High-spin Cyclopentadienyl Complexes, Part 6. σ/π-Rearrangement of Aryl Ligands Connected to Cyclopentadienyliron Fragments

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

Dimeric tri(*tert*-butyl)cyclopentadienyliron(II) bromide $[Cp'''Fe(\mu\text{-}Br)]_2$ (**1**) reacts with phenylmagnesium bromide to give the dinuclear di(cyclohexadienylidene) complex $[(Cp'''Fe)_2(\mu,\eta^5{:}\eta^5\text{-}H_5C_6{=}C_6H_5)]$ (**2**), and with mesitylmagnesium bromide either to the dinuclear complex $[Cp'''Fe(\mu,\eta^5{:}\eta^1\text{-}C_6H_2Me_3)Fe(Br)Cp''']$ (**3**) or to the mononuclear mesityl complex $[Cp'''FeC_6H_2Me_3]$ (**4**), depending on the reaction conditions. The mesityl complex **4** undergoes rearrangement and adds *via* the mesityl *ipso* carbon atom to bromide **1** with formation of **3**. A similar reaction occurs with the nickel analog of bromide **1**. In the latter case, however, mesityl is replaced by tolyl during reaction in toluene, with phenyl in benzene, and remains unchanged if the reaction is carried out in pentane solution. An electrophilic attack at the arene solvent used is discussed for the exchange reaction. For the crystallographically characterized complexes **3** and $[Cp'''Fe(\mu,\eta^1{:}\eta^5\text{-}C_6H_4Me)Ni(Br)Cp''']$ (**5**) with a *meta*-tolyl ligand a significant deviation of the $Cp'''Fe$ fragment from a symmetrical position above the six-membered ring ligand raises questions regarding a possible contribution of a cyclohexadienylylidene resonance structure.

Key words: Crystal Structure, Dienyliron Complexes, Aryl Complexes, Carbene Complexes, Tri(*tert*-butyl)cyclopentadienyl

Introduction

The dinuclear iron compound $[\{^4CpFe(\mu\text{-}Br)\}_2]$ [1] $\{^4Cp = \eta^5\text{-}C_5H(CHMe_2)_4\}$ is one of very few high-spin cyclopentadienyl complexes of iron(II) [2] and exhibits a high reactivity towards nucleophilic reagents. The structural diversity of complexes formed in reactions of the dimer $[\{Cp'''Fe(\mu\text{-}Br)\}_2]$ (**1**) with both substituted and unsubstituted phenolates [3], especially the oxocyclohexadienyl complex formed by π coordination of 2,6-di(*tert*-butyl)phenolate, stimulated us to carry out similar reactions with aryl anions.

Results and Discussion

When tri(*tert*-butyl)cyclopentadienyliron(II) bromide (**1**) was reacted with phenylmagnesium bromide in tetrahydrofuran, dark-blue blocks of the dinuclear complex $[\{Cp'''Fe\}_2(\mu,\eta^5{:}\eta^5\text{-}H_5C_6{=}C_6H_5)]$ (**2**) could be isolated in good yield. While coupling of two phenyl anions to a dianionic dicyclohexadienylidene ligand has rarely been observed in transition metal chemistry [4, 5], the coupling product **2** is analogous to the known dinuclear pentamethylcyclopentadienyliron complex $[\{Cp^*Fe\}_2(\mu,\eta^5{:}\eta^5\text{-}H_5C_6{=}C_6H_5)]$ obtained by two-electron reduction of the dicationic biphenyl complex $[\{Cp^*Fe\}_2(\mu,\eta^6{:}\eta^6\text{-}H_5C_6\text{-}C_6H_5)]^{2+}$ [6]. Full characterization of **2** along with an investigation of its behavior under mass spectrometry conditions and theoretical calculations will be the subject of a separate communication [7].

In order to suppress the carbon-carbon coupling reaction by steric protection, mesitylmagnesium bromide was selected for reactions with **1**. A test reaction was carried out by addition of solid mesitylmagnesium bromide to a toluene solution of **1** which yielded a complex product mixture, from which only one compound could be isolated in low yield as black crystals. The paramagnetic product was characterized by C, H analysis and ^{1}H NMR spectra and identified by crystal structure analysis as $[(C_5H_2R_3)Fe(\mu,\eta^5{:}\eta^1\text{-}C_6H_2Me_3)FeBr(C_5H_2R_3)]$ (**3**) (R = CMe_3), a rare example with cyclopentadienyliron(II) moieties of differ-

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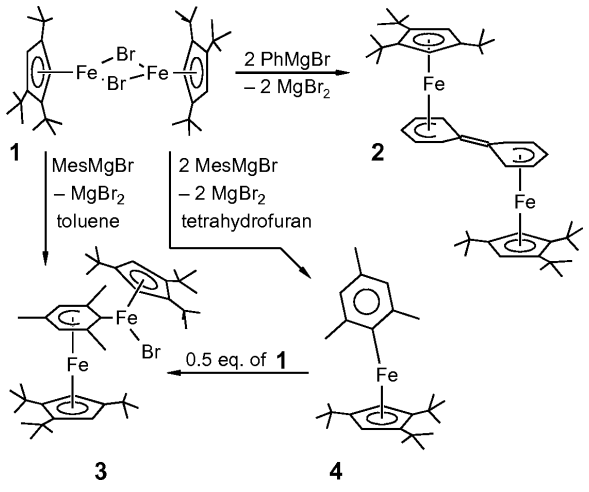


Scheme 1. Formation of complexes **2**–**4** from **1**.

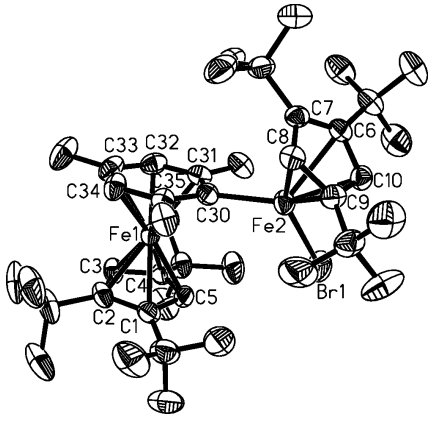


Fig. 1. Crystal structure of the diiron complex **3**. Selected distances (Å) and angles (deg): Fe1–C1 2.117(3), Fe1–C2 2.116(3), Fe1–C3 2.058(2), Fe1–C4 2.113(2), Fe1–C5 2.057(3), Fe1···C30 2.210(2), Fe1–C31 2.135(3), Fe1–C32 2.086(3), Fe1–C33 2.112(3), Fe1–C34 2.099(2), Fe1–C35 2.138(2), Fe2–C6 2.395(3), Fe2–C8 2.424(3), Fe2–C9 2.303(2), Fe2–C10 2.251(2), Fe2–C30 2.128(2), Fe2–Br1 2.4824(5), C30–C31 1.428(4), C31–C32 1.414(4), C32–C33 1.398(4), C33–C34 1.392(4), C34–C35 1.420(3), C35–C30 1.422(4), Fe1–Cp ring plane (C1–C5) 1.71, Fe1–ring plane (C30–C35) 1.59, Fe2–Cp ring plane (C6–C10) 2.04; Br1–Fe2–C30 107.5(1).

ent spin states in one molecule [8] (Scheme 1). This is obvious from the iron-Cp‴ ring distances in the crystal structure of **3** (Fig. 1, Table 1), which is 1.71 Å for the sandwich substructure, and 2.04 Å for the iron bromide fragment with 16 valence electrons. The latter value is unprecedented for cyclopentadienyliron complexes, and the difference between both numbers resembles Mn-ring plane distances in the low-spin and high-spin isomers of 1,1′-dimethylmanganocene (1.73 *vs.* 2.05 Å [9]).

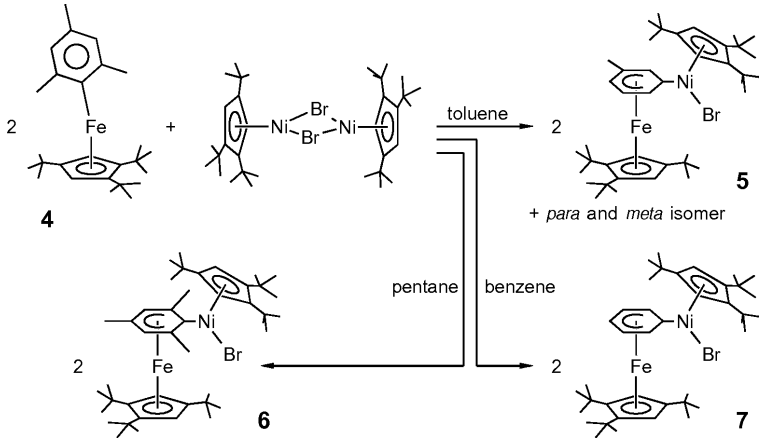
Table 1. Crystal structure data for **3**–**5**.

	3	**4**	**5**
Formula	$C_{43}H_{69}BrFe_2$	$C_{26}H_{40}Fe$	$C_{41}H_{65}BrFeNi$
M_r	777.59	408.43	752.40
Crystal size, mm^3	0.44 × 0.35 × 0.20	0.30 × 0.25 × 0.20	0.50 × 0.50 × 0.20
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$I2/m$	$P2_1/n$
a, Å	10.2833(6)	8.6216(5)	14.0239(10)
b, Å	24.7872(18)	64.711(6)	17.757(1)
c, Å	6.7515(9)	11.2537(7)	16.5828(12)
β, deg	101.677(6)	106.804(7)	106.030(8)
V, Å^3	4181.5(4)	6010.5(7)	3968.9(5)
Z	4	10	4
D_{calcd}, g cm^{-3}	1.235	1.128	1.259
μ(MoK_α), cm^{-1}	16.76	6.35	18.72
F(000), e	1656	2220	1600
hkl range	±12, ±30, ±20	$-9 \le h \le +10$ $-78 \le k \le +78$ $-13 \le l \le +13$	±18, ±23, ±21
$((\sin\theta)/\lambda)_{max}$, Å^{-1}	0.6097	0.6097	0.6577
Refl. measured	58437	23907	68286
Refl. unique	7599	9842	9465
R_{int}	0.1216	0.0808	0.0875
Param. refined	436	655	416
$R(F)$ / $wR(F^2)$[a] (all refl.)	0.0610 / 0.0817	0.0898 / 0.1851	0.0610 / 0.0888
GoF (F^2)[b]	0.864	1.018	0.911
$\Delta\rho_{fin}$ (max/min), e Å^{-3}	0.35/−0.22	1.67/−0.48	0.80/−0.43

[a] $R_1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$, $wR_2 = \Sigma[w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (AP)^2 + BP]$ 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.

The *ipso* carbon atom of the former mesityl ligand (C30) displays a rather weak interaction with Fe1 and establishes an η^1-coordination to Fe2. The C30–Fe2 distance of 2.128(2) Å found for **3** is comparable to Fe–C distances of 2.147(7) and 2.104(6) Å found for $[Fe(1\text{-naphthyl})_4]^{2-}$ [10] as an example for high-spin Fe(II)-aryl bond lengths, but compares also well with the 2.13/2.14 Å Fe–C distances found for the paramagnetic *N*,*N*′-diisopropyl-dimethylimidazolylidene complex $[FeCl_2(NHC)_2]$ [11]. Low-spin iron complexes with Fischer carbene ligands have much shorter Fe–C bonds and are not comparable [12, 13].

The location of Fe1 above the six-membered ring (C30–C35 are coplanar with deviations of less than 0.01 Å) leads to distinctly different Fe1–C distances, the longest being Fe1···C30 with 2.210(2) Å. The three Fe–C bonds to carbon atoms on the opposite side of the ring (C32–C34) are significantly shorter



Scheme 2. Formation of complexes **5** – **7** from **4** and $[Cp'''Ni(\mu\text{-}Br)]_2$.

(2.086(3) – 2.112(3) Å), and the two *ortho* neighbors of C30 reside at Fe1–C distances of 2.135(3) and 2.138(2) Å (Fig. 1). Moreover, the projection of Fe1 onto the ring plane is much closer to C33 (*para*, 1.379 Å) than to C30 (*ipso*, 1.525 Å).

The most acute C–C–C angle in the six-membered ring is at the *ipso* position (C30, 115.46°, average of the other five C–C–C angles 120.90°). The longest C–C bonds are also found at C30 (C30–C31 and C30–C35 with 1.428(4)/1.422(4) Å), and the two shortest C–C bonds are those connecting *para* C33 with its neighbors (1.398(4)/1.391(4) Å).

A magnetic moment of 2.95 B. M. in solution [14] corresponding to two unpaired electrons indicates an intermediate spin situation [15].

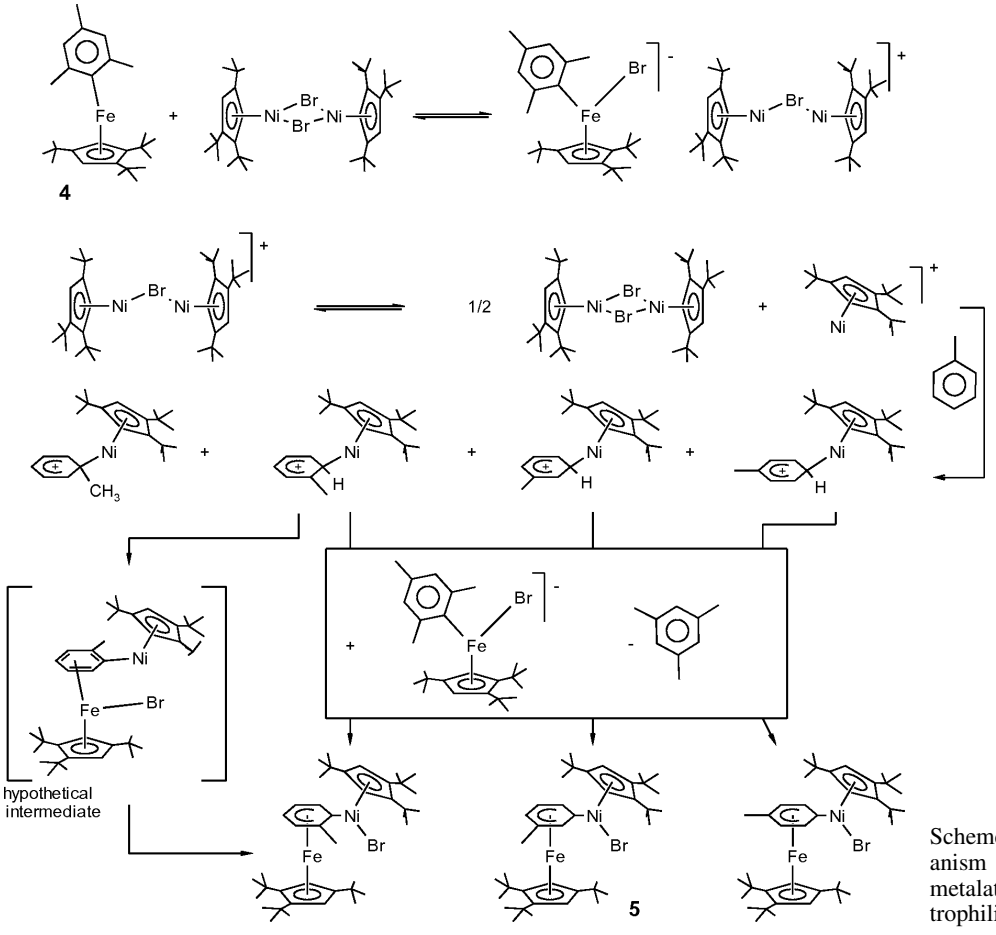
The formation of dinuclear complexes **2** and **3** requires a reactive intermediate formed from bromide **1** and the phenyl- or mesitylmagnesium reagent. In an attempt to isolate this reactive intermediate, the reaction of **1** with one equivalent of mesitylmagnesium bromide was carried out in tetrahydrofuran by rapid addition of a solution of mesitylmagnesium bromide to a solution of **1**. The σ-mesityl complex $[(C_5H_2R_3)FeC_6H_2Me_3]$ (**4**) could be isolated in high yield from the reaction solution (Scheme 1). The light-green crystals of **4** gave rather poor diffraction data which allowed identification of **4** as a monomeric σ-mesityl complex as drawn in Scheme 1, but do not permit a discussion of structural details.

A magnetic moment of 5.50 B. M. in the solid state confirmed the Fe(II) high-spin configuration with four unpaired electrons. In EI mass spectra of **4** the molecular ion (m/z = 408.2) was found with 12 % intensity. The parent peak corresponded to loss of one methyl group (m/z = 393.2). A control reaction of the mesityl complex **4** with the bromo complex **1** in toluene afforded a 57 % yield of the paramagnetic diiron complex **3** (Scheme 1), which was identified by its proton NMR signals (see Experimental Section).

When the mesityl complex **4** was reacted with $[\{Cp'''Ni(\mu\text{-}Br)\}_2]$ [16] (the nickel analog of **1**) in toluene (Scheme 2), the red-brown reaction solution turned purple within 48 h at r. t. A proton NMR spectrum of the crude product revealed a mixture of three diamagnetic complexes with similar and partially overlapping sets of signals. By X-ray crystal structure analysis one of the products could be shown to be the iron/nickel analog **5** of the diiron species **3** with one significant difference: Instead of the expected complex $[Cp'''Fe(C_6H_2Me_3)NiBrCp''']$ with a bridging mesityl unit, the crystalline component contained only one methyl group on the bridging six-membered ring ligand. Since the reagents used had been tested for tolyl impurities with negative result, the toluene solvent is proposed as source of the new ligand, whose metalation most likely follows an electrophilic route (Scheme 3).

In pentane the reaction proceeds as expected. If toluene or benzene are used as solvents, the mesityl ligand is replaced by a tolyl or phenyl moiety, respectively. For a mechanistic interpretation see Scheme 3.

The 14 valence electron iron mesityl complex **4** abstracts a bromide ligand from $[\{Cp'''Ni(\mu\text{-}Br)\}_2]$ with formation of a ferrate $[\mathbf{4}\text{-}Br]^-$. The ensuing cationic nickel electrophile attacks the toluene solvent, where four different isomers are possible. Attack in *ortho* po-



Scheme 3. Proposed mechanism for arene solvent metalation through an electrophilic attack.

sition is sterically hindered, the *para* position is disfavored by statistics, therefore attack in *meta* position is most prominent. The resulting complex is deprotonated by [**4**-Br]$^-$ with liberation of mesitylene. Attack at the *ipso* carbon of toluene is not only sterically hindered, but has probably no consequence other than the reverse reaction. A bromide migration from the iron center of the putative intermediate to nickel affords the observed products.

When the same reaction was carried out in pentane solution, [Cp‴Fe($C_6H_2Me_3$)NiBrCp‴] (**6**) could be isolated in 53 % yield. A test reaction in benzene solution afforded the C_6H_5 derivative [Cp‴Fe(C_6H_5)-NiBrCp‴] (**7**).

NMR spectra of **6** and **7** show the expected signal patterns for two Cp‴ ligands each, and the signals for the six-membered ring, whose *ipso*-C signals are found at 165 (**6**) and 160 (**7**) ppm. ^{13}C NMR signals of the carbene C atom of N-heterocyclic carbene ligands in cyclopentadienylnickel complexes [CpNi-(NHC)X] (X = Br, I; NHC = 2,5-di- or 2,3,4,5-tetraalkyl-imidazolylidene ligand) are found at 179 – 180 ppm [17], whereas the signal of the mesityl *ipso*-C atom in the dimethylaminoethylcyclopentadienyl complex [($H_4C_5CH_2CH_2NMe_2$)Ni($C_6H_2Me_3$-2,4,6)] appears at 125.4 ppm [18].

The crystal structure of **5** shows that the sandwich part of the molecule is very similar to the corresponding part of the diiron complex **3** (Fig. 2). The projection of Fe1 onto the planar six-membered ring lies much closer to *para* C33 (1.365 Å) than to *ipso* C30 (1.570 Å). The effect is even stronger than for complex **3**, probably because of an increased steric interactions with the second metal fragment due to the short bond Ni–C30 (1.89 Å). This value compares well with 1.92 Å for the 1,3-dimesitylimidazol-2-ylidene complex [(C_5H_5)NiCl{C($NMes)_2(CH)_2$}] [19] and with 1.89 Å for the Fischer carbene complex [($C_2H_4)_2$-

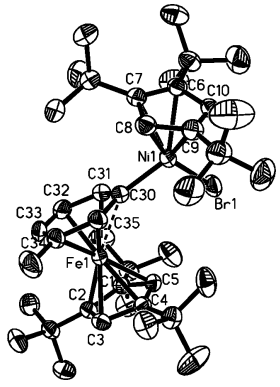


Fig. 2. Crystal structure of the heterodinuclear complex **5**. Selected distances (Å) and angles (deg): Fe1–C1 2.090(2), Fe1–C2 2.083(2), Fe1–C3 2.055(2), Fe1–C4 2.093(2), Fe1–C5 2.055(2), Fe1–C30 2.231(2), Fe1–C31 2.106(2), Fe1–C32 2.079(2), Fe1–C33 2.093(2), Fe1–C34 2.102(2), Fe1–C35 2.106(2), Ni1–C6 2.224(2), Ni1–C7 2.177(2), Ni1–C8 2.059(2), Ni1–C9 2.173(2), Ni1–C10 2.125(2), Ni1–C30 1.892(2), Fe1–Cp ring plane (C1–C5) 1.68, Fe1–dienyl plane (C31–C35) 1.57, C30–dienyl plane 0.09, Ni1–dienyl plane 0.55, Ni1–Cp ring plane (C6–C10) 1.78; C30–Ni–Br 98.8(1).

Ni{CPh(NMeCMe$_3$)}] [20], but also with 1.91 Å for the tris(phenylpyrazolyl)nickel(II) aryl complex [Tp^{Ph}Ni(*o*-tolyl)PPh$_3$] [21].

The bridging six-membered rings seen in the diiron complex **3** and in the iron/nickel complex **5** can be considered as metalated arene ligands. The sandwich part is then regarded as a [CpFe(arene)]$^+$ complex, whose arene moiety is part of an anionic complex, *e. g.* the nickelate(II) moiety [Cp‴NiBr(C$_6$H$_5$)]$^-$ of complex **7**. Arguments for this interpretation of the experimental results are the planarity of the six-membered ring and the short C–C bonds (1.407(3)/1.411(3) Å) between the *ipso* carbon atom and its neighbors.

From another point of view, the bridging ring of the complex is a pentadienyl anion, whose ends are linked together by a carbene function to a cyclohexadienylylidene ligand. This view finds some support in the unsymmetric coordination of Fe1 to the six ring carbon atoms and in the pattern of intra-ring C–C distances and C–C–C angles. The π electrons of the pentadienyl part of a half-open ferrocene provide resonance stabilization for the carbene function bridging the ends of the pentadienyl moiety. A parallel to N-heterocyclic carbenes (NHC) may be drawn, where the carbene is stabilized by π donation from the nitrogen lone pairs as discussed by Frenking *et al.* [22]. The parallel does not extend, however, to the pull-push situation of NHCs including the σ acceptor behavior of the hetero atoms [23], but a structural analogy can be drawn according to which the dinuclear coupling product **2** corresponds to NHC dimers with a C=C double bond, the oxocyclohexadienyl complex [Cp‴Fe(η^5-OC$_6$^{t}Bu$_2$H$_3$)][3] to urea derivatives, and the complexes **3** as well as **5** – **7** to metal complexes of N-heterocyclic carbenes.

It has to be admitted, however, that steric interactions between the two complex fragments involved could be responsible for the dislocation of Fe1 out of a symmetric coordination to the six-membered ring ligand. This possibility weakens the strongest argument for the carbocyclic carbene character of the bridging six-membered ring and calls for complexes with less bulky metal fragments coordinating to the *ipso* carbon atom of the same sandwich moiety. Such complexes and theoretical calculations concerning structure and bonding will be discussed in the following publication of this issue [24].

Experimental Section

*Tri(tert-butyl)cyclopentadienyliron bromide dimer (**1**)*

To a solution of FeBr$_2$(DME) (1.66 g, 4.6 mmol) in DME (30 mL) [25] a solution of NaC$_5$H$_2$(CMe$_3$)$_3$ [26] (1.17 g, 4.6 mmol) was added dropwise during 30 min at −30 °C. The dark-green mixture was stirred for another 30 min at −30 °C and then allowed to warm to ambient temperature. Removal of the solvent *in vacuo* and extraction of the solid residue with pentane (20 mL), followed by centrifugation and evaporation gave 1.19 g (1.61 mmol, 70 %) of an orange, microcrystalline solid. – Anal. for C$_{34}$H$_{58}$Br$_2$Fe$_2$: calcd. C 55.31, H 7.92; found C 54.70, H 7.95. – ^{1}H NMR (400 MHz, 298 K, C$_6$D$_6$): δ = 47.2 (br, 4H, ring-H, $\nu_{1/2}$ = 974 Hz), −7.49 (br, 36H, CH$_3$), −12.64 (br, 18H, CH$_3$).

*Tri(tert-butyl)cyclopentadienyliron(μ,η^5:η^1-1,3,5-trimethylcyclohexadienyl-6-ylidene)bromotri(tert-butyl)cyclopentadienyliron (**3**)*

To an orange-red solution of **1** (228 mg, 0.31 mmol) in toluene (5 mL) solid **4** (250 mg, 0.61 mmol) was added, and the solution was stirred for 12 h at ambient temperature. After centrifugation the black solution was evaporated to dryness. The black residue was washed with a small amount of pentane and dissolved in a minimum amount of toluene. Slow evaporation at ambient temperature gave 274 mg (0.34 mmol, 57 %) of **3** as a black, microcrystalline solid. – Anal. for C$_{43}$H$_{69}$BrFe$_2$: calcd. C 66.47, H 8.96; found C 64.90, H 9.10. – ^{1}H NMR (400 MHz, 298 K, C$_6$D$_6$): δ = 25.7 ($\nu_{1/2}$ = 183 Hz), 9.7 ($\nu_{1/2}$ = 131 Hz), 7.7, 4.86 ($\nu_{1/2}$ = 334 Hz), −18.7 ($\nu_{1/2}$ = 392 Hz).

*Mesityl{tri(tert-butyl)cyclopentadienyl}iron (**4**)*

To a forest-green solution of **1** (300 mg, 0.41 mmol) in tetrahydrofuran (5 mL) a solution of $C_6H_2Me_3MgBr(THF)$ (240 mg, 0.82 mmol) in tetrahydrofuran (5 mL) was added dropwise, and the mixture was stirred for *ca.* 5 min at ambient temperature. The solution turned dark green and was evaporated to dryness. Extraction of the solid residue with pentane (20 mL), centrifugation and reduction of the extract in volume to *ca.* 2 – 3 mL produced light-green crystals of **4** upon standing at ambient temperature for 1 d in 210 mg (0.51 mmol, 63 %) yield. – ^{1}H NMR (400 MHz, 298 K, C_6D_6): δ = 204.6 ($\nu_{1/2}$ = 859 Hz), 198.3 ($\nu_{1/2}$ = 660 Hz), 98.5 ($\nu_{1/2}$ = 1702 Hz), −32.9 (2 CMe_3), −34.8 (CMe_3). Satisfactory elemental analyses could not be obtained due to slow decomposition of pentane solutions and of the solid at r. t., and due to the extreme air sensitivity of the compound.

*Tri(tert-butyl)cyclopentadienyliron($\mu,\eta^5:\eta^1$-3-methylcyclohexadienyl-6-ylidene)bromotri(tert-butyl)cyclopentadienylnickel (**5**)*

To a dark-brown solution of $[Cp'''Ni(\mu\text{-}Br)]_2$ (230 mg, 0.31 mmol) in toluene (5 mL) solid **4** (250 mg, 0.61 mmol) was added, and the solution was stirred for 48 h at ambient temperature. After centrifugation the purple solution was evaporated to dryness. The dark, waxy residue was washed with a small amount of pentane and dissolved in a minimum amount of toluene/pentane (1 : 1). Slow evaporation at ambient temperature gave 271 mg (0.36 mmol, 59 %) of a mixture of isomers, which could not be separated by repeated crystallization. A single crystal of **5** could be selected from the mixture. – Anal. for $C_{41}H_{65}BrFeNi$: calcd. C 65.45, H 8.71; found C 64.10, H 8.89.

*Tri(tert-butyl)cyclopentadienyliron($\mu,\eta^5:\eta^1$-1,3,5-trimethylcyclohexadienyl-6-ylidene)bromotri(tert-butyl)cyclopentadienylnickel (**6**)*

To a dark-brown solution of $[Cp'''Ni(\mu\text{-}Br)]_2$ (230 mg, 0.31 mmol) in pentane (5 mL) solid **4** (250 mg, 0.61 mmol) was added, and the solution was stirred for 12 h at ambient temperature. The purple precipitate formed during this time was isolated by centrifugation, washed with pentane (2 mL) and dried *in vacuo*. Recrystallization from toluene/pentane (1 : 1, 2 mL) afforded **6** as a purple, microcrystalline solid (252 mg, 0.32 mmol, 53 %). – Anal. for $C_{43}H_{69}BrFeNi$: calcd. C 66.18, H 8.91; found C 65.17, H 8.87. – ^{1}H NMR (400 MHz, 298 K, C_6D_6): δ = 5.10 (br, 2H, Cp ring H), 5.03 (s, 2H, *meta* H), 4.41 (br, 2H, Cp ring H), 3.58 (2, 6H, *ortho* CH_3), 1.63 (br, 18H, $C(CH_3)_3$), 1.39 (s, 18H, $C(CH_3)_3$), 1.11 (s, 18H, $C(CH_3)_3$). The signal of the *para* CH_3 substituent may be hidden under the signal at 1.63 ppm, which is a superposition of two CMe_3 signals.

*Tri(tert-butyl)cyclopentadienyliron($\mu,\eta^5:\eta^1$-cyclohexadienyl-6-ylidene)bromotri(tert-butyl)cyclopentadienylnickel (**7**)*

To a dark-brown solution of $[Cp'''Ni(\mu\text{-}Br)]_2$ (46 mg, 0.062 mmol) in benzene (2.5 mL) a solution of **4** (50 mg, 0.12 mmol) in benzene (2.5 mL) was added, and the solution was stirred for 72 h at ambient temperature. After centrifugation the purple solution was evaporated to dryness. The dark residue was washed with a small amount of pentane and dissolved in deuterobenzene for characterization by ^{1}H NMR (600 MHz, 298 K, C_6D_6): δ = 6.65 ("d", 2H, *ortho* H), 4.88 ("t", 2H, *meta* H), 4.86 (s, 2H, FeCp, ring H), 4.64 ("t", 1H, *para* H), 4.52 (s, 2H, NiCp, ring H), 1.69 (br, 9H, $C(CH_3)_3$), 1.49 (s, 18H, $C(CH_3)_3$), 1.34 (s, 9H, $C(CH_3)_3$), 1.25 (s, 18H, $C(CH_3)_3$). – ^{13}C NMR: (150 MHz, C_6D_6): δ = 159.7 (s, C-*ipso*), 128.6 (*o*-Ph), 124.2 (4-*C*-^{t}Bu; NiCp'''), 116.7 (Ni-1,2-*C*-^{t}Bu), 101.7 (4-*C*-^{t}Bu; FeCp'''), 99.7 (1,2-*C*-^{t}Bu; FeCp'''), 85.3 (*m*-Ph), 81.2 (3,5-*C*-H; NiCp'''), 80.5 (*p*-Ph), 71.0 (3,5-*C*-H; FeCp'''), 33.7 (1,2-C(*C*H_3)$_3$), 33.6 (1,2-C(*C*H_3)$_3$), 33.1 (1,2-*C*(CH_3)$_3$), 32.8 (1,2-*C*(CH_3)$_3$), 32.5 (4-C(*C*H_3)$_3$), 31.9 (4-C(*C*H_3)$_3$), 31.7 (4-*C*(CH_3)$_3$), 31.3 (4-*C*(CH_3)$_3$).

Crystal structure determination

Details of the crystal structure determinations have been listed in Table 1. CCDC 699659 and 699660 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.

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