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Is ferrocene more aromatic than benzene?†

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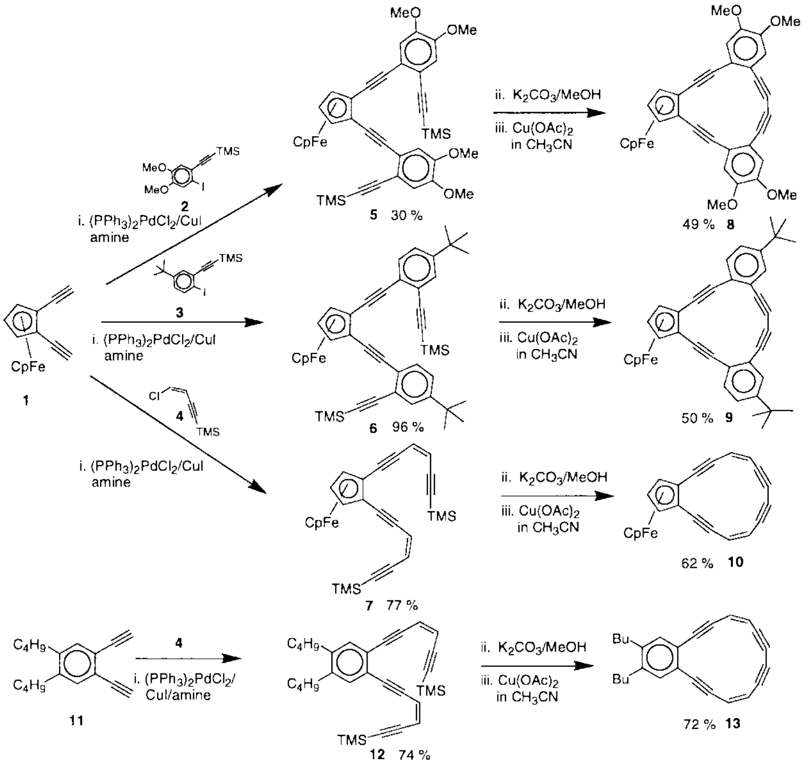
A combination of Pd-catalyzed arene–alkynyl couplings and $Cu(OAc)_2$-promoted internal alkyne dimerization furnishes novel ferrocene-based dehydroannulenes in high yield.

The notion of aromaticity in sandwich and half-sandwich complexes dates back to their observed Friedel–Crafts reactivity and was computationally explored by Bursten and Fenske, leading to the concept of metalloaromaticity,[1] reinforced both by Mitchell's[2] fundamental experiments utilizing chromotrene, cymantrene, and ruthenocene-fused dimethyldihydropyrenes and Schleyer's recent NICS calculations on organometallic π-complexes.[3] While there is little doubt that ferrocene is aromatic, its *degree* of aromaticity is less clear (more or less aromatic than benzene?), and experimental measures are lacking, due to the specific problem of *making* suitable ferroceno-fused dehydroannulenes or dehydrobenzoannulenes.[2] We present herein the synthesis and characterization of ferrocene-based benzodehydro[14]annulenes (**8**,**9**), a ferrocene-based dehydro[14]annulene (**10**), as well as the hitherto unknown 1,2-benzo-3,4,7,8,9,10,13,14-hexadehydro[14]annulene **13**.

The fusion of a [14]dehydroannulene to any π-system offers the unique opportunity to elucidate the (relative) aromaticity of the latter by examining (a) the ^1H NMR chemical shifts and b) the coupling constants of the vinylic H-5,6 protons in the dehydroannulene. According to both Mitchell[2] as well as to Günther and Scott,[4] the disruption of aromaticity under increasing bond fixation can lead to an increase in the observed $^3J_{HH}$ values of the coupling constants[4] and an upfield shift of the vinylic protons.[5] Dehydroannulenes **10** and **13** allow to directly compare the effects of benzo-*vs*. ferroceno-annelation onto an aromatic [14]dehydroannulene, which should be a measure of the relative aromaticity of ferrocene *vs*. that of the epitome of aromaticity, benzene.

Vollhardt and coworkers and others[6,7] developed a powerful route to hexadehydro[14]annulenes. Pd-catalyzed coupling of two C_4-fragments to an unsaturated 2,5-hexadiyne, a C_6-fragement (**1**, **11**) is followed by an internal Glaser[8] type cyclization, which leads to dehydro[14]annulene-derivatives. While originally reported for the synthesis of *benzo*dehydroannulenes we have exploited this concept to make **8**–**10** and **13** (Scheme 1).[9] Starting from 1,2-diethynylferrocene[10] (**1**), Pd/Cu-catalyzed coupling with **2**–**4** furnishes the open tetraynes **5**–**7** in yields of 30–96% (ESI)†. The relatively low yield of **5** is probably due to the electron-donating character of the iodide **2**. The coupling products **5**–**7** are stable oils, which were purified by column chromatography. Removal of the trimethylsilyl groups by potassium carbonate or NBu_4F proceeds smoothly and in high yields. Efficient, copper-catalyzed ring closure by $Cu(OAc)_2$ in acetonitrile[8] furnishes the cycles **8**–**10** in 50–62%



Scheme 1

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† Electronic supplementary information (ESI) available: experimental including details of preparation and spectroscopic characterization of all new compounds. See http://www.rsc.org/suppdata/cc/b0/b009696m/

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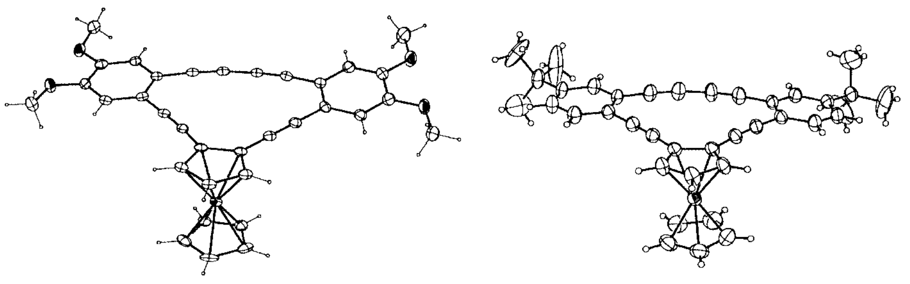
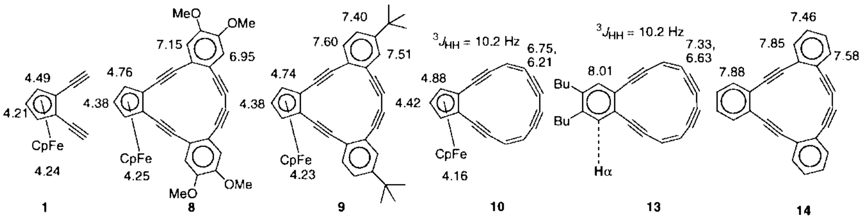


Fig. 1 ORTEP of the organometallic dehydroannulenes **8** and **9**



Scheme 2

yield as sole isolable products. The remainder of these reactions is black, insoluble, and intractable, a consequence of the partial oxidative decomposition of the ferrocene nuclei by the Cu^{II} salts, and low yields in the copper-catalyzed homocoupling reactions of ethynylated ferrocene derivatives have been observed earlier.[10,11] If instead of **1**, 1,2-diethynyl-4,5-dibutylbenzene **11** is coupled to **4**, we obtain the novel hexadehydrobenzo[14]annulene **13** in an overall yield of 53% after Cu-catalyzed coupling.[8] The material is orange–yellow and stable in dilute solution, but unstable as a solid at ambient temperature. Surprisingly, this is the first reported hexadehydrobenzo[14]annulene.

The cycles **8** and **9** are stable in the solid state and crystallize well from hexane–dichloromethane mixtures to give a specimen suited for single-crystal X-ray analysis.‡ Fig. 1 shows the ORTEPs of **8** and **9**. The bond angles and bond lengths are in excellent agreement with the expected values showing distinct bond alternation between triple, double and single bonds. The large hydrocarbon ligand is planar, as expected for a [14]-dehydroannulene. In the solid state, the diyne units of the cycles do not show unusual contacts, and we did not observe solid-state polymerization of these dehydroannulenes.

Most interesting with respect to ferrocene's aromaticity are the ^1H NMR spectra of **8**–**10**. Comparison of the ^1H NMR spectrum of Vollhardt's cyclyne (**14**)[5,6] and that of the benzo–fused dehydro[14]annulene **13** allows extraction of the relative aromaticity of ferrocene with respect to benzene. When the ^1H NMR spectrum of **14** is compared to that of **9**, a small upfield shift is observed for H_α (the protons adjacent to the dehydro[14]annulene), suggesting that, if no other effects are present, ferrocene has a similar, or bigger localizing influence on the dehydroannulenic core than benzene (Scheme 2). This measure is clear but relatively indirect. A proton attached to the reporter annulene would increase the effect, and thus the compounds **10** and **13** offer a much more direct comparison. The ^1H NMR spectrum of the benzo compound **13** shows two doublets at δ 7.33 and 6.63, while in the ^1H NMR spectrum of **10** the *same* vinylic protons appear at δ 6.75 and 6.21, respectively. In the same wake we can compare the ^1H NMR spectrum of **7** (open, non-aromatic) to that of **10** (closed) and the ^1H NMR spectrum of **12** to that of **13**. Upon conversion of **7** $\rightarrow$**10** the annulenic vinyl protons experience a modest downfield shift ($\Delta\delta_{\text{vinyl-H}}$ = 0.40 and 0.77) and the vinylic $^3J_{HH}$ coupling decreases slightly by ΔJ_{HH} = 0.7 Hz, while for the conversion of **12** $\rightarrow$ **13** the shift of the vinyl protons is much bigger ($\Delta\delta_{\text{vinyl-H}}$ = 0.78 and 1.32 respectively). Here the coupling constant decreases by ΔJ_{HH} = 0.8 Hz. These data show that upon ring closure to **10** the downfield shift of the vinyl protons is relatively small, while the downfield shift in the ^1H NMR spectra, when closing the benzo-fused ring (**12** $\rightarrow$ **13**), is almost twice of these values. Consequently a benzene ring disturbs the aromaticity of the fused dehydro[14]annulene *less* than a ferrocene ring. Both sets of data suggest, that in the ferrocene case there is a stronger localization of the dehydro[14]annulene than for benzo-fused **13**, and thus ferrocene is *more* aromatic than benzene by this measure. These arguments are in line with Mitchell's findings.[2] In future we will report the electrochemistry, Bergman rearrangement and the products of the pyrolysis of the ferrocene-fused dehydroannulenes **8**–**10**.

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‡ *Crystal data*: CCDC 157834 and 157835. See http://www.rsc.org/suppdata/cc/b0/b009696m/ for crystallographic data in .cif or other electronic format.

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