Synthesis of Organometallic Dehydroannulenes Containing Ferrocene or (Cyclopentadienylcobalt)cyclobutadiene Moieties

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First synthesized three decades ago, dehydroannulenes[1] continue to stimulate interest in highly ethynylated carbon-rich compounds. Cycles which contain triple bonds and bridging units (such as Scott's pericyclynes,[2] Diederich's dehydroannulenes,[3a,b] and Rubin's diethynylated fullerenes[3c]) have evoked particular interest, because they can serve as precursors for novel carbon allotropes, with applications as materials for the study of electronic interactions, and building blocks for molecular scaffoldings.[4,5]

Arrays of metals held at fixed distances by polypeptide chains[6] carry out vital biological functions such as redox processes and energy transfer; important recent examples include the determination of crystal structures of two different cytochrome *c* oxidases.[7] While biological systems utilize highly sophisticated multimetallic systems, linear and cross-shaped alkyne-bridged organometallics have evolved as functional materials to study energy transfer. Examples are those designed by Lindsey *et al.*,[8] mimicking photosynthetic centers. The incorporation of organometallic or inorganic moieties into *cyclic* structures held together by alkynes[9] may be used to elucidate the spatial dependence of electron or energy transfer between metals, and therefore the development of synthetic routes to such rigid structures is attractive.[10] In this communication we report on the synthesis and preliminary electrochemistry of novel dehydroannulenes containing either ferrocene or (cyclobutadiene)(cyclopentadienyl)cobalt units in the perimeter.

Diyne **1a** (R = SiMe$_3$)[11] was subjected to Hay coupling (122 °C, TMEDA, O$_2$, 4 h)[12,13] and resulted in cyclic oligomers **3−5** according to mass spectroscopic analysis. Repeated chromatography of the crude product led to the isolation of *trans*-**3a** (*n* = 1, 10.1%), *cis*-**3b** (*n* = 1, 4.4%), and a fraction containing **4** and **5**. Both isomers of **3** show distinct sets of signals in their respective ^{13}C NMR spectra that reflect the differences in molecular symmetry. The *trans/cis* isomeric ratio (2.3:1) found in **3** (3:1 ratio expected) suggests a statistical arrangement of the monomers in **3**, and indicates that no steric interactions occur between the subunits during the reaction. This conclusion is reinforced by the X-ray crystal structure of **3a** (Figure 1),[14] which displays no short nonbonded contacts between Cp rings. The butadiyne bridges appear to bend slightly, a phenomenon also observed by Diederich *et al.* in a topologically similar structure.[3a] The hydrocarbon ligand in **3a** is not planar but slightly bent with trimethylsilyl groups directed away from the Cp−Co fragment.[15a] Bond lengths and angles are in agreement with literature values.[15b] Deprotection of **3a** by NMe$_4$$^+F^-$ in DMSO gave **6** (*n* = 1, R = H) in 97% yield; cyclic oligomer **6** was unexpectedly robust as it was found to be thermally stable up to 150 °C in air. Attempts to form **6** and its higher homologs directly by utilizing **1b** (R = H) under identical conditions were (to our surprise) unsuccessful.
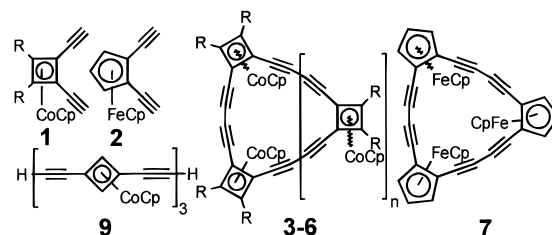

Size exclusion chromatography (SEC) and HPLC were used extensively to isolate products **4a** and **4d**, while **4b,c** sufficiently resolved to obtain their NMR spectra, permitting assignments of the stereoisomers. A statistical distribution of the diastereomeric tetramers 1:4:2:1 for products **4a:4b:4c:4d**[16] was expected, and accordingly 4.0% of **4a**, 17.8% of **4b** + **4c**, and 4.7% of **4d** were actually isolated.

A nearly statistical distribution of products was also observed for the isomers of cyclopentamer **5**, although the low yield (12%) precluded preparative purification. Analytical HPLC shows three pentameric isomers in the ratio 1:1:1. Statistics implies an occurrence of four isomers in the ratio 5:5:5:1. The minor *all-cis* isomer is probably not separable from the directly

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(14) The obtained *R* value (0.086) is higher than expected for high-quality well-ordered crystals. The unit cell of **3a** contains disordered solvent, and the data suffer from the strong X-ray fluorescence of the Co atoms (Mo radiation was not available).
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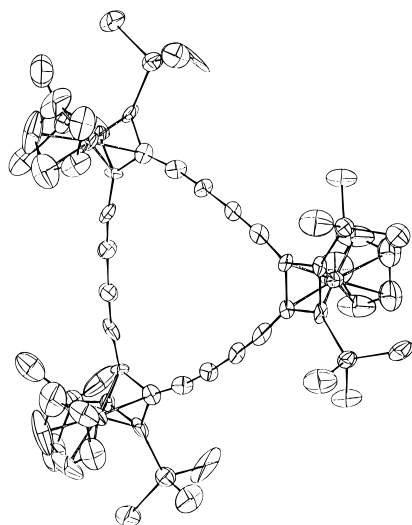(16) The four different stereoisomers of **4** are depicted for clarity:
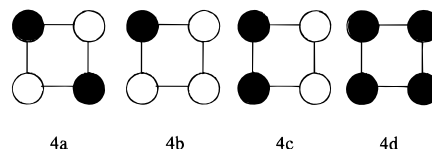
Figure 1. Molecular structure of **3a** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms and solvate moleculesd are omitted for clarity.

preceding one. When the cyclooligomerization of **1a** was conducted using the Vögtle[12d] coupling, the yield of the members was 87% after filtration over aluminum oxide. Yields of the respective cycles (determined by HPLC) were 16.6% (**3a**), 7.9% (**3b**), 6.6% (**4a**), 26.8% (**4b** + **4c**), 7.5% (**4d**), and 13% (**5**), indicating that the Vögtle cyclization is a more efficient method of preparing structures **3**−**5**.

Coupling of **2**[17] under conditions described by Eglinton[12c] yielded 13.1% of *trans*-**7a**, 3.3% of *cis*-**7b**, and 3.6% of higher cycles (unresolved) after separation by column chromatography. In contrast to the oligomerization of tricarbonyl(*o*-diethynylcyclopentadienyl)manganese (**8**),[10c] a linear polymer of **2** was not obtained, resulting only in black infusible material formed by oxidative degradation of the ferrocene nucleus as side product. Nevertheless, trimeric **7** represents the first cyclic and metal ligated segments of fullerenynes which belong to a class of exploded fullerenes.[4c,10c]

The cyclization/polymerization propensities of the monomers **1a,b**, **2**, and **8** lend themselves to some interesting observations: the failure of the Hay coupling of **1a** cannot be attributed to the instability of the product(s) formed (*vide supra*). Differences in the reactivity of monomers **1a,b** as well as in **2** and **8** appears to be a function of steric congestion. In the chemistry of medium-sized hydrocarbon rings it has been previously observed that the introduction of a *gem*-dimethyl group in an open precursor promotes ring closure. Known as the Thorpe−Ingold effect, it has been studied in detail.[18]

The improved propensity of cyclization is caused by the steric rigidity, the exclusion of free volume, and the *gauche* effect of the *gem*-dimethyl group in the open precursor. Monomers **1**, **2**, and **8** are rigid and do not have conformational freedom. Open oligomers, the formation of which must precede the closure to cycles **3**−**7**, *are* conformationally mobile, allowing free rotation around the butadiyne linkages. The function of the bulky TMS groups in **1b** and the CpFe unit in **2**, in comparison to the sterically unhindered Mn(CO)$_3$ ligate, could be similar (despite the absence of *gauche* interactions) to that of the *gem*-dimethyl groups in the cycloalkane case. The restriction of conformational freedom by the bulky substituents

(i.e., an entropic reason) forces cyclization, while the stabilization of the products is not a crucial factor. The failure of the direct cyclization of **1b** (R = H) to **6** is a proof combined with the chemical stability observed for this cycle.

The UV−vis spectrum of **3a** contained a transition at 255−265 nm that was assigned to the butadiyne chromophore. An additional feature at 390 nm shows a shoulder with a weaker ϵ value at 449 nm. For **4** and **5** the electronic spectra display absorptions at λ 266, 361, and 400 nm as well as a shoulder at λ 460 nm. The UV−vis spectrum of **7** shows features at 296, 319, 382, and 465 nm, with the one at 319 nm having the highest ϵ value. The UV−vis spectra of **3a** and **3b** are almost superimposable; the same is true for the electronic spectra of **7a** and **7b**. The spatial position of the organometallic fragment thus does not exert an influence upon the electronic transitions.

The electrochemistry of **6** is complicated, showing irreversible one-electron oxidation[19] at 0.91 V, while **9** displays two oxidations (irreversible) at 1.00 and 1.17 V, indicating an almost independent charging of two rings. The first oxidation potentials of **6** and **9** are similar, suggesting only minor influence of the cyclic arrangement of the CpCo units on the oxidation potential. Reduction of **9**[13b] occurred irreversibly at −2.00 and −2.29 V, while **6** takes up two electrons in a reversible fashion at −1.90 and −2.12 V.

Diastereomer *trans*-**7a** displays three reversible oxidations at 0.61, 0.74, and 0.83 V (one electron each), while in *cis*-**7b** only two reversible steps at 0.61 (one electron) and 0.78 V (two electrons) can be resolved. The first oxidation potentials of cycles **7a** and **7b** are identical to that of **2** (0.62 V) and shifted (0.30 V) relative to that of ferrocene by the electron-accepting nature of the alkyne groups.

The split of 0.17 and 0.22 V, respectively, in **7a,b** leads to the conclusion that these cations belong to type I ferrocene derivatives with weak to moderate interactions between the charged centers as a function of the spatial arrangement of the CpFe units.[20] It is remarkable that despite the relatively large distance between the electrophores, there *is* a difference in the electrochemistry of **7a** and **7b** which differ only in their geometry but not in their overall bonding. Compounds with alkyne bridges will be crucial in the basic analysis of through space and through bond interactions as well as the influence of cyclic conjugation upon the electron transfer in *oligo*ferrocenes.

We have been able to prepare the first organometallic dehydroannulenes, an attractive class of compounds. A future report will focus upon reactivity, demetalation, and materials properties of **3**−**7**. Synthetic efforts to produce larger and more elaborate segments out of organometallic all-carbon nets are underway.

Supporting Information Available: Tables giving crystallographic data, positional parameters, *U* values, bond distances and angles for **3a** and detailed synthetic procedures and complete spectroscopic characterization for all new compounds (16 pages). See any current masthead page for ordering and Internet access instructions.

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