Synthesis and cyclic voltammetry of some new metal carbene substituted cyclopentadienyliron half sandwich complexes

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Dedicated to Professor Günther Wilke on the occasion of his 80th birthday

Abstract

The syntheses of a number of cyclopentadienylcarbene iron half sandwich complexes are described. In addition to their spectroscopic characterization an X-ray crystal structure analysis is provided. The complexes prepared include chromium, molybdenum, and tungsten carbene complexes. The dicarbonyliron unit is substituted by benzyl, butyl or trimethylsilylmethyl groups. In two cases tetrametallic dimeric complexes connected by a propyl chain are presented. The reaction of the formylcyclopentadienyliron complex with a chromium carbene complex provided a vinylogous representative. Cyclic voltammetry was performed, and the data obtained are discussed in comparison to similar ferrocene based complexes.
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1. Introduction

Oligometallic transition metal complexes deserve interest with respect to electronic interactions between the metal atoms. This might have a significant bearing for areas such as catalysis [1–6], molecular electronics [7–12], nonlinear optics [13,14] and electron transfer chemistry [15]. Among the complexes without direct metal–metal bonds in particular those with connecting π systems are promising candidates for electronic interactions. Such interactions might result in new properties deriving from either participating metal and might therefore be different from a formal sum of the distinct properties caused by the single metal. In many cases, metals of oligonuclear complexes are connected by π ligands such as fulvalenes [7,14,16–19], biphenyl [7,20–25], stilbene [26], oligophenylenes [27], etc. Alternatively there are complexes, in which the metals are directly incorporated in the connecting π system, for example in bimetallic cumulenylidene or oligoalkynediyl complexes [28–35].

Cyclopentadienylcarbene complexes combine both possibilities in that the carbene bearing metal is part of the ligand π system of the substituted cyclopentadienyl ligand. Based on our interest in functionalized cyclopentadienyl complexes [36–40], we recently reported on the synthesis of some cyclopentadienylcarbene half sandwich complexes [41]. While this line of thought has been pursued with ferrocene derivatives [42–46], there are only few further reports about half sandwich complexes of this kind [47]. Here, we report on the synthesis and characterization of some cyclopentadienylcarbene half sandwich iron complexes.

The dicarbonylcyclopentadienyliron (Fp) system is among the most broadly explored organometallic complex fragments. The system is easily prepared from cyclopentadiene and pentacarbonyliron and following
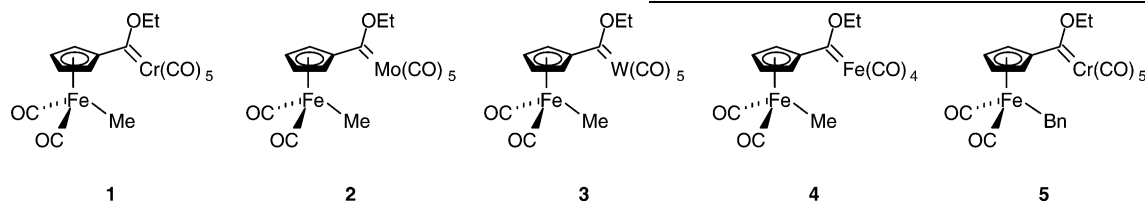
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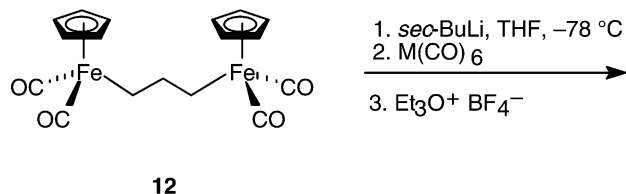E-mail address: holger.butenschoen@mbox.oci.uni-hannover.de (H. Butenschön).

dissociation of the obtained dimer, Fp_2 [48,49]. The chemistry of the Fp system includes the Fp^+ cation, σ-bound alkyl complexes, Fp^- ferrates, Fp carbene complexes, and asymmetric induction by the derived acyl phosphane complexes and has been extensively reviewed [48–52]. However, comparatively few reports about related systems with substituted cyclopentadienyl ligands have been published. The corresponding pentamethylcyclopentadienyl system has occasionally been used [53], and there are a few reports about chiral Fp-like complexes [54].
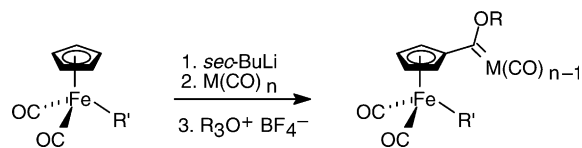
2. Results and discussion

Bimetallic complexes **1**–**5** were already known from our earlier work, there is an X-ray structure analysis of **1** [41]. We now succeeded in a crystallization of benzyl derivative **5** from pentane/diethyl ether at −20 °C, which gave crystals suitable for an X-ray crystal structure analysis (Fig. 1).

1   **2**   **3**   **4**   **5**

The structure clearly shows that in contrast to the structure of **1** a conformation is adopted, in which the bulky benzyl ligand and the carbene pentacarbonylchromium fragment point away from one another. The car-
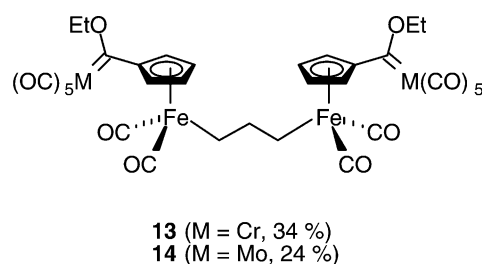

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bene carbon chromium bond deviates from the plane of the cyclopentadienyl ring by a torsional angle of 12°. Remarkably, the ethyl group points towards the iron atom, although this is clearly not the sterically least hindered conformation. The pentacarbonylchromium moiety adopts a staggered conformation with respect to the ethoxy substituent.

Some related complexes were obtained by deprotonation of the cyclopentadienyl ligand in FpR′ with *sec*-butyllithium followed by treatment with metal carbonyl and alkylation using triethyl or trimethyloxonium tetra-

fluoroborate. Along with some diagnostic spectroscopic data the complexes obtained are listed in Table 1.

The spectroscopic properties of the complexes correspond to those of **1**–**4** and to those of related ferrocene derivatives [42–46] with characteristic chemical shifts for the carbene carbon atom. There is only a small effect of the carbene bearing metal on the wavenumber of the Fe–CO vibration.

Tetrametallic complexes **13** and **14** were obtained in 34% and 24% yield, respectively, by similar reactions starting from diiron complex **12** [56]. These yields correspond to an average of 58% and 49%, respectively, for the single reaction steps and are comparable to or even higher than those of the formation of **1**–**11**. These com-

plexes are the first ones with two cyclopentadienylcarbene moieties in one molecule. The spectroscopic properties of the tetrametallic complexes are quite similar to those of their bimetallic counterparts.

13 (M = Cr, 34 %)
14 (M = Mo, 24 %)

In order to prepare a vinylogous cyclopentadienylcarbene complex, we resorted to the method established by Aumann and Heinen [57]. To achieve this (benzyl)dicarbonyl(cyclopentadienyl)iron(II) (**15**) was formulated in 96% yield by deprotonation with *sec*-butyllithium followed by treatment with DMF. Aldehyde **16** was then treated with triethylamine/chlorotrimethylsilane and the carbene complex **17** [58] resulting in the formation of the vinylogous cyclopentadienylcarbene complex **18** in 37% yield. Complex **18** was characterized spectroscopically. In the IR spectrum, a strong absorption at
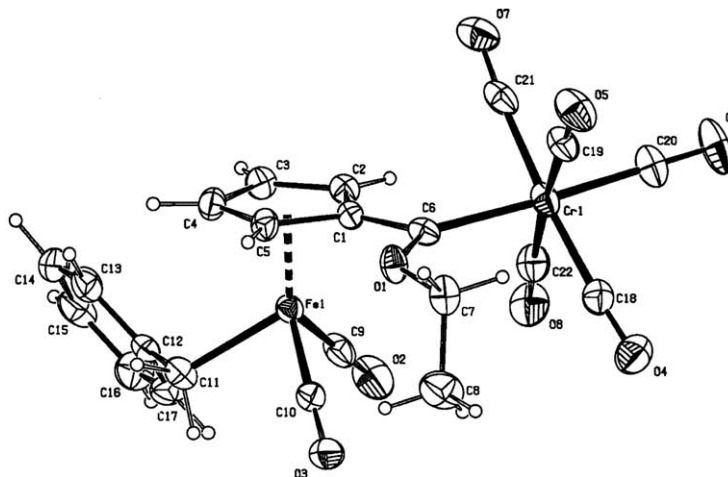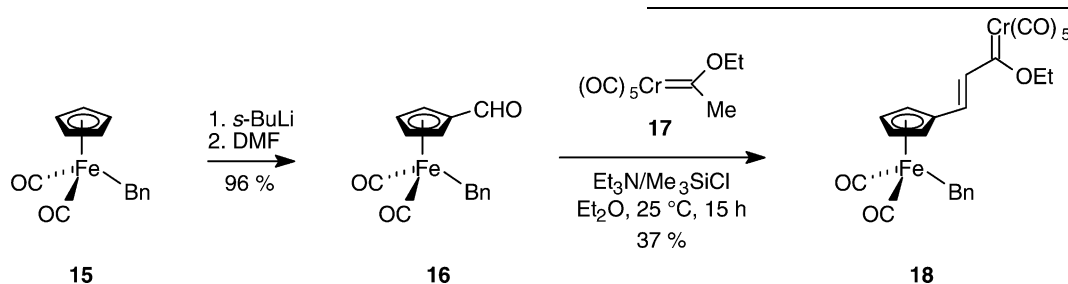
Fig. 1. Structure of **5** in the crystal [55]. Selected bond lengths (Å) angles (°) and dihedral angles (°): C1–C2 1.410(4), C2–C3 1.401(4), C3–C4 1.404(4), C4–C5 1.374(4), C1–C5 1.451(4), C1–C6 2.044(3), C6–Cr 2.044(3), C6–O1 2.044(3), Cr–C18 1.874(5), Cr–C20 1.864(4), Fe–C1 2.112(3), Fe–C2 2.086(3), Fe–C3 2.106(4), Fe–C4 2.119(4), Fe–C5 2.097(3), Fe–C9 1.737(4), Fe–C10 1.738(4), Fe–C11 2.096(3); C2–C1–C6 129.8(3), C5–C1–C6 125.6(3), C1–C6–Cr 125.7(2), C1–C6–O1 104.2(3), C6–O1–C7 124.2(3), C18–Cr–C21 174.8(2), C19–Cr–C22 175.7(2), Fe–C11–C12 115.6(2); C2–C1–C6–Cr 12.2(5), C5–C1–C6–Cr −169.3(3).

2052 cm^{-1} is assigned to the chromium carbonyl ligands. In the ^{1}H NMR spectrum, the olefinic protons give rise to doublets at δ = 6.23 and 7.60 ppm (^3J = 15.3 Hz) confirming the *trans* configuration of the double bond.

reversible reduction processes were reported to take place at $E = -1.34$ V (Hg/HgCl$_2$) for [(CO)$_5$Cr=C(OMe)Ph] and at $E = -1.25$ V (Hg/HgCl$_2$) for [(CO)$_5$W=C(OMe)Ph] [67].

Cyclic voltammetry has proven to be a powerful tool in order to investigate the electronic influence of substituents at the Cp-ring system of transition metal complexes. In particular substituted ferrocenes were described in the literature [59–63]. Ferrocene substituted Fischer-type carbene complexes [(CO)$_5$Cr=C(OEt)Fc] were investigated showing that both metals communicate via the connecting π-system as indicated by the cyclic voltammetry measurements [64]. Despite the fact that two redox active metals (Fe and Cr) are present only one reversible one electron transfer process is observed at $E = 0.70$ V using dichloromethane as solvent. Electrochemical investigations on monometallic Fischer-type carbene complexes were reported in the literature: irreversible oxidation at $E = 0.40$ V and $E = 0.92$ V (Hg/HgCl$_2$) for [(CO)$_5$Cr=C(O)Ph][NEt$_4$] [65] in MeCN and $E = 0.90$ V (Hg/HgCl$_2$) for [(CO)$_5$Cr=C(OEt)Ph] [66] in dichloromethane. Quasi-

So far only a few results on *half* sandwich iron complexes substituted with a carbene functionality at the cyclopentadienyl ligand like [(CO)$_5$M=C(OR)Fp] were synthesized and analyzed using electrochemical methods. In 1999 cyclic voltammetry measurements of heterobimetallic Fischer-type carbene complexes showed that the substitution of the cyclopentadienyl ligand by a chromium carbene moiety [(CO)$_5$Cr=C(OEt)–] decreases the oxidation potential as compared to the unsubstituted Fp complex [41]. The result is remarkable because analogous substituted ferrocenes showed the reverse trend. The oxidation potential increases for electron withdrawing substituents [15]. Some of the bimetallic carbene complexes prepared in this study were investigated by cyclic voltammetry. The data obtained are summarized in Table 2. As representative examples the CV plots of **10** and **13** are given in Figs. 2 and 3, respectively.

Table 1
Cyclopentadienylcarbene complexes

Complex	R′	M(CO)$_n$	R	Yield (%)	$\delta(^{13}C)^a$ (ppm)	ν^b (cm^{-1})	Literature
1	Me	Cr(CO)$_6$	Et	38	331.3	2060	[41]
2	Me	Mo(CO)$_6$	Et	35	321.8	2068	[41]
3	Me	W(CO)$_6$	Et	26	304.6	2068	[41]
4	Me	Fe(CO)$_5$	Et	23	311.7	2072	[41]
						2052	
5	Bn	Cr(CO)$_6$	Et	60	329.3	2059	[41]
6	Bn	Mo(CO)$_6$	Et	40	320.2	2067	–
7	Bn	W(CO)$_6$	Et	46	303.3	2066	–
8	Bn	Cr(CO)$_3$	Me	32	332.4	2060	–
9	Bu	Cr(CO)$_6$	Et	48	329.3	2054	–
10	CH$_2$SiMe$_3$	Cr(CO)$_6$	Et	12	330.7	2058	–
11	CH$_2$SiMe$_3$	W(CO)$_6$	Et	20	303.8	2067	–

[a] ^{13}C NMR signal of the carbene carbon atom in C$_6$D$_6$.
[b] IR absorption of the M–CO band.

Table 2
Cyclic voltammtery of cyclopentadienylcarbene complexes

Complex	v (V/s)	E_A (V)	E_K (V)
5	1	0.696	−2.088
5	2	0.683	−2.054
9	1	0.566	−1.988
9	2	0.553	−2.097
10	1	0.653	−1.798
10	2	0.693	−1.862
13	0.1	0.471	0.333–1.032
13	0.2	0.506	0.302–1.179
14	0.1	0.226	−1.908
14	0.2	[a]	[a]

$T = 25$ °C, $c = 0.1$ mmol/l, $c_{TBAHFP} = 0.1$ mol/l, number of scans = 1, solvent acetonitril, potentials vs. F_c/F_c^+.
[a] Cyclovoltammogram not obtained.

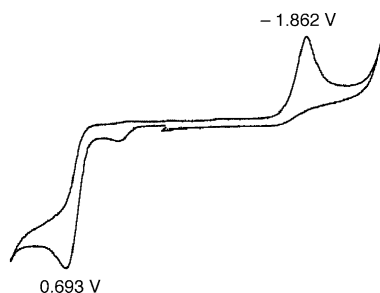Fig. 3. CV plot of **13**. 0.1 V/s, $T = 25$ °C, $c = 0.1$ mmol/l, $c_{TBAHFP} = 0.1$ mol/l, 1 scan, solvent acetonitrile, potential vs. F_c/F_c^+.

Fig. 2. CV plot of **10**. 2 V/s, $T = 25$ °C, $c = 0.1$ mmol/l, $c_{TBAHFP} = 0.1$ mol/l, 1 scan, solvent acetonitrile, potential vs. F_c/F_c^+.

The cyclovoltammogram of the heterobimetallic complex **10** recorded in acetonitrile shows one irreversible oxidation at $E = 0.693$ V. Although irreversible, this oxidation is comparable with the potential measured for structurally analogous ferrocene complexes [64]. The irreversibility observed for **10** is in accord with earlier observations [41] and may be due to the reactivity of the radical formed. In addition, an irreversible reduction is observed at −1.862 V. The fact that there is only one
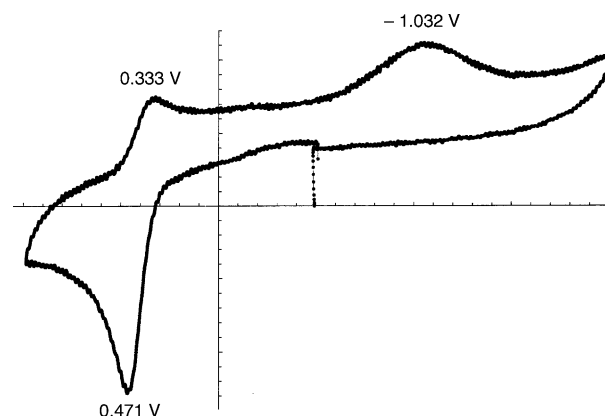
reduction and only one oxidation although there are two redox active metal atoms in the molecule leads to the conclusion that both metal atoms participate in one molecular orbital. The oxidation potential for the unsubstituted half sandwich complex FpBn is reported at $E = 0.688$ V in dichloromethane [41]. Obviously the oxidation in **10** takes place at a comparable potential. A comparison of the reduction potential of **10** of −1.862 V vs. F_c/F_c^+ with that of the chromium carbene complex [(CO)$_5$Cr=C(OMe)Ph] of $E = -1.34$ V (vs. Hg/HgCl$_2$) [67] requires a correction due to the different standards, which is $E_{F_c/F_c^+} = 0.45$ V (vs. Hg/HgCl$_2$) [59]. Remarkably, addition of E_{F_c/F_c^+} to the reduction potential of **10** results in −1.412 V, a value quite close to that of the phenyl substituted carbene complex. Although, the cyclovoltammograms of complexes **5** and **9** show some numerical differences to that of **10**, the overall shape of the cyclovoltammograms is rather similar for these three complexes.

It is interesting to see that the cyclovoltammograms of the tetrametallic complexes **13** and **14** differ considerably from their bimetallic counterparts. The cyclovoltammograms obtained for diirondimolybdenum complex **14** do

not look very nice and are barely reproducible, presumably due to decomposition reactions of the complex or its oxidation or reduction products. However, it was possible to obtain reasonable cyclovoltammograms of the diirondichromium complex **13** (Fig. 3). Complex **13** shows an oxidation at 0.471 V, which is at considerably lower potential as compared to **10**. In contrast to **10** tetrametallic complex **13** shows a reduction wave at 0.333 V which might correspond to the oxidation process at 0.471 V, although, the difference of the two potentials is somewhat high for a fully reversible process with an ideal value of 0.059 V. In addition, another irreversible reduction is observed at −1.032 V, which is a value significantly higher than the reduction observed for **10**. Obviously the tetrametallic complex **13** is reduced much more easily as compared to the dimetallic complex **10**. One might speculate that this could be due to a different reduction mechanism involving either one of the two bimetallic subunits of the system. This line of thought raises questions, e.g., about the influence of the chain length between the iron atoms on the reduction potential and on the reversibility of the redox process observed at higher potential for **13**. These questions are currently pursued in our laboratory.

3. Experimental

3.1. General

Unless otherwise indicated all operations were carried out under argon using standard Schlenk techniques. Halogen free solvents were distilled from sodium–potassium alloy with a small amount of benzophenone. Dichloromethane was dried over P_4O_{10} and distilled under argon. ^{1}H NMR: Bruker AVS 400 (400.1 MHz), AVS 200 (200.1 MHz); ^{13}C NMR: Bruker AM 400 (100.6 MHz), AVS 200 (50.3 MHz), signal multiplicities were determined with the APT [68] technique were indicated. IR: Bruker ISS 25, Perkin–Elmer FTIR spectrometers 580 and 1710. MS: Finnigan MAT 112, MAT 312; elemental analyses: Hareaeus CHN Rapid, Analysensysteme GmbH Elementar Vario EL. CV: Potentiostat Heka PG 285, reference electrode Ag/AgCl (Alfa), counter electrode Pt wire, 0.1 M tetrabutylmmonium hexafluorophosphate (Fluka, electrochemical grade), dichloromethane, potential normalized to ferrocene/ferrocenium ion (E_0 = 0.35 V vs. Ag/AgCl).

3.2. Crystal structure analysis of 5: [55]

$C_{22}H_{16}CrFeO_8$, molecular weight 516.20, crystal system monoclinic, space group $P2_1/n$, a = 7.276(2) Å, α = 90°, b = 10.132(2) Å, β = 91.02(3)°, c = 29.882(6) Å, γ = 90°, V = 2202.6(9) Å^3, Z = 4, d_{calc} = 1.557 g/cm^3, $F(000)$ = 1048e, μ = 1.197 mm^{-1}, crystal color red, crys-

tal size $0.37 \times 0.17 \times 0.06$ mm, Stoe IPDS (Area Detector) diffractometer, T = 303(2) K, Mo Kα = 0.71073 Å, θ_{min} = 2.12, θ_{max} = 24.13°, $-8 \leqslant h \leqslant 8$, $-11 \leqslant k \leqslant 11$, $-34 \leqslant l \leqslant 34$, absorption correction semiempiric, no extinction correction, 19,564 collected, 3415 unique reflections, [R(int) = 0.0749], refinement program: SHELXL-93, refinement by least squares method (F^2), R indices: [$I > 2\sigma(I)$] R_1 = 0.0330, wR_2 = 0.0463, R indices (all data): R_1 = 0.0724, wR_2 = 0.0493, residual electron density: −0.196/0.212 Å^{-3}, completeness of data 96.9%.

3.3. General procedure

A 1.3 M solution of *sec*-butyllithium in cyclohexane is added dropwise to a solution of benzyldicarbonylcyclopentadienyliron(II) (**15**) [48] in THF. The solution becomes dark immediately. After stirring for 1 h the metal carbonyl is added, and after stirring for 1 h the mixture is allowed to warm to 25 °C and is stirred for another 30 min. After solvent removal into a cold trap at reduced pressure the residue is taken up with dichloromethane, and a solution of trialkyloxonium tetrafluoroborate in dichloromethane is added. After 1 h, the solvent is removed into a cold trap at reduced pressure. The crude product is purified by column chromatography at silica gel.

3.4. Pentacarbonyl{[(benzyldicarbonyliron(II))-η⁵-cyclopentadienyl]ethoxycarbene}molybdenum(0) (6)

General procedure (GP), 250 mg (0.9 mmol) of **15**, 30 ml of THF, 1.4 ml (12.9 mmol) of 1.3 M *sec*-butyllithium in cyclohexane, 86 mg (0.9 mmol) of Mo(CO)$_6$, 210 mg (0.9 mmol) of triethyloxonium tetrafluoroborate in 10 ml of dichloromethane. Column chromatography (20×5 cm, petroleum ether/*tert*-butylmethyl ether $10:1 \rightarrow 2:1$) yields 200 mg (0.4 mmol, 40%) of **6** as a black solid, m.p. 93 °C (dec.).

IR (ATR): ν = 2965 cm^{-1} (w, CH), 2932 (w, CH), 2875 (w), 2067 (m, C=O), 2010 (m, FeC=O), 1930 (s, br, C=O), 1775 (w), 1595 (w), 1449 (w), 1230 (w) 1204 (m), 1145 (w), 802 (w), 761 (w) 698 (w). ^{1}H NMR (400 MHz, C$_6$D$_6$): δ = 1.05 (t, $^3J_{6,7}$ = 7.0 Hz, 3H, 7-H), 2.65 (s, 2H, Fe CH$_2$), 3.93 (s, 2H, Cp), 4.57 (q, $^3J_{6,7}$ = 7.0 Hz, 2H, 6-H), 4.98 (s, 2H, Cp), 6.96–7.18 (m, 5H, arom.-H). ^{13}C NMR (100.6 MHz, APT, C$_6$D$_6$): δ = 7.5 (+, FeCH$_2$), 14.8 (−, C-7), 78.3 (+, C-6), 90.0 (−, Cp), 90.6 (−, Cp), 105.5 (+, *ipso* Cp), 124.3–129.6 (−, 5 C arom.C), 151.9 (+, *ipso* Bn), 206.0 (+, FeCO), 212.6 (+, MoCO$_{trans}$), 215.0 (+, MoCO$_{cis}$), 320.2 (+, Mo=C). MS (70 eV, 130 °C): m/z (%) = 532(3) [M$^+$ − CO], 448(5) [M$^+$ − 4CO], 416(10) [M$^+$ − 5CO], 388(11) [M$^+$ − 6CO], 360(10) [M$^+$ − 7CO], 267(68), 239(42), 212(40), 148(20), 121(46), 94(7) [Mo], 91(100) [C$_7$H$_7^+$], 65(31) [Cp]. HRMS C$_{21}$H$_{16}$O$_7$FeMo: Calc. 533.9368; found: 533.9299.

3.5. Pentacarbonyl{[(benzyldicarbonyliron(II))-η^5-cyclopentadienyl]ethoxycarbene}tungsten(0) (7)

GP, 1.0 g (3.7 mmol) of **15**, 30 ml of THF, 3.2 ml (12.9 mmol) of 1.3 M *sec*-butyllithium in cyclohexane, 1.3 g (3.7 mmol) of W(CO)$_6$, 0.7 g (3.8 mmol) of triethyloxonium tetrafluoroborate in 50 ml of dichloromethane. Column chromatography (40 × 3 cm, petroleum ether/*tert*-butylmethyl ether 5:1) yields 1.1 g (1.7 mmol, 46%) of **7** as a deep red solid, m.p. 89 °C (dec.).

IR (ATR): v = 2962 cm^{-1} (w, CH), 2066 (m, C=O), 2004 (m, C=O), 1916 (s, br, C=O), 1487 (w), 1443 (w), 1257 (m) 1223 (m), 1188 (w), 799 (w), 761 (w) 700 (w). ^{1}H NMR (400 MHz, C$_6$D$_6$): δ = 1.09 (t, $^3J_{6,7}$ = 7.0 Hz, 3H, 7-H), 2.71 (s, 2H, FeCH$_2$), 4.01 (s, 2H, Cp), 4.55 (q, $^3J_{6,7}$ = 7.0 Hz, 2H, 6-H), 5.02 (s, 2H, Cp), 7.0–7.28 (m, 5H, arom.H). ^{13}C NMR (100.6 MHz, APT, C$_6$D$_6$): δ = 7.6 (+, FeCH$_2$), 14.6 (−, C-7), 79.1 (+, C-6), 86.0 (−, Cp), 86.01 (−, Cp), 90.2 (−, Cp), 90.3 (−, Cp), 107.1 (+, *ipso* Cp), 123.5–128.7 (−, 5C, arom.C), 151.9 (+, *ipso* Bn), 197.5 (+, WCO$_{cis}$), 202.2 (+, WCO$_{trans}$), 215.0 (+, FeCO), 303.3 (+, W=C). HRMS C$_{22}$H$_{16}$FeO$_8$W: Calc. 647.9600; found: 647.9704.

3.6. Pentacarbonyl{[(benzyldicarbonyliron(II))-η^5cyclopentadienyl]methoxycarbene}chromium(0) (8)

GP, 3.9 g (14.6 mmol) of **15**, 30 ml of THF, 13.5 ml (17.6 mmol) of 1.3 M *sec*-butyllithium in cyclohexane, 3.2 g (14.6 mmol) of Cr(CO)$_6$, 2.6 g (17.6 mmol) of triethyloxonium tetrafluoroborate in 10 ml of dichloromethane. Column chromatography (20 × 5 cm, petroleum ether/*tert*-butylmethyl ether 10:1 → 2:1) yields 2.3 g (4.6 mmol, 32%) of **8** as a deep red oil.

IR (ATR): v = 2961 cm^{-1} (w, CH), 2931 (w, CH), 2875 (w), 2060 (m, C=O), 1999 (s, C=O), 1931 (s, br, C=O), 1773 (m), 1594 (m), 1450 (m), 1236 (w), 1148 (m), 830 (m), 765 (m) 696 (m). ^{1}H NMR (400 MHz, C$_6$D$_6$): δ = 2.64 (s, 2H, FeCH$_2$), 3.93 (s, 2H, Cp), 4.05 (s, 3H, CH$_3$), 4.94 (s, 2H, Cp), 7.11–6.96 (m, 5H, arom.H). ^{13}C NMR (100.6 MHz, APT, C$_6$D$_6$): δ = 7.5 (+, FeCH$_2$), 65.9 (−, CH$_3$), 88.8 (−, Cp), 90.5 (−, Cp), 105.9 (+, *ipso* Cp), 126.0, 126.1, 127.9, 128.7, 129.8 (−, 5C, arom.C), 151.9 (+, *ipso* Bn), 215.1 (+, FeCO), 216.8 (+, CrCO$_{cis}$), 223.0 (+, CrCO$_{trans}$), 332.4 (+, Cr=C). MS (70 eV, 90 °C): m/z (%) = 502 (2) [M$^+$], 474 (4) [M$^+$ − CO], 418 (3) [M$^+$ − 3CO], 390 (2) [M$^+$ − 4CO], 362 (6) [M$^+$ − 5CO], 334 (5) [M$^+$ − 6CO], 306 (9) [M$^+$ − 7CO], 263 (18), 212 (100), 148 (17), 121 (91), 91 (88) [C$_7$H$_7^+$], 65 (39) [Cp]. HRMS C$_{20}$H$_{14}$O$_7$FeCr: Calc. 473.9668; found: 473.9494.

3.7. Pentacarbonyl{[(butyldicarbonyliron(II))-η^5-cyclopentadienyl]ethoxycarbene}chromium(0) (9)

GP, 1.2 g (5.1 mmol) of butyldicarbonylcyclopentadienyliron(+2) [56], 50 ml of THF, 1.7 ml (6.4 mmol) of 1.3 M *sec*-butyllithium in cyclohexane, 1.1 g (5.0 mmol) of Cr(CO)$_6$, 1.0 g (5.0 mmol) of triethyloxonium tetrafluoroborate in 15 ml of dichloromethane. Column chromatography (20 × 5 cm, petroleum ether/*tert*-butylmethyl ether 10:1 → 2:1) yields 1.2 g (2.4 mmol, 48%) of **9** as a deep red oil.

IR (ATR): v = 2935 cm^{-1} (m, CH), 2054 (m, C=O), 1986 (s, C=O), 1944 (s, br, C=O), 1927 (s, br, C=O), 1771 (s), 1584 (m), 1453 (m), 1262 (w), 1055 (w), 824 (w), 752 (w), 697 (s). ^{1}H NMR (400 MHz, C$_6$D$_6$): δ = 0.70–1.01 (m, 9H, CH$_2$, CH$_3$), 1.09 (t, $^3J_{6,7}$ = 7.0 Hz, 3H, 7-H), 4.11 (s, 2H, Cp), 4.71 (q, $^3J_{6,7}$ = 7.0 Hz, 2H, 6-H), 5.05 (s, 2H, Cp). ^{13}C NMR (100.6 MHz, APT, BB, C$_6$D$_6$): δ = 5.2 (+, FeCH$_2$), 13.3 (+, CH$_2$), 14.1 (−, C-7), 27.3 (+, CH$_2$), 40.0 (+, CH$_2$), 66.5 (−, CH$_3$), 75.9 (+, C-6), 88.0 (−, Cp), 88.4 (−, Cp), 106.7 (+, *ipso* Cp), 215.2 (+, FeCO), 217.5 (+, CrCO$_{trans}$), 222.5 (+, CrCO$_{cis}$), 329.3 (+, Cr=C). HRMS C$_{19}$H$_{18}$O$_8$CrFe: Calc. 481.9713; found: 481.9756. CV: T = 25 °C, c = 0.1 mmol/l, c_{TBAHFP} = 0.3 mol/l, number of scans = 1: E_A = 0.566 V (v = 1 V/s), 0.553 V (v = 2 V/s).

3.8. Pentacarbonyl{[((trimethylsilylmethyl)-dicarbonyliron(II))-η^5-cyclopentadienyl]ethoxycarbene}-chromium(0) (10)

GP, 0.90 g (3.4 mmol) of (trimethylsilylmethyl)dicarbonylcyclopentadienyliron(+2) [56], 30 ml of THF, 2.9 ml (3.7 mmol) of 1.3 M *sec*-butyllithium in cyclohexane, 0.75 g (5.0 mmol) of Cr(CO)$_6$, 0.70 g (3.7 mmol) of triethyloxonium tetrafluoroborate in 10 ml of dichloromethane. Column chromatography (20 × 5 cm, petroleum ether/*tert*-butylmethyl ether 10:1 → 2:1) yields 0.20 g (0.4 mmol, 12%) of **10** as a deep red oil.

IR (ATR): v = 2961 cm^{-1} (w, CH), 2875 (w), 2058 (m, C=O), 1998 (s, C=O), 1935 (s, br, C=O), 1777 (m), 1596 (m), 1454 (m), 1239 (w), 835 (m), 765 (m), 690 (m). ^{1}H NMR (400 MHz, C$_6$D$_6$): δ = −0.21 (s, 2H, FeCH$_2$), 0.16 (s, 9H, CH$_3$), 1.08 (t, $^3J_{6,7}$ = 7.0 Hz, 3H, 7-H), 4.40 (s, 2H, Cp), 4.75 (q, $^3J_{6,7}$ = 7.0 Hz, 2H, 6-H), 5.07 (s, 2H, Cp). ^{13}C NMR (100.6 MHz, BB, C$_6$D$_6$): δ = −18.8 (FeCH$_2$), 2.0 (SiCH$_3$), 14.8 (C-7), 76.7 (C-6), 87.6 (Cp), 89.0 (Cp), 106.2 (*ipso* Cp), 215.7 (FeCO), 216.9 (CrCO$_{cis}$), 223.1 (CrCO$_{trans}$), 330.7 (Cr=C). HRMS C$_{19}$H$_{20}$CrFeSiO$_8$: Calc. 511.9628; found: 511.9682. C$_{19}$H$_{20}$CrFeSiO$_8$ (511.9628): Calc. C, 44.53; H, 3.90; found: C, 44.57; H, 4.41. CV: T = 25 °C, c = 0.1 mmol/l, c_{TBAHFP} = 0.3 mol/l, number of scans = 1: E_A = 0.653 V (v = 1 V/s); E_A = 0.693 V (v = 2 V/s).

3.9. Pentacarbonyl{[((trimethylsilylmethyl)-dicarbonyliron(II))-η⁵-cyclopentadienyl]ethoxycarbene}-tungsten(0) (11)

GP, 0.90 g (3.4 mmol) of (trimethylsilylmethyl)dicarbonylcyclopentadienyliron(+2) [56], 30 ml of THF, 2.9 ml (3.7 mmol) of 1.3 M *sec*-butyllithium in cyclohexane, 1.20 g (5.0 mmol) of $W(CO)_6$, 0.70 g (3.7 mmol) of triethyloxonium tetrafluoroborate in 10 ml of dichloromethane. Column chromatography (20×5 cm, petroleum ether/*tert*-butylmethyl ether $10:1 \rightarrow 2:1$) yields 0.43 g (0.7 mmol, 20%) of **11** as a black red oil.

IR (ATR): $v = 2960$ cm^{-1} (w, CH), 2067 (s, C=O), 2012 (s, C=O), 1909 (s, br, C=O), 1721 (w), 1442 (w), 1256 (m), 1056 (w), 822 (m), 764 (m), 679 (m). ^{1}H NMR (400 MHz, APT, BB, C_6D_6): $\delta = -0.23$ (s, 2H, FeCH$_2$), 0.12 (s, 9H, CH$_3$), 1.09 (t, $^3J_{6,7} = 7.0$ Hz, 3H, 7-H), 4.26 (s, 2H, Cp), 4.53 (q, $^3J_{6,7} = 7.0$ Hz, 2H, 6-H), 5.07 (s, 2H, Cp). ^{13}C NMR (100.6 MHz, APT, C_6D_6): $\delta = -18.5$ (+, FeCH$_2$), 2.0 (−, SiCH$_3$), 14.7 (−, C-7), 79.2 (+, C-6), 84.8 (−, Cp), 87.6 (−, Cp), 108.3 (+, *ipso* Cp), 197.5 (+, WCO$_{cis}$), 202.3 (+, WCO$_{trans}$), 303.8 (+, W=C). $C_{19}H_{20}CrFeO_8Si$ (644.3432): Calc. C, 36.50; H, 3.37; found: C, 36.68; H, 3.67.

3.10. Complex 13

GP, 1.20 g (3.0 mmol) of **12** [56], 50 ml of THF, 5.2 ml (6.8 mmol) of 1.3 M *sec*-butyllithium in cyclohexane, 1.20 g (6.0 mmol) of $Cr(CO)_6$, 1.60 g (6.4 mmol) of triethyloxonium tetrafluoroborate in 20 ml of dichloromethane. Column chromatography (20×5 cm, petroleum ether/*tert*-butylmethyl ether $10:1 \rightarrow 2:1$) yields 0.93 g (1.0 mmol, 34%) of **13** as a red orange solid (m.p. 98 °C, dec.).

IR (ATR): $v = 2943$ cm^{-1} (w, CH), 2905 (w, CH), 2057 (s, C=O), 1993 (s, C=O), 1905 (s, br, C=O), 1772 (s), 1467 (m), 1446 (m), 1223 (s) 1203 (s), 1142 (m), 840 (m), 766 (m), 697 (m). ^{1}H NMR (400 MHz, C_6D_6): $\delta = 0.40$ (s, br, 2H, FeCH$_2$ or CH$_2$), 1.09 (t, 6H, CH$_3$), 1.58 (s, 4H, FeCH$_2$ or CH$_2$), 4.15 (s, 2H, Cp), 4.71 (q, $^3J = 7.0$ Hz, 4H, OCH$_2$), 5.08 (s, 2H, Cp). ^{13}C NMR (100.6 MHz, BB, C_6D_6): $\delta = 1.2$ (FeCH$_2$), 9.2 (CH$_2$), 14.8 (CH$_3$), 76.6 (CH$_2$), 88.6 (Cp), 88.8 (Cp), 107.4 (*ipso* Cp), 216.1 (FeCO), 217.0 (CrCO$_{cis}$), 223.1 (CrCO$_{trans}$), 330.2 (Cr=C). MS (70 eV, 140 °C): m/z (%) = 468 (2), 437 (2), 411 (7) [M$^+$ − 14CO − 2OEt], 384 (2), 354 (13), 326 (7), 242 (21), 220 (100, Cr(CO)$_6$), 186 (44), 149 (24), 121 (93), 99 (4), 52 (25) [Cr$^+$]. $C_{33}H_{24}Cr_2Fe_2O_{16}$ (892.2287): ber. C, 44.39; H, 2.69; gef. C, 44.78; H, 3.95.

3.11. Complex 14

GP, 1.20 g (3.0 mmol) of **12** [56], 30 ml of THF, 5.2 ml (6.8 mmol) of 1.3 M *sec*-butyllithium in cyclohex-

ane, 1.60 g (6.0 mmol) of $Mo(CO)_6$, 1.60 g (6.4 mmol) of triethyloxonium tetrafluoroborate in 25 ml of dichloromethane. Column chromatography (20×5 cm, petroleum ether/*tert*-butylmethyl ether $10:1 \rightarrow 2:1$) yields 0.71 g (0.7 mmol, 24%) of **14** as a red orange solid (m.p. 93 °C).

IR (ATR): $v = 2942$ cm^{-1} (w, CH), 2905 (w, CH), 2065 (s, C=O), 1990 (s, C=O), 1929 (s, br, C=O), 1771 (s), 1227 (s) 1209 (s), 1139 (m), 839 (m). ^{1}H NMR (400 MHz, C_6D_6): $\delta = 0.38$ (s, br, 2H, FeCH$_2$ or CH$_2$), 1.08 (t, 6H, CH$_3$), 1.59 (s, 4H, FeCH$_2$ or CH$_2$), 4.17 (s, 2H, Cp), 4.62 (q, 4H, OCH$_2$), 5.09 (s, 2H, Cp). ^{13}C NMR (100.6 MHz, BB, C_6D_6): $\delta = 1.2$ (FeCH$_2$) 9.2 (CH$_2$), 14.8 (CH$_3$), 77.3 (CH$_2$), 88.9 (Cp), 89.6 (Cp), 107.2 (*ipso* Cp), 206.2 (MoCO$_{cis}$), 212.7 (MoCO$_{trans}$), 216.2 (FeCO), 320.6 (Mo=C). MS (70 eV): 354 (8) [Mo=CCpFeCH$_3$ + 4CO], 352 (18), 326 (10) [Mo=CCpFeCH$_3$ + 3CO], 324 (27), 298 (12) [Mo=CCpFeCH$_3$ + 2CO], 296 (28), 270 (5) [Mo=CCpFeCH$_3$ + CO], 266 (16) [Mo(CO)$_6$], 242 (16) [Mo=CCCpFeCH$_3$], 238 (65) [Mo(CO)$_6$ − CO], 210 (100) [Mo(CO)$_6$ − 2CO], 182 [Mo(CO)$_6$ − 3CO], 180 (52), 162 (15) [CpFeCH$_2$CH$_2$CH$_3$], 151 (43), 149 (26) [CpFeCH$_2$CH$_3$], 134 (25) [CpFeCH$_3$], 121 (22) [CpFe$^+$], 115 (53), 106 (32). m/z (%) = 352 ($C_{33}H_{24}O_{16}Fe_2Mo_2$) (972.6754): Calc. C, 40.74; H, 2.47; found: C, 40.50; H, 2.11.

3.12. Benzyldicarbonyl(formylcyclopentadienyl)iron(II) (16)

To 1.00 g (3.7 mmol) of **15** in 50 ml of THF 3.2 ml of 1.3 M *sec*-butyllithium in cyclohexane is added dropwise at −78 °C. The black solution is stirred for 1 h at −78 °C, then 0.41 g (5.6 mmol) of *N,N*-dimethylformamide is added via syringe. After 30 min, 10 ml of 2 M hydrochloric acid is added, and the mixture is allowed to warm to 25 °C. 20 ml of water is added, and the mixture is extracted three times with 30 ml of diethyl ether each. The collected organic layers are dried over MgSO$_4$ and filtered. After solvent removal at reduced pressure 0.80 g (2.7 mmol, 73%) of **16** is obtained as a brown black.

IR (ATR): $v = 2841$ cm^{-1} (w, CH), 2066 (w), 1998 (s, C=O), 1940 (s, br, C=O), 1689 (m, CHO), 1593 (m), 1487 (m), 1257 (m) 1215 (m), 1032 (m), 851 (w), 762 (m) 700 (m). ^{1}H NMR (400 MHz, C_6D_6): $\delta = 2.67$ (s, 2H, FeCH$_2$), 3.81 (s, br, 2H, Cp), 4.54 (s, br, 2H, Cp), 6.91–7.10 (m, 5H, arom.H), 8.93 (s, 1H CHO). ^{13}C NMR (100.6 MHz, BB, C_6D_6): $\delta = 5.2$ (FeCH$_2$), 85.0 (Cp), 88.3 (Cp), 89.4 (*ipso* Cp), 122.2–127.3 (5C, arom.C), 150.2 (*ipso* Bn), 184.8 (CHO), 213.1 (FeCO). MS (70 eV, 90 °C): m/z (%) = 268 (11) [M$^+$ + 1 − CHO], 240 (21) [M$^+$ + 1 − CHO − CO], 212 (98) [M$^+$ + 1 − CHO − 2CO], 186 (6), 168 (4), 149 (14), 121 (100), 91 (78) [C$_7$H$_7^+$], 65 (28). HRMS $C_{14}H_{12}FeO_2$: ber. 268.0184, gef. 268.0187.

3.13. Complex 18

0.90 g (3.0 mmol) of **16**, 1.4 ml of triethylamine, and 1.4 ml of chlorotrimethylsilane in 30 ml of THF is stirred at 25 °C for 1 h. Then 0.84 g (3.2 mmol) of pentacarbonyl(ethoxyethylidene)chromium(0) (**17**) is added. The solution changes its color from orange yellow to red over 12 h. The solvent is removed at reduced pressure. Column chromatography (SiO$_2$, 20 × 5 cm, petroleum ether/*tert*-butylmethyl ether 10:1 → 2:1) yields 0.60 g (1.1 mmol, 37%) of **18** as a black solid.

IR (ATR): $v = 2962$ cm^{-1} (w, CH), 2052 (s, C=O), 2002 (s, C=O), 1906 (s, br, C=O), 1586 (m), 1488 (w), 1258 (s), 1011 (m), 939 (w), 701 (w), 666 (w). ^{1}H NMR (400 MHz, C$_6$D$_6$): $\delta = 1.17$ (t, 3H, $^3J = 7.0$ Hz, CH$_3$), 2.82 (s, 2H, FeCH$_2$), 4.02 + 4.34 (AA'BB', 2 × 2H, Cp), 4.72 (q, $^3J = 7.1$ Hz, 2H, OCH$_2$), 6.23 (d, $^3J = 15.3$ Hz, 1H, CH), 6.89–7.68 (m, 5H, arom.H), 7.60 (d, 1H, CH). ^{13}C NMR (100.6 MHz, APT, BB, C$_6$D$_6$): $\delta = 5.8$ (FeCH$_2$), 12.7 (CH$_3$), 74.3 (CH$_2$), 84.0 (Cp), 88.0 (Cp), 90.8 (*ipso* Cp), 121.9 (arom.-C), 122.7 (CH), 125.9–126.8 (arom.-C), 137.9 (CH), 150.6 (*ipso* Bn), 211.1 (FeCO), 215.4 (CrCO$_{cis}$), 223.2 (CrCO$_{trans}$), 328.7 (Cr=C). HRMS C$_{24}$H$_{18}$O$_8$CrFe: Calc. 541.9643; found: 541.9756. C$_{24}$H$_{18}$CrFeO$_8$ (541.9643): Calc. C, 53.14; H, 3.32; found: C, 53.53; H, 3.54.

Acknowledgments

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