Reactions of complex ligands part 106. Heterobimetallic fused arenes: Chromium-templated benzannulation of a ferrocene-type metal carbene ☆

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Abstract

The heterobimetallic iron cyclopentadienyl(indenyl)carbene chromium complex **3** was synthesized from 5-bromoindene by via metalation with $C_5H_5Fe(CO)_2I$, photodecarbonylation and chromium carbene functionalization of the π-bromoindenyl(cyclopentadienyl)iron intermediate **2**. The chromium-templated benzannulation with 3-hexyne afforded *syn-* and *anti-*diastereomers of heterobimetallic hydroquinoid arene $Cr(CO)_3$ complexes **4a** and **4b** which were characterized by X-ray, spectroscopic and electrochemical means.
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1. Introduction

Due to its structural peculiarity, its redox properties and its ready availability the ferrocene moiety plays a major role in both organometallic chemistry, stereoselective organic synthesis and material science [2]. The chiral information provided by the Togni ligand is widely exploited in asymmetric hydrogenation and C–C bond formation [3]. Ferrocene building blocks are prominent organometallic features superconductors [4], magnetic materials [5], and devices in nanodimensions [6]. The ferrocene unit has been incorporated in redox-active metal carbenes [7]; moreover, it has been disclosed as chemodirecting substitution pattern in chromium-templated cyclization reactions: upon reaction with alkynes (alkoxy)ferrocenylcarbene chromium complexes

in which the ferrocene moiety is directly connected to the carbene carbon atom prefer an alkyne, carbene and CO cyclization mode to form the furan skeleton over the customary benzannulation to chromium-coordinated hydroquinones [8]. In this paper, we report on the synthesis and structure of heterobimetallic fused arenes resulting from the benzannulation of ferrocene-type chromium carbenes.

2. Results and discussion

The synthesis of chromium carbene **3** bearing a cyclopentadienyl–indenyl sandwich skeleton starts from 5-bromoindene [9] which is metalated by cyclopentadienyl(dicarbonyl)iron iodide to give the σ-indenyl iron complex **1** which is subsequently rearranged upon photodecarbonylation to the bromoindenyl sandwich complex **2**. Lithiation with *tert*-butyl lithium, addition of hexacarbonyl chromium followed by *O*-alkylation

of the resulting acyl chromate affords the cyclopentadie-nyl–iron–indenylcarbene chromium complex **3** as a dark-green solid (Scheme 1). Substitution of the standard alkylation reagent trimethyloxonium tetrafluoroborate by methyl triflate increases the yield of the Fischer carbene to 65%.

The bromoindenyl(cyclopentadienyl)iron complex **2** was characterized by X-ray. It forms monoclinic crystals in which the five-membered rings of both arene ligands deviate by 9° from their eclipsed conformation (Fig. 1). The iron center displays a linear coordination with respect to the central positions of the cyclopenta-dienyl and the five-membered indenyl ring as indicated by an angle of 179° and Fe–C distances ranging from 203 to 209 pm.

Upon reaction with 3-hexyne the ferrocene-type chromium carbene **3** undergoes benzannulation as indicated by a colour change of the solution from deep green to deep red. According to the NMR-analysis of the crude reaction mixture two diastereomers differing in their relative orientation of both metal fragments have been formed in a 1:2 ratio. Without further purification the benzannulation products were protected with *tert*-butyl-dimethylsilyl triflate leading to diastereomers **4a** and **4b** in 23% and 34% isolated yields (Scheme 2). The benzannulation is strictly regioselective; as well-known for naphthylcarbene ligands [1] only the angular annulation products are observed [10]. Selective cleavage of the Cr(CO)$_3$ fragment affords the benz[e]indenyl(cyclopentadienyl)iron complex **4c** as demonstrated for warming
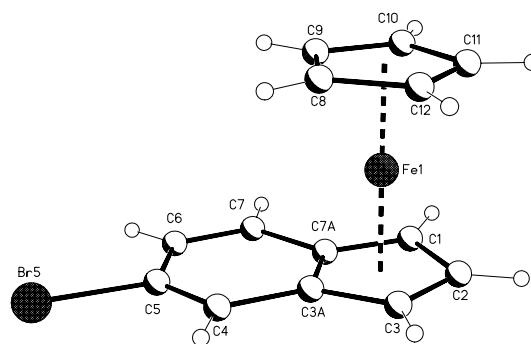

Fig. 1. Molecular structure of 5-bromoindenyl complex **2**. Selected bond lengths (pm) and angles (°): Fe···Cp: 164.8 (4); Fe···Ar^a: 167.1 (4); (Cp–Fe–Ar^a): 178.6 (3); φ[C(3)–C(3A)–C(7A)–C(7)]: 3.1 (6); φ[C(4)–C(3A)–C(7A)–C(1)]: −2.8 (7). ^{a} Ar = 5-bromoindenyl.

an *n*-Bu$_2$O-solution of the *anti* complex **4b** to 115 °C. The benzindenyl complexes were characterized by spectroscopic methods, by X-ray analysis and by cyclic voltammetry.

Crystals of benzoindenyl complexes **4a**, **4b** and **4c** suitable for X-ray analysis were grown from acetone/heptane mixtures. The *syn*-bimetallic complex **4a** crystallizes in a triclinic lattice revealing a torsion of 15° of both five-membered rings. The angle connecting the iron and the center of both five-membered rings slightly deviates from linearity (175°); the iron–carbon distances range from 203 to 212 pm. The chromium-complexed ring shows a slight deviation from planarity. While the Cr–C(1) bond is elongated to 233 pm
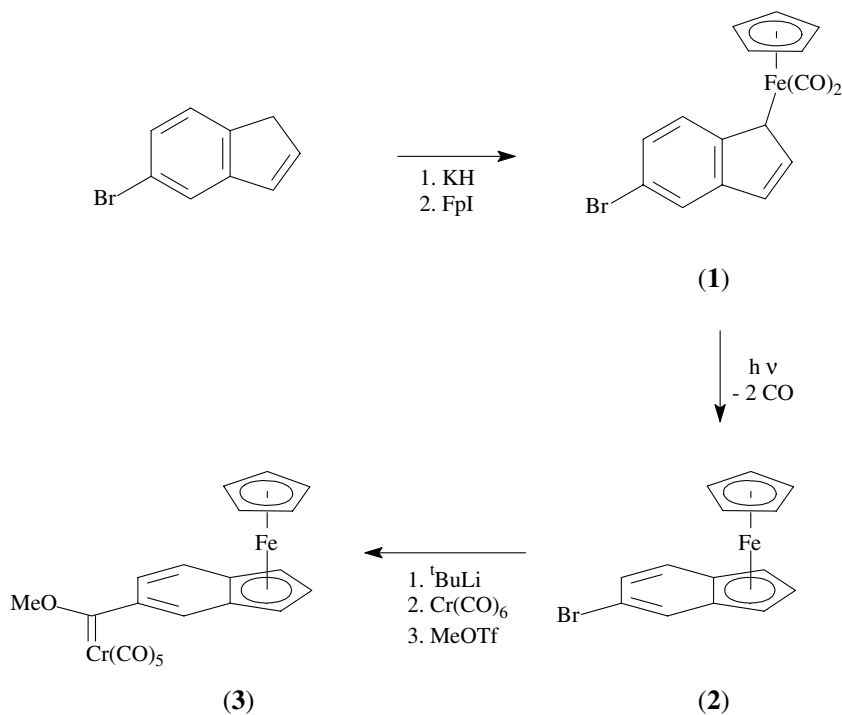
Scheme 1. Synthesis of 5-bromoindenyl(cyclopentadienyl)iron (**2**) and chromium carbene complex **3** (FpI = dicarbonyl(iodo)(η^5-cyclopenta-dienyl)iron).

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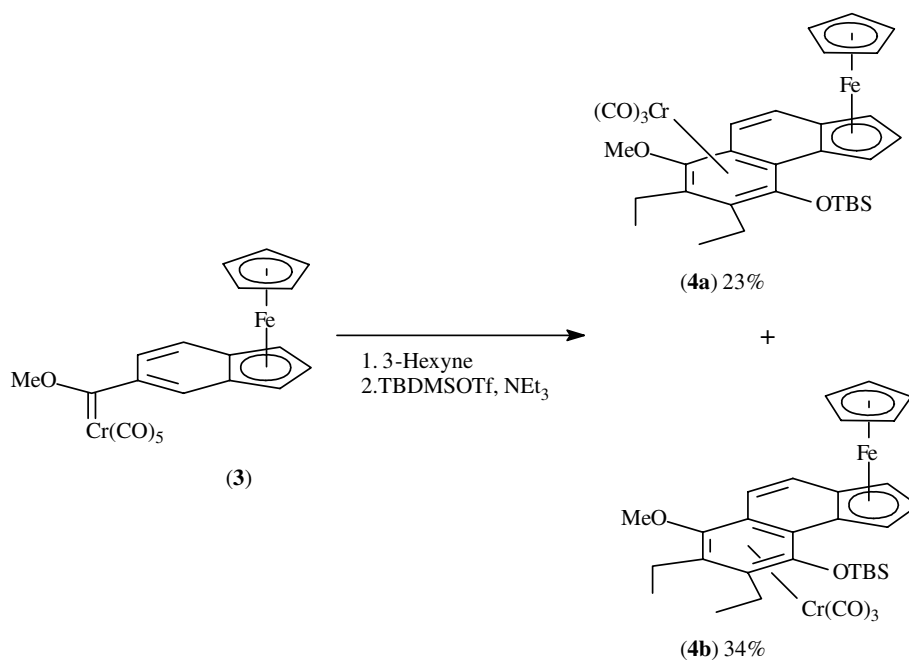
Scheme 2. Chromium-templated benzannulation of indenylcarbene complex **3**.

reflecting the slipping of C(1) out of the plane of the terminal benzene ring, the remaining Cr–C(arene) distances are shorter by 4–13 pm. The *peri*-substitution by the bulky TBDMS-protective group – and in some respect also the Cr(CO)$_3$ fragment – induce a helical twist of the tricyclic arene skeleton as indicated by a torsion angle C(9)–C(9A)–C(9B)–C(1) of 13°.

The *anti*-diastereomer **4b** crystallizes in a monoclinic lattice containing two structural isomers in a 68:32 ratio. The major isomer differs by 25° and the minor isomer by 16° from the eclipsed conformation of the two five-membered rings coordinated to the iron. The axis described by the centers of both rings and the iron is close to linear (178° and 177°); the Fe–C distances range from 201 to 207 pm. The helical twist of the benz[e]indenyl skeleton imposed by the bulky *peri*-protective group amounts to a torsion angle of the carbon atoms C(9)–C(9A)–C(9B)–C(1) of 10°. It is only slightly decreased in comparison to that of its diastereomer **4a** which might reflect the absence of relevant steric interactions arising from the *syn*-configuration of both metal fragments.

Similar structural features are encountered for benz[e]indenyl iron complex **4c** which also crystallizes in a monoclinic lattice. The ferrocene entity is characterized by a nearly linear axis defined by both ring centers and the iron atom, by Fe–C bond lengths varying from 202 to 208 pm and by a deviation from an eclipsed configuration of both five-membered rings by 13°. In comparison with the chromium tricarbonyl complexes **4a** and **4b** the torsion angle C(9)–C(9A)–C(9B)–C(1) is reduced to 6° suggesting that – in addition to the *peri*-interactions of the TBDMS-group – the coordination of the

Cr(CO)$_3$ fragment also contributes to some extent to the helical twist. The molecular structures of benz[e]indenyl complexes **4a**–**c** are presented in Figs. 2–4; selected bond lengths and angles are given in Table 1.

A comparative electrochemical study (given potentials refer to decamethylferrocenium/decamethylferrocene) based on the cyclovoltammograms of benz[e]indenyl-(cyclopentadienyl)iron **4c** and its Cr(CO)$_3$-coordinated diastereomers **4a** and **4b** (Fig. 5(b)–(d)) demonstrates the influence of both the electron-acceptor properties
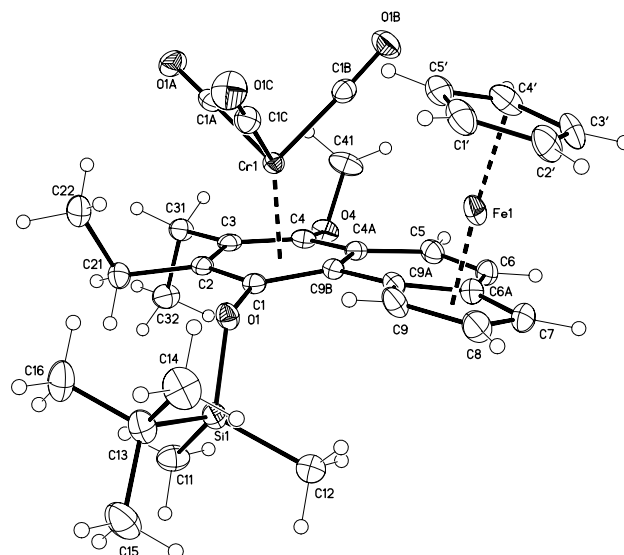
Fig. 2. Molecular structure of heterobimetallic complex **4a**.
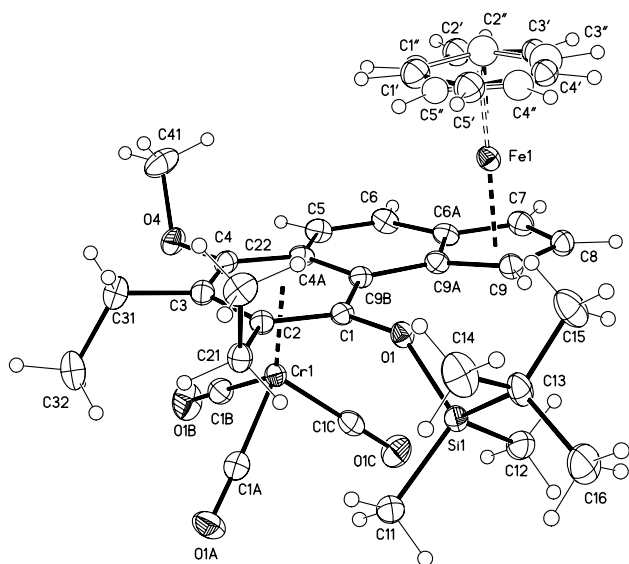
Fig. 3. Molecular structure of heterobimetallic complex **4b**.
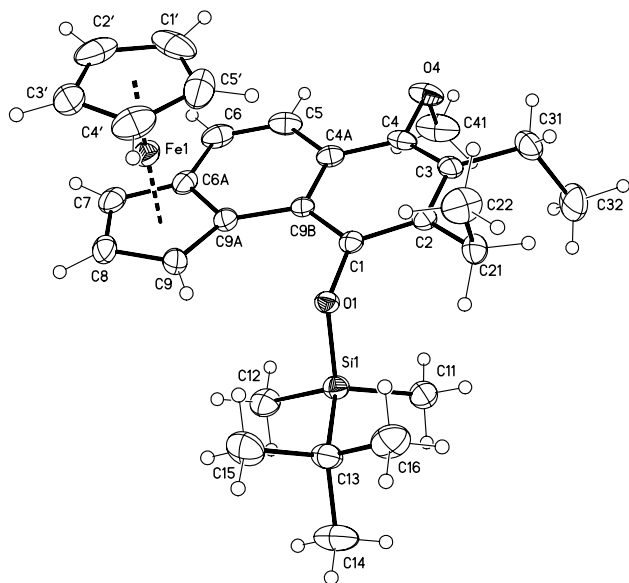
Fig. 4. Molecular structure of iron complex **4c**.

Table 1
Selected bond lengths (pm) and angles (°) for **4a**, **4b** and **4c**

	4a	**4b**	**4c**
Fe···Cp	166.3 (2)	167.2 (1) [164.1 (1) for **4b'**]	164.6 (2)
Fe···Ar[a]	166.2 (2)	165.7 (1)	165.6 (2)
Cr···Ar[a]	176.4 (2)	175.9 (1)	–
φ(Cp–Fe–Ar[a])	175.1 (2)	178.5 (1) [177.0 (1) for **4b'**]	178.2 (1)
C(9)–C(9A)–C(9B)–C(1)	−12.9 (4)	−10.1 (3)	6.2 (4)

[a] Ar = benz[e]indenyl.

of the chromium fragment and the relative stereochemistry of both metal fragments. While a formal oxidation potential $(E_{1/2})$ of 476 mV is observed for the

benz[e]indenyl iron complex **4c**, it is considerably shifted by 103 to 579 mV (**4a**) and by 247 to 723 mV (**4 b**), respectively, upon $Cr(CO)_3$-coordination. These results indicate a metal–metal interaction between iron and chromium through the π-system [11]. It is conspicuous that the oxidation potentials of both diastereomers differ considerably by 143 mV (Table 2). The first peak potential observed at 513 mV (Fig. 5c) for the *anti*-heterobimetallic complex **4b** suggests the formation of minor amounts of a redox-active iron species. The ferrocene moiety in the benz[e]indenyl complexes is more reluctant towards oxidation than in chromium carbene **3** which reveals a formal oxidation potential of 492 mV [measured as 406 mV relative to saturated calomel electrode (SCE)] (Fig. 5(a)); a feed rate of 3000 mV/s (Table 2) is essential to ensure the reversibility of the redox process which illustrates the tendency for side reactions of the oxidized carbene complex **3**. In general, the electrochemical reversibility is established by the difference of the anodic and cathodic peak potentials ΔE_p expected to range between 60 and 90 mV as well as by the ratio of peak currents I_{pK} and I_{pA} being close to unity.

3. Conclusions

Whereas the steric bulk of the ferrocenyl substituent directly attached to the chromium carbene carbon atom blocks the customary chromium-templated benzannulation upon reaction with alkynes in favor of formation of the furan ring, the incorporation of an *ortho*-phenylene spacer allows for the benzannulation to give the benz[e]indenyl skeleton coordinated to CpFe- and $Cr(CO)_3$-fragments at the terminal rings. An angular regiochemistry is observed as generally encountered for the annulation of chromium (alkoxy)naphthylcarbenes to give hydroquinoid phenanthrenes. *Peri*-protection of the primary phenolic benzannulation products by a bulky silyl group induces a helical twist of the tricyclic arene which is further increased by $Cr(CO)_3$coordination. Two diastereomeric benzannulation products are formed characterized by their *syn*- and *anti*-configuration with respect to their metal moieties and by different anionic peak potentials indicating a distinct influence of the relative stereochemistry on the heterometal–metal interaction.

4. Experimental

4.1. General experimental conditions and instruments

All experiments were performed under argon atmosphere by using standard Schlenk techniques. Solvents were dried according to standard procedures and stored under argon. Silica gel (Macherey-Nagel silica
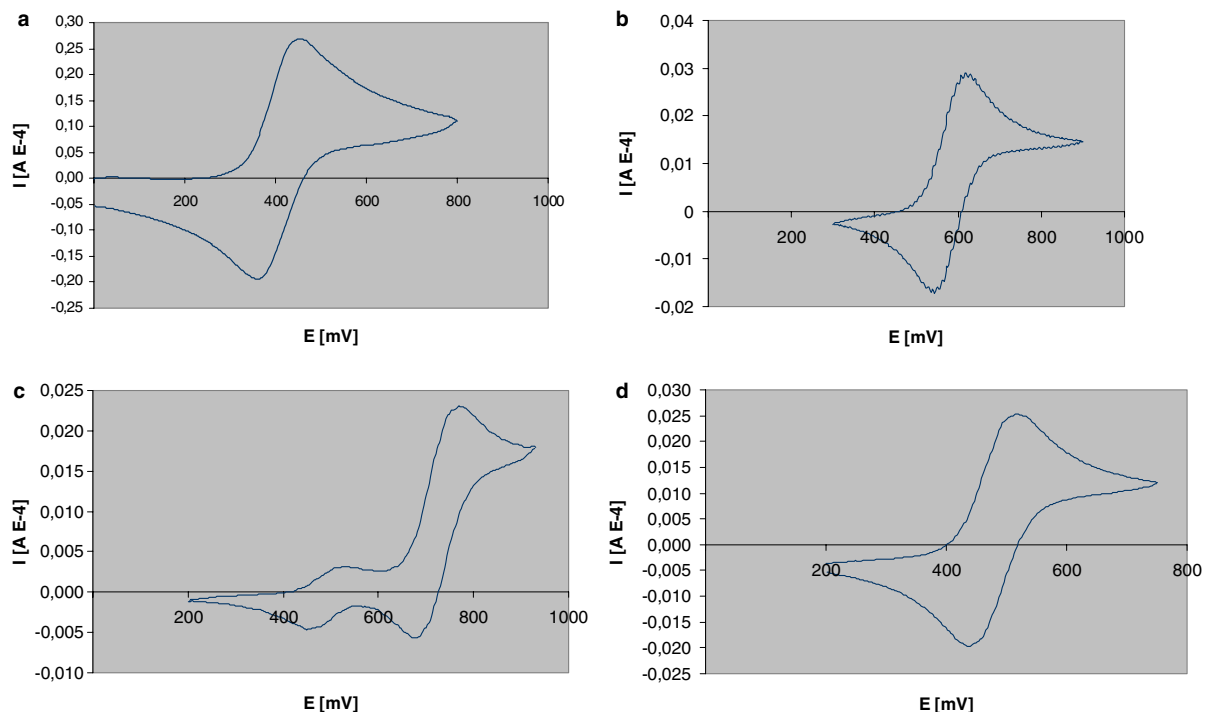
Fig. 5. Cyclovoltammograms of indenyl and benz[e]indenyl complexes **3** and **4a–c**. (a) Cyclovoltammogram of **3** in THF vs. SCE (saturated calomel electrode); $c = 3$ mmol L^{-1}, Bu$_4$N$^+$PF$_6^-$ = 0.2 mol L^{-1}, 3000 mV s^{-1}, glassy carbon electrode, ø = 2 mm; (b) cyclovoltammogram of **4a** in CH$_2$Cl$_2$ vs. decamethylferrocenium/decamethylferrocene (1:1) 0.004 M in acetonitrile; $c = 3$ mmol L^{-1}, Bu$_4$N$^+$PF$_6^-$ = 0.2 mol L^{-1}, 100 mV s^{-1}, glassy carbon electrode, ø = 2 mm; (c) cyclovoltammogram of **4b** in CH$_2$Cl$_2$ vs. decamethylferrocenium/decamethylferrocene (1:1) 0.004 M in acetonitrile; $c = 3$ mmol L^{-1}, Bu$_4$N$^+$PF$_6^-$ = 0.2 mol L^{-1}, 100 mV s^{-1}, glassy carbon electrode, ø = 2 mm; (d) cyclovoltammogram of **4c** in CH$_2$Cl$_2$ vs. decamethylferrocenium/decamethylferrocene (1:1) 0.004 M in acetonitrile; $c = 3$ mmol L^{-1}, Bu$_4$N$^+$PF$_6^-$ = 0.2 mol L^{-1}, 100 mV s^{-1}, glassy carbon electrode, ø = 2 mm.

Table 2
Redox potentials (CV-E_{max}) of indenyl and benz[e]indenyl complexes **3** and **4a–c**

Compound	$E_{1/2}$ (mV)	E_{pA} (mV)	E_{pK} (mV)	ΔE_p (mV)	I_{pA} (µA)	I_{pK} (µA)	I_{pK}/I_{pA}	Feed rate v (mV/s)
3	492[a]	435[a]	377[a]	58	249.2	−274	1.1	3000
4a	579[b]	613[b]	546[b]	67	28.1	−28.1	1	100
4b	723[b]	761[b]	685[b]	76	20.6	−20.38	0.989	100
4c	476[b]	510[b]	442[b]	68	26.8	−27.14	1.02	100

$E_{1/2}$, formal oxidation potential; E_{pA}, anodic peak potential; E_{pK}, cathodic peak potential; I_{pA}, anodic peak current; I_{pK}, cathodic peak current.
[a] Refers to decamethylferrocenium/decamethylferrocene (calculated from 406 mV relative to SCE).
[b] Refers to decamethylferrocenium/decamethylferrocene.

gel 60 0.015–0.025 mm) was used for chromatography in all cases except for compound **2** that was purified by aluminium oxide (Macherey-Nagel aluminium oxide neutral). NMR Spectra were recorded on Bruker DRX 500, Bruker DPX 400 and Bruker DPX 300 (^{13}C and ^{1}H nuclei) spectrometers at room temperature. IR spectra were measured with a Nicolet Magna 550 FT spectrometer. Mass spectra were recorded at the Analytical Center of the Chemical Institutes of the University of Bonn (FAB+ and EI). X-ray structures were solved on a Enraf-Nonius Type Kappa CCD diffractometer. A 350 W USH-350DP

mercury lamp was used for UV-irradiation. Cyclovoltammetry: Potentiostat/Galvanostat Model Autolab PGSTAT 100, Eco Chemie B.V. Melting-points were determined with a Reichert Austria apparatus and are uncorrected.

4.2. Synthesis of [η^5-1,2,3,3a,7a-(6-bromoindenyl)-η^5-cyclopentadienyl]iron (**2**)

A suspension of potassium hydride 1.19 g (29.7 mmol) in 80 mL of dry THF was cooled to −10 °C. Then, 5.78 g (29.7 mmol) of 5-bromoindene

were added, and the mixture was allowed to warm to room temperature. After 3 h the solution was cooled to $-78\,°C$, and 9.02 g (29.7 mmol) of dicarbonyl(iodo) (η^5-cyclopentadienyl)iron were added. After stirring for 18 h, the solvent was removed to give the crude σ-complex intermediate which was used without further purification.

A suspension of the crude intermediate (**1**) in 400 mL petroleum ether (40/60) was irradiated with a 350 W UV-Lamp at $-40\,°C$ for 6 h. Removal of the solvent yielded a dark red-brown residue. Chromatography on neutral Al_2O_3 at $0\,°C$ with petroleum ether and then with petroleum ether/diethylether (7/2) as eluent afforded 4.60 g (49% yield) of the purple air-sensitive product **2**. Recrystallization from diethylether at room temperature afforded purple crystals suitable for X-ray analysis. M.p.: $77\,°C$. ^1H NMR (acetone-d_6, 400 MHz): δ 7.77 (m, 1H), 7.59 (d, 1H, $^3J = 9.1$ Hz), 6.94 (dd, 1H, $^4J = 1.7$ Hz, $^3J = 9.1$ Hz), 5.01 (m, 2H), 4.13 ("t", 1H, $^3J = 2.5$ Hz), 3.85 (s, 5H). ^{13}C NMR (acetone-d_6): δ 132.9, 131.2, 127.2, 116.0, 90.1, 86.3, 71.9, 69.1 (5C), 63.1, 62.8. MS (EI): m/z 313 [M^+, 81], 234 [$M^+ - Br$, 65], 178 [$M^+ - Br - Fe$, 100]. HRMS (EI): Calc. for $C_{14}H_{11}BrFe$ [M^+] 313.9393. Found: 313.9397. $C_{14}H_{11}BrFe$: Calc. C, 53.38; H, 3.52. Found: C, 53.19; H, 3.55%.

4.3. Synthesis of pentacarbonyl(η^5-1,2,3,3a,7a-indenyl-η^5-cyclopentadienyl)iron-(methoxy)-carbene]chromium (3)

After cooling a solution of **2** (0.86 g, 2.7 mmol) in 50 mL diethylether to $-70\,°C$, 4.0 mL of a 1.5 molar solution (5.94 mmol) of tert-butyllithium (in pentane) was added. The mixture was stirred for 15 min, and 0.90 g (4.1 mmol) chromium hexacarbonyl were added. The temperature was raised to $-60\,°C$ and kept for 2 h. After alkylation with 0.89 g (5.4 mmol) methyl triflate the mixture was stirred overnight at $-40\,°C$. Removal of the solvent afforded to a black residue which was purified by column chromatography (SiO$_2$, $-5\,°C$, petroleum ether/diethylether 5/1) affording 0.82 g (63%) of air-sensitive dark green **3**. m.p.: $115\,°C$ (dec.). IR (petroleum ether): $v(CO)$ 2056 (m), 1950 (s), 1940 (sh) cm^{-1}. ^1H NMR (acetone-d_6, 400 MHz): δ 8.22 (s, 1H), 7.65 (d, 1H, $^3J = 9.2$ Hz), 7.11 (dd, 1H, $^4J = 1.6$ Hz, $^3J = 9.2$ Hz), 5.24 (m, 1H), 5.20 (m, 1H), 4.82 (s, 5H), 4.42 ("t", 1H, $^3J = 2.6$ Hz), 3.93 (s, 3H). ^{13}C NMR (acetone-d_6): δ 342.3, 225.2, 217.9, 149.0, 136.1, 129.5, 120.1, 89.2, 86.0, 74.2, 69.5 (5C), 68.3, 65.6, 64.6. MS (FAB): m/z 469.9 [M^+, 49], 441.9 [$M^+ - CO$, 22], 413.9 [$M^+ - 2CO$, 13], 385.9 [$M^+ - 3CO$, 6], 357.9 [$M^+ - 4CO$, 86], 329.9 [$M^+ - 5CO$, 100]. $C_{21}H_{14}$-CrFeO$_6$: Calc. C, 53.65; H, 3.00. Found: C, 53.91; H, 3.19%.

4.4. Benzannulation of chromium indenylcarbene 3

A solution of the carbene complex **3** (0.51 g, 1.1 mmol) and 3-hexyne (0.90 g, 11 mmol) in 50 mL tert-butyl-methylether was warmed to $65\,°C$ (oil bath temperature). After 2 h the dark green solution turned red. An NMR spectrum of the crude solution indicated the formation of a 1:2 mixture of diastereomeric benzannulation products. The phenolic group was protected by addition of 0.11 g (1.1 mmol) triethylamine and tert-butyl-dimethylsilyl triflate (0.87 g, 3.3 mmol). After stirring for 3 h at room temperature chromatography on silica gel at $-5\,°C$ with petroleum ether/tert-butyl-methyl ether (5/1) afforded first 0.16 g (23%) of syn-complex **4a** followed by 0.24 g (34%) of anti-complex **4b** as air-sensitive red-orange products. Recrystallization from an acetone/heptane mixture at room temperature gave crystals suitable for X-ray analysis. Minor diastereomer **4a**: m.p.: 170 (dec.). IR (petroleum ether): $v(CO)$ 1952 (s), 1886 (s), 1875 (s) cm^{-1}. ^1H NMR (dichloromethane-d_2, 400 MHz): δ 7.75 (dd, 1H, $^4J = 0.5$ Hz, $^3J = 9.5$ Hz), 7.18 (d, 1H, $^3J = 9.5$ Hz), 5.76 (m, 1H), 4.73 (dd, 1H, $^4J = 1.1$ Hz, $^3J = 2.4$ Hz), 4.34 ("t", 1H, $^3J = 2.5$ Hz), 4.16 (s, 3H), 3.92 (s, 5H), 2.84 (dq, 1H, $^3J = 7.6$ Hz, $^2J = 13.9$ Hz), 2.63 (dq, 1H, $^3J = 7.3$ Hz, $^2J = 14.7$ Hz), 2.62 (dq, 1H, $^3J = 7.3$ Hz, $^2J = 14.1$ Hz), 2.29 (dq, 1H, $^3J = 7.3$ Hz, $^2J = 14.6$ Hz), 1.38 (t, 3H, $^3J = 7.4$ Hz), 1.19 (t, 3H, $^3J = 7.5$ Hz), 0.94 (s, 9H), 0.28 (s, 3H), 0.03 (s, 3H). ^{13}C NMR (dichloromethane-d_2): δ 236.0, 141.3, 134.8, 127.4, 116.3, 112.2, 106.2, 101.0, 95.2, 86.6, 81.1, 71.0 (5C), 68.6, 68.1, 66.5, 63.1, 26.1, 21.7, 20.1, 19.2, 14.4, 0.9, -0.6, -1.4. MS (EI): m/z 638.1 [M^+, 22], 554.2 [$M^+ - 3CO$, 88], 502.2 [$M^+ - 3CO - Cr$, 100]. HRMS (EI): Calcd. for $C_{32}H_{38}CrFeO_5Si$ [M^+] 638.1243. Found: 638.1251. $C_{32}H_{38}CrFeO_5Si$: Calc. C, 60.19; H, 6.00. Found: C, 60.04; H, 6.30%. Major diastereomer **4b**: m.p.: $170\,°C$ (dec.). IR (petroleum ether): $v(CO)$ 1961 (s), 1955 (sh), 1901 (s), 1882 (s) cm^{-1}. ^1H NMR (acetone-d_6, 400 MHz): δ 7.42 (dd, 1H, $^4J = 0.6$ Hz, $^3J = 9.3$ Hz), 7.16 (d, 1H, $^3J = 9.3$ Hz), 5.79 (m, 1H), 4.95 (dd, 1H, $^4J = 1.2$ Hz, $^3J = 2.6$ Hz,), 4.44 ("t", 1H, $^3J = 2.7$ Hz), 3.89 (s, 5H), 3.77 (s, 3H), 3.11 (dq, 1H, $^3J = 7.4$ Hz, $^2J = 14.0$ Hz), 2.72–2.60 (m, 3H), 1.38 (t, 3H, $^3J = 7.4$ Hz), 1.37 (t, 3H, $^3J = 7.6$ Hz), 1.27 (s, 9H), 0.65 (s, 3H), 0.38 (s, 3H). ^{13}C NMR (acetone-d_6): δ 235.6, 138.6, 129.7, 122.6, 120.3, 111.7, 111.6, 105.5, 94.3, 85.7, 77.8 71.1 (5C), 70.9, 69.6, 67.1, 63.2, 26.9, 21.5, 20.7, 19.9, 17.9, 16.0, 0.5, -1.5. MS (EI): m/z 638.1 [M^+, 10], 554.2 [$M^+ - 3CO$, 58], 502.2 [$M^+ - 3CO - Cr$, 100]. HRMS (EI): Calc. for $C_{32}H_{38}CrFeO_5Si$ [M^+] 638.1243. Found: 638.1248. $C_{32}H_{38}CrFeO_5Si$: Calc. C, 60.19; H, 6.00. Found: C, 60.46; H, 6.11%.

Table 3
Crystallographic data for indenyl and benz[e]indenyl complexes **2** and **4a–c**

Compound	2	4a	4b	4c
Empirical formula	$C_{14}H_{11}BrFe$	$C_{32}H_{38}CrFeO_5Si$	$C_{32}H_{38}CrFeO_5Si$	$C_{29}H_{38}FeO_2Si$
Formula weight	314.99	638.56	638.56	502.53
Temperature (K)	123(2)	123(2)	123(2)	123(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
Unit cell dimensions				
a (Å)	7.5129(5)	11.2983(2)	7.3627(1)	15.2171(4)
b (Å)	15.7237(9)	11.5984(2)	24.4692(3)	16.8773(4)
c (Å)	9.9166(7)	12.0145(3)	16.9881(2)	10.7396(2)
α (°)	90	89.103(1)	90	90
β (°)	109.640(3)	85.568(1)	98.989(1)	106.054(1)
γ (°)	90	71.242(1)	90	90
V (Å^3)	1103.30(12)	1486.25(5)	3022.98(7)	2650.62(11)
Z	4	2	4	4
$D_{calcd.}$ (g cm^{-3})	1.896	1.427	1.403	1.259
μ (mm^{-1})	4.952	0.933	0.918	0.637
Crystal size (mm)	$0.40 \times 0.20 \times 0.10$	$0.25 \times 0.20 \times 0.15$	$0.40 \times 0.25 \times 0.15$	$0.30 \times 0.10 \times 0.05$
Diffractometer	Nonius KappaCCD	Nonius KappaCCD	Nonius KappaCCD	Nonius KappaCCD
2θ Max (°)	50	50	50	50
Limiting indices	$-8 \leqslant h \leqslant 8$	$-13 \leqslant h \leqslant 13$	$-8 \leqslant h \leqslant 8$	$-16 \leqslant h \leqslant 18$
	$-18 \leqslant k \leqslant 17$	$-13 \leqslant k \leqslant 13$	$-29 \leqslant k \leqslant 29$	$-20 \leqslant k \leqslant 18$
	$-11 \leqslant l \leqslant 9$	$-14 \leqslant l \leqslant 14$	$-20 \leqslant l \leqslant 20$	$-9 \leqslant l \leqslant 12$
Reflections collected/unique	5155/1878 [$R_{int} = 0.0950$]	20887/5227 [$R_{int} = 0.0485$]	39216/5326 [$R_{int} = 0.0559$]	12900/4579 [$R(int) = 0.0430$]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Parameters/restraints	145/0	361/0	339/45	298/0
Goodness-of-fit on F^2	1.060	1.042	1.063	0.912
Final indices [$I > 2\sigma(I)$]	$R_1 = 0.0649$	$R_1 = 0.0302$	$R_1 = 0.0298$	$R_1 = 0.0372$
	$wR_2 = 0.1611$	$wR_2 = 0.0800$	$wR_2 = 0.0764$	$wR_2 = 0.0649$
R indices (all data)	$R_1 = 0.0841$	$R_1 = 0.0399$	$R_1 = 0.0392$	$R_1 = 0.0745$
	$wR_2 = 0.1696$	$wR_2 = 0.0836$	$wR_2 = 0.0795$	$wR_2 = 0.0722$
Largest difference in peak and hole (e Å^{-3})	1.605 and −0.873	0.771 and −0.370	0.408 and −0.300	0.244 and −0.274

4.5. Decomplexation of heterobimetallic complex 4b

A solution of the major diastereomer **4b** (0.51 g, 1.1 mmol) in di-*n*-butylether was warmed to 115 °C for 3 h. Chromatography on SiO$_2$ at 0 °C with petroleum ether/*tert*-butyl-methyl ether (5/1) yielded 0.38 g (68%) of benz[e]indenyl iron complex **4c**. Recrystallization from an acetone/heptane mixture at room temperature afforded red crystals suitable for X-ray analysis. m.p.: 137 °C. ^{1}H NMR (acetone-d_6, 300 MHz): δ 7.39 (m, 2H), 5.78 (ddd, 1H, $^4J = 1.1$ Hz, $^4J = 0.4$ Hz, $^3J = 2.4$ Hz), 4.80 (dd, 1H, $^4J = 1.2$ Hz, $^3J = 2.5$ Hz), 4.20 ("t", 1H, $^3J = 2.4$ Hz), 3.84 (s, 5H), 3.54 (s, 3H), 3.12 (dq, 1H, $^3J = 7.5$ Hz, $^2J = 13.4$ Hz), 2.96 (dq, 1H, $^3J = 7.5$ Hz, $^2J = 13.4$ Hz), 2.69 (dq, 1H, = 7.5 Hz, $^2J = 13.3$ Hz), 2.67 (dq, 1H, $^3J = 7.3$ Hz, $^2J = 13.1$ Hz), 1.25 (t, 3H, $^3J = 7.4$ Hz), 1.21 (t, 3H, = 7.3 Hz), 1.20 (s, 9H), 0.00 (s, 3H), −0.18 (s, 3H). ^{13}C NMR (acetone-d_6): δ 150.9, 146.2, 134.4, 132.9, 127.8, 125.7, 119.6, 84.8, 83.3, 70.1 (5C), 69.2, 67.7, 64.0, 62.6, 26.6, 21.6, 20.6, 19.1, 16.3, 15.9,

−2.1, −4.1. MS (EI): *m/z* 502.2 [M$^+$, 100], 487.2 [M$^+$ − CH$_3$, 5], 372.1 [M$^+$ − CH$_3$ − (CH$_3$)$_3$CSi(CH$_3$)$_2$,8] 292.2 [M$^+$ − CH$_3$O − (CH$_3$)$_3$C − FeCp, 20]. HRMS (EI): Calc. for $C_{29}H_{38}FeO_2Si$ [M$^+$] 502.1990. Found: 502.1993. $C_{29}H_{38}FeO_2Si$: Calc. C, 69.31; H, 7.62. Found: C, 69.15; H, 7.79%.

4.6. Crystal structure determinations of indenyl and benz[e]indenyl complexes 2 and 4a–c

The data were collected on a Nonius KappaCCD diffractometer at −150 °C using Mo Kα radiation ($\alpha = 0.71073$ Å). The structures were solved by direct methods (**2**, **4a**, **4c**) or Patterson methods (**4b**) (SHELXS-97) [12]. The non-hydrogen atoms were refined anisotropically, H atoms were refined using a riding model (full-matrix least-squares refinement on F^2, SHELXL-97) [13]. In **4b**, the cyclopentadienyl ring is disordered. An empirical absorption correction was applied for **2**, **4a** and **4b**. Details of data collection and refinement are given in Table 3.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication Nos. CCDC-272216 (**2**), CCDC-272217 (**4a**), CCDC-272218 (**4b**) and CCDC-272219 (**4c**). Copies of the data can be obtained free of charge at www.ccdc.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK, fax: int. code +44 1223 336 033, e-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

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