Organometallics **2008,** *27,* 4173–4182

Syntheses, Structures, and Dimerizations of Ferrocenyl- and Fluorenylideneallenes: Push−Pull Multiple Bonds?

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Received April 2, 2008

Protonation of 9-(ferrocenylethynyl)fluoren-9-ol (**9**) yields the conjugated enone derived from a Meyer−Schuster rearrangement. However, treatment of **9** with thionyl chloride at −30 °C proceeds with elimination of SO_2 to furnish 3,3-biphenylene-1-chloro-1-ferrocenylallene (**14**), the ^{13}C NMR data of which indicate that the central carbon does not have markedly carbenic character. Upon warming, this allene readily forms the sterically highly encumbered head-to-head dimer **15**, whereby the 1,2-bis(alkylidene)cyclobutane adopts a butterfly conformation with two exocyclic Cl(Fc)C═ moieties and a very long (~1.65 Å) C(3)−C(4) bond linking the two spiro-bonded fluorenyl fragments. In contrast, attempts to generate the analogous ferrocenylbromoallene **16** instead yielded the hexa-1,2-dien-5-yne **17**, the product of allenyl radical head-to-tail coupling. Protonation of ferroceno[2,3]inden-1-ol (**25**) confirmed a proposal, originally put forward by Caïs in 1965, concerning the possible diradical nature of the resulting cation; the unambiguous characterization of the ferroceno[2,3]inden-1-yl dimer (**29**) provides experimental verification of Caïs's hypothesis. The X-ray crystal structures of 9-(ferrocenylethynyl)fluoren-9-ol (**9**) and of its isomer 1-(phenylethynyl)ferroceno[2,3]inden-1-ol (**26**) are reported along with, among others, the structures of **15**, **17**, **25**, and **29**. The possible role of these allenes as precursors to ferrocenyl-containing electroluminescent tetracenes is discussed.

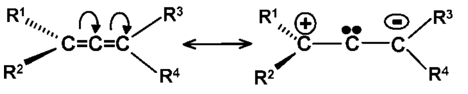
Introduction

As first suggested by Salisbury more than 30 years ago,[1] an extreme resonance form of an allene would place opposite charges at the terminal positions, thus engendering carbene character at the central carbon atom. Such a scenario might be enhanced by incorporating substituents R^1 and R^2 that are particularly efficient at tolerating a neighboring positive charge, while R^3 and R^4 would need to be capable of efficient delocalization of negative charge (Chart 1).

"Push-pull" allenes of this type are known and have been comprehensively reviewed by Saalfrank.[2] However, thus far there is no compelling evidence that the carbene-like structure is a predominant resonance contributor. For example, one might expect diminished barriers to rotation about the formal double bonds to the central carbon or a geometric distortion of the orthogonally positioned R_2C═ fragments toward planarity.

It is well established that organometallic moieties, such as ferrocenyl,[3] or tetrahedral alkynyl dimetallic clusters, (RC≡C)-$(ML_n)_2$, where ML_n = $Co(CO)_3$, $Mo(CO)_2(C_5H_5)$,[4] are quite 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.

Chart 1. Carbene Resonance Form of an Allene



Results and Discussion

Potential Routes to Ferrocenylallenes. The initial plan was to add dibromocarbene to a highly polarized alkene, such as FcCH═C(CN)$_2$ (**1**), FcCH═C(CO$_2$Me)$_2$ (**2**), or FcCH═$C_{13}H_8$ (**3**), and such molecules are readily synthesizable via the Knoevenagel condensation of ferrocenecarboxaldehyde with malononitrile, dimethyl malonate, or fluorene, respectively.[5] The fluorenylidene complex **3** was characterized by X-ray crystallography (Figure 1); the C(9)−C(10) double bond length is 1.349(2) Å, the C(10)−C(11) length is 1.460(3) Å, and the twist angle about the double bond is 11°. The most closely analogous complexes that have been structurally characterized (see Chart 2) are the 2,7-dinitro- and 2,4,5,7-tetranitrofluorenylidene

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(1) Salisbury, L. *J. Org. Chem.* **1972**, *37*, 4075–4077.

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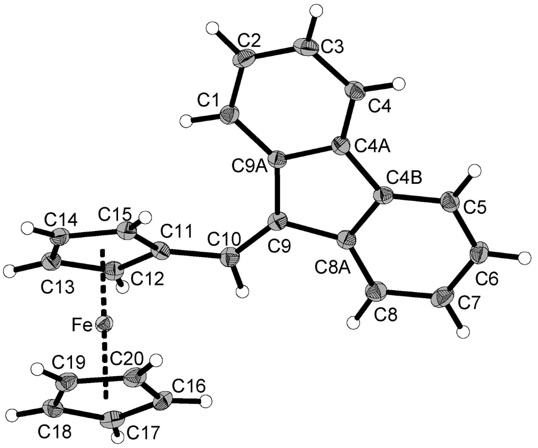
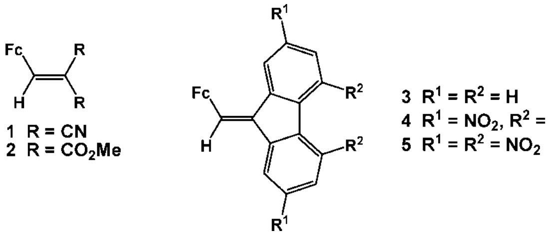
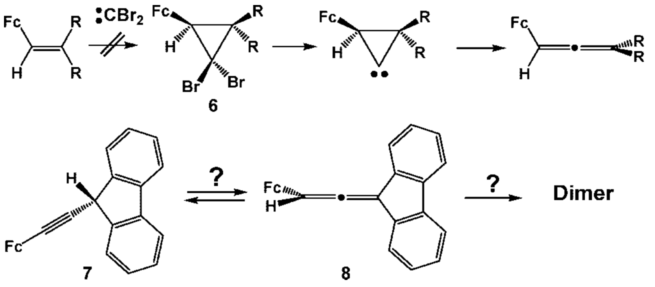


Figure 1. Molecular structure of 9-ferrocenylmethylidenofluorene (**3**). Thermal ellipsoids are drawn at the 50% probability level.

Chart 2. Knoevenagel Products from Ferrocenylcarboxaldehyde



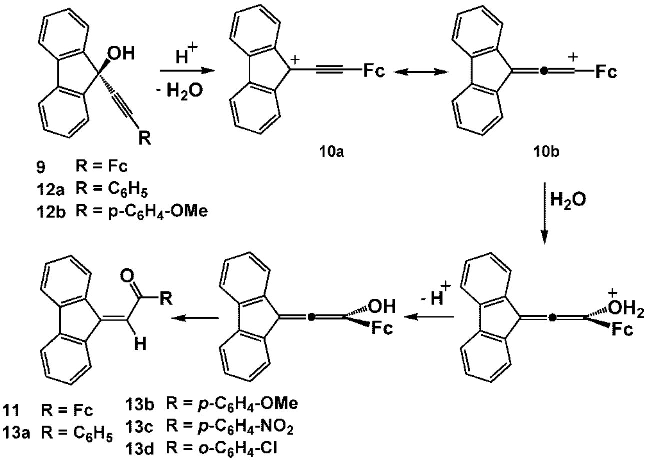
Scheme 1. Cyclopropylidene Carbene Route to Allenes



systems **4** and **5**, in which the corresponding C(9)−C(10) distances are 1.370(7) and 1.350(3) Å, the C(10)−C(11) values are 1.434(7) and 1.453(3) Å, and the twist angles are 12.6 and 3.3°, respectively.[6] It has been suggested that in NLO vinylferrocene derivatives the planarity of the π system is stabilized because it facilitates the intramolecular charge transfer from the ferrocenyl moiety through the C=C bond of the vinyl linkage to the electron acceptor substituents.[7]

The next step would involve debromination of the dibromocyclopropane **6**, to form the corresponding cyclopropylidene carbene that should collapse to the desired allene,[8] as in Scheme 1. However, the carbene addition step proved to be very difficult, and so this route was discontinued. An alternative route to allenes proceeds via the rearrangement of alkynes, and indeed it has been suggested that 9-(ferrocenylethynyl)fluorene (**7**) may be in equilibrium with the allene **8**. Unfortunately, this is apparently not a clean process and is complicated by formation of an unidentified allene dimer.[9]

Scheme 2. Meyer−Schuster Rearrangements of 9-Alkynylfluoren-9-ols



As a first approach toward a convenient synthesis of **8**, we chose to prepare 9-(ferrocenylethynyl)fluoren-9-ol (**9**), which upon protonation should initially generate the antiaromatic 12-π-electron fluorenyl carbocation **10a**, which is perhaps more realistically viewed as the ferrocenyl-stabilized vinylic cation **10b**. After the reaction mixture was worked up, the major product was identified as the ferrocenyl-substituted conjugated ketone **11**. This is readily rationalized as the product of a Meyer−Schuster rearrangement,[10] whereby the initially eliminated molecule of water attacks the vinylic cation **10b**; as shown in Scheme 2, subsequent tautomerization generates **11**. This observation parallels the early report by Abram and Watts, who noted that protonation of 3-ferrocenylprop-2-yn-1-ol yields ferrocenyl vinyl ketone.[11]

In a similar vein, 9-(phenylethynyl)fluorene-9-ol and 9-(*p*-anisylethynyl)-fluorene-9-ol (**12a**,**b**, respectively) also undergo a Meyer−Schuster rearrangement to the corresponding aryl ketones, **13a**,**b**, whose X-ray crystal structures are shown in Figures 2 and 3, respectively. It is noticeable not only that, in both cases, the ketonic moieties are twisted by ∼36° out of the fluorenylidene plane but also that the C(11)−C(12) bond is significantly shorter in **13b** (1.473(2) Å) than in **13a** (1.495(2) Å), presumably as a consequence of conjugation between the methoxy substituent and the carbonyl group. The analogous *p*-nitrophenyl and *o*-chlorophenyl systems **13c**,**d**, respectively, have previously been synthesized but via a different route, namely the aldol condensation of fluorenone with the appropriately substituted acetophenone.[12]

The structure of 9-(ferrocenylethynyl)fluoren-9-ol (**9**), prepared from lithioethynylferrocene and fluorenone,[9] is shown in Figure 4; it exhibits an interesting crystal packing motif, illustrated in Figure 5, whereby four molecules combine to form a hydrogen-bonded rhomboidal pattern with O···O distances of 2.723(2) and 2.877(2) Å. A similar tetrameric arrangement has been seen in several nickel- and platinum-complexed

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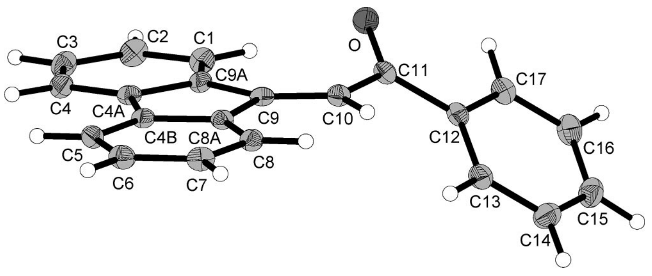

Figure 2. Molecular structure of fluorenylideneacetophenone (**13a**). Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): C(9)−C(10) = 1.348(2), C(10)−C(11) = 1.481(2), C(11)−C(12) = 1.495(2); C(9)−C(10)−C(11)−O(1) = 36.4.

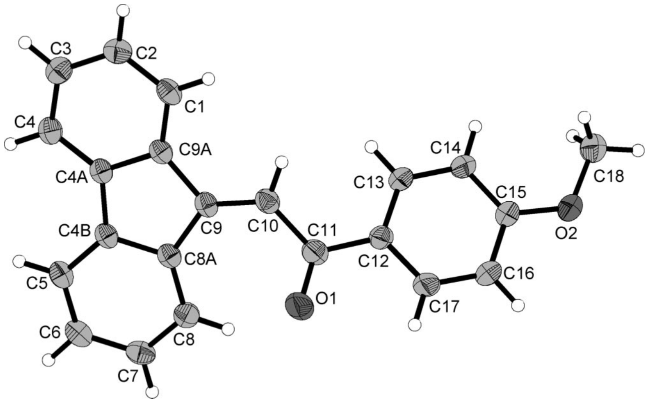

Figure 3. Molecular structure of fluorenylidene-*p*-methoxyacetophenone (**13b**). Thermal ellipsoids are drawn at the 25% probability level. Selected bond lengths (Å) and angles (deg): C(9)−C(10) = 1.340(2), C(10)−C(11) = 1.478(2), C(11)−C(12) = 1.473(2); C(9)−C(10)−C(11)−O(1) = 37.

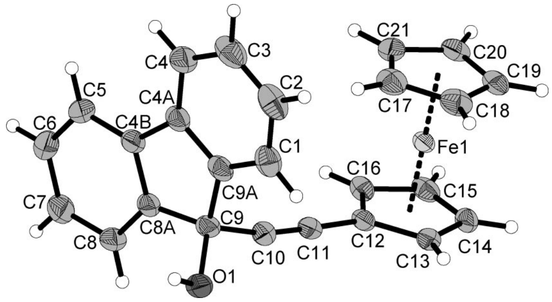

Figure 4. Molecular structure of 9-(ferrocenylethynyl)fluoren-9-ol (**9**). Thermal ellipsoids are drawn at the 70% probability level. Selected bond lengths (Å) and angles (deg): C(9)−C(10) = 1.477(2), C(10)−C(11) = 1.197(2), C(11)−C(12) = 1.425(2); C(9)−C(10)−C(11) = 178.7(2), C(10)−C(11)−C(12) = 178.0(2).

propargyl alcohol systems[13] and also in the hydrogen-bonded dimer of $Fe(C_5H_4C{\equiv}CCMe_2OH)_2$, in which the two O···O distances are 2.801(4) and 2.845(4) Å.[14,15]

The conversion of propargyl alcohols into chloroallenes can be achieved by treatment with thionyl chloride to form a chlorosulfite that subsequently eliminates SO_2 (Scheme 3).[16] To this end, 9-(ferrocenylethynyl)fluoren-9-ol (**9**) was allowed to react with thionyl chloride and the resulting chloroallene **14** was identified from its NMR spectra at −20 °C. One might have predicted that the chloroallene **14**, represented by the canonical form **14a** with an aromatic fluorenyl anion and metal-stabilized cation, would be an ideal candidate to exhibit carbenic character at the central allene carbon. However, the ^{13}C NMR data are more typical of a normal allene, whereby the characteristic resonance for the central sp-hybridized carbon is observed at ~200 ppm. It would be interesting to see what high-level calculations might tell us about this molecule, and we defer to our more theoretical colleagues for further exegesis.

Attempts to crystallize **14** were thwarted because, as the solution was warmed to ambient temperature, a solid residue formed that, eventually, yielded crystals of the head-to-head dimer **15**. The structure of **15** was determined by X-ray crystallography (see Figures 6 and 7) and 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 Cl(Fc)C(5)═C(1)−C(2)═C(16)(Fc)Cl between the two (ferrocenyl)chloromethylidene moieties is 45°; moreover, 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[17] connecting the spiro positions of the fluorenyl groups, which are themselves severely arced away from each other. Nevertheless, the fluorenyl moieties gave rise to only four proton NMR resonances in solution, thus indicating time-averaged C_{2v} symmetry.

A commonly used method for converting propargyl alcohols into their corresponding alkynes involves the use of boron trifluoride and triethylsilane;[18] these alkynes readily undergo isomerization to the corresponding allene, and we have used this approach to generate 3,3-biphenylene-1-phenylallene (and its numerous dimers) from 9-(phenylethynyl)fluoren-9-ol.[19] However, this approach fails with 9-(ferrocenylethynyl)fluoren-9-ol (**9**). As depicted in Scheme 4, an alternative route to such allenes proceeds via treatment of the precursor alcohol with HBr to generate the corresponding bromoallene;[20] subsequent lithiation and quenching with water yields the required allene.[21]

Thus, 9-(ferrocenylethynyl)fluoren-9-ol (**9**) was allowed to react with cold aqueous HBr in the expectation of producing 3,3-biphenylene-1-bromo-1-ferrocenylallene (**16**). However, the major product that was isolated after chromatographic separation and recrystallization was characterized as 3,3-biphenylene-1-ferrocenyl-1-[9-(ferrocenylethynyl)-9*H*-fluorenyl]allene (**17**), whose structure is shown in Figure 8. Several such hexa-1,2-dien-5-ynes have previously been prepared via the reaction of

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(20) Toda, F.; Motomura, H.; Oshima, H. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 467–470.

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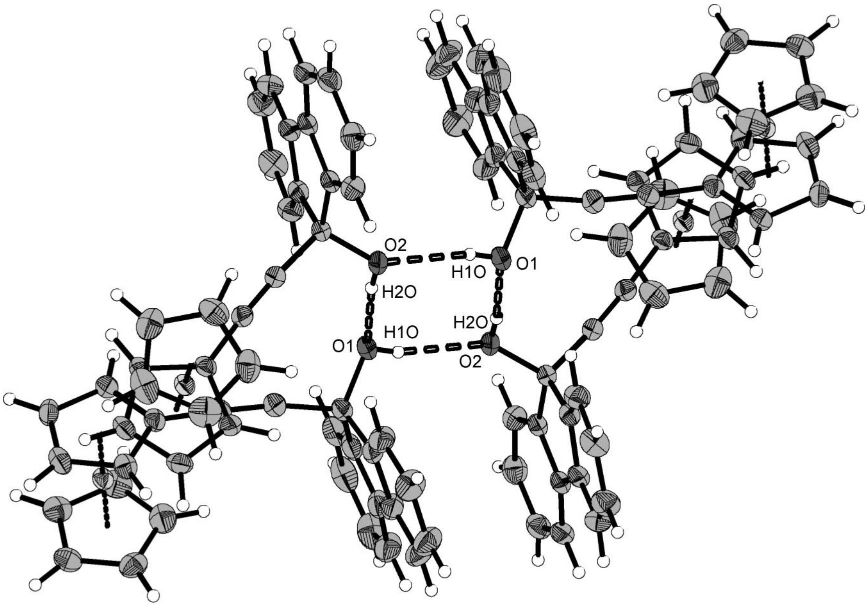
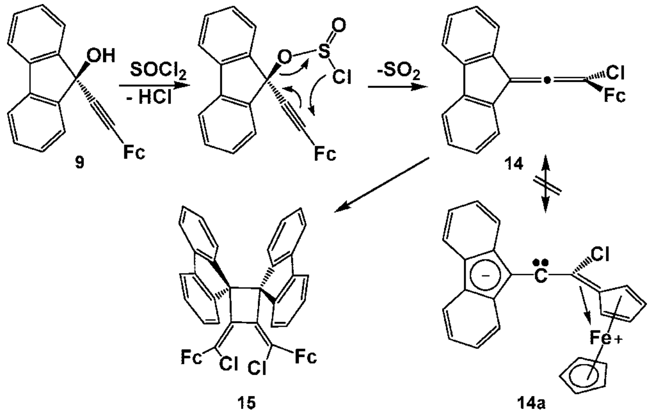


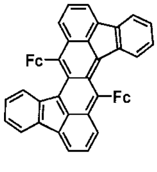
Figure 5. Hydrogen-bonded tetrameric structure of **9**.

Scheme 3. Formation and Dimerization of 3,3-Biphenylene-1-chloro-1-ferrocenylallene (14)



3,3-biphenylene-1-chloro-1-aroylallenes with copper(I) chloride, presumably via the coupling of two canonical forms of the 9-alkynylfluorenyl radical.[22] Interestingly, these head-to-tail allenyl dimers exhibit photochromism in the solid state.[23] Moreover, it has been reported that treatment of 3,3-biphenylene-1-bromo-1-(trimethylsilyl)allene (**18**) with a thiolate anion produced not only the spiro-bonded fluorenylcyclopropene **19** but also 3,3-biphenylene-1-(trimethylsilyl)-1-[9-((trimethylsilyl)ethynyl)-9*H*-fluorenyl]allene (**20**).[24]

Reactivity of Ferroceno[2,3]inden-1-one. In a continuation of our studies on the dimerization of allenes to produce electroluminescent tetracenes,[19] we wished to incorporate ferrocenyl moieties as redox-active substituents. The aforementioned ferrocenylallenes represent one facet of the project, in that they should generate tetracenes in which the organometallic sandwich fragment is a peripheral substituent, as in **21**. Another approach would be to incorporate the ferrocenyl moiety into the fluorenyl framework, thus potentially generating a tetracene **22**, isomeric with **21**.



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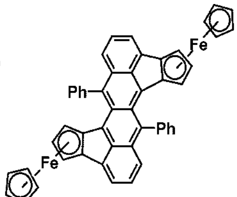

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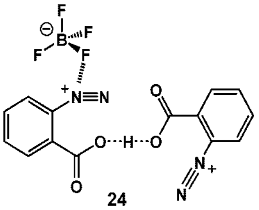

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To this end, ferroceno[2,3]inden-1-one (**23**) was prepared by the reaction of ferrocene with benzenediazonium-2-carboxylic acid. As depicted in Scheme 5, subsequent conversion of 2-ferrocenylbenzoic acid to the corresponding acyl chloride, and Friedel−Crafts ring closure, furnished **23**.[25,26]

Interestingly, the initial step of the synthesis also yielded X-ray-quality crystals of the hydrogen-bridged dimer of 2-carboxylatebenzenediazonium tetrafluoroborate, **24**, and the structure appears as Figure 9. A previous study of the analogous chloride salt revealed a short O···O distance of 2.436 Å,[27] and in the BF_4 salt **24**, the O···O distance is now 2.446(2) Å. In general, unsymmetrical hydrogen bonds between two oxygen atoms lead to O···O distances of 2.6−2.7 Å, while symmetrical hydrogen bonds tend to have shorter O···O distances of ~2.5 Å.[27] Thus, even though in this particular case the data preclude a clear distinction between the possibilities, one might suggest that the bridging hydrogen in **24** is probably symmetrically bonded. As depicted in Figure 10, the shortest N···F distance in **24** (2.752 Å) arises from an interaction of the tetrafluoroborate counterion with the inner nitrogen of the diazonium moiety. Related systems have been analyzed in terms of a Bürgi−Dunitz

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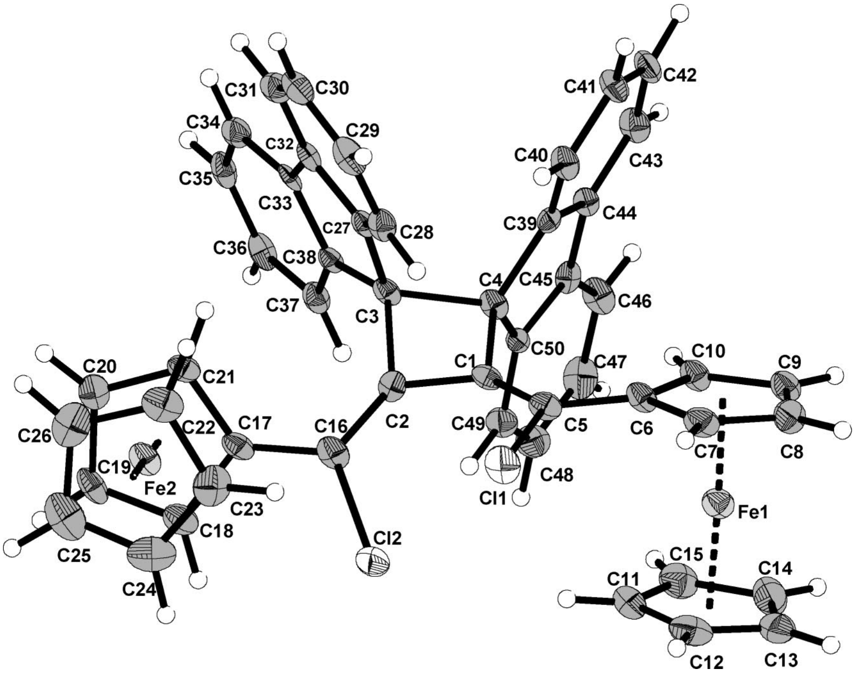

Figure 6. Bird's eye view of the structure of the ferrocenylchloroallene dimer **15**. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): C(1)−C(2) = 1.453(6), C(2)−C(3) = 1.537(5), C(3)−C(4) = 1.647(5), C(1)−C(4) = 1.519(5); C(1)−C(2)−C(16) = 135.9(4), C(2)−C(1)−C(5) = 135.6(4), C(5)−C(1)−C(2)−C(16) = 45.0.

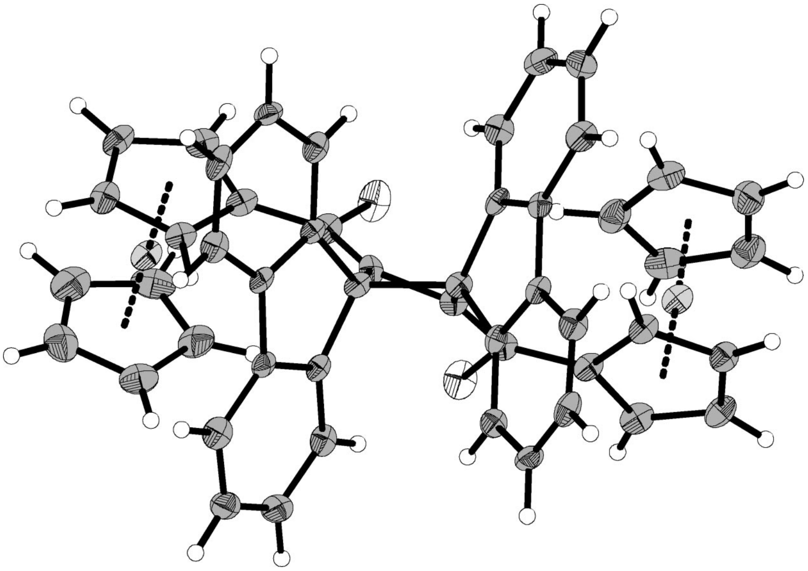

Figure 7. Structure of **15** viewed along the pseudo-C_2 axis.

type trajectory whereby an incipient nucleophile is poised to attack at the formally positive internal nitrogen.[28]

It has previously been reported[25] that ferroceno[2,3]inden-1-one (**23**) can be reduced to the corresponding indenol **25**; the structure is shown in Figure 11 and reveals that the hydroxyl substituent in ferroceno[2,3]inden-1-ol is positioned endo with respect to the metal.

Likewise, reaction of ferroceno[2,3]inden-1-one with (phenylethynyl)lithium yielded the alkynol **26**, in which nucleophilic attack occurred on the exo face of the ligand, as had been the case with the analogous ethynyl complex.[29] The molecular structure and crystal packing of 1-(phenylethynyl)ferroceno-[2,3]inden-1-ol (**26**) are depicted in Figure 12, and one can now directly compare the structurally isomeric alcohols whereby the ferrocenyl moiety is either an alkynyl substituent, as in 9-(ferrocenylethynyl)fluoren-9-ol (**9**), or as a component of the tricyclic ligand, as in **26**. Thus, in **9** each hydroxyl moiety functions both as a hydrogen bond donor and as a hydrogen acceptor. In contrast, in **26** one OH unit acts as only a donor, while the other is only an acceptor. As a result, intermolecular hydrogen bonding leads to dimer formation in **26** rather than the tetrameric rhomboidal pattern observed previously in **9**. We note also that ferroceno[2,3*a*]inden-1-ones are chiral, but the

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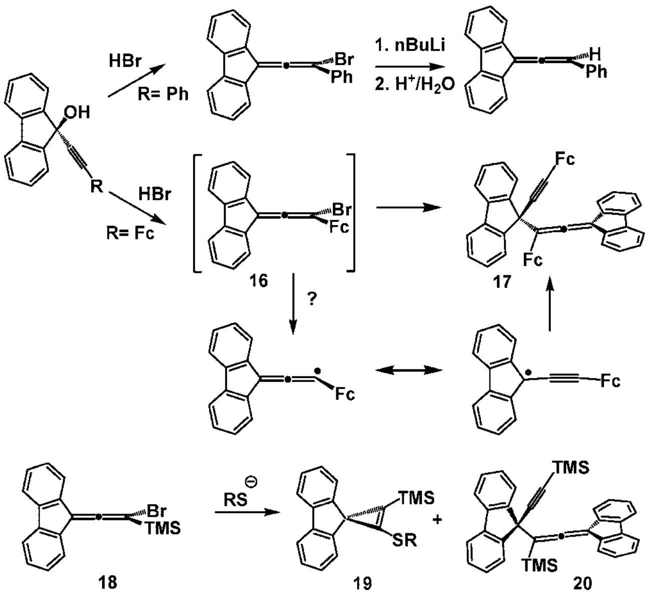
[28] Glaser, R.; Horan, C. J *Can. J. Chem.* **1996**, *74*, 1200–1214.

[29] The structure of the analogous 1-(ethynyl)ferroceno[2,3]inden-1-ol has already been reported by the reaction of **23** with ethynyllithium. Interestingly, the corresponding ethynylmagnesium reagent yields the exo isomer.[14]

Scheme 4. Syntheses and Reactivity of 3,3-Biphenylene-1-bromoallenes



enantiomers have been separated chromatographically on a β-cyclodextrin-based polymer support.[30]

Cations resulting from the protonation of ferroceno[2,3]-inden-1-ol and its derivatives pose an interesting dilemma. It is, of course, well-known that a ferrocenyl moiety can efficiently stabilize a cation in the α-position,[3] however, the ferroceno-[2,3]indenyl system also possesses characteristics of the fluorenyl skeleton whereby a benzo ring has been replaced by a ferroceno fragment. One might thus anticipate that, while the 14-π-electron ferroceno[2,3]indenyl anion **27**(−) should be electronically stable, the corresponding 12-π-electron cation **27**(+) should be disfavored. Indeed, as shown in Scheme 6, **27**(−) has been prepared and shown to react with chlorotrimethylsilane to yield the expected silyl derivative **28**.[31] In contrast, it has been proposed that the cation **27**(+) has radical character and dimerizes.[25] Interestingly, addition of a second ferrocenyl substituent directly bonded to the 1-position of the ferroceno[2,3]-

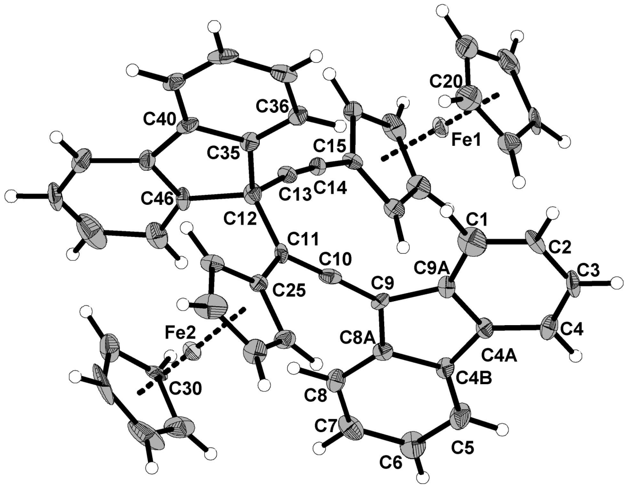
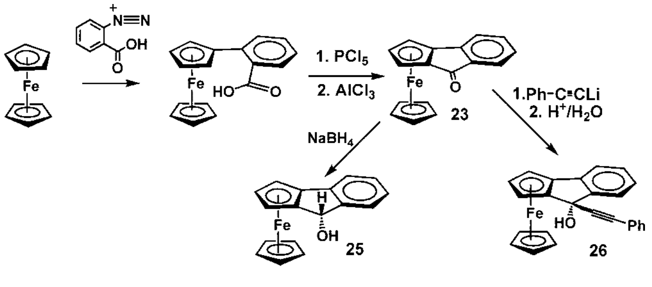


Figure 8. Molecular structure of the ferrocenylallenyl radical dimer **17**. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): C(9)−C(10) = 1.330(7), C(10)−C(11) = 1.304(7), C(11)−C(12) = 1.535(10), C(11)−C(25) = 1.487(7), C(12)−C(13) = 1.469(9), C(13)−C(14) = 1.195(7), C(14)−C(15) = 1.432(8); C(9)−C(10)−C(11) = 177.5(7), C(10)−C(11)−C(12) = 118.2(5), C(10)−C(11)−C(25) = 119.0(5), C(11)−C(12)−C(13) = 109.4(5), C(12)−C(13)−C(14) = 172.2(7), C(13)−C(14)−C(15) = 175.6(6).

Scheme 5. Synthesis and Reactivity of Ferroceno[2,3]-inden-1-one (23)



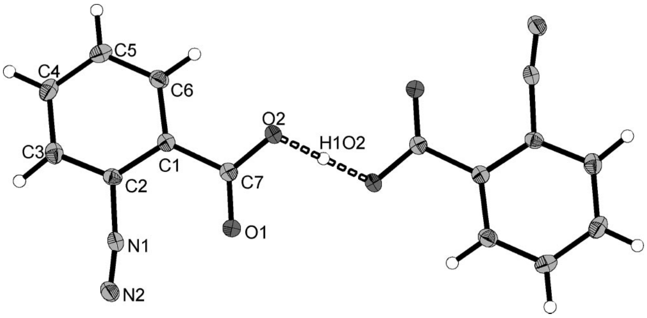


Figure 9. Molecular structure of the hydrogen-bridged dimer **24**. Thermal ellipsoids are drawn at the 50% probability level.

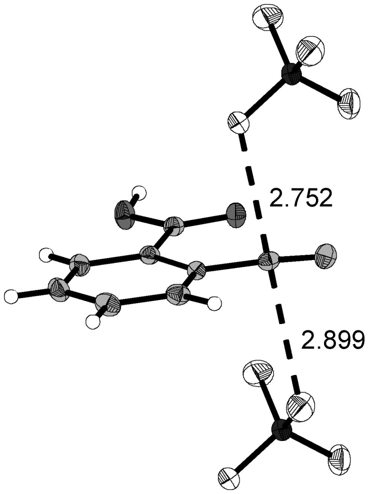


Figure 10. Long-range N···F interactions in 2-carboxylatebenzenediazonium tetrafluoroborate (**24**).

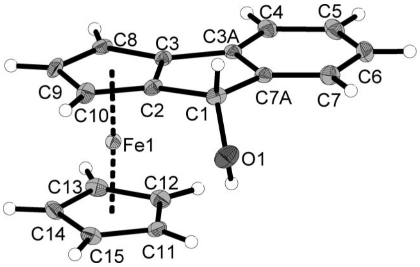


Figure 11. Molecular structure of *endo*-ferroceno[2,3]inden-1-ol (**25**). Thermal ellipsoids are drawn at the 15% probability level.

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(30) Mayr, B.; Schottenberger, H.; Elsner, O.; Buchmeiser, M. R. *J. Chromatogr. A* **2002**, *973*, 115–122.

(31) Kondo, T.; Yamamoto, K.; Kumada, M. *J. Organomet. Chem.* **1973**, *61*, 347–354.

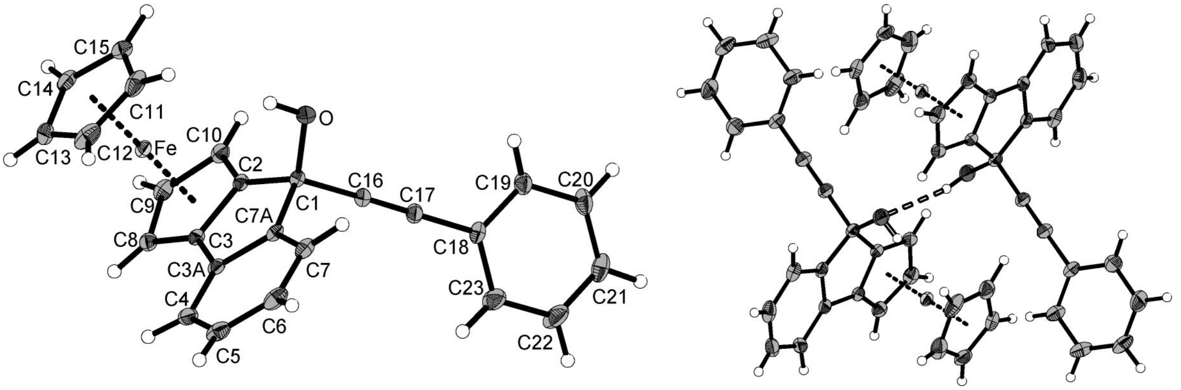
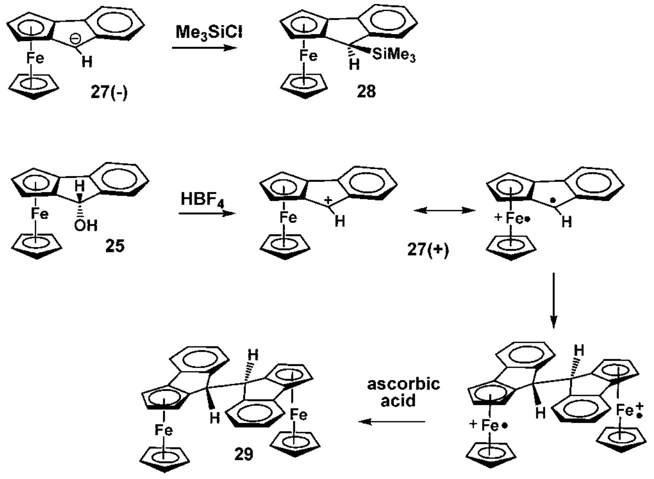


Figure 12. Molecular structure of 1-(phenylethynyl)ferroceno[2,3]inden-1-ol (**26**), showing also its hydrogen-bonded dimer. Thermal ellipsoids are drawn at the 15% probability level. Selected bond lengths (Å) and angles (deg): C(1)−C(16) = 1.485(3), C(16)−C(17) = 1.187(3), C(17)−C(18) = 1.441(3); C(1)−C(16)−C(17) = 178.8(2), C(16)−C(17)−C(18) = 179.2(2).

Scheme 6. Protonation of Ferroceno[2,3]inden-1-ol To Form Dimer 29



indenyl cation apparently suffices to stabilize the system.[32] Presumably, the formal positive charge is alleviated primarily by the second ferrocenyl moiety.

Even at the relatively unsophisticated extended Hückel level of calculation, it is apparent that the HOMO and LUMO of **27**(+) are rather close in energy (approximately 0.9 eV), whereas in the anion **27**(−) the HOMO−LUMO gap is now approximately 3.1 eV, as anticipated for an aromatic system. Figure 13 depicts the EHMO-derived HOMO's and LUMO's for the anion **27**(−) and the cation **27**(+). In the latter, the HOMO is ~79% localized on the iron, having mostly d_{z^2} character, whereas the LUMO is essentially within the π manifold of the tricyclic ligand with a 40% p_z contribution from the formally cationic carbon C(1). However, the relatively small energy difference between these two orbitals suggests that both would be partially occupied and that **27**(+) should have cation diradical character, as represented somewhat simplistically in Scheme 6. Higher level calculations will be the subject of a future report.

To test this hypothesis, the alcohol **25** was protonated and, as previously reported,[25] yielded a green product. Since the initial green product was paramagnetic, presumably because of the presence of two Fe^{3+} centers, it was reduced with ascorbic acid to give a red material that, after chromatographic separation, yielded **29**, which exhibits simple ^{1}H and ^{13}C NMR spectra implying formation of a dimeric product with either C_2 or mirror symmetry (C_s). Such a distinction is difficult to resolve by NMR; however, the X-ray crystal structure of **29**, shown in Figure 14, revealed a dimer of pseudo-C_2 symmetry.

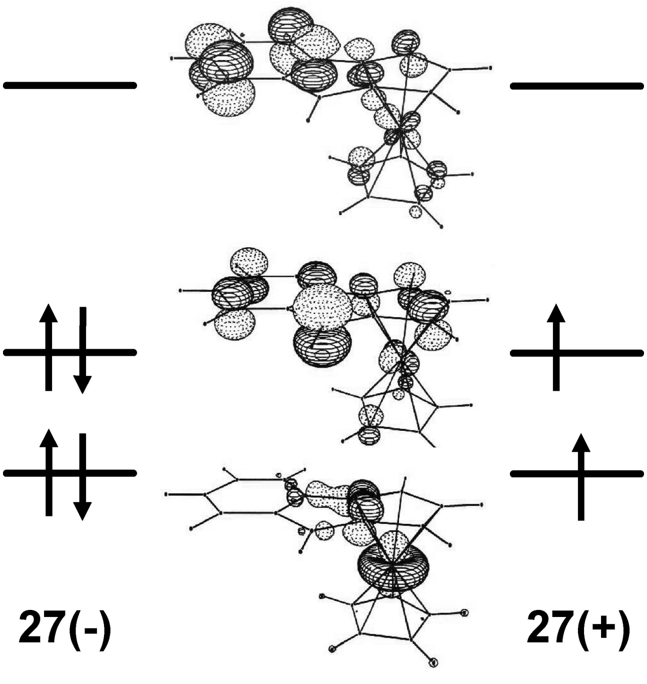


Figure 13. Frontier orbitals of the ferroceno[2,3]indenyl anion **27**(−) and cation **27**(+).

The overall molecular geometry is very reminiscent of bifluorenyl,which adopts a gauche conformation such that the H−C−C−H dihedral angle is 60°.[33] In **29**, the corresponding torsion angle is 61°, and the ferrocenyl substituents are both oriented in an exo fashion so as to minimize steric interactions. As suggested previously,[33] the rationale for the favored gauche conformation in bifluorenyl (and presumably also in the ferrocenoindenyl dimer) is based on the "back-clamping" which disallows aryl ring stacking. In the anti conformation, the hydrogens in the 1,8 (or 7,8)-positions of one fluorenyl (or ferrocenoindenyl) are forced to point directly at their counterparts in the other half of the molecule. These severe H···H nonbonded interactions are greatly relieved in the gauche

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(32) Herber, R. H.; Bildstein, B.; Denifl, P.; Schottenberger, H. *Inorg. Chem.* **1997**, *36*, 3586–3594.

(33) (a) Dougherty, D. A.; Llort, F. M.; Mislow, K.; Blount, J. F. *Tetrahedron* **1978**, *34*, 1285–1300. (b) Harrington, L. E.; Britten, J. F.; McGlinchey, M. J. *Tetrahedron Lett.* **2003**, *44*, 8057–8060.

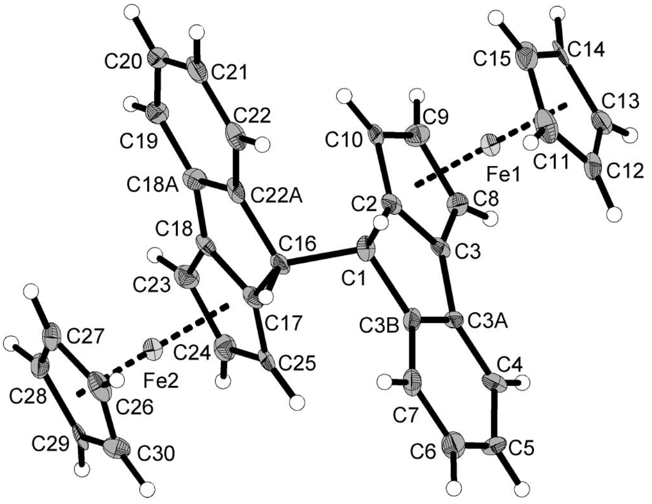

Figure 14. Molecular structure of ferrocenoindenyl gauche dimer **29**. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): C(1)−C(16) = 1.551(8); C(2)−C(1)−C(16)−C(22A) = 61.0, C(3B)−C(1)−C(16)−C(17) = 61.7°, H−C(1)−C(16)−H = 60.6.

conformation and contrast with the situation for unclamped tetraarylethanes, which uniformly favor the anti conformation.[33]

The isolation and unambiguous characterization of the dimer **29** provide convincing support for the diradical character of the precursor cation **27**(+). We acknowledge the prescient report in 1965 by Caïs, who first suggested the possibility of such a radical dimerization of **27** upon treatment with acid;[24,34] however, definitive experimental verification is only now available.

Concluding Remarks. The ^{13}C NMR data on 3,3-biphenylene-1-chloro-1-ferrocenylallene (**14**) do not indicate that the central carbon has markedly carbenic character. Moreover, this allene readily forms the sterically highly encumbered head-to-head dimer **15**, whereby the 1,2-bis(alkylidene)cyclobutane adopts a butterfly conformation with a very long (∼1.65 Å) C(3)−C(4) bond linking the two spiro-bonded fluorenyl moieties. Attempts to generate the analogous ferrocenylbromoallene **16** instead yielded the hexa-1,2-dien-5-yne radical-coupling product **17**. Protonation of ferroceno[2,3]inden-1-ol (**25**) resolved a long-standing question, originally posed by Caïs in 1965, concerning the possible diradical nature of the resulting cation; the X-ray characterization of the ferroceno[2,3]inden-1-yl dimer **29** provides experimental verification of Caïs's hypothesis. The reactivity of 9-(ferrocenylethynyl)fluoren-9-ol (**9**) and of 1-(phenylethynyl)ferroceno[2,3]inden-1-ol (**26**) as potential precursors to allene dimers and, ultimately, the isomeric tetracenes **21** and **22** is an ongoing study in this laboratory.

Experimental Section

^1H and ^{13}C NMR spectra were recorded on Varian 300, 400, or 500 MHz spectrometers. Assignments were based on standard two-dimensional NMR techniques ($^1H-^1H$ COSY, $^1H-^{13}C$ HSQC and HMBC, NOESY). Electrospray mass spectrometry was performed on a Micromass Quattro micro instrument. 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) 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.

9-(Ferrocenylethynyl)fluoren-9-ol (**9**),[9] 9-(ferrocenylmethylideno)fluorene (**3**),[6] 9-(phenylethynyl)fluoren-9-ol (**12a**),[21] 9-(*p*-anisylethynyl)fluoren-9-ol (**12b**),[21] ferroceno[2,3]inden-1-one (**21**),[14,25] and *endo*-ferroceno[2,3]inden-1-ol (**25**)[25] were prepared according to literature procedures.

Meyer−Schuster Rearrangements of 9 and 12a,b. To a solution of 9-(ferrocenylethynyl)fluoren-9-ol (**9**; 0.1 g, 0.25 mmol) in THF (5 mL) was added at 0 °C a solution of concentrated hydrochloric acid (1 drop, 37% in water). After it was stirred for 10 min, the solution was warmed to room temperature, extracted with dichloromethane, and washed with water. The organic layers were combined, dried over $MgSO_4$, filtered, and concentrated. Chromatography of the resulting oil on alumina using pentane/diethyl ether (50:50) as eluent gave 2-(9*H*-fluoren-9-ylidene)-1-ferrocenylethanone (**11**; 0.78 g, 0.20 mmol; 80%) as a violet product. A sample suitable for an X-ray diffraction structural determination was obtained by recrystallization from diethyl ether/pentane. Analogously, the enones **13a**,**b** were prepared from the alkynols **12a**,**b** in yields of 65% and 85%, respectively. Samples suitable for X-ray diffraction structural determinations were obtained by recrystallization from diethyl ether/pentane. **11**: ^1H NMR (300 MHz, $CDCl_3$) δ 8.77 (d, 1H, $J = 8.0$ Hz), 7.79 (d, 2H, $J = 8.0$ Hz), 7.66 (d, 2H, $J = 6.0$ Hz), 7.46−7.23 (m, 4H), 4.98 (m, 2H, Cp H), 4.63 (m, 2H, Cp H), 4.25 (s, 5H, Cp H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.9 (CO), 144.8, 142.3, 141.1, 139.4, 135.7 (ring C's), 130.8, 130.4, 128.6, 128.2, 127.4, 120.9, 120.0, 119.8, 119.8 (CH's), 81.7 (Fc ipso-C), 73.12 (Fc 2CH's), 70.19 (C_5H_5), 70.06 (Fc 2CH's). Anal. Calcd.for $C_{24}H_{18}Fe$: C, 79.56; H, 4.97. Found: C, 79.41: H, 4.83. **13a**: ^1H NMR (300 MHz, $CDCl_3$) δ 8.33 (d, 1H, $J = 7.8$ Hz, fluorenyl H), 8.07 (dd, 2H, $J = 8.1$ Hz, $J = 0.9$ Hz, phenyl *o*-H), 7.77 (d, 1H, $J = 7.5$ Hz, fluorenyl H), 7.68−7.58 (m, 4H, fluorenyl H, phenyl *p*-H, CH), 7.52 (td, 2H, $J = 6.9$ Hz, $J = 1.2$ Hz, phenyl *m*-H), 7.42 (td, 1H, $J = 7.5$ Hz, $J = 0.9$ Hz, fluorenyl H), 7.38 (td, 1H, $J = 7.5$ Hz, fluorenyl H), 7.30 (td, 1H, $J = 7.5$ Hz, $J = 0.9$ Hz, fluorenyl H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.6, 146.1, 142.3, 140.9, 138.8, 138.3, 135.4, 133.5, 130.9, 130.6, 128.9, 128.1, 127.7, 127.6, 121.3, 120.0, 119.8, 119.6.; mp 136−138 °C. Anal. Calcd for $C_{21}H_{14}O$: C, 89.34; H, 5.007. Found: C, 89.26; H, 5.08.

Synthesis of 3,3-(Biphenyl-2,2′-diyl)-1-chloro-1-ferrocenylallene (14) and of the Ferrocenylchloroallene Dimer 15. At 0 °C, a thionyl chloride solution (0.5 M in pentane, 1.0 mL, 0.5 mmol) was added to a solution of 9-(ferrocenylethynyl)fluoren-9-ol (0.2 g, 0.5 mmol) in diethyl ether (9 mL) and pyridine (0.1 mL, 1.2 mmol) in pentane (17 mL). After it was stirred for 1 h at 0 °C, the mixture was warmed to room temperature and stirred overnight. A dark precipitate formed and was filtered off, and the filtrate was concentrated on a rotary evaporator to give a red solid. After trituration of the red solid in pentane, the NMR and IR spectra of the new filtrate revealed the presence of the chloroallene **14**. Numerous attempts to crystallize **14** yielded the head-to-tail dimer **15**, and a sample of **15** suitable for an X-ray diffraction structural determination was eventually obtained after multiple recrystallizations from diethyl ether/pentane. **14**: ^1H NMR (300 MHz, $CDCl_3$) δ 7.66 (d, $J = 7.0$ Hz), 7.53 (d, $J = 7.0$ Hz), 7.35−7.22 (m, 4H) (fluorenylidene CH's), 4.43 (m, 2H, Cp H), 4.23 (s, 5H, C_5H_5), 3.96 (m, 2H, Cp H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.2 (C=*C*=C), 129.2, 127.5, 124.6 (fluorenyl CH's), 71.4, 69.8, 69.1 (Fc CH's); IR (solid, KBr) ν 1940 cm^{-1} (C=C=C). **15**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, 4H, $J = 7.5$ Hz), 7.31 (br, 4H), 7.16 (t, 4H, $J = 7.0$ Hz), 6.99 (br, 4H) (fluorenyl H's), 4.09 (s, 10H, Cp H), 3.87 (br, 8H, Cp H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.4 (C−Cl), 140.5, 133.4 (fluorenyl C's), 127.8, 125.8, 125.3, 119.6 (fluorenyl CH's), 82.2 (Fc ipso-C), 70.2 (C_5H_5), 69.4 (Fc 2CH's), 68.9 (Fc 2CH's); MS (ES+) *m*/*z* calcd for $C_{50}H_{34}Cl_2Fe_2$ 816.0736, found 816.0744.

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(34) Kerber, R. C.; Ehntholt, D. J. *Synthesis* **1970**, *9*, 449–465.

Table 1. Crystallographic Data for 3, 13a,b, 9, and 15

	3	**13a**	**13b**	**9**	**15**
formula	$C_{24}H_{18}Fe$	$C_{21}H_{14}O$	$C_{22}H_{16}O_2$	$C_{25}H_{18}OFe$	$C_{50}H_{34}Cl_2Fe_2$
M_r	362.23	282.32	312.35	390.24	817.37
cryst syst	monoclinic	monoclinic	monoclinic	triclinic	triclinic
space group	$C2/c$ (No. 15)	$P2_1/c$ (No. 14)	$P2/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a (Å)	16.3657(11)	8.8665(8)	22.353(3)	11.1696(7)	8.5552(10)
b (Å)	9.7933(7)	16.4000(14)	4.2632(6)	12.1768(7)	12.9575 (14)
c (Å)	21.6578(15)	10.0460(9)	16.519(2)	14.8291(9)	17.632(2)
α (deg)	90	90	90	70.2570(10)	74.008(2)
β (deg)	99.704(1)	103.9660(1)	94.393(2)	76.1170(10)	80.465(2)
γ (deg)	90	90	90	70.5140(10)	84.882(4)
V (Å^3)	3421.5(4)	1417.6(2)	1569.5(4)	1771.11(19)	1850.1(4)
Z	8	4	4	4	2
ρ_{calcd} (g cm^{-3})	1.406	1.323	1.322	1.464	1.467
T (K)	100(2)	100(2)	293(2)	100(2)	100(2)
μ (mm^{-1})	0.883	0.080	0.084	0.863	0.966
F(000)	1504	592	656	808	840
θ range for data collecn (deg)	1.91−28.57	2.37−28.22	1.83−21.97	2.25−29.48	1.64−21.00
index ranges	$-20 \le h \le 21$	$-11 \le h \le 11$	$-23 \le h \le 23$	$-15 \le h \le 15$	$-8 \le h \le 8$
	$-12 \le k \le 12$	$-21 \le k \le 21$	$-4 \le k \le 4$	$-16 \le k \le 16$	$-13 \le k \le 13$
	$-27 \le l \le 28$	$-13 \le l \le 12$	$-17 \le l \le 17$	$-20 \le l \le 20$	$-17 \le l \le 17$
no. of rflns measd	14 318	11 871	7922	32 458	9815
no. of indep rflns	4048	3325	1928	9113	3959
R_{int}	0.0249	0.0178	0.0207	0.0230	0.0436
no. of data/restraints/params	4048/0/298	3325/0/255	1928/0/218	9113/0/631	3959/300/487[a]
final R values ($I > 2\sigma(I)$)					
R1	0.0369	0.0430	0.0316	0.0360	0.0383
wR2	0.0851	0.1052	0.0800	0.0956	0.0798
R values (all data)					
R1	0.0415	0.0493	0.0395	0.0399	0.0654
wR2	0.0877	0.1098	0.0849	0.0987	0.0878
GOF on F^2	1.093	1.039	1.034	1.060	0.952

[a] DELU restraints were used to fit "rigid bond" thermal displacements.

Table 2. Crystallographic Data for 17, 24−26, and 29

	17	**24**	**25**	**26**	**29**
formula	$C_{50}H_{34}Fe_2$	$C_{14}H_9BN_4O_4F_4$	$C_{17}H_{14}OFe$	$C_{25}H_{18}OFe$	$C_{34}H_{26}Fe_2$
M_r	746.47	384.06	290.13	390.24	546.25
cryst syst	triclinic	monoclinic	monoclinic	triclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
a (Å)	10.7366(13)	16.0959(10)	10.044(8)	9.5739(13)	6.311(7)
b (Å)	11.7389(15)	7.1079(4)	12.341(9)	10.4470(14)	19.272(19)
c (Å)	14.6319(18)	14.3430(9)	20.732(16)	10.6029(14)	20.099(16)
α (deg)	100.457(2)	90	90	102.072(2)	90
β (deg)	95.144(2)	109.097(1)	104.054(11)	115.407(2)	98.35(4)
γ (deg)	105.829(2)	90	90	96.572(2)	90
V (Å^3)	1725.8(4)	1550.65(16)	2493(3)	911.4(2)	2418(4)
Z	2	4	8	2	4
ρ_{calcd} (g cm^{-3})	1.437	1.645	1.546	1.422	1.500
T (K)	100(2)	100(2)	293(2)	293(2)	100(2)
μ (mm^{-1})	0.878	0.152	1.196	0.839	1.222
F(000)	772	776	1200	404	1128
θ range for data collecn (deg)	1.43−24.00	2.68−28.51	1.65−26.0	2.05−28.27	2.05−21.99
index ranges	$-12 \le h \le 12$	$-21 \le h \le 21$	$-12 \le h \le 12$	$-12 \le h \le 12$	$-6 \le h \le 6$
	$-13 \le k \le 13$	$-9 \le k \le 9$	$-15 \le k \le 15$	$-13 \le k \le 13$	$-20 \le k \le 20$
	$-16 \le l \le 16$	$-18 \le l \le 19$	$-25 \le l \le 25$	$-13 \le l \le 14$	$-21 \le l \le 21$
no. of rflns measd	21 252	12 747	33 847	15 645	23 636
no. of indep rflns	5435	3656	5024	4256	2974
R_{int}	0.0444	0.0142	0.0554	0.0255	0.1108
no. of data/restraints/params	5435/208/688[a]	3656/0/284	5024/168/511[a]	4256/0/314	2974/247/325[b]
final R values ($I > 2\sigma(I)$)					
R1	0.0565	0.0359	0.0478	0.0407	0.0665
wR2	0.1259	0.0908	0.1375	0.0996	0.1524
R values (all data)					
R1	0.0700	0.0395	0.0528	0.0462	0.0842
wR2	0.1312	0.0934	0.1423	0.1033	0.1625
GOF on F^2	1.198	1.041	1.078	1.081	1.049

[a] SAME restraints were used to fit the less occupied molecules into the shape of the higher occupied ones. [b] DELU restraints were used to fit "rigid bond" thermal displacements.

Synthesis of 3,3-(Biphenyl-2,2′-diyl)-1-ferrocenyl-1-[9-(ferrocenylethynyl)-9*H*-fluorenyl]allene (17). To a cooled solution of 9-(ferrocenylethynyl)-9*H*-fluoren-9-ol (**9**; 200 mg, 0.51 mmol) in acetic acid (3 mL) was added dropwise a solution of hydrobromic acid (47%, 353 mg, 2.05 mmol) in water (1 mL). After the mixture was stirred for 2 h with cooling, the precipitate was filtered, washed with water, and dried to give an orange solid that was purified by chromatography on silica gel with chloroform/pentane to yield 3,3-(biphenyl-2,2′-diyl)-1-ferrocenyl-1-[9-(ferrocenylethynyl)-9*H*-fluorenyl]allene (**17**) as the major product (53.4 mg, 0.07 mmol; 28%). A sample suitable for an X-ray crystal structure determination was obtained by recrystallization from diethyl ether/pentane/dichloromethane. **17**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98−7.91 (m, 4H), 7.88−7.83 (m, 2H), 7.79−7.74 (m, 2H), 7.51−7.42 (m, 8H), 3.85 (s, 5H), 3.89−3.80 (m, 4H), 3.68 (s, 5H), 3.66−3.61 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.8, 147.6, 140.7, 139.2, 138.3, 128.6, 128.3, 128.2, 127.6, 125.7, 123.0, 120.5, 120.4, 117.0, 109.2, 85.0, 81.0, 71.2, 69.8, 69.7, 69.0, 68.2, 68.2, 67.9, 65.3, 54.7; IR (KBr) 2247 ($C{\equiv}C$), 1934 cm^{-1} ($C{=}C{=}C$). Anal. Calcd for $C_{50}H_{34}Fe_2\cdot 0.5CH_2Cl_2$: C, 77.05; H, 4.45. Found: C, 77.41; H, 4.90.

Synthesis of 1-(Phenylethynyl)ferroceno[2,3]inden-1-ol (26). Analogously to the previously reported preparation of 1-(ethynyl)ferroceno[2,3]inden-1-ol,[14] *n*-BuLi (3.55 mL of a 1.6 M hexane solution, 5.68 mmol) was added dropwise to a solution of phenylacetylene (566 μL, 5.16 mmol) in diethyl ether (40 mL) at 0 °C. After 15 min of stirring at 0 °C, a solution of 2,3-ferrocenoindenone (1.49 g, 5.16 mmol) in diethyl ether (10 mL) was added via cannula. The solution was stirred at room temperature overnight, quenched with water, and extracted with diethyl ether several times. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated to give a brown oil that was purified by chromatography on silica gel using pentane/dichloromethane to yield 1-(phenylethynyl)ferroceno[2,3]inden-1-ol (**26**; 817 mg, 2.09 mmol; 41%), mp 144−147 °C, as a brown solid. A sample suitable for an X-ray crystal structure determination was obtained by recrystallization from diethyl ether/pentane. **26**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61−7.57 (m, 1H, H_7), 7.40−7.36 (m, 2H, phenyl *m*-H), 7.34−7.30 (m, 2H, H_4, phenyl *p*-H), 7.28−7.21 (m, 4H, H_6, H_8, phenyl *o*-H), 4.63 (d, 1H, J = 2.0 Hz, H_{10}), 4.61 (d, 1H, J = 2.5 Hz, H_8), 4.39 (t, 1H, J = 2.0 Hz, H_9), 4.13 (s, 5H, Cp H), 3.06 (s, 1H, H_{OH}); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.3 (C_{7a}), 138.6 (C_{3a}), 132.0 (phenyl *m*-C), 129.1 (C_8), 128.4 (phenyl *p*-C), 128.2 (phenyl *o*-C), 126.6 (C_6), 124.5 (C_7), 122.7 (phenyl *ipso*-C), 120.5 (C_4), 100.9 (C_2), 89.7 (C_3), 89.1 ($C_{2'}$), 83.4 ($C_{3'}$), 71.0 (C_1), 70.6 (C_9), 69.9 (C_{Cp}), 62.4 (C_8), 60.5 (C_{10}). Anal. Calcd for $C_{25}H_{18}FeO\cdot 0.25C_4H_{10}O$: C, 76.39; H, 5.05; Fe, 13.66. Found: C, 76.01; H, 4.75; Fe, 13.63.

Synthesis of the Dimer Bis(ferroceno[2,3]inden-1-yl) (29). To a solution of *endo*-ferroceno[2,3]inden-1-ol (**25**; 638 mg, 2.20 mmol) in diethyl ether (22 mL) was added, at 0 °C, a 1 M solution of HBF_4 in diethyl ether (245 μL, 3.30 mmol). The mixture was stirred for 20 min at 0 °C, and a green precipitate was isolated under nitrogen after filtration via cannula. The fluoroborate salt, dissolved in acetone (7 mL), was mixed with a solution of ascorbic acid (1000 mg) in water (2 mL). The reaction mixture was stirred at room temperature for 30 min and, after dilution with water, was extracted several times with diethyl ether. The organic layers were combined, washed with brine, dried over $MgSO_4$, filtered, and concentrated to give a dark red solid. The crude material was purified by chromatography on alumina gel using pentane/dichloromethane as eluent. The dimer bis(ferroceno[2,3]inden-1-yl) (**29**; 120 mg, 0.22 mmol; 20%), mp >360 °C, was isolated as an orange solid after trituration in diethyl ether. A sample suitable for an X-ray crystal structure determination was obtained by recrystallization from diethyl ether/dichloromethane. **29**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, 4H, J = 8.0 Hz, indenyl H), 7.19 (td, 2H, J = 0.8 Hz, J = 7.6 Hz, indenyl H), 4.58 (s, 2H, CH), 4.26 (d, 2H, J = 2.0 Hz, Cp H), 3.84 (t, 2H, J = 2.0 Hz, Cp H), 3.79 (s, 10H, Cp H), 3.40 (d, 2H, J = 2.0 Hz, Cp H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.2, 142.8, 127.1, 124.6, 124.3, 119.9, 93.9, 91.4, 70.1, 69.5, 63.1, 58.6, 48.9. Anal. Calcd for $C_{34}H_{26}Fe_2\cdot 0.5CH_2Cl_2$: C, 70.38; H, 4.63; Fe, 18.97. Found: C, 70.50; H, 4.70; Fe, 18.67.

X-ray Crystallography. X-ray crystallographic data[35] for **3** (CCDC 656352), **9** (CCDC 656351), **13a** (CCDC 656354), **13b** (CCDC 656355), **15** (CCDC 56360), **17** (CCDC 656358), **24** (CCDC 656353), **25** (CCDC 656357), **26** (CCDC 656356), and **29** (CCDC 656359) were collected using a Bruker SMART APEX CCD area detector diffractometer and are given in Tables 1 and 2. A full sphere of reciprocal space was scanned by $\varphi-\omega$ scans. Pseudoempirical absorption correction based on redundant reflections was performed by the program SADABS.[36] The structures were solved by direct methods using SHELXS-97[37] and refined by full-matrix least squares on F^2 for all data using SHELXL-97.[38] Anisotropic displacement parameters were refined for all non-hydrogen atoms. Hydrogen atom treatment varied from compound to compound, depending on the crystal quality. In **3**, **9**, and **13a**, all hydrogen atoms were located in the difference Fourier map and refined freely with isotropic thermal displacement parameters. The same applies to the hydrogen atoms attached to carbon in **24** and **26**. The bridging hydrogen atom in **24** was defined to occupy the inversion center, its thermal displacement parameter being fixed to 1.5 times that of the oxygen atom bearing it. All other hydrogen atoms were added at calculated positions and refined using a riding model. Their isotropic thermal displacement parameters were fixed to 1.2 times (1.5 times for methyl and OH groups) the equivalent isotropic displacement parameters of the atom to which they are attached.

Acknowledgment. We thank Science Foundation Ireland and University College Dublin for generous financial support. JN thanks the University of Hamburg for an exchange fellowship.

Supporting Information Available: CIF files and tables giving X-ray crystal data for **3**, **9**, **13a**,**b**, **15**, **17**, **24**−**26**, and **29**. This information is available free of charge via the Internet at http://pubs.acs.org.

OM800293M

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[35] CCDC Nos. 656351−656360 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif, by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax: +44−1223−336033).

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