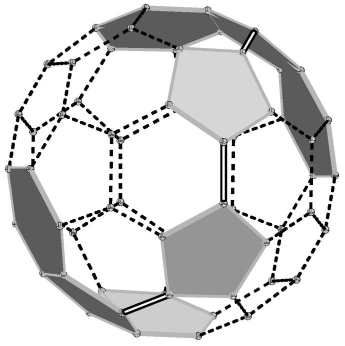
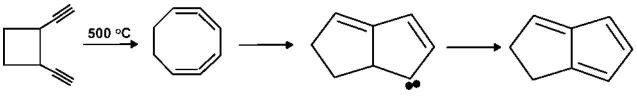


Figure 5. C_{36} skeletal framework of **17** mapped onto C_{60}.

Scheme 5. Cyclization of a Diallene to a Carbene



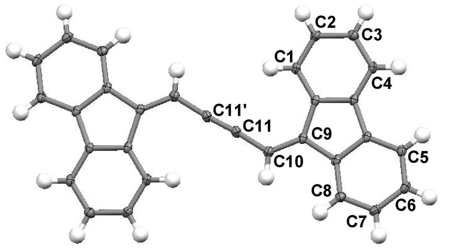
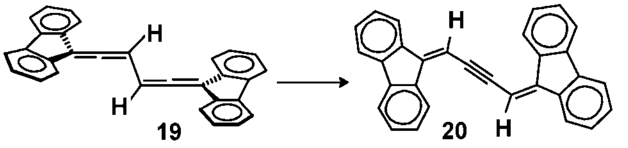


Figure 6. *Mercury* representation of the molecular structure of the bis-fluorenylidene-alkyne **20** (30% thermal ellipsoids). Selected bond lengths (Å) and angles (deg): C(9)−C(10) 1.354(2), C(10)−C(11) 1.408(2), C(11)−C(11′) 1.215(3), C(9)−C(10)−C(11) 126.2(1), C(10)−C(11)−C(11′) 175.0(2).

Scheme 6. Prototropic Shifts to Isomerize 19 into 20



respectively] are significantly shorter than to C(6) and C(7) [2.249(6) and 2.213(5) Å, respectively], and the Fe−ring-centroid distance is 1.792 Å. By comparison, in (η^5-fluorenyl)Fe(η^5-cyclopentadienyl) the Fe−fluorenyl-ring-plane distance is 1.681 Å, and the metal−ring carbon distances range only from 2.052 to 2.100 Å.[22] The η^5-fluorenyl ligand in **21** is not planar, but rather is slightly arced away from the metal such that the interplanar angle between the six-membered rings is 8°. The iron−acyl-carbon distance is rather long [Fe(1)−C(16) = 1.997(5) Å], and the possible relative weakness of this linkage may account for the somewhat fragile character of the molecule, which, as discussed below, gradually decomposes in solution, even at room temperature.

Molecule **21** is not actually mirror-symmetric in the solid state, but it evidently adopts time-averaged C_s symmetry in solution, whereby the two fluorenyl moieties straddle the mirror plane, which contains the two nonequivalent silyl groups. The most closely analogous systems of which we are aware are **22** and **23**, in each case the product of the iron carbonyl-promoted ring-opening of a spiro[2.4]hepta-4,6-diene such that a carbon of the cyclopropyl ring migrates onto a carbonyl ligand, as in Scheme 7. In **22** and **23**, the Fe−bridging-CO distances were found to be 1.978 and 1.960 Å, and the acyl ν_{CO} absorptions were at 1663 and 1630 cm^{-1}, respectively.[27,28]

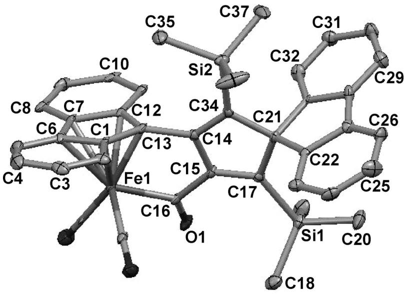
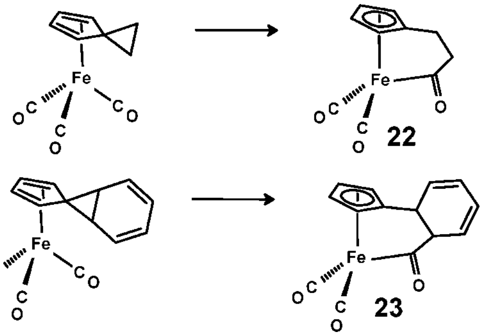


Figure 7. *Mercury* representation of the molecular structure of the η^5-fluorenyl complex **21** (30% thermal ellipsoids). Hydrogens have been removed for clarity. Selected bond lengths (Å) and angles (deg): C(13)−C(14) 1.482(7), C(14)−C(15) 1.454(7), C(14)−C(34) 1.327(7), C(15)−C(17) 1.355(7), C(17)−C(21) 1.542(8), C(21)−C(34) 1.545(7), C(17)−Si(1) 1.883(6), C(34)−Si(2) 1.878(6), C(34)−C(14)−C(15) 112.6(5), C(14)−C(15)−C(17) 111.0(5), C(14)−C(15)−C(16) 117.7(4).

Scheme 7. Metal-Promoted Ring-Opening of Spiro[2.4]hepta-4,6-dienes



The formation of the iron complex **21** directly from the diallene **13** poses a challenging mechanistic problem since it would be necessary to postulate a complex rearrangement process by which the second fluorenyl inserts into the carbon−carbon bond that links the two trimethylsilyl substituents. However, if one were to invoke the existence of an equilibrium between the diallene **13** and the propargyl-allene **12**, the situation becomes more tractable. Thus, reaction of $Fe_2(CO)_9$ with **12** could yield **24**, in which both the alkyne and one of the allene double bonds are coordinated to an iron tricarbonyl unit. Now, as shown in Scheme 8, migration of the terminal trimethylsilyl group onto the internal alkyne carbon generates the vinylidene complex **25** and also positions the spiro-bonded fluorenyl fragment between two carbons, each bearing a trimethylsilyl substituent, as required to attain the structural motif found in **21**. (There is ample precedent for the isomerization of trimethylsilyl-alkyne complexes of Ru, Rh, and Ir into vinylidene ligands.[29]) Subsequent cyclization, to form **26**, and migration of the linkage connecting the five-membered ring to the metal onto a terminal carbonyl group yields the observed product, **21**. Gratifyingly, the reaction of the propargyl-allene **12** directly with di-iron nonacarbonyl also yields complex **21**.

When the fluorenyl-iron complex **21** was left in chloroform solution at room temperature for several hours, it gradually

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(21) Knölker, H.-J. *Chem. Soc. Rev.* **1999**, *28*, 151–157.

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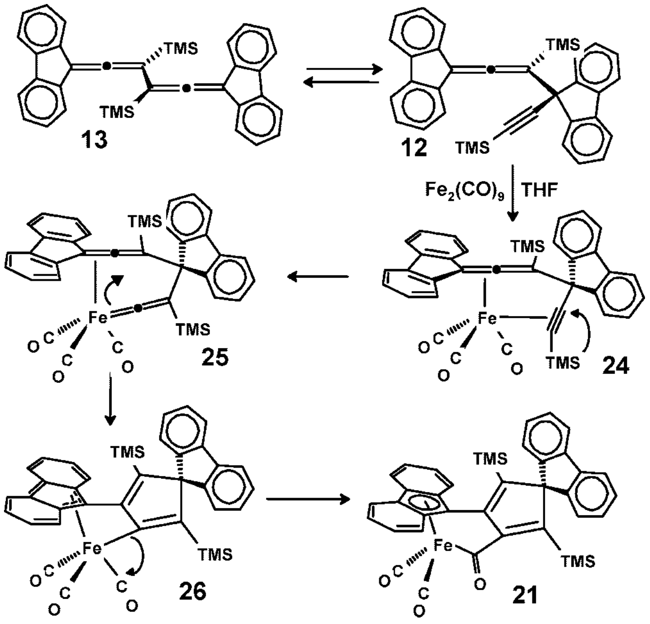
Scheme 8. Proposed Rearrangement Mechanism Leading to the Formation of 21



decomposed with loss of the metal to yield an organic compound, **27**, whose ^1H and ^{13}C NMR spectra again revealed the presence of two fluorenyl moieties and two nonequivalent trimethylsilyl substituents, as well as an infrared absorption at 1760 cm^{-1}, possibly suggesting the presence of a cyclic conjugated carbonyl moiety. The structure of **27** was unequivocally resolved by X-ray crystallography and was shown to be a bicyclic lactone clearly derived from **21** by loss of the dicarbonyliron fragment and incorporation of an additional oxygen.

As illustrated in Figure 8, lactone **27** has retained the mirror symmetry of its precursor, **21**, whereby the two spiro-bonded fluorenyl fragments are orthogonal to the central eight-atom bicyclic plane. The carbocyclic ring is fused to the lactone such that the central bond of the 1,3-diene unit is common to both five-membered rings. No such bicyclo[3.3.0]octadienones appear to have been previously described; the most closely related system to have been reported is probably the tricyclic anhydride **28**, mentioned by Barton and Lindsey en route to their establishment of the structure of caryophylene.[30]

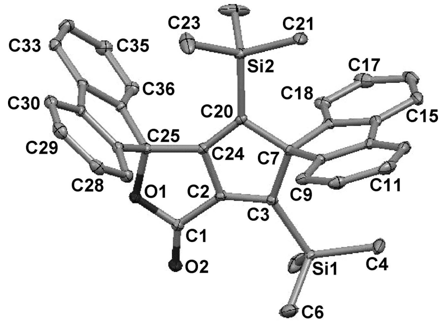
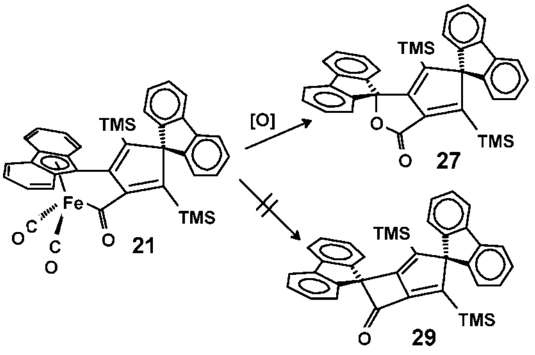
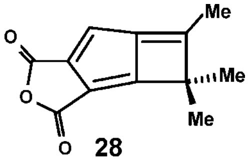


Figure 8. *Mercury* representation of the molecular structure of lactone **27** (30% thermal ellipsoids). Selected bond lengths (Å) and angles (deg): C(1)−O(1) 1.367(2), C(1)−O(2) 1.202(2), C(1)−C(2) 1.475(2), C(2)−C(24) 1.446(2), C(24)−C(25) 1.513(2), C(25)−O(1) 1.493(2), C(2)−C(3) 1.351(2), C(24)−C(20) 1.345(2), C(7)−C(20) 1.548(2), C(3)−C(7) 1.544(2), C(3)−Si(1) 1.885(2), C(20)−Si(2) 1.878(2), C(25)−O(1)−C(1) 113.3(1), O(1)−C(1)−C(2) 107.2(1), O(1)−C(1)−O(2) 121.3(1), C(1)−C(2)−C(24) 108.8(1), C(2)−C(24)−C(25) 107.9(1), O(1)−C(25)−C(24) 102.6(1), C(2)−C(24)−C(20) 111.6(1), C(3)−C(2)−C(24) 112.7(1).

Scheme 9. Decomposition of (η^5-Fluorenyl)iron Complex 21 to Form Lactone 27





Molecule 28

We noted above that the Fe-to-bridging-CO distance in **21** is 1.997(5) Å, considerably longer than was observed in the related (η^5-cyclopentadienyl)iron dicarbonyl complexes **22** and **23**, and is consistent with the relative weakness and ready cleavage of this linkage. However, simple reductive elimination would have led to formation of a very highly strained bicyclo[3.2.0]heptadiene system, **29**; instead, as depicted in Scheme 9, it appears that decomposition of **21** involves concomitant oxidation to the observed lactone **27**.

To conclude, the bis-trimethylsilyl-difluorenylidene-diallene **13** is apparently so sterically crowded that it cannot undergo a conventional electrocyclization to a 3,4-dialkylidene-cyclobutene and instead forms a cyclopentenylidene carbene that dimerizes to yield dihydro-quatercyclopentadienes **15** and **17**, whose C_{36} skeletons can be mapped onto the C_{60} framework and indeed represent 60% of that fullerene. Furthermore, the diallene **13** does not form an $Fe(CO)_3$ complex directly, but rather reverts to its precursor propargyl-allene isomer **12** and rearranges, via a vinylidene carbene, to the novel η^5-fluorenyl complex **21**, which in turn decomposes to furnish the lactone **27**. It has long been known that bis-allenes isomerize in the presence of metal salts,[31] and other reactions of **12** and **13** with organometallic reagents will be the subject of future reports.

Experimental Section

All reactions were carried out under an atmosphere of dry nitrogen employing conventional benchtop and glovebag techniques. Merck silica gel 60 (230−400 mesh) was used for flash chromatography. ^1H and ^{13}C NMR spectra were recorded on Varian Inova 300, 400, or 500 MHz spectrometers. Assignments were based on standard two-dimensional NMR techniques ($^1H-^1H$ COSY, $^1H-^{13}C$ HSQC, HMBC, NOESY). Infrared spectra were recorded on a Perkin-Elmer Paragon 1000 FT-IR spectrometer and were calibrated with polystyrene. High-resolution mass spectra were acquired on a Waters Micromass LCT spectrometer. Melting points were determined on an

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Table 1. Crystallographic Data for 13, 15, 17, 20, 21, and 27

	13	15	17	20	21	27
formula	$C_{36}H_{34}Si_2$	$C_{66}H_{52}Si_2$	$C_{60}H_{36}$	$C_{30}H_{18}$	$C_{39}H_{34}O_3Si_2Fe$	$C_{37}H_{34}O_2Si_2$
M	522.81	901.26	756.89	378.44	662.69	566.82
cryst syst	monoclinic	triclinic	triclinic	orthorhombic	monoclinic	triclinic
space group	$P2_1/n$ (#14)	$P\bar{1}$ (#2)	$P\bar{1}$ (#2)	*Pbca* (#61)	$P2_1$ (#4)	$P\bar{1}$ (#2)
a [Å]	8.7746(8)	9.3793(5)	9.9551(8)	17.614(4)	11.3911(14)	11.4318(9)
b [Å]	15.0035(14)	10.8902(6)	12.1672(9)	6.0205(14)	40.922(5)	14.3358(11)
c [Å]	23.312(2)	12.6232(7)	16.7538(14)	18.488(4)	15.1025(19)	20.6890(16)
α [deg]	90	89.0770(10)	84.330(2)	90	90	110.013(2)
β [deg]	96.878(2)	79.5930(10)	85.134(2)	90	104.314(3)	96.216(2)
γ [deg]	90	75.4160(10)	77.975(2)	90	90	98.873(2)
V [Å^3]	3047.0(5)	1226.71(12)	1970.8(3)	1960.6(8)	6821.4(15)	3100.0(4)
Z	4	1	2	4	8	4
ρ_{calcd} [g cm^{-3}]	1.140	1.220	1.275	1.282	1.291	1.214
T [K]	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
μ [mm^{-1}]	0.139	0.115	0.072	0.073	0.549	0.146
F(000)	1112	476	792	792	2768	1200
θ range for data collection [deg]	1.62 to 28.00	1.64 to 27.00	1.72 to 23.30	2.20 to 24.11	1.39 to 23.40	1.83 to 28.28
index ranges	$-11 \le h \le 11$	$-11 \le h \le 11$	$-10 \le h \le 11$	$-16 \le h \le 20$	$-12 \le h \le 12$	$-15 \le h \le 15$
	$-19 \le k \le 19$	$-13 \le k \le 13$	$-13 \le k \le 12$	$-6 \le k \le 6$	$-45 \le k \le 45$	$-19 \le k \le 19$
	$-30 \le l \le 30$	$-16 \le l \le 16$	$-18 \le l \le 18$	$-10 \le l \le 21$	$-16 \le l \le 16$	$-27 \le l \le 27$
reflns measd	29 648	22 908	18 311	6355	44 991	31 872
indep reflns	7348	5334	5682	1557	19 717	15 247
R_{int}	0.0216	0.0245	0.0280	0.026	0.0416	0.0261
data/restraints/parameters	7348/3/401	5334/0/411	5682/0/541	1557/0/136	19 717/709 /1646[a]	15 247/0/751
final *R* values [$I > 2\theta(I)$]:						
R1	0.0455	0.0504	0.0353	0.0355	0.0504	0.0477
wR2	0.1177	0.1298	0.0824	0.0886	0.1139	0.1195
R values (all data):						
R1	0.0510	0.0565	0.0459	0.0455	0.0609	0.0594
wR2	0.1240	0.1354	0.0878	0.0931	0.1191	0.1274
GOF on F^2	1.038	1.058	1.019	1.085	1.039	1.036

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

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, **12**, was prepared as previously described.[11]

Preparation of 1,6-Bis(biphenyl-2,2′-diyl)-3,4-bis(trimethylsilyl)-1,2,4,5-hexatetraene (13). A solution of **12** (1 g, 1.913 mmol) in toluene (20 mL) was heated at reflux for 48 h; upon cooling to room temperature and trituration with diethyl ether, colorless crystals were deposited and were washed in pentane to give bis(fluorenylidene)bis(trimethylsilyl)diallene **13** (750 mg, 1.43 mmol; 75%) as a white solid, mp 177−179 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85−7.80 (m, 4H, fluorenyl-H), 7.64−7.59 (m, 4H, fluorenyl-H), 7.41−7.34 (m, 8H, fluorenyl-H), 0.13 (s, 18H, TMS). ^{13}C NMR (100 MHz, $CDCl_3$): δ 204.7 (C_{10}), 138.4, 138.1 (C_{4a}, C_{4b}, C_{8a}, C_{9a}), 127.3, 127.1, 122.8, 120.4 (C_1, C_2, C_3, C_4), 103.5, 102.5 (C_9, C_{11}), 0.15 (TMS). IR ($CDCl_3$): 1919 cm^{-1} ($C=C=C$). Anal. Calcd for $C_{36}H_{34}Si_2 \cdot (CH_3CH_2)_2O$: C, 81.52; H, 7.02. Found: C, 81.67; H, 6.48. A sample suitable for an X-ray crystal structure determination was obtained by recrystallization from dichloromethane/pentane.

Preparation of Tetrabenzodihydroquatercyclopentadiene 15. A solution of the bis-allene **13** (300 mg, 0.574 mmol) in toluene (10 mL) was heated at reflux for 5 days and then allowed to cool to room temperature. The precipitate was filtered and washed with toluene to give bis(fluorenylidene)-bis(trimethylsilyl)-diallene **13** (18.3 mg, 0.035 mmol; 6%), recovered as a white solid. The filtrate was concentrated and the crude material was purified by chromatography on a silica column using pentane/dichloromethane. Trituration of the dark blue main fraction with diethyl ether gave the tetrabenzodihydroquatercyclopentadiene **15** (64 mg, 0.07 mmol; 26%) as a rather insoluble green solid, mp >360 °C. UV/vis: λ = 560 nm. ϵ = 300 400 L mol^{-1} cm^{-1}. HRMS: calcd for $C_{66}H_{52}Si_2$ [M$^+$], 900.3608; found, 900.3591. Anal. Calcd for $C_{66}H_{52}Si_2 \cdot 0.5CH_2Cl_2$: C, 84.62; H, 5.67. Found: C, 84.37; H, 5.68. A sample suitable for an X-ray crystal structure determination was obtained by recrystallization from dichloromethane/diethyl ether.

Preparation of Tetrabenzodihydroquatercyclopentadiene 17. To a solution of the bis-allene **13** (125 mg, 0.24 mmol) in THF (10 mL) was added sodium fluoride (11 mg, 0.26 mmol) at room temperature. Almost immediately, the solution became orange and then blood-red. After stirring overnight, the solution was concentrated and the crude material was purified by chromatography on a silica column using pentane/dichloromethane to yield purple crystals of the quatercyclopentadiene **17** (6.4 mg, 0.008 mmol; 7%), orange crystals of the bis(fluorenylidene)but-2-yne **19** (5 mg, 0.013 mmol; 5%), and several other currently unidentified products. Data for **17**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.97 (4H, d, J = 7.6 Hz, $H_{23,26}$), 7.78 (2H, d, J = 7.5 Hz, H_7), 7.70 (2H, d, J = 5.7 Hz, H_3), 7.53 (2H, d, J = 7.5 Hz, H_{10}), 7.44 (4H, t, J = 7.6 Hz, $H_{21,28}$), 7.38 (2H, d, J = 7.4 Hz, H_{13}), 7.18 (2H, m, H_8), 7.18 (2H, m, H_9), 7.18 (4H, m, $H_{22,27}$), 6.98 (4H, d, J = 7.6 Hz, $H_{20,29}$), 6.91 (2H, t, J = 7.3 Hz, H_{14}), 6.50 (2H, t, J = 7.7 Hz, H_{15}); 6.41 (2H, m, H_2), 6.40 (2H, m, H_{16}). ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.81 (C_4), 148.78 (C_{24},C_{25}), 142.22 (C_{18},C_{19}), 141.79 (C_1), 140.27 (C_3), 140.12 (C_6), 140.08 (C_{11}), 139.53 (C_{17}), 137.12 (C_2), 136.74 (C_{12}), 130.60 (C_5), 128.63 (C_{22},C_{27}), 128.18 (C_{21},C_{28}), 126.79 (C_9), 126.57 (C_{14}), 126.36 (C_8), 125.90 (C_{16}), 125.62 (C_{15}), 125.36 (C_7), 124.54 (C_{20}, C_{29}), 120.09 (C_{23}, C_{26}), 119.23 (C_{10}), 118.47 (C_{13}), 68.04 (C_{18}). HRMS: calcd for $C_{60}H_{37}$ [M + H$^+$], 757.2895; found, 757.2930. Samples of **17** and **19** suitable for X-ray crystal structure determinations were obtained by recrystallization from dichloromethane/pentane.

Preparation of (η^5-Fluorenyl)Fe Complex 21. A solution of the bis(fluorenylidene)-bis(trimethylsilyl)-diallene **13** (222 mg, 0.43 mmol) and $Fe_2(CO)_9$ in THF (5 mL) was stirred at room temperature for 36 h. The solvent was removed on a rotary evaporator, and the crude material was purified by silica chromatography using dichloromethane/pentane as eluent to give recovered starting material **13** (118.5 mg, 0.23 mmol; 53%) as a white solid and the η^5-fluorenyl complex **21** (68.8 mg, 0.104 mmol; 52%) as a red solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.84 (d, 2H, J = 8.5 Hz, fluorenyl-H), 7.80

(d, 2H, $J = 7.5$ Hz, fluorenyl-H), 7.65 (d, 2H, $J = 8.5$ Hz, fluorenyl-H), 7.43 (t, 2H, $J = 7.5$ Hz, fluorenyl-H), 7.38 (t, 2H, $J = 8.0$ Hz, fluorenyl-H), 7.33 (t, 2H, $J = 7.5$ Hz, fluorenyl-H), 7.30−7.24 (m, 4H, fluorenyl-H), −0.40 (s, 9H, TMS), −0.55 (s, 9H, TMS). ^{13}C NMR (125 MHz, $CDCl_3$): δ 249.8 (bridging CO), 213.7 (CO), 185.6, 152.1, 149.2, 147.5, 143.0, 142.7, 128.7, 128.3, 127.8, 125.8, 124.2, 124.1, 120.6, 105.5, 97.1, 86.0, 84.3, −0.9, −1.3. IR ($CDCl_3$): 2017, 1965, 1649 cm^{-1} (CO). Anal. Calcd for $C_{39}H_{34}FeO_3Si_2 \cdot 0.5CH_2Cl_2$: C, 67.27; H, 5.01. Found: C, 67.61; H, 5.00. A sample of the complex suitable for an X-ray crystal structure determination was obtained by recrystallization from pentane/diethyl ether/dichloromethane.

Preparation of the Bicyclic Lactone 27. A solution of η^5-fluorenyl complex **21** was left in deuteriated chloroform solution at room temperature for 24 h. The mixture was concentrated, and the crude product was purified by chromatography on silica using pentane/dichloromethane as eluent to give the bicyclic lactone **27** as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74 (d, 2H, $J =$ 7.0 Hz, fluorenyl-H), 7.66 (d, 2H, $J = 7.5$ Hz, fluorenyl-H), 7.52 (d, 2H, $J = 7.5$ Hz, fluorenyl-H), 7.44 (t, 2H, $J = 7.5$ Hz, fluorenyl-H), 7.39 (t, 2H, $J = 7.0$ Hz, fluorenyl-H), 7.37 (t, 2H, $J = 7.5$ Hz, fluorenyl-H), 7.25 (t, 2H, $J = 7.5$ Hz, fluorenyl-H), 7.01 (d, 2H, J $= 7.5$ Hz, fluorenyl-H), −0.23 (s, 9H, TMS), −1.14 (s, 9H, TMS). ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.1, 164.7, 159.3, 148.1, 147.6, 145.6, 143.4, 141.0, 140.1, 130.6, 128.8, 128.6, 127.7, 125.1, 123.8, 120.7, 120.6, 90.9, 90.7, −1.3, −1.9. IR ($CDCl_3$): 1649 cm^{-1} (CO). HRMS: calcd for $C_{37}H_{35}O_2Si_2$ [M$^+$], 567.2176; found, 567.2172. A sample suitable for an X-ray crystal structure determination was obtained by recrystallization from pentane/diethyl ether.

X-ray Measurements for 13, 15, 17, 20, 21, and 27. Crystal data were collected using a Bruker SMART APEX CCD area detector diffractometer and are listed in Table 1. A full sphere of the reciprocal space was scanned by phi-omega scans. A pseudoempirical absorption correction based on redundant reflections was performed by the program SADABS.[32] The structures were solved by direct methods using SHELXS-97[33] and refined by full matrix least-squares on F^2 for all data using SHELXL-97.[34] In **15**, all hydrogen atoms were located in the difference Fourier map and allowed to refine freely with isotropic thermal displacement factors. All other hydrogen atoms were added at calculated positions and refined using a riding model. Their isotropic displacement parameters 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 temperature factors were used for all non-hydrogen atoms.

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-675654 (**13**), CCDC-675655 (**15**), CCDC-688696 (**17**), CCDC-689382 (**20**), CCDC-675656 (**21**), and CCDC-675657 (**27**). This information is available free of charge from http://www.ccdc.cam.ac.uk.

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