Some bimetallic half sandwich iron complexes with metal carbene substitution at the cyclopentadienyl ligand: synthesis, characterization, structure, and cyclic voltammetry†

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The first half sandwich cyclopentadienyl complexes **2**–**5** with a carbene complex subtituent at the cyclopentadienyl ring are presented. These complexes deserve interest because one metal atom (Cr, Mo, W, Fe) is incorporated in the π system of the ligand in conjugation to the cyclopentadienyl ring complexed to iron. In addition to intermetallic interactions these complexes offer the possibility of reactions at both metal atoms. An X-ray structure analysis of **2** reveals, however, that the carbene–chromium π bond is not perfectly coplanar with the cyclopentadienyl ring. Cyclic voltammetry of some of the complexes prepared shows a decrease in oxidation potential upon carbene complex substitution at the cyclopentadienyl ring for **2** and **7** by 118 and 63 mV, respectively. A ligand exchange reaction with bis(diphenylphosphino)ethane (dppe) under irradiation results in the incorporation of two dppe molecules.

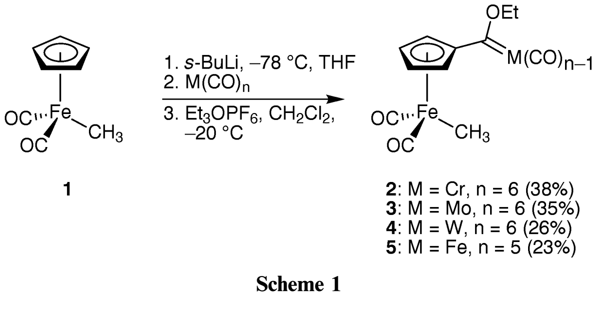
Transition metal complexes with more than one metal atom incorporated raise the question of interactions between the metal atoms. This deserves interest in connection with possible applications of multinuclear metal complexes in topical fields such as electron transfer chemistry,[1] catalysis, molecular electronics,[2] and nonlinear optics.[3,4] Considering intermetallic interactions, complexes lacking a direct chemical bond between the metal atoms are interesting with respect to the role of the ligands as possible communication paths between the metal atoms. Such communication might facilitate new properties that cannot appear when such complexes are regarded as just the sum of some mononuclear complexes that are chemically bound to one another.

Experience from organic chemistry teaches us that π systems are especially prone to act as transfer units for electronic interactions, and therefore metal complexes of various π systems are frequently used to investigate such interactions. A number of systems have been investigated in which π complex subunits are connected directly or by conjugated π systems as conductive spacers. Examples are bimetallic complexes of fulvalenes,[2,4–6] biphenyl,[2,7–12] stilbene,[13] oligophenylenes,[14] *etc.* Alternatively, one might consider systems in which the metal atoms are integrated in the π systems as is the case in bi- or oligometallic carbene and carbyne complexes.[15–19]

In the context of our interests in half sandwich complexes with functionalized cyclopentadienyl ligands[20–27] we saw the possibility to combine the two principles: half sandwich complexes with a cyclopentadienyl ligand bearing a carbene complex substituent might show interesting chemical and physical properties. Here we report the syntheses of some cyclopentadienyliron complexes with chromium, molybdenum, tungsten, and iron carbene moieties bound directly to the cyclopentadienyl ring. We were especially interested in half sandwich complexes because these bear some potential in terms of ligand exchange at the metal and of functionalization reactions at the other ligands. This might become important if one considers intramolecular reactions between a ligand and the metal carbene moiety. We note that few carbene complexes bearing a ferrocenyl substituent at the carbene carbon atom are known.[28–32] However, these do not offer much possibility for further chemistry at the iron atom. We regarded the well investigated dicarbonylcyclopentadienyliron(II)[33,34] system more attractive as it allows for chemistry at the cyclopentadienyl ligands as well as at the iron atom.

Results and discussion

Dicarbonylcyclopentadienylmethyliron(II) (**1**) was deprotonated at the cyclopentadienyl ring by treatment with *sec*-butyllithium at −78 °C. The anion was then treated with hexacarbonylchromium(0), hexacarbonylmolybdenum(0), hexacarbonyltungsten(0), or pentacarbonyliron(0). Finally, triethyloxonium hexafluorophosphate was added to afford complexes **2**–**5** in 23–38% yield (Scheme 1). The Group 6 metal carbene complexes were obtained as crystalline materials with melting points at 83 °C (**2**, M = Cr), 85 °C (**3**, M = Mo), and 87 °C (**4**, M = W). These complexes are air stable when crystalline; they decompose within a few hours when their solutions are exposed to air.



Scheme 1

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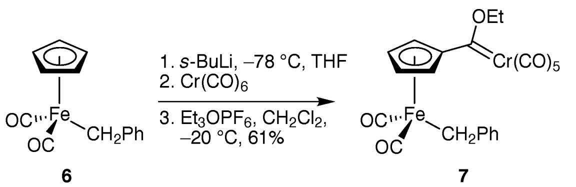
† Dedicated to Professor Dirk Walther on the occasion of his 60th birthday.



Scheme 2

In a similar manner, starting from benzyliron complex **6**,[35] chromium carbene complex **7** (Scheme 2) was obtained in 61% yield as a dark red solid, which is air stable for some days.

All spectroscopic data obtained are in accord with the expected compositions of **2**–**5** and **7**. The IR spectra are somewhat more complicated due to the number of carbonyl ligands. The A_1 absorptions of the carbene metal carbonyl ligands correspond rather closely to those reported for the ferrocenylcarbene complexes,[28,30] taking into account that the data reported in the literature were obtained from a hexane solution whereas chloroform was used in this study. A band at 2016 cm^{-1} is observed for all complexes and is assigned to the dicarbonyliron moiety.

The mass spectrum of chromium complex **2** clearly shows the molecular ion peak and those resulting from losses of up to seven CO ligands, leading to the base peak at $m/z = 244$ corresponding to the completely decarbonylated complex. In the ^{13}C NMR spectrum carbonyl absorptions are observed at $\delta = 216.2$ (Fe–CO) and at $\delta = 217.6$ (*cis*-Cr–CO) as well as at $\delta = 223.8$ (*trans*-Cr–CO). The carbene carbon atom gives rise to a signal at $\delta = 331.3$. The corresponding signals of **7** do not differ much from those of **2**, the carbene carbon resonance is observed at δ 330.8. Although the carbene carbon chemical shifts are in the usual range of chromium carbene complexes, the data indicate a significantly increased shielding of the carbene carbon atom when compared with the ethoxyphenylcarbene pentacarbonylchromium complex.[36]

Mixed valence diiron complex **5** was obtained by treatment with $Fe(CO)_5$ in 23% yield, in addition to a small amount (4%) of $Fe_3(CO)_{12}$. Here iron carbonyl signals are observed at $\delta = 215.0$ and 216.2; the carbene carbon atom signal shows up at $\delta = 311.7$.

It was possible to obtain crystals of chromium complex **2**, which were suitable for an X-ray crystal structure analysis (Fig. 1). The structure shows an octahedral coordination around the chromium atom. The axis O(7)–C(15)–Cr–C(14)–O(6) is linear, whereas the geometry is disturbed by the steric bulk of the carbene ligand, leading to an angle of 172.5° for C(12)–Cr–C(13). In addition, the Cr–C(12)–O(4) subunit also significantly deviates from linearity (173.8°). The special position of the C(12)–O(4) carbonyl ligand also becomes visible by a comparison of the angles between the C(6)–Cr bond and the carbonyl ligands. Three of these angles are about 90°, whereas that of C(6)–Cr–C(12) is 97.4°, indicating the steric repulsion between this carbonyl ligand and the ethoxy group. On the other hand, bond angle O(1)–C(6)–C(1) is 103.8°, considerably smaller than the usual 120° angle. The Cr–C(6) π bond and the π system of the cyclopentadienyl ligand are *not* coplanar; the dihedral angle C(5)–C(1)–C(6)–Cr is 150.3°. A possible reason for this deviation from ideal conjugation might be the steric bulk of the dicarbonylmethyliron fragment, to avoid close interaction with the C(14)–O(6) carbonyl ligand at chromium.

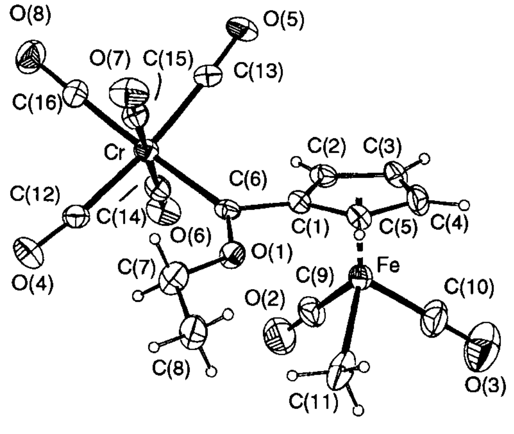


Fig. 1 Molecular structure of **2** in the crystal. Selected bond lengths (Å) and angles (°): Fe–C(1) 2.105(5), Fe–C(2) 2.095(5), Fe–C(3) 2.099(5), Fe–C(4) 2.094(6), Fe–C(5) 2.084(6), Fe–C(11) 2.130(6), C(1)–C(2) 1.418(6), C(1)–C(5) 1.417(7), C(2)–C(3) 1.393(7), C(3)–C(4) 1.384(7), C(4)–C(5) 1.396(9), C(1)–C(6) 1.483(8), C(7)–C(8) 1.394(9), C(6)–O(1) 1.329(6), C(7)–O(1) 1.443(7), Cr–C(6) 2.038(7); C(12)–Cr–C(13) 172.5(2), Cr–C(12)–O(4) 173.7(5), Cr–C(6)–C(1) 125.0(4), Cr–C(6)–O(1) 130.7(4), C(1)–C(6)–O(1) 103.8(4).

In order to investigate if electronic properties of the cyclopentadienyliron complexes were affected by the carbene complex substitution, cyclic voltammetry measurements were performed with bimetallic iron–chromium complexes **2** and **7**, and for comparison, with the unsubstituted iron complexes **1** and **6** (Fig. 2, 3). The voltammograms of **2** and **7** are rather similar and show oxidation peaks at 640 and 625 mV, respectively. Both oxidations are irreversible, presumably a result of the high reactivity of the radical cations formed.

In Table 1 the results are summarized, and the data indicate a decrease in oxidation potential of 118 and 63 mV for **1** and **6**, respectively, upon substitution of the cyclopentadienyl ligand with an ethoxycarbene(pentacarbonyl)chromium moiety. As chromium carbene complexes normally are less easily oxidized than cyclopentadienyldicarbonyliron complexes and therefore air stable, the observed oxidation step is assigned to the Fe(II)–Fe(III) oxidation. It is remarkable that the substitution of the cyclopentadienyl ligand by a chromium carbene moitey *decreases* the oxidation potential. Data

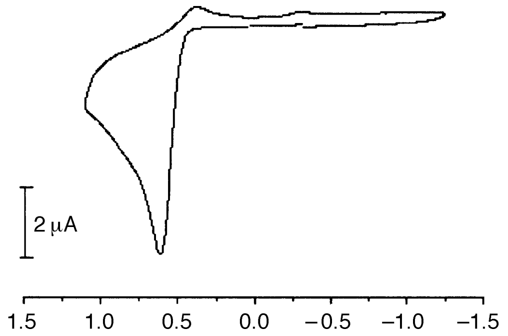


Fig. 2 Cyclic voltammogram of **2**. Potential *vs.* ferrocene/ferrocenium ion

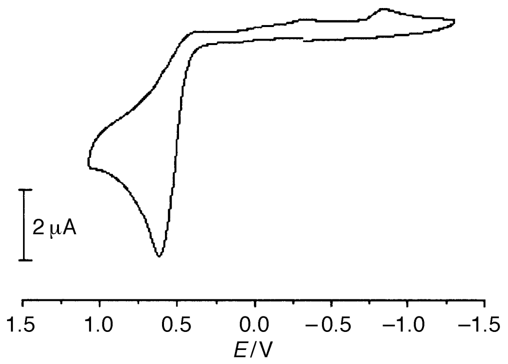


Fig. 3 Cyclic voltammogram of **7**. Potential *vs.* ferrocene/ferrocenium ion

Table 1 CV data of complexes **1**, **2**, **6**, and **7**[a]

	E_{AP}/mV
1	758
2	640
6	688
7	625

[a] Conditions: $-20\,°C$, $c_{complex} = 0.1$ mmol L^{-1}, CH_2Cl_2, $Bu_4N^+PF_6^-$ (0.1 mol L^{-1}), 1 scan, 100 mV s^{-1}. E_{AP} = anodic potential *vs.* ferrocene/ferrocenium ion.

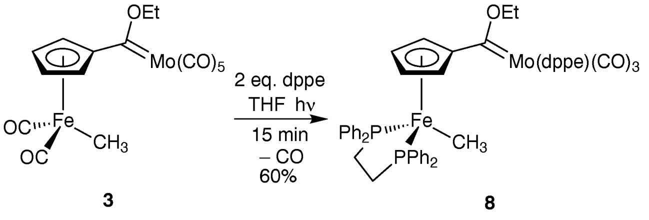
obtained for substituted ferrocenes show the reverse trend in that the oxidation potential *increases* for electron withdrawing substituents.[1]

Although the extent of decrease observed is not extremly high, it is significant. For an explanation one has to take into account all factors that might influence the redox potential. These include the unusual steric bulk of the substituent at the cyclopentadienyl ring in **2** and **7** and possible consequences for the diffusion coefficient, as well as a possibly different mechanism of electron transfer from the complex to the positively charged anode because of the presence of a much larger number of cabonyl ligands with negatively polarized oxygen atoms as compared to **1** and **6**. Electronic effects of substituents at aromatic systms are traditionally divided into inductive and resonance influences, the latter normally being considered more important. However, resonance effects require conjugation between the aromatic system and the π system of the respective ligand. As the X-ray analysis of **2** indicates only partial conjugation in this case, the reason for the observed electronic effect could be a change in the balance of resonance and inductive contributions resulting in a relative decrease of the resonance part as compared with the inductive effect. Clearly, more studies directed to a detailled understanding of resonance and inductive effects of Fischer type carbene complexes are required.

In a ligand exchange reaction molybdenum complex **3** was treated with two equivalents of bis(diphenylphosphino)ethane (dppe) under irradiation in THF. After 15 min ligand exchange had occurred to give complex **8** in 60% yield (Scheme 3). **6** was identified spectroscopically on the basis of IR and NMR spectra, all data are in accord with a double ligand exchange reaction. A FAB MS spectrum showed a signal corresponding to CpFe(dppe), no molecular ion peak was observable. **6** is more sensitive than the other bimetallic complexes prepared, some losses occurred during the column chromatography.

Conclusion

We have prepared and characterized some bimetallic complexes in which iron(II) is bound to a substituted cyclopentadienyl ligand, which bears a metal carbene substituent. Further investigations in this field are directed towards possible intermetallic communication in the complexes and the reactivity of these complexes especially with respect to intra- and intermolecular Dötz type anellation reactions, which might lead to heterobimetallic indenyl complexes.[37–45]



Scheme 3

Experimental

Unless otherwise indicated all operations were carried out under argon using standard Schlenk techniques. Halogen-free solvents were distilled from sodium–potassium alloy wth a small amount of benzophenone. Dichloromethane was dried over P_4O_{10} and distilled under argon. ^1H NMR: Bruker AM 400 (400.1 MHz); ^{13}C NMR: Bruker AM 400 (100.6 MHz); signal multiplicities were determined with the APT[46] technique where indicated; NMR samples were prepared under argon and sealed under vacuum. IR: Perkin–Elmer FTIR spectrometers 580 and 1710. MS: Finnigan MAT 112, MAT 312, MAT SSQ 7000. 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).

Synthesis

{Ethoxy[pentacarbonylchromium(0)]carbenylcyclopentadienyl}dicarbonylmethyliron(II) (2). At $-78\,°C$ 5.1 mL of a 0.47 M (2.4 mmol) solution of *sec*-butyllithium in cyclohexane was added dropwise to 415 mg (2.34 mmol) of cyclopentadienyldicarbonylmethyliron(II) (**1**) in 20 mL of THF. After stirring for 20 min the cold solution was added to a $-60\,°C$ cold suspension of 515 mg (2.34 mmol) of $Cr(CO)_6$ in 15 mL of THF. The mixture was allowed to warm to 10 °C, while the $Cr(CO)_6$ dissolved, and a change in colour from dark brown to yellow-brown was observed. The solvent was removed under reduced pressure, and the residue was dissolved in 15 mL of dichloromethane. At 25 °C a solution of 615 mg (2.45 mmol) of triethyloxonium hexafluorophosphate in 15 mL of dichloromethane was added, and the mixture was stirred for 15 min. Then the mixture was extracted with three portions of *tert*-butylmethyl ether (MTBE)–water (1 : 1), and the collected organic layers were dried over $MgSO_4$. The crude product was purified by column chromatography (15 × 4 cm, petroleum ether–MTBE 10 : 1 to 2 : 1). The product was obtained as a red solution, whose volume was reduced to 15 mL. The solution was stored at $-30\,°C$. After some days dark red needles crystallized, 395 mg (38%) of **2** was obtained (mp 83 °C).

IR ($CHCl_3$): $\tilde{\nu}$ = 2980 cm^{-1} (w), 2900 (w), 2060 (s, CrCO), 2016 (s, FeCO), 1940 (br s, CrCO and FeCO), 1444 (w), 1376 (w), 1252 (m), 1228 (m), 1056 (w), 648 (m), 584 (m). ^1H NMR (400.1 MHz, C_6D_6): δ = 0.37 (s, 3H, $FeCH_3$), 1.14 (t, 3H, 8-H, $^3J_{7,8}$ = 7.0 Hz), 4.13 (s, 2H, Cp), 4.76 (q, 2H, 7-H), 5.09 (s, 2H, Cp). ^{13}C NMR (100.6 MHz, C_6D_6, APT): δ = −20.0 (−, $FeCH_3$), 15.5 (−, C-8), 77.3 (+, C-7), 88.2 (−, Cp), 89.9 (−, Cp), 107.4 (+, Cp), 216.2 (+, FeCO), 217.6 (+, $CrCO_{cis}$), 223.8 (+, $CrCO_{trans}$), 331.3 (+, Cr=C). MS (70 eV, 90 °C): *m*/*z* (%) = 441 (3) [$M^+ + 1$], 440 (10) [M^+], 412 (1) [$M^+ - CO$], 356 (21) [$M^+ - 3$ CO], 328 (8) [$M^+ - 4$ CO], 313 (4) [$M^+ - 4$ CO $-CH_3$], 300 (21) [$M^+ - 5$ CO], 285 (12) [$M^+ - 5$ CO $-CH_3$], 272 (19) [$M^+ - 6$ CO], 257 (7) [$M^+ - 6$ CO $-CH_3$], 244 (100) [$M^+ - 7$ CO], 216 (6), 200 (10) [$M^+ - 7$ CO $-C_2H_5$ $-CH_3$], 187 (26), 172 (23), 131 (17), 108 (9), 52 (16) [Cr^+]. $C_{16}H_{12}CrFeO_8$ (440.11): calcd C 43.67, H 2.75; found C 43.66, H 2.80%. CV (100 mV s^{-1}, $T = -20\,°C$): E_{AP1} = 640 mV.

{Ethoxy[pentacarbonylmolybdenum(0)]carbenylcyclopentadienyl}dicarbonylmethyliron(II) (3). At $-78\,°C$ 4.7 mL of a 0.47 M (2.2 mmol) solution of *sec*-butyllithium in cyclohexane was added dropwise to 400 mg (2.08 mmol) of cyclopentadienyldicarbonylmethyliron(II) (**1**) in 20 mL of THF. After stirring for 20 min the brown solution was added to a 20 °C warm suspension of 550 mg (2.08 mmol) of $Mo(CO)_6$ in 15 mL of THF. The mixture was stirred at −50 °C for 60 min, then at 10 °C for 30 min. The solvent was removed at reduced pressure, and the brown residue was dissolved in 15 mL of dichloromethane. At 20 °C a solution of 550 mg (2.2 mmol) of triethyloxonium hexafluorophosphate in 15 mL of dichloromethane was added, and the mixture was stirred for 15 min. Then the mixture was extracted with three portions of MTBE–water (1 : 1), and the collected organic layers were dried over $MgSO_4$. The crude product was purified by filtration through a 8 cm thick layer of silica gel, and the solvent was removed under reduced pressure: 460 mg (0.94 mmol, 35%) of **3** was obtained as an amorphous red solid (mp 85 °C).

IR ($CHCl_3$): $\tilde{\nu} = 3112$ cm^{-1} (w), 2976 (w), 2068 (s, MoCO), 2016 (s, FeCO), 1944 (br s, MoCO and FeCO), 1444 (w), 1376 (w), 1260 (m), 1228 (m), 1056 (w), 628 (w), 600 (m), 584 (m), 564 (w). ^1H NMR (400.1 MHz, $[D_6]$-acetone): $\delta = 0.28$ (s, 3H, $FeCH_3$), 1.69 (t, 3H, 8-H, $^3J_{7,8} = 6.99$ Hz), 5.15 (q, 2H, 7-H), 5.32 (s, 2H, Cp), 5.72 (s, 2H, Cp). ^{13}C NMR (100.6 MHz, $[D_6]$-acetone, APT): $\delta = -19.9$ (−, $FeCH_3$), 16.2 (−, C-8), 80.6 (+, C-7), 90.3 (−, Cp), 92.5 (−, Cp), 107.9 (+, Cp), 207.3 (+, $CrCO_{cis}$), 214.5 (+, $CrCO_{trans}$), 217.1 (+, FeCO), 321.8 (+, Mo=C). MS (70 eV, 100 °C): m/z (%) = 488 (3), 486 (7), 486 (3), 484 (6), 483 (5), 482 (3), 480 (5), $[M^+]$ for the 7 Mo isotopes; in the following only the largest peak is given: 430 (18) $[M^+ - 2\ CO]$, 403 (38) $[M^+ - 3\ CO]$, 388 (7) $[M^+ - 3\ CO\ -CH_3]$, 374 (23) $[M^+ - 4\ CO]$, 359 (9) $[M^+ - 4\ CO\ -CH_3]$, 346 (42) $[M^+ - 5\ CO]$, 331 (11) $[M^+ - 5\ CO\ -CH_3]$, 316 (30) $[M^+ - 6\ CO]$, 302 (12) $[M^+ - 6\ CO\ -CH_3]$, 288 (83) $[M^+ - 7\ CO]$, 273 (19) $[M^+ - 7\ CO\ -CH_3]$, 260 (42), 246 (50), 231 (100) $[M^+ - 7\ CO\ -OCH_2CH_3\ -CH_3]$, 218 (55), 192 (35), 163 (33), 134 (45) $[FeC_6H_6^+]$, 121 (78) $[FeCp^+]$, 98 (17) $[Mo^+]$, 94 (21) $[Mo^+]$, 71 (24). $C_{16}H_{12}FeMoO_8$ (484.05): calcd C 39.70, H 2.50; found C 39.31, H 2.61%.

{Ethoxy[pentacarbonyltungsten(0)]carbenylcyclopentadienyl}dicarbonylmethyliron(II) (4). At −78 °C 6.4 mL of a 0.47 M (3.0 mmol) solution of *sec*-butyllithium in cyclohexane was added dropwise to 550 mg (2.86 mmol) of cyclopentadienyldicarbonylmethyliron(II) (**1**) in 20 mL of THF. After stirring for 15 min the cold solution was added to a −70 °C cold suspension of 1006 mg (2.86 mmol) of $W(CO)_6$ in 20 mL of THF. After stirring for 60 min at −70 °C, the mixture was allowed to warm to 20 °C and stirred for another 30 min. The solvent was removed under reduced pressure, and the residue was dissolved in 15 mL of dichloromethane. At 25 °C a solution of 750 mg (3.0 mmol) of triethyloxonium hexafluorophosphate in 20 mL of dichloromethane was added, and the mixture was stirred for 20 min. The crude product was purified by column chromatography (20 × 4 cm, petroleum ether–MTBE 10 : 1 to 3 : 1). The product was obtained as a red solution, whose volume was reduced to 15 mL. The solution was stored at −78 °C; 420 mg (26%) of **4** was obtained as dark red needles (mp 87 °C).

IR ($CHCl_3$): $\tilde{\nu} = 2964$ cm^{-1} (w), 2896 (w), 2068 (s, WCO), 2016 (s, FeCO), 1928 (br s, WCO and FeCO), 1444 (w), 1376 (w), 1260 (m), 1200 (m), 1096 (w), 1056 (m), 1012 (w), 944 (w), 808 (w), 628 (m), 584 (m). ^1H NMR (400.1 MHz, C_6D_6): $\delta = 0.38$ (s, 3H, $FeCH_3$), 1.11 (t, 3H, 8-H, $^3J_{7,8} = 6.99$ Hz), 4.14 (s, 2H, Cp), 5.57 (q, 2H, 7-H), 5.07 (s, 2H, Cp). ^{13}C NMR (100.6 MHz, C_6D_6, APT): $\delta = -19.8$ (−, $FeCH_3$), 15.3 (−, C-8), 79.7 (+, C-7), 88.2 (−, Cp), 91.4 (−, Cp), 109.4 (+, Cp), 198.3 (+, WCO_{cis}), 203.1 (+, WCO_{trans}), 216.0 (+, FeCO), 304.6 (+, W=C). MS (70 eV, 140 °C): m/z (%) = 574 (6), 572 (7), 571 (4), 570 (5), $[M^+]$ of the 4 main isotopes of W; in the following only the largest peak is given: 544 (11) $[M^+ - CO]$, 516 (39) $[M^+ - 2\ CO]$, 501 (6) $[M^+ - 2\ CO,\ -CH_3]$, 488 (24) $[M^+ - 3\ CO]$, 460 (30) $[M^+ - 4\ CO]$, 444 (11) $[M^+ - 4\ CO\ -CH_3]$, 433 (83) $[M^+ - 5\ CO]$, 418 (13) $[M^+ - 5\ CO\ -CH_3]$, 405 (42) $[M^+ - 6\ CO]$, 389 (44) $[M^+ - 6\ CO\ -CH_3]$, 375 (59) $[M^+ - 7\ CO]$, 361 (74), 348 (75), 333 (58), 317 (100) $[M^+ - 7\ CO\ -OCH_2CH_3\ -CH_3]$, 304 (92), 288 (21), 248 (17), 222 (16), 186 (7), 134 (6), 121 (15), 94 (9), 71 (12). $C_{16}H_{12}FeWO_8$ (571.96): calcd C 33.60, H 2.12; found C 34.23, H 2.26%.

{Ethoxy[tetracarbonyliron(0)] carbenylcyclopentadienyl}dicarbonylmethyliron(II) (5). At −78 °C 6.2 mL of a 0.47 M (2.9 mmol) solution of *sec*-butyllithium in cyclohexane was added dropwise to 520 mg (2.71 mmol) of cyclopentadienyldicarbonylmethyliron(II) (**1**) in 20 mL of THF. After stirring for 15 min the cold solution was added to a −60 °C cold suspension of 531 mg (2.71 mmol) of $Fe(CO)_5$ in 15 mL of THF. After stirring for 60 min at −70 °C, the mixture was allowed to warm to 20 °C and was stirred for another 30 min. The solvent was removed under reduced pressure, and the residue was dissolved in 15 mL of dichloromethane. At −15 °C a solution of 750 mg (3.0 mmol) of triethyloxonium hexafluorophosphate in 20 mL of dichloromethane was added, and the mixture was stirred for 20 min at −10 °C. The mixture was extracted with 70 mL of water–MTBE (1 : 1) three times, and the collected organic layers were dried over $MgSO_4$. The black crude product was purified by column chromatography (20 × 4 cm, petroleum ether–MTBE 10 : 1 to 5 : 1). After an 18 mg fraction of green $Fe_3(CO)_{12}$, the product is obtained as a brown-red fraction, and the solvent is removed at reduced pressure: 260 mg [23%, purity *ca.* 90% (NMR)] of **5** was obtained as a viscous brown oil.

IR ($CHCl_3$): $\tilde{\nu} = 2980$ cm^{-1} (w), 2896 (w), 2360 (w), 2072 (m, FeCO), 2052 (s, FeCO), 2016 (s, FeCO), 1964 (s, FeCO), 1172 (w), 588 (w). ^1H NMR (400.1 MHz, C_6D_6): $\delta = 0.41$ (s, 3H, $FeCH_3$), 1.15 (br s, 3H, 8-H), 4.09 (br s, 2H, Cp), 4.63 (br s, 2H, 7-H), 5.03 (s, 2H, Cp). ^{13}C NMR (100.6 MHz, C_6D_6, APT): $\delta = -20.1$ (−, $FeCH_3$), 15.0 (−, C-8), 78.0 (+, C-7), 86.9 (−, Cp), 91.9 (−, Cp), 108.1 (+, Cp), 215.0 (+, FeCO), 216.2 (+, FeCO), 311.7 (+, Fe=C). MS (70 eV, 100 °C): m/z (%) = 416 (3) $[M^+]$, 360 (4) $[M^+ - 2\ CO]$, 332 (22) $[M^+ - 3\ CO]$, 317 (4) $[M^+ - 3\ CO\ -CH_3]$, 304 (23) $[M^+ - 4\ CO]$, 289 (8) $[M^+ - 4\ CO\ -CH_3]$, 276 (7) $[M^+ - 5\ CO]$, 274 (5) $[M^+ - 4\ CO\ -2CH_3]$, 260 (6) $[M^+ - 5\ CO\ -CH_3]$, 248 (100) $[M^+ - 6\ CO]$, 236 (24), 220 (18), 208 (25), 193 (37), 176 (31), 165 (33), 135 (44), 121 (80) $[FeCp^+]$, 94 (27), 84 (52) $[FeCO^+]$.

{Ethoxy[pentacarbonylchromium(0)]carbenylcyclopentadienyl}dicarbonylbenzyliron(II) (7). At −78 °C 2.3 mL of a 1.3 M (2.99 mmol) solution of *sec*-butyllithium in cyclohexane was added dropwise to 733 mg (2.74 mmol) of (benzyl)cyclopentadienyldicarbonyliron(II) (**6**) in 30 mL of THF. After stirring for 30 min 410 mg (2.75 mmol) of $Cr(CO)_6$ was added. The mixture was stirred for 60 min at −78 °C, then the mixture was allowed to warm to 25 °C and stirred for another 30 min. The solvent was removed at reduced pressure, and the residue was dissolved in 40 mL of dichloromethane. At 25 °C a solution of 746 mg (2.90 mmol) of triethyloxonium hexafluorophosphate in 10 mL of dichloromethane was added, and the mixture was stirred for 30 min. The solvent was removed at reduced pressure, and the crude product was purified by column chromatography (20 × 5 cm, petroleum ether–MTBE 10 : 1 to 2 : 1): 862 mg (61%) of **7** was obtained as a red solid (mp 96 °C).

IR ($CHCl_3$): $\tilde{\nu} = 2984$ cm^{-1} (w), 2964 (w), 2060 (s, CrCO), 2016 (s, FeCO), 1966 (sh), 1944 (br s, CrCO and FeCO), 1592 (w), 1444 (w), 1376 (w), 1248 (w), 1056 (w), 580 (m). ^1H NMR (200.1 MHz, C_6D_6): $\delta = 1.27$ (t, 3H, 8-H, $^3J_{7,8} = 7.0$ Hz), 2.84 (s, 2H, CH_2), 4.14 (s, 2H, Cp), 4.88 (q, 2H, 7-H), 5.17 (s, 2H, Cp), 7.33 (m, 5H, C_6H_5). ^{13}C NMR (100.6 MHz, C_6D_6, APT) $\delta = 8.04$ (+, $FeCH_2$–), 15.51 (−, C-8), 77.36 (+, C-7), 89.67

(−, Cp), 91.26 (−, Cp), 106.42 (+, C-1), 124.99 (−, Ph), 129.37 (−, Ph), 152.64 (+, Ph), 215.85 (+, FeCO), 217.57 (+, $CrCO_{cis}$), 223.83 (+, $CrCO_{trans}$), 330.80 (+, C-6). MS-FAB: 488 [$M^+ - CO$], 432 [$M^+ - 3\ CO$], 404 [$M^+ - 4\ CO$], 376 [$M^+ - 5\ CO$], 348 [$M^+ - 6\ CO$]. HRMS ($C_{22}H_{16}CrFeO_8$) calcd 515.959967, found 515.960083. CV (100 mV s^{-1}, $T = -20\,°C$): $E_{AP1} = 625$ mV.

{Ethoxy [tricarbonyl(bis(diphenylphosphino)ethane)-molybdenum(0)] carbenylcyclopentadienyl} [bis(diphenylphosphino)ethane] methyliron(II) (8). A solution of 300 mg (0.62 mmol) of **3** and 320 mg (0.8 mmol) bis(diphenylphosphino)ethane (dppe) in 100 mL of THF was irradiated [Hg high pressure lamp, quarz filter]. After 10 min the solution became darker, and in addition to adduct two products were detected by TLC. Dppe (320 mg, 0.8 mmol) was added to the solution, and irradiation was continued for 5 min. The solvent was removed at reduced pressure, and the residue was purified by column chromatography (22 × 4 cm, petroleum ether–MTBE 5 : 1, then pure MTBE, product losses during chromatography): 470 mg (0.39 mmol, 60%) of **8** was obtained as a green solid.

IR ($CHCl_3$): $\tilde{\nu} = 2964\ cm^{-1}$ (w), 2060 (m, MoCO), 1936 (s, MoCO), 1436 (w), 1264 (s), 1096 (m), 1016 (w). ^1H NMR (400.1 MHz, [D_8]-THF): $\delta = -0.65$ (t, 3H, $FeCH_3$, $^3J_{H,P} = 6.44$ Hz), 1.18 (t, 3H, 8-H, $^3J_{7,8} =$ 7.08 Hz), 2.35–2.80 (m, 8H, 9-H bis 12-H), 4.49 (m, 2H, Cp), 4.62 (q, 2H, 7-H), 4.89 (m, 2H, Cp), 7.15–7.70 (m, 40H, dppe). ^{13}C NMR (100.6 MHz, [D_8]-THF, APT): $\delta = -13.4$ (−, t, $FeCH_3$, $J_{P,C} = 24.2$ Hz), 15.5 (−, C-8), 28.4 (+, m, C-11 and C-12), 29.3 (+, t, C-9 and C-10, $J_{P,C} = 21.0$ Hz), 76.9 (+, C-7), 80.8 (−, Cp), 91.1 (−, Cp), 102.2 (+, Cp), 128–135 (−, dppe), 137–143 (+, dppe), 210.1 (+, t, MoCO, $J_{P,C} = 8.6$ Hz), 218.2 (+, dd, MoCO, $J_{P,C} =$ 25.5 Hz and 8.7 Hz), 307.6 (+, Mo=C). FAB-MS: 922 (3), 826 (4), 743 (5), 649 (5), 606 (20), 519 (22), 469 (55), 399 (72), 185 (100).

Crystal structure analysis of 2

$C_{16}H_{12}CrFeO_8$, $M = 440.1\ g\ mol^{-1}$, crystal system monoclinic, space group $P2_1/n$ (no. 14), $a = 6.865(1)$, $b = 10.751(2)$, $c = 24.700(4)$ Å, $\alpha = 90$, $\beta = 92.26(2)$, $\gamma = 90°$, $U = 1821.6(5)$ Å^3, $d_{calcd.} = 1.605\ g\ cm^{-3}$, $\mu = 14.3\ cm^{-1}$, $F(000) = 888$, $Z = 4$, $Mo_{K\alpha}$, $\lambda = 0.71073$ Å, $T = 300$ K, 11149 measured reflections (±7, ±12, ±28), 2824 independent and 1264 observed reflections [$I > 2\sigma(I)$], completeness of data: 99.8%, $R(I) = 0.074$, absorption correction: none, extinction correction: none, refinement: SHELXL-93, $N_{ref} = 2824$, $N_{par} = 237$, $R_{gt}(F) = 0.0444$, $R_w(F^2) = 0.0636$ [$w = 1/\sigma^2(F_0^2)$], $S = 1.11$, min./max. residual electron density $-0.45/0.68$ e Å^{-3}.

CCDC reference number 440/124. See http://www.rsc.org/suppdata/nj/1999/891/ for crystallographic files in .cif format.

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