Metallocenes

DOI: 10.1002/anie.200705743

Dibenzo[*c*,*g*]fluorenyliron: An Organometallic Relative of Pentahelicene

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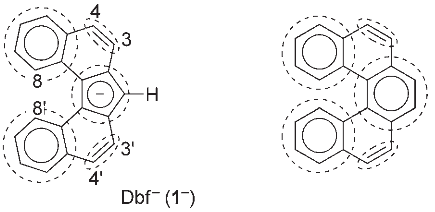
Dedicated to Professor Wolfgang A. Herrmann on the occasion of his 60th birthday

Benzannulated cyclopentadienides such as indenide (Ind^-) and fluorenide (Flu^-) are important ligands in organometallic chemistry. They have found broad application in a series of transition-metal-catalyzed processes mainly in olefin polymerization.[1] However, the ring annulations in the 10 and 14 π-electron systems of Ind^- and Flu^-, respectively, give rise to a less symmetrical charge distribution compared to Cp^-. Thus, the barriers for $\eta^5 \rightarrow \eta^3$ ($\rightarrow \eta^1$) shifts are decreased, making the transition-metal complexes of indenide and fluorenide less stable and more difficult to access than the analogous cyclopentadienide complexes.[2] This may be avoided by extending the π system by a formal further benzannulation of Flu^-.

Recently we published the first organometallic compounds of dibenzo[*c*,*g*]fluorenide (**1**$^-$, Dbf^-).[3] There are only a few reports on the organometallic chemistry of other benzannulated fluorenes in the literature, mostly related to early transition-metal chemistry. Although the aromatic π system of **1**$^-$ is extended to 22 electrons, analogously to pentahelicene, its electronic structure is more related to cyclopentadienide (Cp^-) than to fluorenide (Flu^-), as confirmed by quantum-chemical calculations.[3] In Dbf^-, benzannulation occurs at the fluorenide center in such a way, that the whole π system can be formally divided into three aromatic 6π-electron systems; one five-membered $C_5R_4H^-$ ion and two six membered $C_6H_4R_2$ units, as well as two CH=CH fragments (Scheme 1).

We provided evidence for this hypothesis by synthesizing $[(Dbf)_2Fe]$ (**2**), which, unlike $[(Flu)_2Fe]$,[3] is directly accessible, as well as synthesizing allyl complexes of Group 6 of the type $[(Dbf)M(CO)_2(\eta^3\text{-}C_3H_5)]$ (M = Mo, W), which turned out to be thermally quite stable compounds.[4] Furthermore, **1**$^-$ is an intrinsically chiral molecule that has to adopt a twisted conformation due to the repulsion of the protons in the 8- and 8′-position of the binaphthyl system. Although the barrier for the racemization of **1**$^-$ is low (18.8 kJ mol^{-1} by DFT calculation),[5] its structure represents a novel type of chiral Cp ligand, which should be of potential interest for enantioselective catalysis. Racemization can efficiently be blocked as soon as substitutents are introduced in the 8- and 8′-position. Herein, we report on the selective hydrogenation of the "isolated" C=C bonds of $Dbf{-}Fe^{II}$ complexes, which provides additional support for the special electronic situation in Dbf^-.

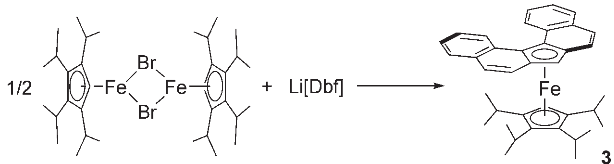


Dbf^- (**1**$^-$)

Scheme 1. Chemical structure of Dbf^- (left) and pentahelicene (right).

Moss green $[(Dbf)_2Fe]$ (**2**) can simply be synthesized by reacting Li(Dbf) with $FeBr_2$. However the compound is almost insoluble in all organic solvents, therefore, all attempts to characterize it by X-ray crystallography up to now were unsuccessful, although we were able to obtain ^{1}H NMR and Mössbauer spectra.[3] Solid-state cyclic voltammetry[6] shows a reversible redox wave at $E_0 = 0.046$ V. Therefore, **2** is more easily oxidized than ferrocene; its redox potential is comparable to that of electron-rich hexaalkyl ferrocenes.[7] This is corroborated by the electrochemical data of deep red $[(Dbf)Fe(^4Cp)]$ (**3**) ($E_0 = 0.040$ V; ^4Cp = 1,2,3,4-tetraisopropylcyclopentadienyl), a well-soluble Dbf–Fe complex that can be obtained in high yields by reaction of Li(Dbf) with the dimeric iron(II) complex $[\{(^4Cp)Fe(\mu^2\text{-}Br)\}_2]$ (Scheme 2).[8]

In the ^{1}H NMR spectrum of **3**, two singlets at $\delta = 3.61$ and 5.02 ppm can be assigned to the CH groups of the five-membered rings of ^{4}Cp and Dbf, respectively. The signal of one aromatic CH unit is shifted significantly to lower field and can therefore be assigned to the protons in the 8- and 8′-position (d, $\delta = 9.27$ ppm), which are affected by the addi-



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Scheme 2. Synthesis of $[(Dbf)Fe(^4Cp)]$ (**3**).

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tional ring current of the neighboring naphthyl wing of the Dbf ligand. Further effects of the Dbf ring currents are observed in the resonances of the CH(*Me*)$_2$ groups ($\delta = 1.36$, 1.28, 0.77, 0.52 ppm), which are shifted to higher field as compared to the -CH(*Me*)$_2$ groups in [(^{4}Cp)$_2$Fe] ($\delta = 1.53$, 1.38, 1.31, 1.05 ppm),[9] as well as for the resonances of the C*H*(Me)$_2$ protons (**3**: $\delta = 2.62$, 2.22 ppm; [(^{4}Cp)$_2$Fe]: $\delta =$ 2.83 ppm, the four protons are superimposed). Recrystallization of **3** from pentane gave crystals suitable for X-ray structure analysis, the results of which are shown in Figure 1.[10]

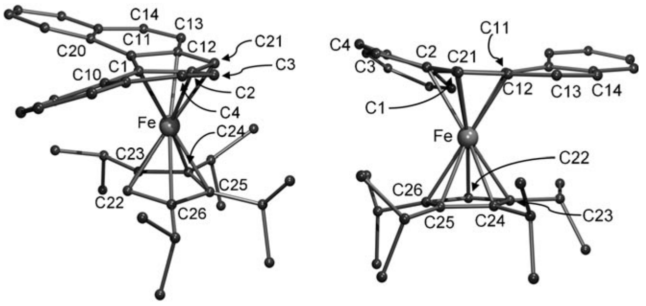
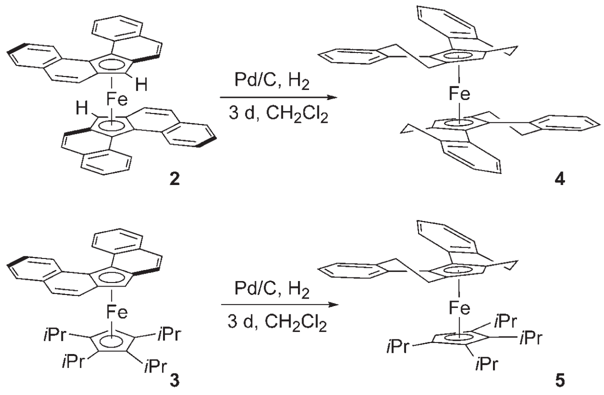


Figure 1. Molecular structure of **3** in the solid state (left: side view; right: front view; hydrogen atoms are omitted for clarity).[11] Characteristic bond lengths [Å] and dihedral angle [°]: Fe–C1 2.0967(14), Fe–C2 2.1334(14), Fe–C11 2.1255(14), Fe–C12 2.0848(15), Fe–C21 2.0641(15), Fe–C22 2.0544(14), Fe–C23 2.0607(13), Fe–C24 2.0707(14), Fe–C25 2.0893(14), Fe–C26 2.0986(14), C3–C4 1.348(2), C13–C14 1.334(2); C10-C1-C11-C20 11.8(3).

The solid-state structure of **3** is determined by the bulkiness of the two η^5-coordinating ligands: to minimize the intramolecular repulsion, the C22–H22 unit of the ^{4}Cp group locates itself below one naphthyl wing of Dbf, which points in the direction of the ^{4}Cp ligand. Nevertheless, one of the isopropyl units still strongly interferes with the binaphthyl system, resulting in a quite small twist of the Dbf ligand (11.8°) although the H8–H8′ distance in **3** (2.034 Å) is comparable to that in other Dbf complexes. This is only possible by a severe distortion of the wing of Dbf pointing towards ^{4}Cp. As shown in Figure 1 (right), the first C$_6$ ring of the left naphthyl unit, which contains the carbon atoms C1–C4, is pushed up, whereas the second ring of the same naphthyl unit is pushed down again. These distortions result in a broad variation of the Fe–C distances for the Dbf ($\Delta d_{\mathrm{FeC}} \approx 7$ pm) as well as for the ^{4}Cp ligand ($\Delta d_{\mathrm{FeC}} \approx 5$ pm). As expected, the distances C3–C4 and C13–C14 are short. Since deprotonation of Dbf–H and coordination to an iron(II) center stabilizes the central aromatic C$_5$R$_4$H$^-$ ring, this leads to a localization of C=C double bonds between the carbon atoms C3/C4 and C3′/C4′ (Scheme 1) and results in a pentahelicene-like structure. Thus, a more-or-less olefin-like reactivity in these positions is expected. We chose to confirm this hypothesis by the selective hydrogenation of these double bonds.

Depending on the catalyst applied, hydrogenation of condensed arenes leads to different products: using Pd on activated charcoal results in the hydrogenation of C=C double bonds of mainly olefinic character, as is the case for the C9–C10 bond in phenanthrene. On the other hand, Pt/C or PtO$_2$ preferentially leads to complete hydrogenation of terminal rings.[12] Such strategies have been used, for example, for the hydrogenation of *ansa*-indenyl and fluorenyl metallocenes of Group 4 by PtO$_2$·H$_2$O to synthesize the corresponding tetrahydroindenyl[13] and octahydrofluorenyl[14] complexes. The reduction of ethylenebis(indenyl)titanium dichloride has likewise been performed with Pd/C, but with a lower yield.[13a] Only one hydrogenation of a benzannulated ferrocene has been described in the literature up to now: Hydrogenation of dinuclear bisbiindenyliron in the presence of Pd/C led to the corresponding tetrahydrobiindenyl derivative.[15]

Reaction of [(Dbf)$_2$Fe] (**2**) and [(^{4}Cp)(Dbf)Fe] (**3**) with dihydrogen at a pressure of 60–65 bar in the presence of 10–15 wt % Pd/C leads to the selective hydrogenation of the C3=C4 and C3′=C4′ double bonds to give the corresponding 3,4,3′,4′-tetrahydrodibenzo[*c*,*g*]fluorenide complexes [(H$_4$-Dbf)$_2$Fe] (**4**) and [(H$_4$-Dbf)Fe(^{4}Cp)] (**5**; Scheme 3). Since the red ferrocene derivative **4** is well soluble in organic solvents, a full spectroscopic and structural characterization of this compound could be carried out.[16] In the ^{1}H NMR spectrum, the resonance of the CH units of the central five-membered rings occurs at $\delta = 3.69$ ppm (in C$_6$D$_6$; $\delta =$ 3.96 ppm in CD$_2$Cl$_2$), a chemical shift typical for highly alkylated electron-rich ferrocenes ([(^{4}Cp)$_2$Fe]: $\delta = 3.84$ ppm in C$_6$D$_6$). In the ^{13}C NMR spectrum, the signals of the quarternary sp^2-hybridized carbon atoms in the Cp ring are observed at $\delta = 87.84$ and 79.12 ppm, and the resonance of the CH unit is detected at $\delta = 70.32$ ppm. Resonances at $\delta = 31.19$ and 22.73 ppm can be assigned to the four methylene groups, which give three centrosymmetric multiplets at $\delta = 2.64$ (8H), 2.29 (4H), and 2.08 ppm (4H) in the ^{1}H NMR spectrum. DFT calculations on H$_4$-Dbf$^-$ showed an increased barrier for the racemization (32.5 kJ mol^{-1}) compared to Dbf$^-$ (18.8 kJ mol^{-1}) due to a decrease of the steric strain. The transformation of two rigid C=C double bonds into more flexible C–C single bonds allows a larger twist of the carbon skeleton. When a solution of **4** in CD$_2$Cl$_2$ is cooled down to about −90 °C, a splitting of the resonances into two sets of



Scheme 3. Synthesis of the hydrogenated compounds **4** and **5**.

signals is observed. We assign this to the presence of the *rac* and the *meso* diastereomer (*MM*/*PP*- and *MP*/*PM*-configurations of the binaphthyl systems). This confirms for the first time, that it is, in principle, possible to resolve spectroscopically the chirality of a (substituted) Dbf complex.

Compound **4** crystallizes from toluene to give crystals suitable for X-ray structure analysis. The unit cell contains two crystallographically independent molecules. Figure 2 presents the molecular structure of one of these units in the solid state.[10] In this molecular structure, the Cp units are arranged in an eclipsed conformation. The two H_4-Dbf ligands are rotated by 72° with respect to each other (dihedral angle H21-C21-C42-H42). The hydrogenation of the four C=C double bonds of **2** generates eight novel sp^3-hybridized carbon atoms (C3–C4, C13–C14, C24–C25, C34–C35), resulting in a more flexible ligand backbone allowing rotation around the bonds C1–C10, C11–C20, C22–C31, and C32–C41. Therefore, the dihedral angles describing the twist of the naphthyl units with respect to each other can now be reduced to about 6°, and the variation of the Fe–C bond lengths is less pronounced than for **2**. The two H_4-Dbf ligands in the structure shown in Figure 2 are homochiral, resulting in the *rac* diastereomer with π-stacking of two terminal *ortho*-phenylene rings. Interestingly, the second asymmetric unit found in the solid-state structure (see the Supporting Information) is the *meso* isomer, in which π-stacking is not possible.

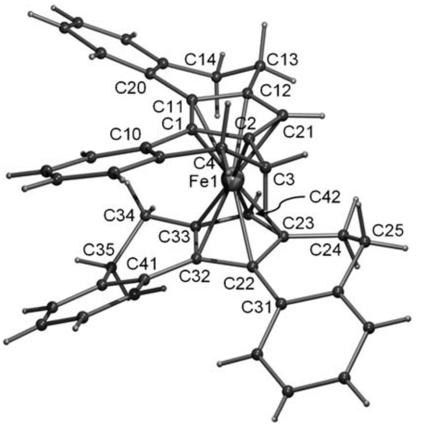


Figure 2. Molecular structure of **4** in the solid state.[11] Characteristic bond lengths [Å] and dihedral angles [°]: Fe1–C1 2.087(2), Fe1–C2 2.052(2), Fe1–C11 2.100(2), Fe1–C12 2.048(2), Fe1–C21 2.056(2), Fe1–C22 2.098(2), Fe1–C23 2.041(2), Fe1–C32 2.074(2), Fe1–C33 2.062(2), Fe1–C42 2.057(2); C10-C1-C11-C20 6.6(4), C31 C22-C32-C41 6.2(4).

H_4-Dbf^- represents another novel and intrinsically chiral Cp ligand, which because of its electron-rich nature is related to cyclopentadienides such as $C_5HMe_4^-$ or $^4Cp^-$. We are presently working on an alternative direct access to this ligand, to obtain it in larger amounts, and thereby to facilitate the investigation of its coordination chemistry. This route should allow the introduction of substituents in the 8- and 8′-position more simply than in the case of Dbf^-. These ligands should be stable against racemization, and thus the derived metal complexes should be promising candidates for the application of Dbf-type systems in enantioselective catalysis.

Experimental Section

[(Dbf)Fe(^{4}Cp)] (**3**): Dbf-H (266 mg, 1 mmol) was dissolved in dry toluene (10 mL) in a Schlenk tube under an atmosphere of nitrogen. The solution was cooled to −15 °C, and *n*-butyllithium (690 μL, 1.1 mmol, $c = 1.6\,\mathrm{mol\,L^{-1}}$ in hexane) was added dropwise. While slowly warming to 25 °C, the solution was stirred for a further two hours. A colorless precipitate of Li(Dbf) appeared, which was dissolved by addition of dry THF (5 mL). The Li(Dbf) solution was cooled to −15 °C and a solution of [{(^{4}Cp)Fe(μ^2-Br)}$_2$] (369 mg, 0.5 mmol), dissolved in dry toluene (10 mL) and dry THF (5 mL) was added through a dropping funnel over a period of 20 min. A black solution was obtained, which was stirred for 7 h at 0 °C and for a further 16 h at 25 °C. Subsequently the solvents were removed in vacuum, the brownish residue was washed with dry pentane (5 mL) and extracted with dry toluene (2 × 10 mL). The combined dark red extracts were concentrated to a volume of about 2 mL and kept at −40 °C overnight. Compound **3** was obtained as dark red microcrystals. After removal of the mother liquor, the crystals were washed with a small quantity of dry toluene. Repetition of the procedure described above allowed further microcrystals to be isolated from the combined mother liquor and the washing solution to give an overall yield of **3** of 464 mg (0.84 mmol, 84 %). The pentane fraction contained [(^{4}Cp)$_2$Fe] as a side product. Single crystals suitable for analysis by X-ray diffraction were obtained from a solution of **3** in pentane at −40 °C.

[(H_4-Dbf)$_2$Fe] (**4**): Green, finely powdered [(Dbf)$_2$Fe] (**2**; 25 mg, 43 μmol) was dissolved in dry CH_2Cl_2 (10 mL) in an autoclave equipped with a magnetic stirrer. Owing to the poor solubility of **2** in CH_2Cl_2, it initially formed a pale green suspension, to which Pd/C (3.2 mg) was added. The autoclave was flushed twice with dihydrogen, and the dihydrogen pressure was adjusted to 60–65 bar. The solution was stirred for 70 h at this pressure. After the hydrogenation, the resulting red solution was transferred into a Schlenk tube, the solvent was removed in vacuum, and the residue was extracted with dry pentane (2 × 10 mL). The combined extracts were evaporated to dryness to yield pure **4** (12 mg, 20 μmol; 47 %)) as a red solid. Complex **4** is well soluble in pentane, toluene, and dichloromethane, and relatively air-stable as a solid. Single crystals suitable for analysis by X-ray diffraction were obtained by dissolving the compound in toluene and slow absorption of the solvent in dry paraffin oil.

[(H_4-Dbf)Fe(^{4}Cp)] (**5**): The same procedure as for **4** was applied; **3** (98 mg, 177 μmol) was dissolved in dry CH_2Cl_2 (20 mL) and Pd/C (38 mg) was added. The reaction mixture was worked-up as described for **4** to yield **5** as a red solid (42 mg, 75 μmol; 42 %).

Received: December 14, 2007

Keywords: chiral ligands · iron · metallocenes · polycycles · structure elucidation

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