High-spin Cyclopentadienyl Complexes, Part 7. Ambivalent Interpretation of the Bonding in Iron-Copper Complexes: Metalated Arene *versus* Carbocyclic Carbene

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Z. Naturforsch. **2009**, *64b,* 18 – 24; received September 15, 2008

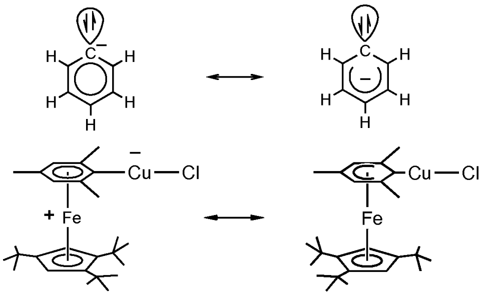
Dedicated to Professor Otto J. Scherer on the occasion of his 75th birthday

The electron distribution within a mesityl ligand bridging a cyclopentadienyliron fragment attached to the mesityl π system and a second metal fragment connected to the *ipso* carbon of the mesityl ring has been probed using a copper(I) halide as a component in $[Cp'''Fe\ (\mu,\eta^5:\eta^1\text{-}C_6H_2Me_3)CuCl]$ (**2**) and its copper bromide derivative **3**. This approach minimizes steric effects and allows for DFT calculations the results of which are in very good agreement with structural data. The calculations show a significant carbene character already for the bare phenyl anion as a result of electrostatic repulsion of the lone pair pushing the π electrons away from the *ipso* carbon towards the *para* carbon atom of the aromatic ring. π Coordination of a cyclopentadienyliron(II) fragment to the phenyl anion to form a hypothetical sandwich complex does not change this situation. The iron center rather follows the unsymmetric distribution of π charge with an unsymmetrical coordination to the π system. Coordination of a copper(I) chloride moiety to the phenyl anion or to the hypothetical π complex $[CpFe(C_6H_5)]$ in both cases equally lowers that carbene character by attracting the lone pair of the *ipso* carbon and thus decreasing its repulsive influence on the π electrons.

Key words: Iron Complexes, Copper Complexes, Tri(*tert*-butyl)cyclopentadienyl, DFT Calculations, Carbene

Introduction

The σ-mesityl complex $[Cp'''Fe(C_6H_2Me_3\text{-}2,4,6)]$ (**1**, $Cp''' = C_5H_2{}^tBu_3\text{-}1,2,4$; Scheme 1) has been synthesized as the first example of a cyclopentadienyliron-σ-aryl complex without additional ligands. Complex **1** has been shown to undergo σ/π-rearrangement with the 14 VE fragment $\{Cp'''FeBr\}$ and with the 16 VE fragment $\{Cp'''NiBr\}$, as discussed in more detail in the accompanying paper [1]. In the resulting complexes of the $[Cp'''Fe(\mu\text{-}C_6H_2Me_3)MCp'''Br]$ (M = Fe, Ni) type the mesityl unit occupies a bridging position and is usually interpreted as a metalated arene moiety $[(C_6H_2Me_3)MCp'''Br]^-$ (a bromo-mesityl-tri{*tert*-butylcyclopentadienyl}ferrate(II) or nickelate(II) anion) exhibiting η^6 coordination to the $\{Cp'''Fe\}^+$ fragment of the sandwich part of the dinuclear molecule.



Scheme 1. Metalated arene *versus* metal cyclohexadienylylidene forms of complex **2**.

X-Ray data of the complexes $[Cp'''Fe(\mu\text{-}C_6H_2Me_3)MCp'''Br]$ (M = Fe, Ni), however, show significantly different Fe–C bond lengths for the *ipso* and *para* carbon atoms of the six-membered ring. This observation led us to consider an alternative resonance structure, where the mesityl ring is regarded as a trimethylcyclohexadienyl-ylidene ligand exhibiting η^5 coordination to iron and therefore to some extent acting as a carbocyclic carbene ligand towards the second metal center [2]. Formal representations of the two points of view are outlined in Scheme 1. An earlier submission of a paper discussing this proposal for publication in October 2005 met with criticism regarding the data as insufficient evidence for a rather unconventional interpretation.

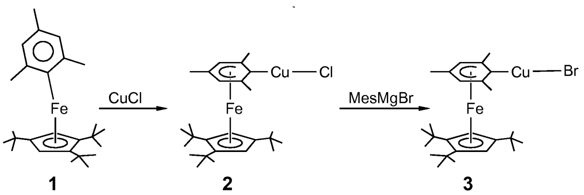
Results and Discussion

In this communication we present well-resolved structural data for novel copper complexes of the same iron sandwich fragment with the aryl group as the bridging unit. These complexes have been designed in order to test the two interpretations outlined above by (i) introduction of an ML_n fragment consisting of only two atoms in order to remove steric bulk as a possible reason for distortion from η^6 towards η^5 coordination and (ii) by theoretical calculations regarding structure and bonding.

When the mesityliron complex **1** was reacted with copper(I) chloride in tetrahydrofuran the diamagnetic heterodinuclear complex [FeCp‴($\mu,\eta^5:\eta^1$-$C_6H_2Me_3$)CuCl] (**2**) was obtained (Scheme 2).

By X-ray crystal structure determination (Table 1) **2** was shown to be a monomeric copper(I) chloride complex (Fig. 1).

The copper-carbon bond length (Cu–C60) of 1.900(6) Å and the Cu–Cl distance of 2.148(2) Å compare well with those found for the bis(2,6-diisopropylphenyl)imidazol-ylidene complex of copper(1) chloride (Cu–C 1.88 and Cu–Cl 2.11 Å [3]), and the Cu–C distances in diarylcuprate(I) complexes are also comparable, *e. g.* 1.922(5) and 1.957(5) Å in $LiCuAr_2$ as described by Niemeyer [4] (Ar = C_6H_3-2,6-(C_6H_2-Me_3-2,4,6)$_2$). Probably the best reference examples are the 1,3-diisopropyl-4,5-dimethylimidazolylidene-copper(I) aryl complexes [(Dmp)Cu(NHC)] (Dmp = 2,6-dimethylphenyl) and [(Mesityl)Cu(NHC)], where the two Cu–C(aryl) and the two Cu–C(NHC) distances are all between 1.902 and 1.922 Å [5]. The six-membered ring of **2** shows Fe–C distances between 2.062(6) and 2.133(6) Å for C61–C65 and a longer distance for Fe–C60 (2.206(5) Å).



Scheme 2. Formation of complexes **2** and **3** from [Cp‴Fe($C_6H_2Me_3$)] (**1**).

Table 1. Crystal structure data for copper halide complexes **2** and **3**.

	2	**3**
Formula	$C_{26}H_{40}ClCuFe$	$C_{26}H_{40}BrCuFe$
M_r	507.42	551.88
Cryst. size, mm^3	0.24 × 0.24 × 0.12	0.35 × 0.20 × 0.15
Crystal system	orthorhombic	orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$
a, Å	10.4351(13)	10.2617(6)
b, Å	11.648(3)	11.7510(8)
c, Å	20.839(3)	20.9200(14)
V, Å^3	2532.9(8)	2522.6(3)
Z	4	4
D_{calcd}, g cm^{-3}	1.331	1.453
μ(MoK_α), cm^{-1}	15.27	30.12
F(000), e	1072	1144
hkl range	±12, ±14, ±26	±14, ±16, ±29
$((\sin\theta)/\lambda)_{max}$, Å^{-1}	0.6326	0.7143
Refl. measured/unique	39794/5295	54331/7698
R_{int}	0.107	0.037
Param. refined	275	274
$R(F)/wR(F^2)$[a] (all refl.)	0.0887/0.1134	0.0354/0.0637
GoF (F^2)[b]	0.844	1.066
$\Delta\rho_{fin}$ (max/min), e Å^{-3}	0.78/−0.50	0.66/−0.26

[a] $R(F) = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$; $wR(F^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (AP)^2 + BP]$ with $P = (F_o^2 + 2F_c^2)/3$; [b] GoF = $\{\Sigma[w(F_o^2 - F_c^2)] / (n-p)\}^{1/2}$; n = number of reflections, p = number of parameters.

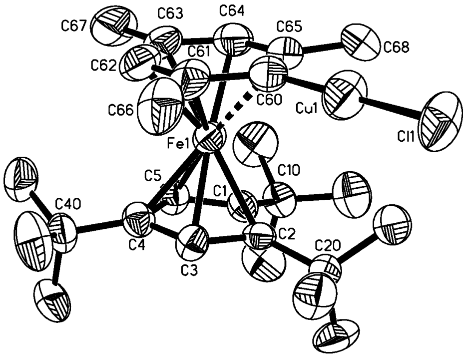


Fig. 1. Crystal structure of the copper chloride complex **2**. Selected distances (Å) and angles (deg): Fe1–C1 2.103(5), Fe1–C2 2.112(4), Fe1–C3 2.066(6), Fe1–C4 2.116(6), Fe1–C5 2.067(5), Fe1–C60 2.206(5), Fe1–C61 2.133(6), Fe1–C62 2.062(6), Fe1–C63 2.081(5), Fe1–C64 2.078(7), Fe1–C65 2.147(6), Cu1–C60 1.900(6), Cu1–Cl1 2.148(2), Fe1–Cp ring plane (C1–C5) 1.70, Fe1–dienyl plane (C61–C65) 1.58, C60–dienyl plane 0.013, Cu1–dienyl plane 0.067; C60–Cu–Cl 179.2(2).

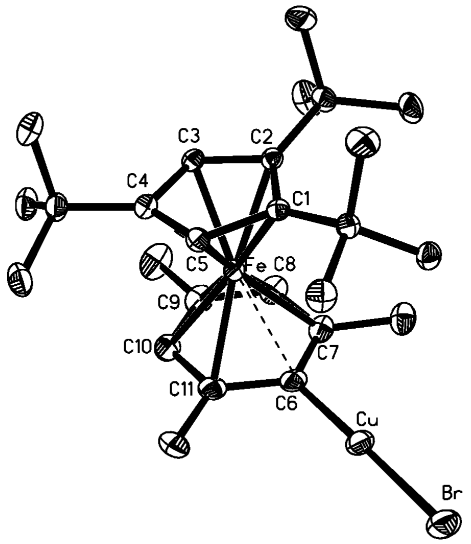


Fig. 2. Crystal structure of the copper bromide complex **3**. Selected distances (Å) and angles (deg): Fe1–C1 2.114(2), Fe1–C2 2.113(2), Fe1–C3 2.061(2), Fe1–C4 2.101(2), Fe1–C5 2.064(2), Fe1–C6 2.200(2), Fe1–C7 2.160(2), Fe1–C8 2.098(2), Fe1–C9 2.1077(18), Fe1–C10 2.081(2), Fe1–C11 2.109(2), Cu1–C6 1.910(2), Cu–Br 2.2390(3), Fe1–Cp ring plane (C1–C5) 1.70, Fe1–dienyl plane (C7–C11) 1.58, C6–dienyl plane 0.018, Cu1–dienyl plane 0.069; C6–Cu–Br 179.1(1).

Table 2. Structure parameters (Å, deg) of the iron-mesityl fragment in four complexes (Fe2, FeNi, **2**, **3**).

	Fe2[a]	FeNi[b]	**2**	**3**
d(Fe–C *ipso*)	2.210(2)	2.231(2)	2.206(5)	2.200(2)
d(Fe–C *ortho*)	2.135(3)	2.106(2)	2.133(6)	2.160(2)
	2.138(2)	2.106(2)	2.147(6)	2.109(2)
d(Fe–C *meta*)	2.086(3)	2.079(2)	2.062(6)	2.098(2)
	2.099(2)	2.102(2)	2.078(7)	2.081(2)
d(Fe–C *para*)	2.112(3)	2.093(2)	2.081(5)	2.108(2)
Intraring C–C				
ipso / ortho	1.428(4)	1.411(3)	1.446(9)	1.423(3)
	1.422(4)	1.407(3)	1.405(9)	1.431(3)
ortho / meta	1.414(4)	1.422(3)	1.406(9)	1.424(3)
	1.420(3)	1.411(3)	1.407(9)	1.423(3)
meta / para	1.398(4)	1.400(4)	1.391(10)	1.401(3)
	1.392(4)	1.398(4)	1.402(10)	1.414(3)
C–C–C angle at				
C *ipso*	115.4(2)	115.3(2)	116.8(6)	116.6(2)
C *ortho*	121.8(3)	122.1(2)	119.6(7)	121.3(2)
	121.6(3)	124.3(2)	121.9(7)	121.3(2)
C *meta*	121.8(3)	119.8(2)	122.8(7)	121.7(2)
	122.0(3)	121.1(3)	121.2(7)	121.2(2)
C *para*	117.3(2)	120.6(2)	117.6(6)	117.8(2)
Fold angle along C *ortho*···C *ortho*	0.9	6.8	0.9	1.3

[a] Fe2 = Cp‴Fe(CH_2Me_3)FeCp‴Br; [b] FeNi = Cp‴Fe(CH_2Me_3)-NiCp‴Br.

The bromo analog [FeCp‴($\mu,\eta^5:\eta^1$-$C_6H_2Me_3$)-CuBr] (**3**) (Table 1, Fig. 2) was obtained from an experiment aiming at replacement of the chloro ligand of **2** with a mesityl ligand by reaction with mesitylmagnesium bromide, which resulted in halide exchange.

As anticipated, the two copper complexes show a distortion of the iron-arene moiety as observed before in the sterically congested nickel and iron analogs (Table 2).

The unsymmetrical coordination of the six-membered ring to iron in the complexes **2** and **3** is in contrast to the structure of the metalated arene complex [(OC)$_3$Cr($\mu,\eta^6:\eta^1$-C_6H_5)TiCl(C_5H_5)$_2$], whose six Cr–C(arene) bond lengths are "identical within experimental error" [6]. In many other examples, like *o*-metalated chromium tricarbonyl complexes of 1-phenylpyridine, there are only small variations of Cr–C(arene) distances like 2.23 Å for five ring C atoms and 2.27 Å for the *ipso* carbon atom for a palladated, or even smaller effects for a mercurated derivative [7]. However, the oxidative addition of the C–Cl bond of the chlorobenzene complex [CpFe(C_6H_5Cl)]$^+$ to a Pd(PPh_3)$_2$ fragment produced the metalated arene complex *cis*-[(Ph_3P)$_2$(Cl)Pd(μ-C_6H_5)FeCp]$^+$, whose Fe–C(arene) distances show significant variations and a long bond Fe–C$_{ipso}$ with 2.16(1) Å. This result prompted the authors to state without further discussion: "*Although the structure of (the) Cp-Fe-(η^6-C_6H_5) moiety is similar to those of related [CpFe(η^6-arene)]$^+$ complexes, the Fe–C$_{21}$ bond is longer than the other Fe–C bonds of Fe(η^6-C_6H_5) (2.04–2.10 Å)*" [8].

In the case of the copper complexes **2** and **3** the deviation from symmetrical η^6 coordination to iron is significant, even larger than in the palladium iron complex mentioned. Steric strain, as present in complexes [Cp‴Fe($\mu,\eta^5:\eta^1$-$C_6H_2Me_3$)MBrCp‴] (M = Fe, Ni) [1], can be ruled out as a possible reason for a distortion towards an η^5 coordination for the complexes **2** and **3**, since they possess sterically undemanding CuX units connected to the *ipso* carbon atom of the mesityl moiety. The crystallographic data show that the copper position does not deviate significantly from the ring plane, suggesting that the Fe–C(*ipso*) bond elongation is not caused by iron-copper repulsion. Therefore, the elongation observed appears to support the proposed $\eta^5:\eta^1$-cyclohexadienyl-ylidene resonance structure, even though the ^{13}C NMR signal of the *ipso* carbon atom at 163.3 ppm does not quite show the low-field shift seen for the carbene C atom

Table 3. Calculated and experimental structures (distances in Å, angles in deg).

	Phenyl anion	$[CpFeC_6H_5]$	Me_3-**2**[a] calculated	**2** (X = Cl) experimental	**3** (X = Br) experimental
Cu–X			2.122	2.148(2)	2.2390(3)
Cu–C			1.890	1.900(6)	1.910(2)
Angle between line C–Cu and plane C_6			173.88	179.2	179.9
Fe-C_6 structure			distances		
d(Fe–ring plane)		1.621	1.586	1.577	1.58
Fe–C *ipso*		2.217	2.190	2.206(5)	2.200(2)
Fe–C *ortho*		2.156	2.137	2.133(6)	2.160(2)
				2.147(6)	2.109(2)
Fe–C *meta*		2.139	2.103	2.062(6)	2.098(2)
				2.078(7)	2.081(2)
Fe–C *para*		2.081	2.130	2.078(7)	2.108(2)
Fe–Cp structure					
d(Fe–ring plane)		1.844	1.690	1.703	1.70
intraring distances	distances calculated		distances calculated	distances experimental	
ipso – ortho	1.427	1.440	1.436	1.446(9)	1.423(3)
				1.405(9)	1.431(3)
ortho – meta	1.406	1.421	1.422	1.406(9)	1.424(3)
				1.407(9)	1.423(3)
meta – para	1.402	1.425	1.416	1.391(10)	1.401(3)
				1.402(10)	1.414(3)

[a] Me_3-**2** = the hypothetical trimethylcyclopentadienyl derivative of complex **2**, $[(C_5H_2Me_3\text{-}1,2,4)Fe(CH_2\text{-}Me_3)CuCl]$.

in copper complexes of N-heterocyclic carbenes (between 177 and 187 ppm) [5, 9 – 12]. The C(*ipso*) signal of copper aryl complexes can be found between 138 and 170 ppm, *e. g.* at 169 ppm for $[ArCuPPh_3]$ with Ar = 2,6-dimesitylphenyl or [(Dmp)Cu(NHC)] (Dmp = 2,6-dimethylphenyl, NHC = 1,3-diisopropyl-4,5-dimethylimidazolylidene) [5], or at 138 ppm for [(Mesityl)Cu(NHC)] with NHC the same as before [5].

In order to verify the extent of the unsymmetrical coordination and to elucidate the reasons for this distortion, DFT calculations have been carried out using the B3LYP density functional with Dunning's double zeta plus polarization basis (DZP, [13]) for chlorine, carbon and hydrogen, and a 6-311G Wachters-Hay basis (14s9p5d/9s5p3d) [14, 15] for iron and copper as included in the GAUSSIAN03 (G03) program package [16] based on the results of Schaefer III *et al.* [17] for the first row transition metallocenes.

Tables 3 and 4 show calculated charge distributions and bond lengths together with experimental bond lengths from crystal structure determinations. Very good agreement has been found for the overall structure, even the unsymmetrical coordination of the six-membered ring to iron could be verified beyond doubt by the calculation. When bulky substituents at the five-membered ring were omitted, the *ipso* carbon atom of the six-membered ring remained in the same position, but the CuCl moiety moved closer to the iron atom.

The discussion of the calculations refers to a charge and bond order analysis based on natural atomic orbitals and their occupation according to Weinhold [18, 19].

In the free phenyl anion, charges of −0.12, −0.10, and −0.14 have been calculated for the CH groups in *ortho*-, *meta*- and *para* position, respectively, while the *ipso* carbon carries −0.40 unit charges. Obviously a charge of *ca.* −0.6 is delocalized over the rest of the ring with equal parts in the σ and the π system. Thus the π system of the phenyl anion can be considered as a combination of an arene and an ylidene resonance structure (see Scheme 1), lending some carbene character to the *ipso* carbon atom. The mixing ratio has been calculated to 69 : 31. The reason for this effect is the presence of a lone pair at C(*ipso*), which destabilizes the π orbital at the same atom and thus distorts the 6π system.

Upon π coordination of a cyclopentadienyliron(II) unit to the six-membered ring the overall charge on the ring changes from −1.00 in the free phenyl anion to −0.61 in the hypothetical complex $[(C_5H_5)Fe(C_6H_5)]$. The *ipso* carbon atom of the aryl fragment now has −0.31 elemental charges, *i. e.* it contributes only −0.09 elemental charges to the net donation (see Table 4). The contribution of the five CH groups amounts to −0.31, although each group carries much less charge than the *ipso* carbon atom. Inspection of the π population of the ring shows that the π sys-

Table 4. Distribution of total charge and occupation of π orbitals[a].

	— Total charge —			— π orbital population —			
	$C_6H_5^-$	[CpFeC_6H_5]	Me_3-**2**	$C_6H_5^-$	[ClCuPh]$^-$	[CpFeC_6H_5]	[CpFeC_6H_5CuCl]
Fe		0.84	0.83				
Cu			0.69				
Cl			−0.73				
Cp		−0.23	−0.13				
C_6H_5	−1.00	−0.61	−0.70	5.99[b]	6.05[c]	5.72[d]	5.88[e]
C *ipso*	−0.40	−0.31	−0.53	0.69	0.87	0.69	0.87
RC *ortho*	−0.14	−0.09	−0.05	1.05	1.02	1.00	1.00
RC *meta*	−0.10	−0.04	−0.02	1.05	1.03	1.00	1.00
RC *para*	−0.12	−0.04	−0.03	1.10	1.07	1.03	1.02
Ylidene character (%):				31	12	29	12

[a] "RC" should be understood as the respective carbon atom (*ortho*, *meta*, or *para*) together with its H or CH_3 substituent, when total charges are listed, but only as the respective carbon atom itself, when π occupation is considered; [b] the occupation numbers do not sum up to 6.00 because of a small population of $3p$ atomic orbitals; [c] the total π electron count exceeds 6.00 because of a small π back donation from the copper atom; [d] π transfer to the iron atom occurs; [e] *cf.* remarks [b] and [c]; π black donation from the copper atom.

tem contributes 0.26 electrons of the total donation of *ca.* 0.40 electrons, but the ylide character of the ligand remains close to 30 % (mixing ratio arene / ylidene = 71 : 29).

Upon coordination of CuCl to the free phenyl anion with formation of [PhCuCl]$^-$ only a very small total donation of 0.06 electrons to the copper chloride fragment takes place, which can be separated into a σ donation of 0.12 electrons and a π back donation of 0.06 electrons mainly into the π function of the *ipso* carbon atom. The mixing ratio of the two resonance structures has changed to 88 : 12.

In the corresponding iron π complex, CuCl coordination causes nearly the same overall changes. In particular the iron charge is not affected, and the mixing ratio of the two resonance structures stays at 88 : 12.

The six-membered ring thus appears much like a phenyl anion coordinated to a practically uncharged CuCl fragment. This charge distribution indicates a stronger contribution from the metalated arene resonance structure than from the cyclohexadienyl-ylidene resonance structure.

In a formal sense the cyclopentadienyliron-stabilized six-membered ring π ligand can be derived from ferrocene, if one carbon-carbon bond is opened and a carbon atom inserted. The idea of stabilizing carbenes by electron-rich ferrocenyl substituents previously led to experiments with ferrocenyl-substituted carbenes as reactive intermediates, which dimerized or could be trapped with fullerene [20]. With their ylidene function in conjugation with a 6π system, N-heterocyclic carbenes of the imidazol-ylidene type [21] are related, and other types of N-heterocyclic carbenes are known [22 – 25], but the closest analogies to the carbocyclic system reported here are found in the cycloheptatrienylidene ligand of a catalytically useful palladium complex [26] and in related cyclopropenylidene palladium complexes published recently [27].

Conclusion

Whereas we expected, that π coordination of the cyclopentadienyliron cation to the aryl ring in the title compounds would influence the π electron distribution in favor of the ylidene resonance structure, the calculations clearly show that this resonance structure is already contributing to the electronic structure of the phenyl anion $[C_6H_5]^-$ with 31 % weight and is preserved with very little change in its hypothetical π complex [CpFeC_6H_5]. In the chloro-phenylcuprate(I) anion the ylidene resonance structure contributes 12 % weight, which remains unchanged after coordination of the cyclopentadienyliron cation. The iron fragment thus has little influence on the ylidene character, but moves closer to the carbon atoms with more densely populated π orbitals.

Experimental Section

All of the computations were carried out with the GAUSSIAN03 program by applying density functional theory (DFT) to describe correlation effects, using the B3LYP functional.

First row elements and chlorine were described by Dunning's correlation consistent double zeta plus polarization basis for DFT (cc-pVDZ), whereas the Wachters-Hay 6-311G basis was used for the first row transition elements Fe and Cu. Charge distributions were taken from a natural population analysis.

The preparation of complexes **1** – **3** was carried out in a glove box from MBraun, Garching, equipped with a gas purification system and filled with argon.

Mesityl-tri(*tert*-butyl)cyclopentadienyliron(II) (**1**) was prepared as described before [1].

*1,2,4-Tri(tert-butyl)cyclopentadienyliron($\mu,\eta^5:\eta^1$-1,3,5-trimethylhexadienyl-6-ylidene)copper(I) chloride (**2**)*

Copper(I)chloride (46 mg, 0.47 mmol) and complex **1** (190 mg, 0.47 mmol) were stirred in tetrahydrofuran (5 mL) at ambient temperature for 1 d. The red mixture was subjected to centrifugation, and the solution was evaporated to dryness. The crude product was washed with two 1 mL portions of pentane, dried and extracted with dimethoxyethane (5 mL). A white precipitate was removed by centrifugation, and the solvent was evaporated *in vacuo* to afford **2** as a purple, microcrystalline solid (101 mg, 0.20 mmol, 43 %), m. p. 155 °C. – Analysis for $C_{26}H_{40}ClCuFe$ (507.45): calcd. C 61.54, H 7.95; found C 61.50, H 8.24. – ^{1}H NMR (400 MHz, 298 K, C_6D_6): δ = 5.14 (2H, Cp ring H), 3.79 (s, 2H, *meta* H), 2.62 (s, 3H, *para* CH_3), 1.89 (s, 6H, *ortho* CH_3), 1.40 (s, 18H, $C(CH_3)_3$), 1.14 (s, 9H, $C(CH_3)_3$). – $^{13}C\{^1H\}$ NMR (100 MHz, 298 K, C_6D_6): δ = 163.3 (1C, *C*-Cu), 109.7 (1C, C4, Cp ring), 103.7 (2C, *ortho C*-Me), 101.4 (2C, C1/C2, Cp ring), 95.2 (1C, *para C*-Me) 85.4 (2C, *meta C*-H), 70.5 (2C, C3/C5, Cp ring), 33.9 (6C, *C*H_3, ^{t}Bu), 32.8 (2C, *C*Me_3), 31.3 (3C, *C*H_3, ^{t}Bu), 30.9 (1C, *C*Me_3), 30.9 (1C, *para C*H_3), 20.9 (2C, *meta C*H_3).

*1,2,4-Tri(tert-butyl)cyclopentadienyliron($\mu,\eta^5:\eta^1$-1,3,5-trimethylhexadienyl-6-ylidene)copper(I) bromide (**3**)*

To a solution of **2** (51 mg, 0.10 mmol) in tetrahydrofuran (2 mL) mesitylmagnesium bromide was added (30 mg, 0.10 mmol), and the mixture was stirred at r. t. for 12 h. Workup as described for complex **2** yielded **3** (35 mg, 63 μmol, 63 %) as a red powder. – Analysis for $C_{26}H_{40}BrCuFe$ (551.90): calcd. C 56.58, H 7.31; found C 55.64, H 6.89. – ^{1}H NMR (400 MHz, 298 K, C_6D_6): δ = 4.87 (2H, Cp ring H), 3.57 (s, 2H, *meta* H), 2.39 (s, 3H, *para* CH_3), 2.92 (s, 6H, *ortho* CH_3), 1.37 (s, 18H, $C(CH_3)_3$), 1.22 (s, 9H, $C(CH_3)_3$).

Crystal structure determination

Details regarding the crystal structure determinations have been listed in Table 1. CCDC 699662 and 699663 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.

Acknowledgements

This work was funded by the Deutsche Forschungsgemeinschaft (DFG grant Si 366/9-1 and 9-2) and presented in part at the 227. ACS National Meeting on April 1, 2004, in Anaheim [2]. The authors thank Dr. G. Hornung for acquisition of mass spectra.

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