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Exploring the Concept of Aromaticity on Complexes of a Fourfold Benzannulated Cyclopentadienyl Ligand

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Abstract: The ligand dibenzo[*c*,*g*]fluorenide (Dbf^-), combines a cyclopentadienide ligand and 1,1′-binaphthyl fragment in one molecule. Preliminary investigations confirmed the special electronic situation in this 6π-electron donor by way of a series of novel transition-metal complexes. Herein, the electron delocalization was investigated in detail by means of DFT calculations in combination with calculations on the nucleus-independent chemical shifts (NICS). These results clearly prove that the Dbf^- ion gains the largest aromatic stabilization among all benzannulated fluorenides, and there are two almost olefinic C=C bonds in this structure. These bonds undergo cyclopropanation when treated with $ZnEt_2$ and $ClCH_2I$ in a modified Simmons–Smith reaction.

Keywords: aromaticity · binaphthalene · cyclopropanation · ferrocene · helicenes · NICS

Introduction

Since the discovery of ferrocene in 1951,[1] cyclopentadienide (Cp^-) is the paradigm for a 6π-electron donor ligand giving stable transition-metal complexes. Annulated Cp derivatives have also been extensively investigated, although the stability of the corresponding transition-metal complexes usually drops due to an unbalanced charge distribution that facilitates a haptotropic $\eta^5 \rightarrow \eta^3 \rightarrow \eta^1$ shift of the metal center. Recently, we reported the synthesis of complexes containing the chiral, binaphthalene-derived dibenzo[*c*,*g*]fluorenide (Dbf^-) as a metallocene ligand.[2] Therein we pointed out that, due to its special annulation pattern, the Dbf anion might, in terms of its electronic properties, be considered as an intermediate between the Cp^- and the fluorenide ligand (Flu^-).[2c] In fact it seems that in Dbf^- a certain localization of the aromatic system occurs in the Cp ring and the terminal *o*-phenylene rings, while electron delocalization in the internal six-membered rings decreases, leading to a loss of aromaticity and partial olefinic character of the double bonds in the positions 3,4 and 3′,4′. This hypothesis was supported by the fact that the Dbf ferrocenes $[(Dbf)_2Fe]$ and $[(Dbf)Fe(^4Cp)]$ (^4Cp = 1,2,3,4-tetraisopropylcyclopentadienyl) undergo selective hydrogenation in these positions.[2a] Herein, we report further theoretical and experimental evidence for this statement, which has been obtained by quantum-chemical analysis of Dbf^- and related Cp anions and by the selective cyclopropanation of a Dbf ferrocene.

Results and Discussion

The calculation of nucleus-independent chemical shifts (NICS) has become a widely used tool to assess the aromaticity of conjugated π systems.[3] We have employed this method to compare the aromaticity in the rings of the η^5-lithium complexes depicted in Scheme 1 and the corresponding carbanions. We decided to calculate $NICS(0)_{iso}$[4] and $NICS(0)_{zz}$ values.[3b] Since nonplanar systems were examined, the calculation of out-of-plane NICS values, such as $NICS(1)_{iso}$[5] and $NICS(1)_{zz}$[6] seemed inadequate, while the application of $NICS_\pi$ methods[7] on such molecules is nontrivial. Structural optimizations were carried out without symmetry restrictions by using B3LYP/6-31+G*, followed by GIAO-NMR calculations at the same level of theory. Insertion of the Bq-dummy atoms at the ring centroids and calculation of the ring-plane equations and thus the corresponding norm vectors were performed on the refined geometry by using a commercially available X-ray structure analysis program.[8] The examined Cp anions are depicted in Scheme 1, and Table 1 presents the calculated $NICS(0)_{zz}$

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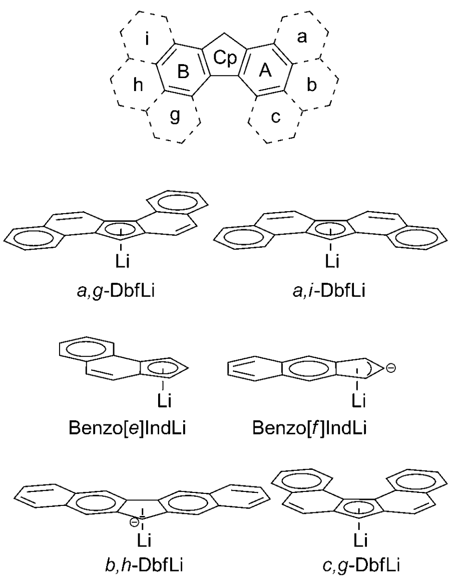


Scheme 1. Predominant aromatic resonance structures of the benzannulated Cp derivatives examined by NICS calculations. The sketch at the top shows the nomenclature for the annulation pattern, which is also used to indicate the corresponding columns in Table 1.

Table 1. $NICS(0)_{zz}$[a] values for the compounds depicted in Scheme 1 and the benzoid parent compounds benzene, anthracene[b] and phenanthrene,[b] values given in ppm.[c]

$NICS(0)_{zz}$	Cp	A	B	a	b	c	g	h	i
benzo[*e*]ind⁻	−18.0	−2.7		−7.7					
benzo[*e*]indLi	−14.1	−0.7		−10.6					
benzo[*f*]ind⁻	−21.9	−17.6			−4.2				
benzo[*f*]indLi	−17.3	−16.2			−4.7				
a,g-Dbf⁻	−14.8	−3.9	−2.6	−9.6			−8.7		
a,g-DbfLi	−12.8	−0.3	1.2	−10.7			−10.9		
a,i-Dbf⁻	−13.2	−2.6	−2.9	−9.6					−9.2
a,i-DbfLi	−11.2	−0.9	−1.2	−10.7					−10.2
b,h-Dbf⁻	3.2	−11.8	−11.6		−5.3			−6.2	
b,h-DbfLi	−3.5	−13.6	−13.9		−8.0			−7.6	
c,g-Dbf⁻	−16.3	−3.4	−2.8			−8.1	−8.5		
c,g-DbfLi	−13.3	−0.8	−1.2			−10.5	−10.3		
benzene		−13.2							
anthracene		−8.7	−18.1						
phenanthrene		−11.7	−1.4						

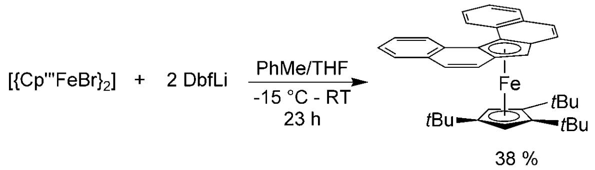
[a] Structure: B3LYP/6-31+G*, NMR: GIAO, B3LYP/6-31+G*. [b] For anthracene and phenanthrene 'A' indicates terminal, 'B' internal rings. [c] Small deviations of the $NICS(0)_{zz}$ values of symmetry equivalent rings in *a,i*-Dbf⁻, *a,i*-DbfLi, *b,h*-Dbf⁻, *b,h*-DbfLi, and *c,g*-Dbf⁻ are attributed to calculations without any symmetry restrictions; the values for equivalent rings in anthracene and phenanthrene were averaged.

values for the carbanions and the corresponding lithium complexes.

Benzo[*e*]indenide and the isomers *a,g*-, *a,i*-, and *c,g*-Dbf⁻, allow the formulation of aromatic resonance structures with electron delocalization in the Cp ring and the terminal six-membered rings. With the exception of *b,h*-Dbf, all Cp anions investigated here show large negative $NICS(0)_{zz}$ values in the five-membered rings, which diminish slightly upon Li^+ coordination. This effect has already been observed for a series of other polyaromatics.[9] Due to the size dependency of the NICS method, the aromaticity of smaller rings is overestimated.[10] It turns out that in the carbanions investigated here, the internal six-membered rings—designated A and B (see Scheme 1)—yield $NICS(0)_{zz}$ values ranging from −3.9 to −2.6 ppm, while the terminal benzoid rings reach values between −7.7 and −9.6 ppm. When the lithium complexes are formed, the ring currents in the internal six-membered rings effectively collapse (−1.2 to −0.3 ppm and 1.2 ppm in case of the B ring in *a,g*-DbfLi), whereas the terminal rings further gain aromaticity (−10.3 to −10.9 ppm). For benzo[*f*]indenide and the *b,h*-Dbf⁻ isomer, delocalization of the negative charge would be possible only at the expense of losing aromaticity in the benzoid ring system. Instead anthracene-like systems are formed, which exhibit maximum aromaticity in the internal A and B rings.[11] As a consequence, the negative charge is less effectively delocalized. This leads in case of *b,h*-Dbf⁻ to a weak ring current in the Cp ring. The $NICS(0)_{iso}$ values show a similar correlation, although less pronounced, due to the smaller absolute range of the obtained chemical shifts (see Supporting Information for details). These findings correspond to experimental results reported by Kuhn et al. some 40 years ago: *b,h*-DbfH ($pK_a \approx 21.4$) was found to be about four orders of magnitude less acidic than *c,g*-DbfH ($pK_a \approx 16.8$) and *a,i*-DbfH ($pK_a \approx 17.4$).[12]

It can thus be concluded that the ability or inability to form a maximum number of local benzoid systems, strongly affects the capability of the corresponding Cp anion to stabilize a negative charge. These findings furthermore corroborate our hypothesis that in complexes of Cp derivatives such as *c,g*-Dbf the loss of aromaticity in the internal six-membered rings should consequently lead to partial olefinic reactivity of the associated double bonds.

To obtain additional experimental verification of this proposition, the application of further olefin-typical reactions to Dbf ferrocenes was investigated. For this the highly soluble unsymmetrical derivative [(Dbf)Fe(Cp‴)] (**1**, Cp‴ = 1,2,4-tri-*tert*-butylcyclopentadienyl) was synthesized according to a published procedure.[2a] Compound **1** can be obtained by reaction of DbfLi with the dimeric iron half-sandwich complex [{Cp‴FeBr}$_2$] (Scheme 2).[13]



Scheme 2. Synthesis of [(Dbf)Fe(Cp‴)] (**1**).

As expected, the dark red compound **1** is well soluble in organic solvents and could be fully characterized. The five-membered rings give singlets in the ^1H NMR spectrum at $\delta = 5.29$ ppm (in C_6D_6) for the Dbf-9-H and at $\delta = 3.31$ ppm for the b,b′-H of the Cp‴ ligand, which can be easily assigned by their signal intensities. HMQC NMR spectroscopy allows the assignment of the ^{13}C resonances at $\delta = 61.14$ and 65.90 ppm to the 9-CH and to the b,b′-CH groups, respectively. By HMBC NMR spectroscopy, the corresponding signals of the quaternary η^5-C_5 carbon nuclei can be identified at $\delta = 87.11$ and 80.29 ppm for the Dbf ligand and at $\delta = 98.83$ and 94.21 ppm for Cp‴. For the 8,8′-protons of the Dbf a doublet is observed at $\delta = 9.37$ ppm, which is the highest chemical shift yet measured for this group. The presence of one set of signals for the two naphthyl fragments indicates rapid racemization at room temperature. The ^1H resonances of the a,a′- and c-*tert*-butyl groups of the Cp‴ ligand are detected at $\delta = 1.10$ and 1.03 ppm, respectively, and correspond to ^{13}C resonances at $\delta = 33.74$ (a,a′-Me), 32.36 (a,a′-C), 31.33 (c-C), and 31.15 ppm (c-Me).

[(Dbf)Fe(Cp‴)] (**1**) crystallized from an oversaturated solution in toluene as dark red prisms in the space group $P2_1/c$. In the solid state, the two Cp ligands assume an almost eclipsed conformation with the c-*tert*-butyl group being co-aligned to the 9-CH bond (H21-C21-C25-C35 4.464(2)°, Figure 1). Consequently, the remaining a- and a′-*tert*-butyl groups are located beneath the naphthyl arms and exert considerable steric pressure on the Dbf ligand. This leads to a bent coordination to the metal site with angles of 8.942° between the two η^5-C_5 ring planes and 174.168(1)° between the ring centers and the iron center. Furthermore, the *tert*-butyl groups are bent away from the iron center, which is also the case for the A and B rings of the Dbf ligand. The C10-C1-C11-C20 dihedral angle that describes the twist of the binaphthyl system is reduced to 10.958(4)° by steric repulsion, which is less than half the value observed in the free ligand DbfH (−23.9657(2)°),[14] while the 8,8′-protons approach each other to 1.949 Å. The 3,4- and 3′,4′-double bonds are shortened to 1.344(3) Å and 1.340(3) Å, values in the same range as those measured for [(Dbf)Fe(^{4}Cp)] (1.348(2) Å, 1.334(2) Å).[2a]

Cyclopropanation of Dbf ferrocenes can be carried out by a modified Simmons–Smith reaction.[15] Although this is a well understood and ubiquitously applied reaction, to the best of our knowledge only one publication by Helquist et al. reports the cyclopropanation of phenanthrene,[16] which can be considered the benzoid model compound for the Dbf chemistry demonstrated here. Formation of cyclopropane derivatives from vinylferrocenes has been described recently;[17] however, to the best of our knowledge a similar reaction has not been applied to a double bond that forms part of a conjugated aromatic system. We chose $ZnEt_2$ and $ClCH_2I$ as reagents to exploit the advantages of a homogenous reaction system; in addition, $ClCH_2I$ has been reported to generate a more efficient cyclopropanation agent than CH_2I_2.[18] Stepwise treatment of [(Dbf)Fe(Cp‴)] with 80 equivalents of $ZnEt_2$ and 120 equivalents of $ClCH_2I$ at −30 °C allows the selective cyclopropanation of the 3,4 and 3′,4′ double bonds in the Dbf ligand to yield the corresponding *meso*-dicyclopropa[*a,i*]-Dbf complex.[19] The carbenoid species can approach the complex [(Dbf)Fe(Cp‴)] only from the *exo*-side of the Dbf ligand. This limits the outcome of the reaction to the formation of the product shown in Scheme 3. Taking into account the rapid racemization of the binaphthyl system, essentially a *meso* compound is obtained. Compound **2** was isolated and completely characterized by MALDI-TOF mass spectrometry, NMR spectroscopy, and X-ray-diffraction. Following the same route [(Dbf)Fe(^{4}Cp)] (^{4}Cp = tetraisopropylcyclopentadienyl) and symmetrical [$(Dbf)_2Fe$] could be converted into the corresponding di- and tetracyclopropanylated derivatives, which were characterized by MALDI-TOF mass spectrometry (see the Supporting Information).

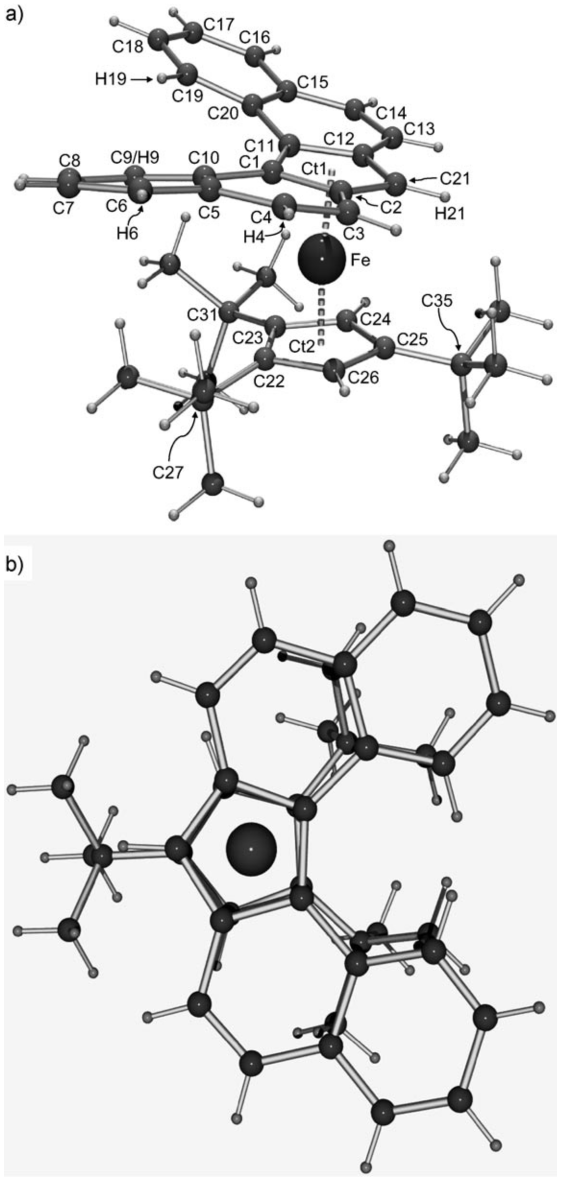
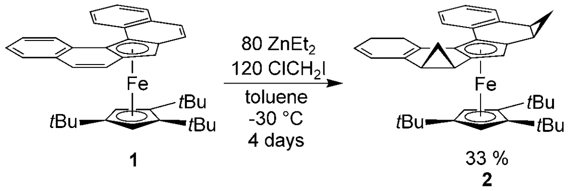


Figure 1. Solid-state structure of [(Dbf)Fe(Cp‴)] (**1**), seen from the side (a) and top down (b). Characteristic bond lengths [Å] and angles [°]: Ct1−Fe 1.7032, Ct2−Fe 1.6786, 8,8′-H 1.949, Fe1−C1 2.1101(15), Fe1−C2 2.1016(15), Fe1−C21 2.0475(15), Fe1−C12 2.0754(15), Fe1−C11 2.1492(15), Fe1−C22 2.1058(16), Fe1−C23 2.0963(15), Fe1−C24 2.0454(15), Fe1−C25 2.0781(15), Fe1−C26 2.0440(15), C3−C4 1.344(3), C13−C14 1.340(3); Ct1-Fe-Ct2 174.168(1), Cp-Cp 8.942, C10-C1-C11-C20 10.957(4).



Scheme 3. Synthesis of **2** by cyclopropanation of [(Dbf)Fe($\mathrm{Cp'''}$)] (**1**).

The bright red complex **2** is very soluble in aprotic organic solvents, with the exception of acetonitrile, wherein it is insoluble. In its ^{1}H NMR spectrum (C_6D_6), compound **2** shows resonances of the eight remaining aromatic protons. The 8,8′-CH group again exhibits the highest observed chemical shift and is detected as a doublet at $\delta = 8.48$ ppm. The resonance of the 9-CH group is shifted by almost 0.7 ppm compared to the starting material and appears at $\delta = 4.60$ ppm, while the b,b′-protons are detected at $\delta = 3.49$ ppm. The signals of the *tert*-butyl groups also experience an upfield shift and are observed at $\delta = 1.30$ and 1.20 ppm. Six resonances of aromatic carbon atoms are observed in the ^{13}C NMR spectrum. The carbon atoms of the η^5-coordinated rings are detected between $\delta = 65$ and 102 ppm and could be individually assigned by HMQC and HMBC NMR spectroscopy. The 9-CH group is observed at $\delta = 65.89$ ppm, while the corresponding quaternary 1,1′- and 2,2′-carbon atoms are detected at $\delta = 75.87$ and 87.49 ppm, respectively. In the $\mathrm{Cp'''}$ ligand, the b,b′-CH groups are detected at $\delta = 70.21$ ppm, and the c- and a,a′-ring carbon atoms yield resonances at $\delta = 96.02$ and 101.71 ppm. The ^{13}C resonances of the attached *tert*-butyl groups are found at $\delta = 34.16$ (CH_3) and 32.46 ppm (C) for the a,a′ positions and at $\delta = 31.56$ (C) and 31.07 ppm (CH_3) for the c position.

The newly formed cyclopropropyl rings yield four resonances in the ^{1}H NMR spectrum at $\delta = 2.29$ (3,3′-H, m_c), 2.12 (4,4′-H, m_c), 1.02 (*exo*-3a,3a′-H, dt), and 0.55 ppm (*endo*-3a,3a′-H, q), each corresponding to two protons. The ^{13}C resonances of the 3,3′-CH and 3a,3a′-CH_2 groups are detected at $\delta = 15.69$ and 15.63 ppm (not assigned individually), the 4,4′-CH group is observed at $\delta = 20.65$ ppm. The *exo*/*endo* assignment is in agreement with the reported chemical shifts for 9,10-methanophenanthrene (9,10-CH: $\delta = 2.30$ ppm, *exo*-H: $\delta = 1.60$ ppm, *endo*-H: $\delta = -0.02$ ppm)[12] and could also be verified by a NOESY NMR experiment, which shows a strong correlation between *exo*-3a,3a′-H and each 3,3′-H and 4,4′-H. For the *endo*-3a,3a′ protons an equally intense interaction is not observed (see Supporting Information).

To obtain crystals suitable for X-ray diffraction, **2** was dissolved in a 1:4 mixture of acetonitrile and Et_2O. The ether was subsequently removed by absorption in paraffin oil, which yielded the complex as red needles. Upon crystallization of the racemic complex spontaneous asymmetric resolution occurred, as becomes evident from the chiral space group $P2_12_12_1$. The most prominent features of the complex are the two cyclopropyl rings C3-C4-C41 and C13-C14-C42, which bridge the former double bonds in positions 3,4 and 3′,4′ (Figure 2). The C_3 ring planes assume angles of 70.885° und 71.487° relative to the planes of the adjacent butadienyl fragments C2-C3-C4-C5 and C12-C13-C14-C15, respectively.

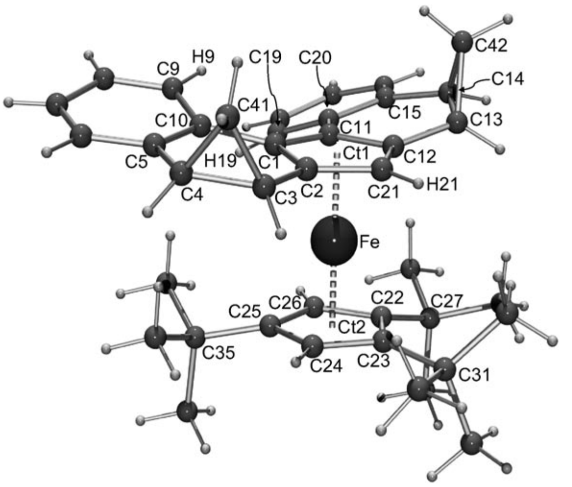


Figure 2. Solid-state structure of **2**. Characteristic bond lengths [Å] and angles [°]: C1−Fe1 2.118(3), C2−Fe1 2.059(3), C11−Fe1 2.073(3), C12−Fe1 2.076(3), C21−Fe1 2.046(3), C22−Fe1 2.110(3), C23−Fe1 2.078(3), C24−Fe1 2.047(3), C25−Fe1 2.092(3), C26−Fe1 2.054(3), Ct1−Fe 1.6806, Ct2−Fe1 1.6836, C3−C4 1.507(4), C13−C14 1.522(4), H9-H19 2.0791; H21-C21-C23-C31 −3.743(1), Cp-Cp 3.752, C10-C1-C11-C20 −16.573(3), Ct1-Fe-Ct2 177.695(1).

The five-membered rings in **2** assume an eclipsed conformation, as has been observed for [(Dbf)Fe($\mathrm{Cp'''}$)] (**1**). This time the a′-*tert*-butyl group is co-aligned to the 9-CH group (H21-C21-C23-C31: −3.743(1)°), while the c-*tert*-butyl group is positioned beneath the upward pointing naphthyl arm. The unequal steric pressure of the *tert*-butyl groups upon the Dbf system leads to a more pronounced dihedral angle of the binaphthyl system of −16.573(3)°, which also allows a greater spatial separation of the 8,8′ protons (2.0791 Å, [(Dbf)Fe($\mathrm{Cp'''}$)]: 1.949 Å) and a more symmetrical coordination geometry at the metal center: The tilt of the Cp ring planes is reduced to 3.752° and the Ct1-Fe-Ct2 angle reaches 177.695(1)°.

Conclusions

The results presented here support the hypothesis of more or less localized aromaticity in certain benzannulated Cp complexes. NICS calculations as well as reactivity studies clearly show the formation of C=C bonds possessing distinctive double-bond character in the corresponding benzannulated Cp anions. This feature becomes even more pronounced by η^5-coordination of such ligands and is one of the reasons for the strongly enhanced stability of the derived complexes compared to analogous flourenide systems.

Experimental Section

Synthesis of [(Dbf)Fe(Cp‴)] (1): DbfH (266 mg, 1.0 mmol) was dissolved in absolute 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, 1.6 M in hexane) was added dropwise. While slowly warming to ambient temperature, the solution was stirred overnight. The colorless precipitate of DbfLi was dissolved by addition of absolute THF (5 mL). The resulting greenish-black solution was again cooled to −15 °C and a solution of [{Cp‴FeBr}$_2$][9] (369 mg, 0.5 mmol) dissolved in absolute toluene (10 mL) and absolute THF (5 mL) was added dropwise over 1 h. The resulting black solution was again stirred overnight while slowly warming to ambient temperature. After the solvent was removed, the residue was extracted with absolute toluene (2 × 10 mL). The combined dark red extracts were evaporated to dryness and the residue was extracted with absolute pentane (2 × 10 mL). The combined extracts were concentrated to about 2 mL and allowed to crystallize at −30 °C, which yielded a dark red microcrystalline solid. Single crystals suitable for examination by X-ray diffraction were obtained by crystallization from an oversaturated solution in toluene at ambient temperature. Yield: 108.2 mg (195 µmol, 38 %); ^{1}H NMR (400 MHz, C_6D_6): $\delta = 9.37$ (d, 2H, $^3J_{HH} = 8.0$ Hz, 8,8′-H), 7.56 (dd, 2H, $^3J_{HH} = 7.7$ Hz/1.3 Hz, 5,5′-H), 7.41 (dt, 2H, $^3J_{HH} = 8.1$ Hz/1.3 Hz, 7,7′-H), 7.35–7.37 (m, 4H, 6,6′-H und 3,3′/4,4′-H), 7.17 (d, 2H, 3,3′/4,4′-H), 5.29 (s, 1H, 9-H) 3.31 (s, 2H, b,b′-H), 1.10 (s, 18H, a,a′-*t*Bu), 1.03 ppm (s, 9H, c-*t*Bu); ^{13}C NMR (100 MHz, C_6D_6): $\delta = 136.76$, 134.22, 129.19, 127.95, 127.48, 127.06, 125.86, 125.47, 98.83 (Cp‴-c-C), 94.21 (Cp‴-a,a′-C), 87.11 (Dbf-C), 80.29 (Dbf-CH), 65.90 (b,b′-CH), 61.14 (9-CH), 33.74 (a,a′-*t*BuMe), 32.36 (a,a′-*t*BuC), 31.33 (c-*t*BuC), 31.15 ppm (c-*t*BuMe); elemental analysis calcd (%) for $C_{38}H_{42}Fe$: C 82.30, H 7.63; found: C 81.68, H 7.67; IR (KBr): $\tilde{\nu} = 3095$ (m), 3046 (m), 3015 (w), 2953 (vs), 2901 (s), 2867 (s), 1892 (w), 1743 (w), 1715 (w), 1604 (m), 1543 (w), 1489 (m), 1458 (s), 1449 (s), 1395 (w), 1383 (w), 1355 (s), 1268 (m), 1246 (s), 1168 (w), 1114 (w), 1152 (w), 1121 (w), 994 (m), 948 (m), 919 (w), 863 (w), 849 (m), 832 (w), 821 (m), 807 (m), 793 (s), 761 (s), 751 (s), 675 (w), 647 (w), 625 (m), 575 (m), 541 (s), 526 (m), 477 (w), 450 (m), 429 (m), 408 cm^{-1} (w); MALDI-TOF MS: *m/z* (%): 552.546 ($[M-2]^+$, 7), 553.550 ($[M-1]^+$, 3), 554.543 ($[M]^+$, 100), 555.558 ($[M+1]^+$, 64), 556.572 ($[M+2]^+$, 18), 557.593 ($[M+3]^+$, 1); calcd ($C_{38}H_{42}Fe$) = 554.27.

Synthesis of 2: [(Dbf)Fe(Cp‴)] (42 mg, 75.7 µmol) as dissolved in absolute toluene (7 mL) in a Schlenk tube and the solution was cooled to −30 °C. Subsequently $ZnEt_2$ (2.28 mL, 2.27 mmol, 30 equiv, 1 M in hexane fractions) and $ClCH_2I$ (2.5 mL, 3.41 mmol, 45 equiv, 10 % solution in absolute toluene) were added. The reaction was monitored by MALDI-TOF MS while two more loads of 30–20 equivalents of $ZnEt_2$ and 30–45 equivalents of $ClCH_2I$ were added in intervals of 16–24 h until the reaction came to completion. Afterwards, while still being kept at −30 °C, degassed, distilled water (0.5 mL) was added, the suspension was stirred at −30 °C for another 30 min and then for one more hour while slowly warming to ambient temperature. To absorb the water Na_2SO_4 (1 g) was added, the solution was filtered, and the solid residue was again extracted with absolute toluene (2 × 10 mL). The combined extracts were concentrated to 2–3 mL and the remaining solvent was slowly removed by absorption in paraffin oil, which yielded **2** as thin red needles. Single crystals suitable for X-ray diffraction were obtained by suspending a small amount of **2** in absolute acetonitrile (1 mL). The complex was then dissolved by addition of absolute Et_2O (ca. 4 mL). Removal of the ether by absorption in paraffin oil yielded the complex as red needles. Yield: 13.3 mg (22.8 µmol, 33 %); ^{1}H NMR (600 MHz, C_6D_6): $\delta = 8.48$ (d, 2H, $^3J_{HH} = 7.3$ Hz, 8,8′-H), 7.24 (dd, 2H, $^3J_{HH} = 7.1$ Hz/$^4J_{HH} = 1.6$ Hz, 5,5′-H), 7.05 (quintd, 2H, $^3J_{HH} = 7.1$ Hz/$^4J_{HH} = 1.5$ Hz, 6,6′,7,7′-H), 4.60 (s, 1H, 9-H), 3.49 (s, 2H, b,b′-H), 2.29 (m_c, 2H, 3,3′-H), 2.12 (m_c, 2H, 4,4′-H), 1.30 (s, 18H, a,a′-*t*Bu), 1.20 (s, 9H, c-*t*Bu), 1.02 (td, 2H, $^3J_{HH} = 8.6$ Hz/$^4J_{HH} = 3.9$ Hz, *exo*-3a,3a′-H), 0.55 ppm (q, $^3J_{HH} = 4.5$ Hz, *endo*-3a,3a′-H); ^{13}C NMR (150 MHz, C_6D_6): $\delta = 137.79$, 134.72, 130.06, 126.14, 125.35, 101.71 (Cp‴-a,a′-C), 96.02 (Cp‴-c-C), 87.49 (2,2′-C), 75.87(1,1′-C), 70.21 (Cp‴-b,b′-CH, 65.89 (Dbf-9-CH), 34.16 (a,a′-*t*Bu-CH_3), 32.46 (a,a′-*t*Bu-C), 31.56 (c-*t*Bu-C), 31.07 (c-*t*Bu-CH_3), 20.65 (4,4′-CH), 15.69 (cyclopropyl), 15.63 ppm (cyclopropyl); elemental analysis calcd (%) for $C_{38}H_{46}Fe$: C 82.46, H 7.96; found: C 81.52, H 7.99; IR (KBr): $\tilde{\nu} = 2957$ (s), 2924 (m), 2868 (m), 1636 (w), 1596 (w), 1542 (w), 1499 (m), 1481 (w), 1462 (m), 1386 (w), 1361 (m), 1246 (m), 1234 (w), 1167 (w), 1100 (w), 1054 (w), 1027 (m), 994 (w), 947 (m), 903 (w), 878 (w), 844 (w), 822 (m), 755 (s), 708 (w), 670 (w), 648 (w), 613 (w), 577 (m), 527 (m), 511 cm^{-1} (w); MALDI-TOF MS: *m/z* (%): 580.433 ($[M-2]^+$, 5), 581.446 ($[M-1]^+$, 2), 582.457 ($[M]^+$, 100), 583.472 ($[M+1]^+$, 53), 584.489 ($[M+2]^+$, 10), 585.499 ($[M+3]^+$, 1); calcd ($C_{40}H_{46}Fe$) = 582.29.

X-ray structure analyses: Crystal data and refinement parameters are collected in Table 2. The structures were solved by using direct methods (SIR92),[20] completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures.[21] Semiempirical absorption corrections from equivalents (Multiscan) were carried out.[22] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms positions were calculated in ideal positions (riding model). CCDC-754517 (**1**) and CCDC-754518 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 2. Crystallographic data for **1** and **2**.

	1	**2**
formula	$C_{38}H_{42}Fe$	$C_{40}H_{46}Fe$
formula weight	554.57	582.62
T [K]	150(2)	150(2)
wavelength [Å]	1.54184	1.54184
crystal size [mm]	0.21 × 0.16 × 0.15	0.28 × 0.06 × 0.03
crystal system	monoclinic	orthorhombic
space group	$P2_1/c$	$P2_12_12_1$
a [Å]	10.1735(3)	8.6048(2)
b [Å]	16.7013(6)	15.8825(3)
c [Å]	17.7647(3)	22.9949(6)
α [°]	90	90
β [°]	105.505(2)	90
γ [°]	90	90
V [Å^3]	2908.56(14)	3142.61(12)
Z	4	4
ρ_{calcd} [g cm^{-3}]	1.266	1.231
µ ($Cu_{K\alpha}$) [mm^{-1}]	4.324	4.025
θ range [°]	3.70/62.66	3.84/62.57
index ranges	$-11 \leq h \leq 11$	$-9 \leq h \leq 9$
	$-19 \leq k \leq 19$	$-18 \leq k \leq 15$
	$-20 \leq l \leq 20$	$-26 \leq l \leq 24$
reflections collected	24 784	9153
unique reflections	4630	4446
	$R_{int} = 0.0376$	$R_{int} = 0.0470$
absorption correction	multiscan	multiscan
data/restraints/parameters	9324/2/366	4446/0/379
GOF on F^2	1.013	0.941
final R indices	$R_1 = 0.0376$	$R_1 = 0.0344$
$[I>2\sigma(I)]$[a]	$wR_2 = 0.0947$	$wR_2 = 0.0634$
R indices[a]	$R_1 = 0.0576$	$R_1 = 0.0526$
(all data)	$wR_2 = 0.1024$	$wR_2 = 0.0690$
Flack parameter	–	−0.001(4)
$\Delta\rho$max/min [eÅ^{-3}]	0.476/−0.380	0.272/−0.274

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

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