Organometallic Chemistry

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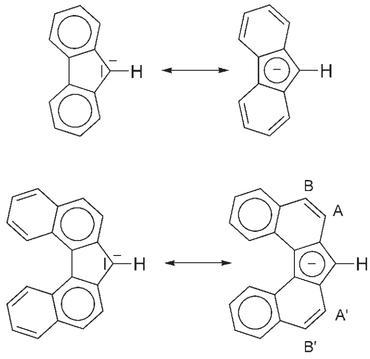
Dibenzo[*c*,*g*]fluorene: The Combination of Cyclopentadiene and 1,1′-Binaphthyl in One Ligand

*Frank Pammer, Yu Sun, Claudia May, Gotthelf Wolmershäuser, Harald Kelm, Hans-Jörg Krüger, and Werner R. Thiel**

The discovery of ferrocene in 1951 was a milestone in organometallic chemistry.[1] During the following years, a multitude of complexes containing 6π-aromatic ligands such as $C_5H_5^-$ and C_6H_6 were synthesized.[2] Nearly parallel to these advances, the coordination chemistry of polycyclic aromatic compounds such as indenide or naphthalene was systematically developed.[3] The organometallic chemistry of fluorene dates to the beginning of the 20th century, when the first compounds of the fluorenyl anion (Flu$^-$) with alkali-metal counterions were synthesized.[4] Fluorenyl complexes of mercury[5] and Group XIV elements[6] followed. The first reports on fluorenyl complexes of the transition metals appeared in the 1960s.[7] The investigation of benzene-annulated cyclopentadienyl anions as ligands in organometallic chemistry has intensified over the last 15–20 years, owing to the application of such systems in "single-site" catalysts for olefin polymerization.[8] Further annulation of aromatic rings to fluorene leads to more extended π systems. However, only a few benzene-annulated fluorenes have been described,[9] and they have rarely been used as ligands.[10] Very recently, Beckhaus et al. reported on the coordination chemistry of tetrabenzo[*a*,*c*,*g*,*i*]fluorene.[11]

Herein, we describe the synthesis of the first transition-metal complexes of the dibenzo[*c*,*g*]fluorenyl anion (Dbf$^-$, **1**$^-$), a ligand that can be considered as an analogue of the cyclopentadienyl anion (Cp$^-$) or as a 2,2′-bridged 1,1′-binaphthyl system. Thus, **1**-H and its derivatives have a chiral axis that passes through the Cp fragment. This chirality is a remarkable feature of these compounds, although the barrier of racemization for **1**$^-$ is low, as we will discuss below on the basis of spectroscopic studies and quantum-mechanical calculations.

Whereas ferrocene is the paradigm for a stable organometallic molecule, difluorenyl iron has not yet been reported. The instability of [(Flu)$_2$Fe] results from the perturbation of the two benzenoid aromatic rings of the fluorenyl ligands that occurs upon the η^5 coordination of the Cp fragment to the metal center. In contrast, the perturbation in benzene-annulated fluorenyl anions such as **1**$^-$ should be less pronounced (Scheme 1). The negative charge should be stabilized more efficiently, leading to a more favorable charge distribution and a more covalent metal–ligand bond than in fluorenyl complexes.



Scheme 1. Mesomeric formulas highlighting the aromatic stabilization of Dbf$^-$ (**1**$^-$; bottom) in comparison to Flu$^-$ (top).

To verify this hypothesis and to investigate the racemization barrier of **1**$^-$, density functional theory (DFT) calculations were carried out.[12] Figure 1 shows the calculated structures of [(Cp)Li], [(Flu)Li], and [(Dbf)Li], and gives the corresponding Li–C bond lengths. The numbering of the carbon atoms in [(Dbf)Li] will be used for the following discussion of the calculated structures.

The Li–C distances for the quaternary carbon atoms in the five-membered ring of [(Flu)Li] are significantly longer than that for the tertiary carbon atom (C1). This result implies that a higher concentration of negative charge is present at the C1 site. The corresponding differences in the Li–C bond lengths are less pronounced for [(Dbf)Li]. A comparison of the charges at the lithium atom and at the carbon atoms of the five-membered rings in the three compounds underlines this effect (Table 1). Independent of the calculation method, the unevenness of the charge distribution in the ring increases from [(Cp)Li] to [(Dbf)Li] to [(Flu)Li]. In particular, the charge concentration at C1 is significantly less pronounced for [(Dbf)Li] than for [(Flu)Li]. This result implies that the Dbf ligand has an enhanced preference for η^5 coordination and, thus, a higher stability against decoordination through a η^5,η^1 shift.

If the mesomeric formula of **1**$^-$ (Scheme 1, bottom), which comprises three aromatic rings, makes a relevant contribution to the electronic structure of the molecule, the bonds C_A–C_B

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[*] Dipl.-Chem. F. Pammer, Dr. Y. Sun, Dipl.-Chem. C. May,
Dr. G. Wolmershäuser, Dr. H. Kelm, Prof. Dr. H.-J. Krüger,
Prof. Dr. W. R. Thiel
Fachbereich Chemie
Technische Universität Kaiserslautern
Erwin-Schrödinger-Strasse, Geb. 54
67663 Kaiserslautern (Germany)
Fax: (+49) 631-2054676
E-mail: thiel@chemie.uni-kl.de

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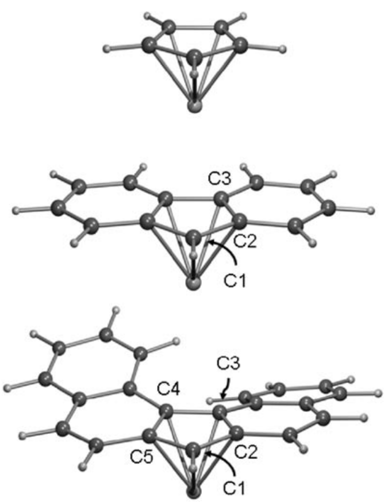


Figure 1. Calculated molecular structures of [(Cp)Li], [(Flu)Li], and [(Dbf)Li] (**1**-Li). Li–C distances [Å]: [(Cp)Li]: C–Li 2.1030; [(Flu)Li]: C1–Li 2.1045, C2–Li 2.1451, C3–Li 2.1626; [(Dbf)Li]: C1–Li 2.1236, C2–Li 2.1557, C3–Li 2.1284, C4–Li 2.1701, C5–Li 2.1232.

Table 1: Mulliken and natural bond orbital (NBO) charges in [(Cp)Li], [(Flu)Li], and [(Dbf)Li] from DFT calculations.[a]

	[(Cp)Li]		[(Flu)Li]		[(Dbf)Li]	
	Mulliken	NBO	Mulliken	NBO	Mulliken	NBO
C1	−0.255	−0.392	−0.409	−0.448	−0.369	−0.398
C2	–	–	+0.084	−0.132	+0.064	−0.141
C3	–	–	−0.077	−0.183	−0.113	−0.173
C4	–	–	–	–	−0.144	−0.163
C5	–	–	–	–	+0.078	−0.150
Li	+0.382	+0.926	+0.520	+0.957	+0.534	+0.957

[a] Atom labels correspond to those in Figure 1.

and $C_{A'}-C_{B'}$ should have enhanced double-bond character. In the calculated structure of [(Dbf)Li], these bonds (1.360 Å) are the shortest C–C bonds. They are also distinctly shorter than the corresponding bonds in [(Flu)Li] (1.378 Å).

The synthesis of **1**-H was accomplished on a multigram scale by following the procedure published by Martin and by Seki et al.[13] An alternative route was published by Harvey et al.[14] The deep red ketone **2** was obtained as an intermediate in the Martin/Seki route. The structure of **2** was determined by single-crystal X-ray diffraction (Figure 2).

The treatment of **1**-H with *n*-butyllithium in toluene precipitates colorless air-sensitive [(Dbf)Li], which is readily soluble in coordinating solvents. The reaction of [(Dbf)Li] with $FeBr_2 \cdot dme$[16] in tetrahydrofuran (THF) at room temperature (Scheme 2) gives a red solution and a green precipitate. After removing the solvent and washing the residue with toluene, water, ethanol, and again with toluene, moss-green $[(Dbf)_2Fe]$ (**3**) is obtained. Complex **3** is nearly air-stable, but virtually insoluble in organic solvents. Solutions of **3** in chlorinated hydrocarbons undergo slow decomposition.

It has not yet been possible to grow single crystals of **3**. However, the compound could be fully characterized by means of elemental analysis, mass spectrometry, and ^1H NMR and Mössbauer spectroscopy. The matrix-assisted laser desorption/ionization (MALDI) time-of-flight (TOF) mass spectrum shows a signal assigned to the molecular cation $[(Dbf)_2Fe]^+$ ($m/z = 586$). Four additional groups of signals at higher m/z values could be assigned to species of the type $[(Dbf)_xFe_y]^+$, which are formed during the mass spectrometry experiment. Complex **3** is only poorly soluble in the solvents commonly used for NMR spectroscopy. In the ^1H NMR spectrum of a benzene solution of **3**, only one set of signals, which includes a singlet for the proton of the η^5-C_5H unit at $\delta = 4.71$ ppm, is detected. In contrast, the resonance of the CH_2 group of **1**-H appears at $\delta = 3.73$ ppm. The single set of signals in the ^1H NMR spectrum of **3** demonstrates that the Dbf ligands undergo rapid racemization on the time scale of the experiment; otherwise, the *rac* and *meso* isomers of **3** should be distinguishable. In the Mößbauer spectrum of **3** at 150 K, a signal at an isomer shift of 0.626(5) $mm\,s^{-1}$ with a quadrupole splitting of 2.376(9) $mm\,s^{-1}$ is detected. These values are in good agreement with those reported for ferrocene and its derivatives.[17]

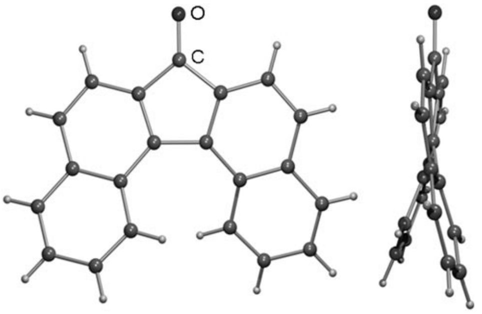
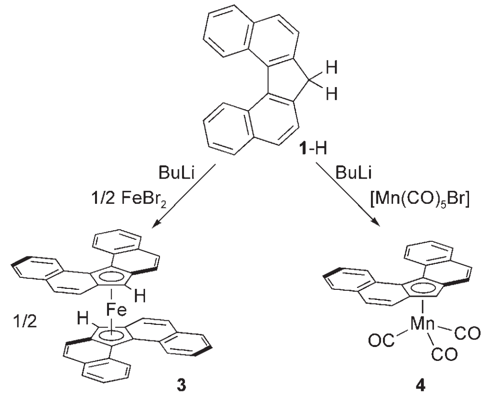


Figure 2. PLUTON[15] plots of the molecular structure of **2** in the solid state. C=O bond length: 1.2238(15) Å; dihedral angle between the two naphthyl rings: 22.7(2)°.



Scheme 2. Synthesis of **3** and **4**.

The reaction of a solution of [(Dbf)Li] in THF/toluene with $[Mn(CO)_5Br]$ at −20 °C gives golden yellow $[(Dbf)Mn(CO)_3]$ (**4**), the doubly benzene-annulated congener of $[(Flu)Mn(CO)_3]$.[18] The ^1H NMR and ^{13}C NMR spectra of **4** each show a single set of resonances for the Dbf ligand. These results are consistent with a rapid racemization of the binaphthyl system, as proposed for **3**. The NMR spectroscopy data for **4** correlate well with those determined for [(η^5-

Flu)Mn(CO)$_3$], and, thus, provide strong evidence for an η^5-coodinated Dbf ligand. In the ^{13}C NMR spectrum of **4**, the three resonances of the five-membered ring are shifted upfield ($\delta = 103.7$, 91.8, 66.7 ppm), and the resonance of the carbonyl ligands is detected at $\delta = 225.4$ ppm. In the ^{1}H NMR spectrum of **4**, the chemical shift of the C$_5$H-proton signal is solvent-dependent (CDCl$_3$: $\delta = 5.65$ ppm; C$_6$D$_6$: $\delta = 4.92$ ppm). The IR spectrum of **4** exhibits two strong absorptions assigned to CO stretching vibrations ($\tilde{\nu} = 2017$ and 1936 cm^{-1}), as expected for a {M(CO)$_3$} complex with local C_{3v} symmetry.

Crystals of **4** are isolated by slow diffusion of pentane into a toluene solution. The complex crystallizes in the monoclinic space group $P2_1/c$ (no. 14); the molecular structure of **4** in the solid state is shown in Figure 3. An axis of chirality is clearly present in the Dbf ligand, passing through atoms C1 and C11.

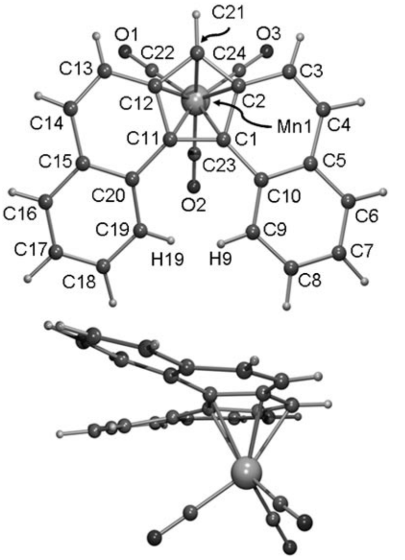


Figure 3. PLUTON[15] plots of the molecular structure of **4** in the solid state. Characteristic bond lengths [Å], angles [°], and torsion angle [°]: C1–Mn1 2.211(3), C2–Mn1 2.150(3), C11–Mn1 2.185(3), C12–Mn1 2.190(3), C21–Mn1 2.130(3), C22–Mn1 1.793(3), C23–Mn1 1.810(3), C24–Mn1 1.800(3), C22–O1 1.155(4), C23–O2 1.138(4), C24–O3 1.143(4), C3–C4 1.351(5), C13–C14 1.340(5); C22-Mn1-C24 90.76(15), C22-Mn1-C23 92.76(14), C24-Mn1-C23 94.20(13), O1-C22-Mn1 179.0(3), O2-C23-Mn1 179.5(3), O3-C24-Mn1 176.7(3); C10-C1-C11-C20 −10.7(5).

However, the torsion angle C10-C1-C11-C20, which describes the twist of the binaphthyl system, is only 10.7°. This angle is less than half as large as that in the ketone **2** (Figure 2); the η^5 coordination of Dbf to manganese in **4** requires that the five-membered ring be as planar as possible. Thus, the distance H9···H19 in **4** (2.034 Å) is significantly shorter than that in **2** (2.110 Å). The range of variation in the distances between the manganese center and the carbon atoms of the five-membered ring is slightly smaller in **4** than it is in [(Flu)Mn(CO)$_3$].[19] The bonds labeled as C$_A$–C$_B$ and C$_{A'}$–C$_{B'}$ in Scheme 1 are by far the shortest C–C bonds in **4** (C3–C4 1.351, C13–C14 1.340 Å), as predicted by the DFT calculations.

As mentioned in the discussion of the NMR spectra of **3** and **4**, the racemization barrier of **1**-H and its derivatives is low, apparently as a result of the strained five-membered ring. Hence, the distance between the hydrogen atoms at the 8 and 8′ positions (IUPAC numbering) in the 1,1′-binaphthyl system of **1**-H and its derivatives is larger than that in conventional 1,1′-binaphthyl compounds. From the solid-state structure of **4**, it is clear that the η^5 coordination of the ligand will lower this barrier. This fact is important if Dbf complexes are to be applied in enantioselective catalysis.

For **1**$^-$, a racemization barrier of $\Delta G^{\ddagger}_{298} = 18.76$ kJ mol^{-1} was calculated,[12] which implies a rapid equilibration of the anion at room temperature. This value does not correlate well with the experimental data of Bringmann et al.[20] They demonstrated that the racemization barriers for 2,2′-bridged 1,1′-binaphthyl systems are distinctly lower than those for unbridged 2,2′-substituted 1,1′-binaphthyl systems, which are often used in enantioselective synthesis and catalysis. For dinaphtho[2,1-*b*:1′,2′-*d*]pyran-4-one, which contains a six-membered lactone ring, a barrier of $\Delta G^{\ddagger}_{298} = (91.1 \pm 1.8)$ kJ mol^{-1} was experimentally determined. Thus, we believe that the actual racemization barrier for **1**$^-$ should be significantly higher than the calculated value (18.76 kJ mol^{-1}); either the value is underestimated by the theoretical method we applied, or it is significantly influenced by the solvent.

To produce a configurationally stable Dbf ligand, substituents must be introduced at the 8 and 8′ positions of the 1,1′-binaphthyl system. Calculations on the derivative of **1**$^-$ with fluorine atoms substituted at these positions gave a racemization barrier of $\Delta G^{\ddagger}_{298} = 104.29$ kJ mol^{-1}, which is also an underestimation, in our opinion. However, the value indicates that this type of substitution should lead to configurationally stable Dbf derivatives. We are currently working on the synthesis of such ligands, which should be of interest for enantioselective catalysis.

Experimental Section

Further details on the X-ray structure analyses of **2** and **4**, the spectroscopic investigations, and the quantum-chemical calculations are included in the Supporting Information.

3: **1**-Li (1.99 g, 7.31 mmol) and FeBr$_2$·dme (1.00 g, 3.65 mmol) were transferred into a Schlenk tube under an inert atmosphere and dissolved in anhydrous THF (20 mL) at room temperature. A black-green solution formed, which was stirred for 3 d. During this time period, the color of the solution turned to red, and a green precipitate appeared. The solvent was removed under vacuum, and the solid residue was transferred onto a glass frit, where it was washed with toluene, water, ethanol, and again with toluene. Pure **3** remained as a moss-green powder (yield: 651 mg, 1.1 mmol, 30 %), which is stable in air for a short time and can be stored under a nitrogen atmosphere at room temperature.

4: **1**-H (266 mg, 1 mmol) was dissolved in anhydrous toluene (10 mL) in a Schlenk tube. After the solution was cooled to −5 °C, *n*-butyllithium (1.6 mol L^{-1} in hexanes, 85 μL, 1.35 mmol) was added. The mixture was slowly warmed to room temperature and stirred for 10 h. The colorless precipitate (**1**-Li) was dissolved in anhydrous THF (2 mL), and the resulting solution was cooled to −20 °C. A solution of [Mn(CO)$_5$Br] (274.9 mg, 1 mmol) in anhydrous THF (5 mL) was slowly added, and the mixture was slowly warmed to room temperature and stirred for a further 20 h. After removing the solvent under vacuum, the brownish-black residue was extracted with anhydrous

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toluene (2 × 15 mL). The combined extracts were concentrated to a volume of 10 mL, resulting in the precipitation of a first crop of yellow microcrystals. Another crop crystallized after the mother liquor was cooled to −20 °C (yield: 97 mg, 24 %).

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[19] Mn−C bond lengths [Å] for **4** and $[(\mathrm{Flu})\mathrm{Mn}(\mathrm{CO})_3]$ (italics): $(d_{\mathrm{Mn1\text{-}C1}} + d_{\mathrm{Mn1\text{-}C11}})/2 = 2.188$ (*2.189*), $(d_{\mathrm{Mn1\text{-}C2}} + d_{\mathrm{Mn1\text{-}C12}})/2 = 2.170$ (*2.185*), $d_{\mathrm{Mn1\text{-}C21}} = 2.130$ (*2.122*).

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