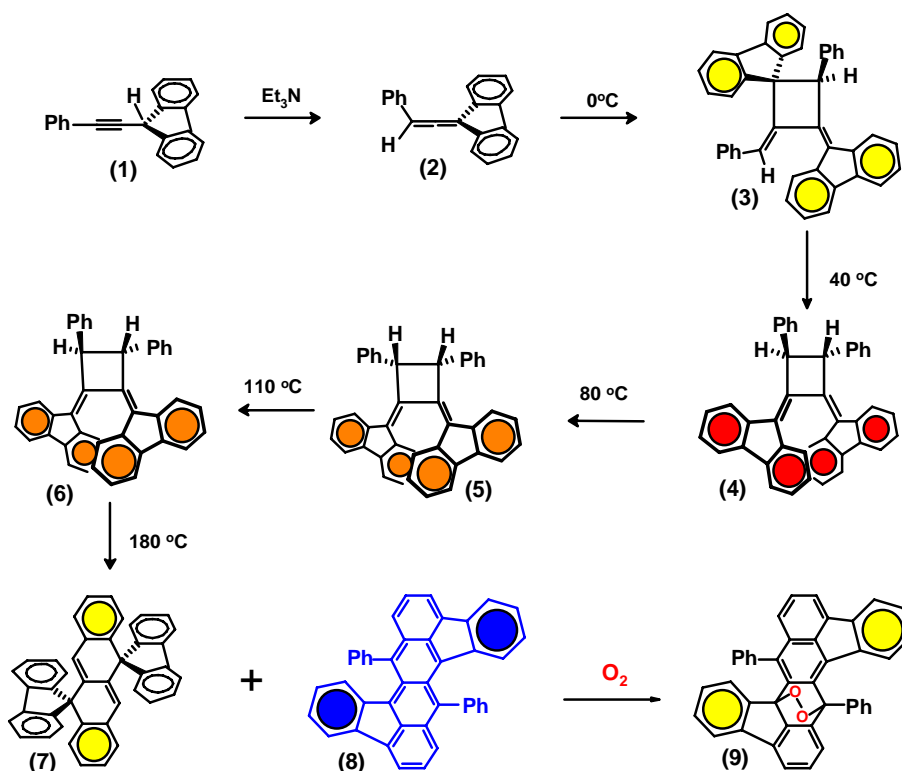


From Allenes to Tetracenes: Syntheses, Structures and Reactivity of the Intermediates

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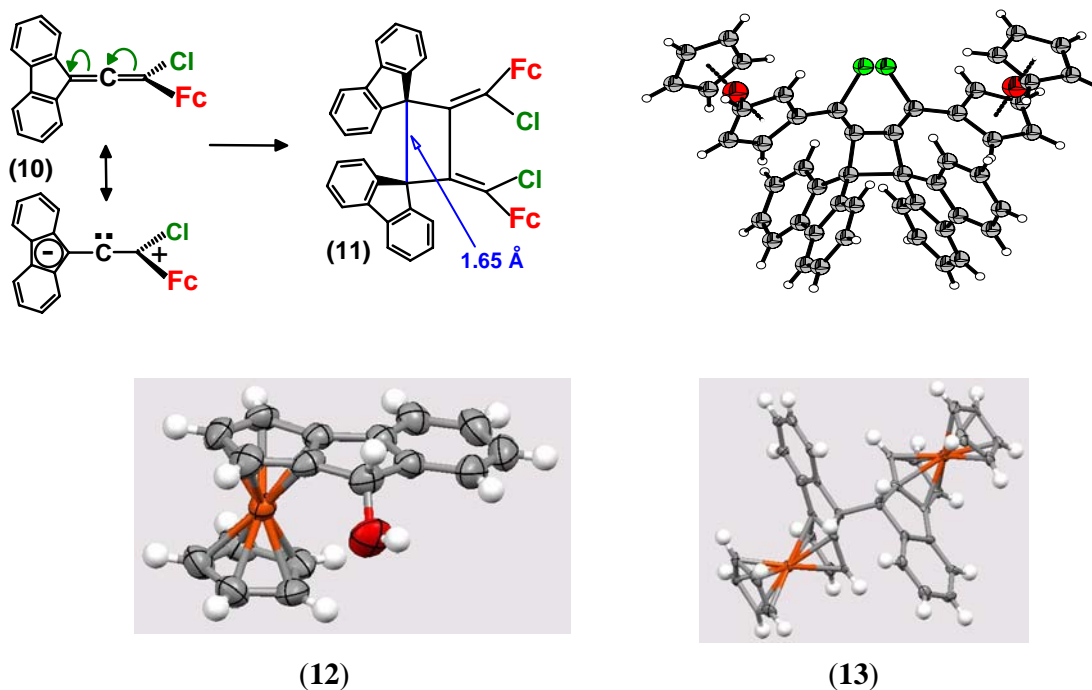
The isolation and characterisation of transient intermediates is the life-blood of mechanistic organic and organometallic chemistry. By such means an entire multi-step pathway can be completely unravelled. Following our serendipitous discovery of a one-pot route from alkynyl-fluorenes to electroluminescent tetracenes (currently the subject of intense commercial interest as organic materials for use in computer display screens), the question arose as to the detailed mechanism of this unexpected process.

The sequence of intermediates depicted in *Scheme 1* was definitively elucidated by NMR spectroscopy and by X-ray crystallography. Thus, the complete three-dimensional structure has been determined for each molecule in the progression: fluorenyl-alkyne (**1**) → fluorenyl-allene (**2**) → yellow head-to-tail dimer (**3**) → red *trans* tail-to-tail dimer (**4**) → orange *cis* tail-to-tail dimer (**5**) → orange *trans* tail-to-tail dimer (**6**) → yellow dispiro-tetracene (**7**) and blue indeno-tetracene (**8**) → peroxide (**9**). The dramatically changing colours of these materials led to picturesque chromatographic separations.



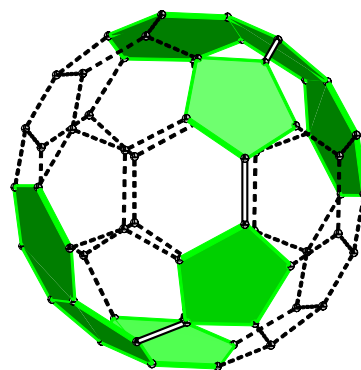
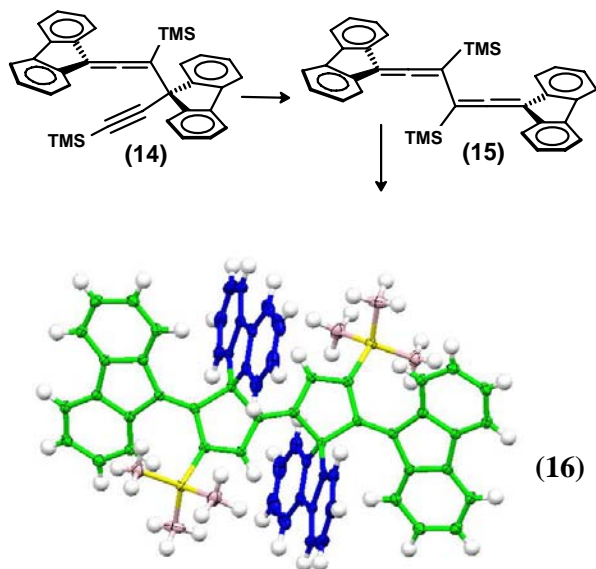
Scheme 1. From alkynyl-fluorenes to tetracenes.

This novel reaction sequence was subsequently generalised to include fluorenyl-allenes containing a wide range of aryl substituents as well as silyl, phosphino (and a related range of metal complexes). Furthermore, the redox-active ferrocenyl moiety was incorporated into allenes both as an alkynyl unit and also as a component of the fluorenyl skeleton; the goal was to prepare tetracenes whose photophysical properties could be modified electrochemically. This aspect of the project led to several novel observations: the push-pull allene (**10**), whereby the stabilisation of the positive and negative charges as a ferrocenyl cation and an aromatic fluorenyl anion, respectively, engendered carbene character at the central carbon, and brought about facile dimerisation to the head-to-head dimer (**11**) which possesses a very long carbon-carbon single bond of 1.65 Å (not quite the world record, but still remarkable). In contrast, the cation derived from the ferrocindenylyl system (**12**) has a small HOMO-LUMO gap and behaves as a diradical, resulting ultimately in formation of the dimer (**13**). Interestingly, such behaviour had been predicted in a prescient report by Cai's in 1965, but only now has it been experimentally verified.



The dimerisation of a silyllallene yielded the anticipated sterically crowded tail-to-tail isomer, as well as the alkynyl-allene (**14**) which underwent thermal rearrangement to a diallene (**15**) and eventually to the tetra-cyclopentadiene (**16**). In this latter molecule, the

C_{36} unit, shown in green, can not only be mapped onto the C_{60} skeleton (depicted in *Figure 1* as folded around the framework) but also, when the two spiro-fluorenyl moieties are included and the silyl groups removed, has the formula $C_{60}H_{36}$. Currently, studies are being undertaken to see whether this system may provide a genuine, designed route to fullerene derivatives.



(16)

Figure 1. The C_{36} portion of (16) mapped onto the C_{60} framework.

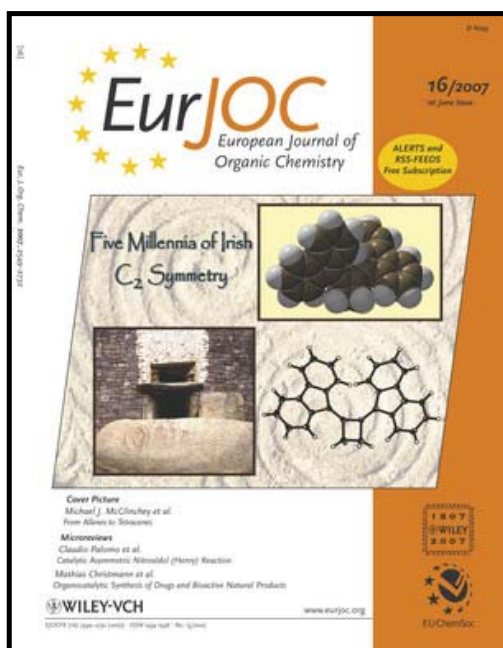
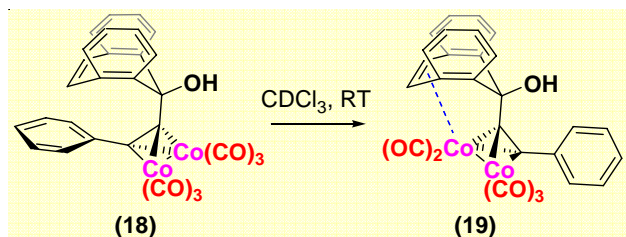


Figure 2. A C_2 -symmetric allene dimer.

Returning to the tail-to-tail silyllallene dimer, removal of the silyl substituents still maintains the intrinsic C_2 symmetry resulting from the overlap of fluorenylidene fragments with their very large wingspans, as in the space-filling model shown in *Figure 2*. This concept is now being extended so as to generate chiral diphosphine ligands, possessing two-fold symmetry, for use in asymmetric catalysis as versatile alternatives to the *binap* systems for which Noyori received his Nobel prize.

Finally, en route to allenes derived from dibenzosuberone, the precursor phenylethynyl-dibenzosuberoneol (**17**) was treated with dicobalt octacarbonyl in the expectation of forming the corresponding hexacarbonyl cluster (**18**); however, it gradually metamorphosed into a second product, the pentacarbonyl-dicobalt complex (**19**), whereby the third ligand site on one of the cobalt centres is now occupied by the C(10)=C(11) double bond of the seven-membered ring. This η^2 -alkene-pentacarbonyldicobalt-alkyne complex is the initial intermediate in Magnus's proposed mechanism for the Pauson-Khand reaction – the most widely-used cyclopentenone synthesis. This result provides the first experimental structural and dynamic data for such a system; gratifyingly, it is in accord with the numerous theoretical predictions of its structure and energetics.



The development of a simple, one-pot synthetic route to allene dimers and tetracenes bearing substituents with commercially desirable electrochemical or photophysical properties, coupled with an enhanced understanding of the mechanism of their formation, opens new vistas in this area. There is a continuing need for novel organic materials for use in the electronics industry, in particular in screen display systems.

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.