



# Paramagnetic Organometallics

# Iron(III) Half-Sandwich Complexes of the Two-Legged Piano-Stool [CpFe(aryl)Cl] Type from the Corresponding Aryliron(II) Precursors

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**Abstract:** Instead of reacting with the  $\sigma$ -mesityliron(II) complex [Cp<sup>'''</sup>Fe( $\sigma$ -C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>-2,4,6)] (1; Cp<sup>'''</sup> = 1,2,4-tri-*tert*-butylcyclopentadienyl) to form a cyclohexadienyl(cyclopentadienyl)iron(II) sandwich complex with palladium coordination to the *ipso* carbon atom of the six-membered ring, palladium(II) chloride oxidized **1** to the mesityliron(III) complex [Cp<sup>'''</sup>Fe( $\sigma$ -C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>-2,4,6)CI] (**5**) with a two-legged piano-stool geometry. The oxidation of [<sup>4</sup>CpFe( $\sigma$ -C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>-2,4,6)] (**4**; <sup>4</sup>Cp = tetraisopropylcyclopentadienyl) to [<sup>4</sup>CpFe( $\sigma$ -C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>-2,4,6)CI] (**6**) was accom-

plished with hexachloroethane. Two other derivatives, [<sup>4</sup>CpFe-( $\sigma$ -C<sub>6</sub>H<sub>3</sub>*i*Pr<sub>2</sub>-2,6)Cl] (**7**) and [<sup>5</sup>CpFe( $\sigma$ -C<sub>6</sub>H<sub>3</sub>*i*Pr<sub>2</sub>-2,6)Cl] (**8**; <sup>5</sup>Cp = pentaisopropylcyclopentadienyl), could also be obtained by the same method. The molecular structures of **5** and **6** are compared with the structure of the (tetraisopropylcyclopentadienyl)iron(III) dibromide [<sup>4</sup>CpFeBr<sub>2</sub>] (**9**), which was formed from the iron(II) analogue [<sup>4</sup>CpFe( $\mu$ -Br)]<sub>2</sub> during attempted nucleophilic substitution with an arylmagnesium bromide.

#### Introduction

Aryliron(II)-cyclopentadienyl (Cp) complexes with carbonyl ligands of the [CpFe(CO)<sub>2</sub>(aryl)] type have been known for 60 years, and the first example was derived from the reaction of the iodo complex [(C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>I] with phenylmagnesium bromide.<sup>[1]</sup> More recently, aryltin or arylzinc compounds have also been used as sources for aryl ligands, [2-4] and the catalytic activity of such complexes for the hydrogenation of 2-pyridylmethanol has been demonstrated.<sup>[5]</sup> The first aryl(cyclopentadienyl)iron(II) complex without additional donor ligands was the paramagnetic and highly reactive (alkylcyclopentadienyl)-(mesityl)iron complex  $[Cp'''Fe(\sigma-C_6H_2Me_3-2,4,6)]^{[6]}$  (1; Cp''' =1,2,4-tri-tert-butylcyclopentadienyl; Scheme 1). Homo- and heterodinuclear half-open ferrocene derivatives are available from 1 by the addition of a Lewis acid  $ML_n$  ( $ML_n = CuCl$ ,  $AlEt_{3}$ , or other reactive metal complexes with low coordination numbers and valence-electron counts). Examples of the general formula  $[Cp'''Fe(\mu,\eta^5:\eta^1-C_6H_2Me_3-2,4,6)ML_n]$  with a bridging trimethylcyclohexadienyl-ylidene ligand, which can also be regarded as a metal-substituted  $\pi$ -arene ligand, are shown in Scheme 1. When a phenyl ligand was introduced instead of a mesityl ligand, the dimerization of the aryliron intermediate to the diiron complex  $[(Cp'''Fe)_2(\mu,\eta^5:\eta^5-H_5C_6=C_6H_5)]$  with a bridging bis(cyclohexadienyl-ylidene) ligand was observed (Scheme 1).

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Scheme 1. Top:  $\sigma/\pi$  rearrangement of the aryl ligand of the cyclopentadienyliron(II) complex 1. In pentane, 1 adds a Cp<sup>'''</sup>NiBr fragment. In toluene, the same reaction proceeds with the replacement of the mesityl ligand with an *ortho-*, *meta-*, or *para*-tolyl ligand.<sup>[6]</sup> Lewis acids such as the Cp<sup>'''</sup>FeBr fragment<sup>[6]</sup> or copper(I) chloride<sup>[7]</sup> are also added with aryl  $\sigma/\pi$  rearrangement. Bottom: dimerization of an unsubstituted phenyl anion.<sup>[8]</sup>





Two facets of the reactivity of  $(\sigma$ -aryl)(cyclopentadienyl)iron complexes are illustrated in Scheme 1, both of which result in  $\sigma/\pi$  rearrangement: addition of Lewis acids or aryl dimerization. In this manuscript, we describe another reaction pathway available to these aryliron(II) complexes: in addition to nucleophilic aryl anion reactivity, in which the [CpFe(aryl)] species resembles a Grignard reagent, the oxidation to novel iron(III) half-sandwich compounds of the [<sup>R</sup>CpFe(aryl)X] type with a two-legged pianostool geometry was encountered and will be discussed below. The starting compounds **1–4** used in this study are depicted in Scheme 2.



Scheme 2. Four paramagnetic (alkylcyclopentadienyl)(aryl)iron(II) complexes used as starting compounds:  $[Cp'''Fe(\sigma-C_6H_2Me_3-2,4,6)]$  (1),<sup>[6]</sup> [<sup>4</sup>CpFe- $(\sigma-C_6H_2Me_3-2,4,6)]$  (2; this work), [<sup>4</sup>CpFe( $\sigma-C_6H_3iPr_2-2,6)$ ] (3),<sup>[9]</sup> [<sup>5</sup>CpFe- $(\sigma-C_6H_3iPr_2-2,6)]$  (4),<sup>[10]</sup>

As the  $\sigma$ -aryl complex **2** has not been described previously, we report its synthesis and discuss its molecular structure before we proceed to the oxidation of these iron(II) compounds.

#### **Results and Discussion**

During the reaction of the half-sandwich complex  $[{}^{4}CpFe(\mu-Br)]_{2}$ and mesitylmagnesium bromide the color of the reaction mixture changed from orange-red to orange-yellow. The supernatant solution was separated from the solid, and the solvent was evaporated under vacuum to yield **2** in nearly quantitative yield. If further purification is needed, **2** can be recrystallized from small amounts of pentane.

The  $\sigma$ -aryl complex **2** is extremely sensitive towards air and moisture, and even solutions in noncoordinating solvents such as toluene or pentane show decomposition products after several hours without exposure to oxygen or moisture. The <sup>1</sup>H NMR spectrum shows the expected paramagnetic behavior of 2 with broad signals in the range  $\delta$  = 204 to -120 ppm, comparable with the data obtained for the  $\sigma$ -aryl complex **1**.<sup>[6]</sup> The mass spectra and elemental analysis as well as the X-ray diffraction data confirmed the formation of the expected product 2. The concentration of a saturated pentane solution yielded yellow crystals, which allowed for the determination of the molecular structure (Figure 1). Complex 2 crystallizes in the unusual space group Im. Two molecules occupy general positions, and a third molecule is located on a crystallographic mirror plane. The geometries of the three molecules are almost identical, and packing effects may be responsible for the small structural variations.



Figure 1. Molecular structure of **2**. Selected distances [Å] and angles [°]: Fe1–Cp<sub>cent</sub> 1.896, Fe2–Cp<sub>cent</sub> 1.893, Fe3–Cp<sub>cent</sub> 1.888, Fe1–C6 2.030(5), Fe2–C6a 1.993(6), Fe3–C6b 2.012(8); Cp<sub>cent</sub>–Fe1–C6 174.6, Cp<sub>cent</sub>–Fe2–C6a 174.2, Cp<sub>cent</sub>–Fe3–C6b 175.2.

The mesityl ligands of **2** are oriented such that one methyl group in an *ortho* position lies underneath the substitution gap of the cyclopentadienyl ligand, and the other is underneath the two adjacent isopropyl substituents pointing away from each other. With a deviation of 4.8–5.4° from the ideal 180° angle between the Cp centroids and the *ipso*-carbon atom, complex **2** can be considered to have a structure similar to an umbrella, comparable to those of other ( $\sigma$ -aryl)(cyclopentadienyl)iron(II) complexes such as **1**,<sup>[6]</sup> [<sup>4</sup>CpFe( $\sigma$ -C<sub>6</sub>H<sub>3</sub>*i*Pr<sub>2</sub>-2,6)],<sup>[9]</sup> and [<sup>5</sup>CpFe-( $\sigma$ -C<sub>6</sub>H<sub>3</sub>*i*Pr<sub>2</sub>-2,6)], (<sup>5</sup>Cp = pentaisopropylcyclopentadienyl).<sup>[10]</sup>

In an orienting experiment aiming at  $\sigma/\pi$  rearrangement with a palladium-based Lewis acid, the mesityl complex **1** was treated with palladium(II) chloride. From the black reaction solution, the redox product [Cp<sup>'''</sup>Fe( $\sigma$ -C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>-2,4,6)CI] was obtained as a black oil, which was sparingly soluble in pentane and highly soluble in toluene or tetrahydrofuran (THF; Scheme 3).

From a concentrated toluene solution layered with pentane, a few black crystals were obtained. In the unit cell (space group  $P2_1/c$ ), one molecule of the chlorido(mesityl)iron(III) complex **5** was found with a distorted trigonal-planar geometry of the iron–Cp centroid axis, the Fe–Cl bond, and the Fe–C<sub>ipso</sub> bond (Figure 2).

The distance between the cyclopentadienide centroid and the iron atom is 1.871 Å. The Fe–C12 ( $C_{ipso}$ ) bond [1.969(4) Å] is shorter than that (2.043 Å) of the aryliron(II) derivative **4**<sup>[10]</sup> (Scheme 2), as expected from the different ionic radii of high-spin Fe<sup>II</sup> and Fe<sup>III</sup> ions.<sup>[11]</sup> The Fe<sup>III</sup>–C bonds in N-heterocyclic carbene complexes are even longer, for example, the Fe–CH<sub>3</sub>





Scheme 3. Palladium(II) chloride did not rearrange the mesityl ligand to form a heterodinuclear species but resulted in the oxidized aryliron complex **5**.



Figure 2. Molecular structure of **5**. Selected distances [Å] and angles [°]: Fe-Cp<sub>cent</sub> 1.871, Fe-Cl 2.1756(12), Fe-Cl2 1.969(4); Cp<sub>cent</sub>-Fe-Cl 135.1, Cp<sub>cent</sub>-Fe-Cl2 127.2, Cl-Fe-Cl2 97.52(12).

distances are 2.060(11) Å in the 17-valence-electron iron(III) complex [Cp\*Fe( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)(CH<sub>3</sub>)]<sup>[12]</sup> and 2.090(2) Å in the 1,3diisopropylimidazol-2-ylidene complex of iron(III) chloride.<sup>[13]</sup> The *tert*-butyl substituent of C-4 is located directly above the mesityl moiety and bent out of the plane of the cyclopentadienyl ring by ca. 14.4° for steric reasons. The <sup>1</sup>H NMR spectrum shows broad signals between  $\delta$  = 121.30 and -19.37 ppm, in agreement with the expected paramagnetic behavior of the iron(III) complex **5** with a 15-valence-electron count. Although the electron ionization mass spectrum did not display a signal



for the molecular ion, signals for large fragments of **5** could be detected, for example, those derived from the loss of one mesityl or one chlorido ligand in addition to signals of ligand fragments such as  $[Cp''']^+$ ,  $[MesH]^+$ , and  $[tBu]^+$ .

The reducing properties of iron(II) salts in aqueous solution are well known, and the facile oxidation to **5** can be understood as a consequence of its high-spin d<sup>6</sup> electron configuration, which displays unpaired electrons in nonbonding or even antibonding iron d orbitals. From this perspective, there should be no need for a precious oxidizing agent. Complex **2**, obtained in situ from [<sup>4</sup>CpFe( $\mu$ -Br)]<sub>2</sub> with mesitylmagnesium bromide in pentane, could be oxidized by the addition of hexachloroethane to the filtered reaction solution. Black crystals of the chlorido(mesityl)iron(III) half-sandwich complex **6** were obtained in good yield upon cooling (Scheme 4, Figure 3).



Scheme 4. In situ preparation of the mesityl(tetraisopropylcyclopentadienyl)iron(II) derivative  ${\bf 2}$  and subsequent oxidation with hexachloroethane to form the iron(III) half-sandwich complex **6**.



Figure 3. Molecular structure of the chlorido(mesityl)(tetraisopropylcyclopentadienyl)iron(III) derivative **6**. Selected distances [Å] and angles [°]: Fe-Cp<sub>cent</sub> 1.898, Fe-Cl 2.1864(9), Fe-C6 2.012(3); Cp<sub>cent</sub>-Fe-Cl 133.86, Cp<sub>cent</sub>-Fe-C6 127.92, Cl-Fe-C6 97.83(9).

The Fe–Cp<sub>cent</sub> distance of 1.898 Å is slightly longer than that for the Cp<sup> $\prime\prime\prime$ </sup> derivative **5** (1.871 Å; cf. Table 1) and indicates the higher steric demand of the <sup>4</sup>Cp ligand compared with that of



#### Table 1. Comparison of the distances [Å] and angles [°] in 5, 6, and 9.



Distance/angle	<b>5</b> (X1 = Cl, X2 = mesityl)	<b>6</b> (X1 = Cl, X2 = mesityl)	<b>9</b> (X1 = Br1, X2 = Br2)
Fe-Cp <sub>cent</sub>	1.871	1.898	1.883
Fe-X1	2.1756(12)	2.1864(9)	2.3204(16)
Fe–X2	1.969(4)	2.012(3)	2.3246(17)
Cp <sub>cent</sub> –Fe–X1	135.1	133.86	131.30
Cp <sub>cent</sub> –Fe–X2	127.2	127.92	122.91
X1–Fe–X2	97.52(12)	97.83(9)	105.73(6)

the Cp<sup>'''</sup> ligand. The two structures illustrate the cone-angle concept for cyclopentadienyl ligands;<sup>[14]</sup> the bulk of <sup>4</sup>Cp was associated with an average cone angle of 146.4°, and that for Cp<sup>'''</sup> was 132°. Although the individual Cp substituents are the bulkier *tert*-butyl groups for Cp<sup>'''</sup> and isopropyl groups for <sup>4</sup>Cp, the higher number of substituents is important here. The Cp<sup>'''</sup> ligand with two substitution gaps offers more space for the two *ortho* methyl groups of the mesityl ligand and, hence, suffers less from steric crowding (Figure 2). The tetraisopropylcyclopentadienyl ligand offers one gap above one mesityl methyl substituent. The second methyl group points between two isopropyl substituents. These are rotated away from each other to provide as much space as possible, but this is not as effective as a second ring CH position. Therefore, the <sup>4</sup>Cp ligand is bulkier than Cp<sup>'''</sup> in this example and in other cases.

In an analogous experiment, the (diisopropylphenyl)iron(II) analogue [ ${}^{4}CpFe(\sigma-C_{6}H_{3}iPr_{2}-2,6)$ ] (**3**) was generated in situ and oxidized with hexachloroethane to afford black cubes from the pentane reaction solution at -30 °C. The <sup>1</sup>H NMR spectrum showed many broad and partially overlapping signals in the range between  $\delta$  = 175.50 and -145.73 ppm. The elemental analysis agrees with the expected conversion to the iron(III) complex [ ${}^{4}CpFe(\sigma-C_{6}H_{3}iPr_{2}-2,6)Cl$ ] (**7**). The poor-quality diffraction data allow the identification of 7 as a monomeric aryliron(III) complex like 5 and 6 but do not warrant a discussion of structural details. Compared to its mesityl analogue 6, the diisopropylphenyl derivative 7 appears more stable and shows a melting point with decomposition at 150 °C. At 50 °C, 7 decomposes within several days to a brown solid. Crystalline 7 is air-stable at room temperature for approximately 1 h but in solution for less than 5 min with a color change from black to brown.

A pentane solution of the aryliron(II) derivative [5CpFe- $(\sigma-C_6H_3iPr_2-2,6)$ ] (4) turned black within minutes after hexachloroethane addition. The paramagnetic iron(III) complex [<sup>5</sup>CpFe( $\sigma$ -C<sub>6</sub>H<sub>3</sub>*i*Pr<sub>2</sub>-2,6)Cl] (8) shows broad <sup>1</sup>H NMR signals between  $\delta$  = 175.05 and -126.50 ppm. Compared to the tetraisopropylcyclopentadienyl derivative 7, compound 8 shows fewer NMR signals, which agrees with the higher symmetry of the pentaalkylcyclopentadienyl ligand of 8. The chemical shifts for 7 and 8 are similar, as expected for similar compounds. The NMR signals of the mesityl derivative 6 differ markedly from those of 7 and 8. For example, the diisopropylphenyl derivatives **7** and **8** have only one signal downfield from  $\delta = 100$  ppm ( $\delta$  = 175.50 ppm for **7**,  $\delta$  = 175.07 ppm for **8**), whereas complex **6** has four different signals between  $\delta$  = 183 and 100 ppm ( $\delta$  = 109.43, 113.96, 120.86, 182.16 ppm). Furthermore, <sup>4</sup>Cp complex 7 has ten signals with negative shifts, and the <sup>5</sup>Cp derivative 8

has only four owing to the higher symmetry of the cyclopentadienyl ligand.

From the reaction of  $[{}^{4}CpFe(\mu-Br)]_{2}$  with biphenyl-4,4'-diylbis(magnesium bromide), the expected dinuclear biaryldiiron(II) compound could not be detected. Instead, only a few red crystals could be isolated and characterized by X-ray diffraction. The crystallographic data revealed mononuclear dibromido(tetraisopropylcyclopentadienyl)iron(III) (**9**; Figure 4).



Figure 4. Molecular structure of **9**. Selected distances [Å] and angles [°]: Fe–Cp<sub>cent</sub> 1.883, Fe–Br1 2.3204(16), Fe–Br2 2.3246(17); Cp<sub>cent</sub>–Fe–Br1 131.30, Cp<sub>cent</sub>–Fe–Br2 122.91, Br1–Fe–Br2 105.73(6).

The distance of 1.883 Å between the iron atom and the centroid of the cyclopentadienyl ligand is between the values found for the mesityl derivatives **5** and **6** (Table 1). Both Fe–Br bonds of **9** show nearly the same length and are 2.3204(16) and 2.3246(17) Å, respectively. In contrast to the bond lengths, the Cp<sub>cent</sub>–Fe–Br angles are different. The angle to Br1 is 131.30°, whereas the angle to Br2 is significantly smaller (122.91°). The Br–Fe–Br angle is 105.74°. The unsymmetrical arrangement of the bromido ligands with Br1 directly under an isopropyl substituent and Br2 in the gap between two isopropyl substituents orienting their methyl groups away from each other results in a smaller Cp–Fe–Br2 angle.

Further characterization could not be performed owing to the small amount of crystals. The trace amounts of an iron(III) complex formed during the reaction of an iron(III) precursor with an organomagnesium compound raises questions regarding the oxidizing agent. If traces of atmospheric oxygen were responsible, we would expect an oxido bridge, which is not likely to be replaced readily by bromide ions. Another hypothe-





sis assumes the reduction of the [<sup>4</sup>CpFe(µ-Br)]<sub>2</sub> precursor by the organomagnesium component to form an Fe<sup>1</sup> intermediate, followed by oxidative addition of unreacted aryl bromide admitted together with the solution of the Grignard compound. The conversion of a putative [<sup>4</sup>CpFe(aryl)Br] intermediate to the dibromide **9** could then follow by Schlenk equilibria involving heterodinuclear iron(III)-magnesium(II) complexes. The unintended formation of the iron(III) half-sandwich complex **9** underscores the outlook in an earlier report<sup>[15]</sup> on the possible oxidation of cyclopentadienyliron(II) bromides to the corresponding iron(III) dibromides and calls for the development of a procedure for the rational synthesis of **9** and its derivatives.

#### Conclusions

Starting from paramagnetic alkylcyclopentadienyl(o-dialkylphenyl)iron(II) complexes of the [CpFe( $\sigma$ -aryl)] type, a previously unknown reaction pathway was encountered in reactions with palladium(II) chloride and hexachloroethane.

Palladium(II) chloride is too strongly oxidizing to give the Lewis acid reaction with aryliron(II)–cyclopentadienides as previously encountered with copper(I) chloride to form heterodinuclear [CpFe( $\mu$ , $\eta^{5}$ : $\eta^{1}$ -aryl)CuCl] complexes. The facile oxidation by PdCl<sub>2</sub> to form aryliron(III) chloride complexes of the [CpFe(aryl)Cl] type occurs owing to the presence of unpaired electrons in high-lying d orbitals of the high-spin d<sup>6</sup> Fe<sup>II</sup> ion. This interpretation is supported by the hexachloroethane oxidation of aryliron(II) precursors. It remains to be seen whether a palladium(0) starting compound will be able to undergo the rearrangement reaction, which failed with palladium(II) chloride.

The unexpected formation of dibromido(tetraisopropylcyclopentadienyl)iron(III) in low yield during the reaction of the iron(II) bromide precursor [ $^{4}CpFe(\mu-Br)$ ]<sub>2</sub> with the difunctional Grignard reagent biphenyl-4,4'-diylbis(magnesium bromide) was observed as a side reaction and requires an oxidizing agent. The reduction of iron(II) to iron(I) by the organomagnesium reagent, followed by the oxidative addition of residual aryl bromide could produce iron(III). This hypothesis requires subsequent ligand exchange in analogy to the well-known Schlenk equilibria to produce the observed dibromide.

### **Experimental Section**

**General:** For the preparation of air- and moisture-sensitive compounds under an inert gas, Schlenk-line techniques and a glovebox (MBraun) filled with argon were applied. The solvents were dried rigorously and deoxygenated by distillation under an inert gas with molten potassium (THF) or sodium/potassium alloy (pentane) before use. NMR spectra were obtained with a Bruker Avance 400 spectrometer and referenced to the residual proton signals of the deuterated solvents. Half-widths  $\Delta v_{1/2}$  are given in Hz, and chemical shifts  $\delta$  are in ppm. Elemental analyses were performed in the analytical laboratory of the chemistry department of the TU Kaiserslautern with a Vario Micro Cube analyzer (Elementar Analysentechnik). The crystal structures were obtained by XRD measurements with a Stoe IPDS diffractometer (**5**) or an Oxford Diffraction Gemini Ultra diffractometer (others). The mass spectra were recorded with a

Finnigan MAT 90 instrument with an ionization energy of 70 eV. CCDC 1499981 (for **2**), 1499980 (for **5**), 1499981 (for **6**), and 1499982 (for **9**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.  $[{}^{4}CpFe(\mu-Br)]_{2}$ ,<sup>[9]</sup>  $[{}^{5}CpFeBr(dme)]$  (dme = 1,2-dimethoxyethane),<sup>[10]</sup> mesitylmagnesium bromide,<sup>[16]</sup> mesityl(tri-*tert*-butylcyclopentadienyl)iron (**1**),<sup>[6]</sup> (2,6-diisopropyl-phenyl)magnesium bromide,<sup>[10]</sup> (2,6-diisopropylphenyl)(tetraisopropylcyclopentadienyl)iron (**3**),<sup>[8]</sup> and (2,6-diisopropylphenyl)-(pentaisopropylcyclopentadienyl)iron (**4**)<sup>[10]</sup> were synthesized according to literature procedures. Hexachloroethane (Acros, 99 %) was used as purchased.

[<sup>4</sup>**CpFe**( $\sigma$ -**C**<sub>6</sub>**H**<sub>2</sub>-**2**,**4**,**6**-**Me**<sub>3</sub>)] (2): A solution of mesitylmagnesium bromide–diethyl ether (173 mg, 0.82 mmol) in THF (5 mL) was added to a solution of [<sup>4</sup>CpFe( $\mu$ -Br)]<sub>2</sub> (300 mg, 0.41 mmol) in THF (5 mL). After the reaction mixture had turned dark green, the solvent was evaporated, and the residue was extracted with pentane (10 mL) and centrifuged. The yellow solution was concentrated, and the solvent was allowed to evaporate slowly at room temperature. After 1 d, yellow crystals were obtained (221 mg, 0.55 mmol, 67 %). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K)  $\delta$  = 203.95, 196.91, 87.18, 73.97, -23.93 ( $\Delta \nu_{1/2}$  = 556 Hz), -119.73 ( $\Delta \nu_{1/2}$  = 1062 Hz) ppm. C<sub>26</sub>H<sub>40</sub>Fe (408.45): calcd. C 76.45, H 9.87; found C 75.42, H 9.55.

[Cp<sup>'''</sup>Fe( $\sigma$ -C<sub>6</sub>H<sub>2</sub>-2,4,6-Me<sub>3</sub>)CI] (5): A solution of 1 (100 mg, 0.25 mmol) in THF (5 mL) was added to a suspension of palladium dichloride (22 mg, 0.13 mmol) in THF (5 mL). The reaction mixture turned deep black after a few minutes. The reaction mixture was stirred overnight, and the solvent was removed in vacuo. The residue was extracted with toluene (5 mL) and centrifuged. The solution was separated from the black residue, and the solvent was removed in vacuo. A viscous black oil was isolated (81 mg, 0.18 mmol, 73 %). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K)  $\delta$  = 121.30 ( $\Delta \nu_{1/2}$  = 144 Hz), 72.61 ( $\Delta \nu_{1/2}$  = 368 Hz), -13.45 ( $\Delta \nu_{1/2}$  = 322 Hz), -19.37 ( $\Delta \nu_{1/2}$  = 381 Hz) ppm. Satisfactory elemental analysis could not be obtained. MS: m/z = 408.2 [M – CI]<sup>+</sup>, 324.2 [M – Mes]<sup>+</sup>, 234.2 [Cp<sup>'''</sup>H]<sup>+</sup>, 120.1 [MesH]<sup>+</sup>, 105.0 [Mes – CH<sub>3</sub>]<sup>+</sup>, 57.1 [tBu]<sup>+</sup>.

 $[{}^{4}CpFe(\sigma-C_{6}H_{2}-2,4,6-Me_{3})CI]$  (6): A solution of  $[{}^{4}CpFe(\mu-Br)]_{2}$ (738 mg, 1.0 mmol) in pentane (10 mL) was added to a suspension of mesitylmagnesium bromide (with 1 equiv. of Et<sub>2</sub>O, 595 mg, 2.0 mmol) in pentane (10 mL) at 0 °C with stirring. The reaction mixture was allowed to warm slowly to room temperature and then stirred at room temperature for 1 h. After centrifugation, the orange solution was separated from the precipitate. Without further characterization, the solution containing complex 2 was added to a solution of hexachloroethane (239 mg, 1.0 mmol) in pentane (5 mL). After some minutes, the reaction mixture turned black and was stirred at room temperature for 16 h. The mixture was separated from insoluble compounds by centrifugation, concentrated, and stored at -30 °C. After several days, complex 6 was obtained as black crystals (552 mg, 1.24 mmol, 62 %). <sup>1</sup>H NMR (600 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  = 182.16 ( $\Delta v_{1/2}$  = 2663 Hz), 120.86 ( $\Delta v_{1/2}$  = 233 Hz), 113.96  $(\Delta \nu_{1/2} =$  118 Hz), 109.43 ( $\Delta \nu_{1/2} =$  3977 Hz), 61.66 ( $\Delta \nu_{1/2} =$  3852 Hz), 48.48, 18.88, -20.84 ( $\Delta v_{1/2}$  = 3419), -41.07 ( $\Delta v_{1/2}$  = 3378 Hz), -55.97  $(\Delta v_{1/2} = 5300 \text{ Hz})$ , -150.50 ppm. C<sub>26</sub>H<sub>40</sub>ClFe (443.88): calcd. C 70.35, H 9.08; found C 69.86, H 9.19.

[<sup>4</sup>CpFe( $\sigma$ -C<sub>6</sub>H<sub>3</sub>-2,6-*i*Pr<sub>2</sub>)Cl] (7): A solution of [<sup>4</sup>CpFe( $\mu$ -Br)]<sub>2</sub> (369 mg, 0.5 mmol) in THF (10 mL) was added to a solution of (2,6-diisopropylphenyl)magnesium bromide with 1 equiv. of THF (338 mg, 1.0 mmol) in THF (10 mL) at room temperature with stirring. The reaction mixture became lighter, and the solvent was removed after 5 min. The residue was extracted with pentane (2 × 10 mL), and the volume of the combined pentane extracts was



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reduced to 10 mL. This solution of the known complex **3**<sup>[8]</sup> was added to a solution of hexachloroethane (120 mg, 0.5 mmol) in pentane (5 mL). After some minutes, the reaction mixture turned black and was stirred at room temperature for 16 h. After centrifugation, the black solution was concentrated and stored at -30 °C. After some days, complex **7** was obtained as black crystals (150 mg, 0.31 mmol, 31 %). <sup>1</sup>H NMR (600 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  = 175.50 ( $\Delta \nu_{1/2}$  = 1262 Hz), 76.26 ( $\Delta \nu_{1/2}$  = 1454 Hz), 49.69 ( $\Delta \nu_{1/2}$  = 1439 Hz), 42.54 ( $\Delta \nu_{1/2}$  = 1185 Hz), 29.62 ( $\Delta \nu_{1/2}$  = 1064 Hz), 17.19 ( $\Delta \nu_{1/2}$  = 1643 Hz), -15.47 ( $\Delta \nu_{1/2}$  = 993 Hz), -22.08 ( $\Delta \nu_{1/2}$  = 961 Hz), -28.60, -39.45 ( $\Delta \nu_{1/2}$  = 1572 Hz), -46.55 ( $\Delta \nu_{1/2}$  = 1114 Hz), -53.55, -56.15, -74.40 ( $\Delta \nu_{1/2}$  = 2772 Hz), -111.27 ( $\Delta \nu_{1/2}$  = 57 Hz), -145.73 ( $\Delta \nu_{1/2}$  = 1628 Hz) ppm. C<sub>29</sub>H<sub>46</sub>CIFe (485.98): calcd. C 71.67, H 9.54; found C 70.91, H 9.55.

 $[{}^{5}CpFe(\sigma-C_{6}H_{3}-2,6-iPr_{2})CI]$  (9): A solution of  $[{}^{5}CpFeBr(dme)]$ (501 mg, 1.0 mmol) in THF (10 mL) was added to a solution of (2,6diisopropylphenyl)magnesium bromide with 1 equiv. of THF (338 mg, 1.0 mmol) in THF (10 mL) and stirred at 75 °C for 3 h, and the reaction mixture turned orange-red. After the mixture had cooled to room temperature, the solvent was removed in vacuo. The residue was extracted with pentane ( $2 \times 10$  mL), and the volume of the combined pentane extracts after centrifugation was reduced to 10 mL. This solution of the known complex 4<sup>[10]</sup> was added to a solution of hexachloroethane (120 mg, 0.5 mmol) in pentane (5 mL). After some minutes, the reaction mixture turned black and was stirred at room temperature for 16 h. After centrifugation to remove insoluble compounds, the black solution was concentrated and stored at -30 °C. After a few days, complex 9 was obtained as black crystals (110 mg, 0.28 mmol, 28 %). <sup>1</sup>H NMR (600 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  = 175.07 ( $\Delta v_{1/2}$  = 725 Hz), 78.28 ( $\Delta v_{1/2}$  = 835 Hz), 56.22 ( $\Delta v_{1/2}$  = 136 Hz), 21.10 ( $\Delta v_{1/2}$  = 325 Hz), 17.29, 16.25,  $-12.97 (\Delta v_{1/2} = 1673 \text{ Hz}), -26.71 (\Delta v_{1/2} = 280 \text{ Hz}), -54.05 (\Delta v_{1/2} = 280 \text{ Hz}), -56.05 (\Delta v_{1/2} = 280 \text{ Hz}$ 309 Hz), -126.50 ( $\Delta v_{1/2}$  = 1252 Hz) ppm. C<sub>32</sub>H<sub>52</sub>ClFe (528.06): calcd. C 72.79, H 9.93; found C 72.75, H 9.86.

#### Acknowledgments

H. S. is grateful to Professor O. J. Scherer for many years of friendly support.

**Keywords:** Iron · Half-sandwich complexes · Arene ligands · Cyclopentadienyl ligands · Piano-stool complexes

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Received: August 19, 2016 Published Online: ■





#### Paramagnetic Organometallics

- H. Bauer, M. W. Wallasch, G. Wolmershäuser, Y. Sun,
- *H. Sitzmann\** ..... 1–7
- Iron(III) Half-Sandwich Complexes of the Two-Legged Piano-Stool [CpFe(aryl)Cl] Type from the Corresponding Aryliron(II) Precursors



Paramagnetic iron(III) half-sandwich complexes with bulky alkylcyclopentadienyl ligands are available from highspin aryliron(II) precursors by oxidation with hexachloroethane and are characterized as 15-valence-electron monomers with two-legged piano-stool geometries.

# DOI: 10.1002/ejic.201601026