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Synthesis, Reactivity, and Some Photochemistry of

Ortho-$N,N$-dimethylaminomethyl Substituted Aryl and Ferrocenyl Pentamethylcyclopentadienyl

Dicarbonyl Iron Complexes

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Abstract:

Ortho-lithiated \(N,N\)-dimethylaminomethyl ferrocene and benzylidimethylamine react with \(\text{Cp}^*\text{Fe(CO)}_2\text{I}\) to give the new complexes \(((\text{Cp}^*\text{Fe(CO)}_2)_2\text{-2-(CH}_2\text{NMe}_2)\text{C}_5\text{H}_3)\text{Fe(Cp)}\) and \(\text{Cp}^*\text{Fe(CO)}_2\text{-C}_6\text{H}_4(o\text{-CH}_2\text{NMe}_2)\). Access to a wide variety of alkoxy-substituted complexes \(((\text{Cp}^*\text{Fe(CO)}_2)_2\text{-2-(CH}_2\text{OR})\text{C}_5\text{H}_3)\text{Fe(Cp)}\) can be easily achieved by tandem quaternization/alcoholysis of \(((\text{Cp}^*\text{Fe(CO)}_2)_2\text{-2-(CH}_2\text{NMe}_2)\text{C}_5\text{H}_3)\text{Fe(Cp)}\). Preliminary results show that chelated complexes can be obtained by displacement of one of the carbonyl ligands by photolysis. Crystal structures of \(((\text{Cp}^*\text{Fe(CO)}_2)_2\text{-2-(CH}_2\text{NMe}_2)\text{C}_5\text{H}_3)\text{Fe(Cp)}\) (\(R = \text{Ph, Bz, CHPh}_2\) and \(d\)-menthyl) and \([\text{Cp}^*\text{Fe(CO)}_2\text{-C}_6\text{H}_4(o\text{-CH}_2\text{NMe}_2)]\text{[I]}\) are reported.
Graphical Abstract

R = Me, Et, iPr, Ph, Bz, CHMePh, CHPH₂, d-menthyl
Highlights

- \((\text{Cp}^*\text{Fe}(\text{CO})_2)\text{-2-(CH}_2\text{NMe}_2\text{)C}_5\text{H}_3\text{)}\text{Fe(Cp)}\) and \(\text{Cp}^*\text{Fe}(\text{CO})_2\text{-C}_6\text{H}_4(\text{o-CH}_2\text{NMe}_2)\) are synthesized from \(\text{Cp}^*\text{Fe}(\text{CO})_2\text{I}\) and ortho-lithiated \(N,N\)-dimethylaminomethyl ferrocene or benzyldimethylamine.

- Alkoxy-substituted complexes \((\text{Cp}^*\text{Fe}(\text{CO})_2)\text{-2-(CH}_2\text{OR})\text{C}_5\text{H}_3\text{)}\text{Fe(Cp)}\) can be easily obtained by tandem quaternization/alcoholysis of \((\text{Cp}^*\text{Fe}(\text{CO})_2)\text{-2-(CH}_2\text{NMe}_2\text{)C}_5\text{H}_3\text{)}\text{Fe(Cp)}\).

- Photolytic displacement of one of the carbonyl ligands of \(\text{Cp}^*\text{Fe}(\text{CO})_2\text{-C}_6\text{H}_4(\text{o-CH}_2\text{NMe}_2)\) yield the corresponding chelated complex.
1. Introduction

In the last decade the importance of iron in catalysis has grown due to its sustainability, environmentally benign impact, and low-cost. Iron-catalyzed transformations now compete and sometime outperform expensive transition-metal catalyzed processes,[1-11] making iron a viable alternative to rhodium, ruthenium and palladium, for example. In this regard, special attention is given to well-defined complexes possessing a cyclopentadienyl mono- or dicarbonyl iron moiety.[12-29] Among such catalysts, the importance of the neutral complex CpFe(CO)₂Me (1, Cp: cyclopentadienyl = 5-C₅H₅)[14-20] and the cationic complex [CpFe(CO)₂(THF)][BF₄] (2)[21-24] are particularly noteworthy (Figure 1). Indeed, the readily accessible complex 1 has been used as a precursor to more elaborate iron catalysts for various catalytic transformations, and more recently its catalytic activity for the dehydrogenative coupling reaction between thiols and hydrosilanes to form thiosilanes was reported.[15] The commercially available THF adduct 2 of the 16-electron complex [CpFe(CO)]⁺ has been employed extensively as a mild Lewis acid catalyst in many homogeneous reactions such as cyclopropanation of alkenes, epoxidation of aromatic aldehydes, or aziridination of aryl imines. More recently, efficient visible light-promoted reduction of aldehydes, ketones, esters, imines and amides has been described by Darcel et al. using NHC and phosphine complexes 3 and 4 as well as some of their derivatives.[25-30].
In addition to the increasing number of [CpFe(CO)$_n$]-based complexes that are active in catalytic processes, half-sandwich iron carbonyl molecules with modified Cp rings or incorporating the bulky and electron-rich Cp* ligand (Cp*: pentamethylcyclopentadienyl = $\eta^5$-C$_5$Me$_5$) have been recently designed for applications in catalysis.[17, 31, 32] For example, Royo et al. synthesized the iodo carbonyl complexes 5 which display good catalytic activity for the transfer hydrogenation of ketones and reduction of sulfoxides,[33, 34] despite the presence of the sterically demanding N-heterocyclic carbene-functionalized cyclopentadienyl ligand, while Sawamoto et al. have prepared and used complex 6 in the living radical polymerization of methyl methacrylate,[35] showing that superior control of the polymerization reaction is exhibited by a complex bearing a Cp* ligand over that shown by a complex ligated by a Cp ligand (Figure 2).

Figure 2: Selected Cp-modified or Cp* iron carbonyl catalysts. R = H, Me; X = H, Me, OMe.

In a previous communication,[36] we have reported the synthesis of a series of piano-stool iron(II) $\sigma$–aryl complexes of general formula Cp*Fe(CO)$_2$Ar (7-X, X = H, Me, OMe), together with the ferrocenyl analogue 8. This family of molecules was found to display good catalytic activity for the photo-catalyzed reductive etherification of aldehydes;[37] the 16-
electron catalytically-active species were unambiguously shown to originate from photochemical decarbonylation of these complexes. In an attempt to develop this class of catalysts, our attention was drawn to the introduction of new functionalities on the ancillary phenyl or ferrocenyl moieties σ-bonded to the [Cp*Fe(CO)₂] fragment, as a preamble to the exchange of the reactive carbonyl ligands connected to the iron metal center. Hence, we describe herein the synthesis of new pentamethylcyclopentadienyl dicarbonyl iron complexes featuring 2-dimethylaminomethyl-substituted ferrocenyl and phenyl ligands. Their reactivities toward alcohols following quaternization of their amine function are also presented, as an efficient pathway to new ferrocene-based ethers. Electrochemical (from cyclic voltammetry) and structural properties (from single-crystal X-ray structural studies) are reported. Finally, initial results of the UV-promoted intramolecular ligand exchange at these compounds are described.

2. Results and discussion

The synthesis of the 2-(N,N-dimethylamino)methyl-substituted ferrocenyl pentamethylcyclopentadienyl dicarbonyl iron complex 10 was achieved by reaction between the iodo precursor Cp*Fe(CO)₂I 9 [38] and ortho-lithiated N,N-dimethylaminomethyl ferrocene [39] in diethyl ether (Scheme 1). Nucleophilic substitution of the iodide in 9 by lithium reagent readily takes place, 10 being isolated in moderate yield as an air-stable orange solid. Since deprotonation at the 2-position of N,N-dimethylaminomethyl ferrocene with n-BuLi occurs without any diastereoselectivity [40], 10 was obtained as its racemic mixture. The phenyl analogue 11 was obtained by the same method, using (o-(N,N-dimethylaminomethyl)phenyl)lithium [41, 42] as the lithium reagent, but in somewhat higher yield, as a yellow solid with a marked light sensitivity in solution.
Scheme 1: Synthesis of complexes 10 and 11.

The complexes were readily identified by microanalysis, spectroscopy and, in the case of 10, single-crystal X-ray diffraction (vide infra). The ESI spectra contain molecular ions at m/z 489.1 (10, [M]⁺) and 382.1 (11, [M+H]⁺) with, in the case of 10, a fragmentation peak corresponding to the loss of the dimethylamino substituent (m/z = 445.06, 46%). The presence of the [Cp*Fe(CO)] moiety in these complexes is evidenced by two strong νC=O bands at ca. 1990 and 1930 cm⁻¹ in the IR spectra. The Cp* ligand gives typical NMR resonances at δH ca. 1.70 ppm and δC ca. 96 and 10 ppm. The carbonyl ligands are also visible by 13C NMR spectroscopy, with two signals at δC 219.2 and 218.3 ppm for 10 (due to rotational constraints that are also related to the planar chirality) and one for 11 at 218.1 ppm. Resonances at δH 2.20 – 2.30 ppm and δC ca. 46 ppm are related to the dimethylamino moieties whereas the ferroceny (10) and aryl (11) signals are found within the expected ranges. The presence of the substituted redox-active ferrocene in 10 is also confirmed by the observation of a fully reversible wave by cyclic
voltammetry in CH$_2$Cl$_2$ at 0.16 V (vs. SCE in CH$_2$Cl$_2$), a feature absent in the voltammogram of 11. The assignment of the reversible process in the cyclic voltammogram of 10 to the ferrocenic moiety is definitely supported by the observation of a similar chemically reversible wave in the voltammogram of 8,[43] its Cp analogue CpFe(CO)$_2$Fc,[44-47] and for their ruthenium counterparts CpRu(CO)$_2$Fc and Cp*Ru(CO)$_2$Fc.[48] Moreover, in the voltammograms of both 10 and 11 two irreversible waves at higher potential can be seen, likely to be related to the oxidation of the [Cp*Fe(CO)$_2$] and dimethylamino moieties.

Displacement of trimethylammonium groups by nucleophiles such as cyanide or hydroxyl anion is a known reaction at α-dimethylaminomethyl ferrocene methiodide substrates [49-51]. Thus, in order to introduce other functional groups at 10, its quaternization with methyl iodide was attempted. However, these reactions were unsuccessful in most polar solvents, giving only decomposition products, while the reactivity of 10 towards methyl iodide was sluggish in apolar media. However, when methanol was used as the solvent, an orange complex could be isolated in pure form by column chromatography. This complex exhibits typical signatures for the carbonyl ligands (ν$_{C=O}$ bands at 1990 and 1934 cm$^{-1}$, $^{13}$C NMR resonances at δ$_C$ 219.0 and 218.1 ppm) and Cp* ligands (δ$_C$: 96.4 and 9.6 ppm, δ$_H$: 1.71 ppm) of a [Cp*Fe(CO)$_2$] moiety along with those of a 1,2-substituted ferrocene. The reversible wave observed by cyclic voltammetry at 0.13 V (vs. SCE in CH$_2$Cl$_2$), at a very similar potential to that in 10, was also indicative of the presence of the redox-active ferrocenic moiety. Finally, the presence of singlets at δ$_H$ 3.33 ppm and δ$_C$ 58.1 ppm in the NMR spectra and the appearance of bands at 2815 and 1031 cm$^{-1}$ in the IR spectra are consistent with assignment of the compound as the methoxy-substituted complex 13-Me, resulting from solvolysis of the elusive methiodide 12 (Scheme 2). By optimizing the reaction conditions, 13-Me was obtained in up to 71 % yield and changing the solvent to ethanol or
isopropanol led to the isolation of two other alkoxy derivatives 13-Et and 13-iPr in 57 and 68 % yield, respectively.

![Scheme 2: Solvolysis of 10 in the presence of iodomethane.](image)

The reactivity of 10 towards alcohols in the presence of methyl iodide contrasts to that observed with the aryl complex 11, which only gave the corresponding ammonium salt 14 in 92 % yield under similar conditions (Scheme 3). The formulation of 14 as the methiodide of 11 and not the methoxy-substituted complex 15 was clearly established by X-ray analysis on a single crystal (see below), and is in line with the spectroscopic data. The new complex 15 was prepared by an alternative procedure, namely reaction between 9 and 2-(methoxymethyl)phenyl lithium, isolated in 53 % yield, and fully characterized.
To assess if the reactivity of 10 results from the presence of the ferrocenyl substituent, N,N-dimethylaminomethylferrocene (16) was subjected to the same reaction conditions as were successfully utilized for the formation of 13-Me. In accordance with literature reports for these type of substrates [40, 52, 53], N,N-dimethylaminomethylferrocene methiodide (17) was formed in high yield (84 %), but together with a small amount of methoxymethylferrocene (18, 14 % isolated yield). This proves that methanolysis of the ammonium salt 17 occurs under these reaction conditions but is a slow process. Indeed, 17 had to be refluxed for 24 h in methanol in order to obtain a similar yield than that observed for the formation of 13-Me from 10 (Scheme 4) [54], the latter readily taking place at room temperature in a significantly shorter period of time.
Using acetonitrile as the solvent enabled to extend the scope of the dimethylamino/alkoxy substitution reaction at 10 (via the elusive methiodide 12) to other (non-solvent) alcohols. A
variety of them were thus reacted with 10 in the presence of methyl iodide to give the new alkoxy-substituted complexes 13-R in moderate yields (Table 1).
<table>
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<th>Complex</th>
<th>Yield</th>
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<td>57 %</td>
</tr>
<tr>
<td>2</td>
<td>benzyl alcohol</td>
<td>13-Bz</td>
<td>58 %</td>
</tr>
<tr>
<td>3</td>
<td>13-CHMePh</td>
<td>13-CHMePh</td>
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</tr>
<tr>
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<tr>
<td>5</td>
<td>13-Menthyl</td>
<td>13-Menthyl</td>
<td>40 %</td>
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</table>

Table 1: Alcoholysis of 10 in acetonitrile.

No difference in reactivity between the previous aliphatic alcohols and phenol (Entry 1) or benzyl alcohol (Entry 2) was observed. The only limitation of this reaction can be ascribed to steric considerations: with benzhydrol (Entry 4) the yield dropped significantly when compared...
to 1-phenylethanol (Entry 3), and with the spatially demanding triphenylmethanol no reaction took place at all. Finally the introduction of a menthyl group was also achieved using d-menthol (Entry 5). All these complexes were fully characterized and the solid-state structures of four of them (R = Ph, Bz, CHPh₂, Menthyl) were obtained (Figure 6).

The excess of methyl iodide required in this procedure precluded extending the scope to embrace N-, S- and P-nucleophiles. Indeed, these are likely to be quaternized and thereby becoming unreactive toward 12. Nevertheless, this method could also be applied to the trimethylammonium derivative 17. As exemplified in Scheme 5, refluxing an acetonitrile solution of 17 in the presence of excess benzhydrol gave benzhydrolxymethyl ferrocene 19 in 16 % yield (not optimized).

![Scheme 5: Alcoholysis of 17 with benzhydrol.](image)

Next, introduction of simple structural changes within the iron carbonyl coordination sphere of the present complexes was attempted by means of intramolecular ligand exchange reactions. Taking advantage of the easy photodecarbonylation of iron carbonyl piano-stool complexes, clean formation of the chelate 20 was achieved when a toluene solution of 11 was irradiated under UV-light for 16 h (Scheme 6). Compound 20 was isolated in 71 % yield after
purification by precipitation from n-pentane at -90 °C. It is noteworthy that 20 has an asymmetric iron atom and is obtained as a racemic mixture. Unfortunately, such clean and selective photodecarbonylation was not observed when the same procedure was applied to complexes 10 and 15 in various solvents, since some dimeric \([\text{Cp}^*\text{Fe}(\text{CO})_2]_2\) species (resulting from Fe-C bond cleavage) was generated along with unstable side-products and/or incomplete chelate formation.

![Scheme 6: Formation of 20 by photolysis.](image)

In the case of 11, the completeness of the monodecarbonylation/chelation reaction can be assessed in a convenient fashion by IR spectroscopy: the two original \(\nu_{\text{C=O}}\) bands in 11 at 1989 and 1932 cm\(^{-1}\) are replaced by a single band at 1886 cm\(^{-1}\). A molecular ion peak in the ESI spectrum at \(m/z\) 353.1 in addition to fragments corresponding to the loss of the remaining carbonyl ligand (\(m/z\): 325.2; 62 %) and to \([\text{Cp}^*\text{FePh}]\) (\(m/z\): 268.2; 10 %) were also consistent with the formulation of 20 as depicted above. The most visible changes following formation of this metallaclace can still be seen by \(^1\text{H}\) NMR. Around the asymmetric iron center there is constrained rotation, and the signals of the dimethylamino moiety and of the benzylic protons are both split, into two individual singlets and into two doublets (with \(J_{\text{HH}} = 9\) Hz), respectively. The signals found at higher field can be assigned to the protons closest to the \(\text{Cp}^*\) ligand, the ring current deshielding the signals (Figure 3).
Figure 3: Comparison of the $^1$H NMR spectra of 11 (in CDCl$_3$) and 20 (in C$_6$D$_6$).

Coordination of the dimethylamino moiety to the iron centre also induces changes in the redox behavior of the complex: while the CV trace of 11 only shows two irreversible waves at around 0.9 – 1.20 V for both the amino and iron centers (vide supra), an additional perfectly reversible process is observed for 20 at ca. 0.0 V vs. SCE (Figure 4). The chemical reversibility of this redox event is very likely to be related to the Fe(II)/Fe(III) couple, indicating a better stabilization of the Fe(III) species on the measurement timescale when the $\sigma$-donor nitrogen ligand is coordinated to the iron atom, as already observed with mono-phosphine complexes[58, 59].
Figure 4: Left: superimposed CV traces of 11 (top) and 20 (bottom) in CH$_2$Cl$_2$/0.10 M [$n$-Bu$_4$N][PF$_6$] with a -1.0 – 1.6 V scan range. Right: close-up view of the reversible process of 20.

The crystal structures of complexes 10, 13-R (R = Ph, Bz, CHPh$_2$, menthy1) and 14 were determined by single-crystal X-ray diffraction. ORTEP representations of complexes 10 and 14 are displayed in Figure 5, while compounds 13-R are represented in Figure 6. Crystallographic data are combined in Tables 2 and 3. Examination of the packing of racemic ferrocenyl complexes 10 and 13-R (R = Ph, Bz, CHPh$_2$) shows that both enantiomers are present in the unit cell whereas for complex 13-Menthy1 the crystal studied is constituted only from the R$_{Fc-d}$-menthyl diastereomer. In all complexes, the iron atom of the [Cp*Fe(CO)$_2$] moiety is in a pseudo-octahedral environment, with three coordination positions occupied by the Cp* ligand and the three others by the two carbonyls and ferrocenyl (10, 13-R) or aryl (14) ligands. Bond lengths and angles are similar to those found in the parent complexes 7-H and 8 [36], the only significant differences compared with those two unsubstituted complexes being the unequal OC-
Fe-C_{ipso} angles, with the OC-Fe-C_{ipso} angle on the same side of the CH₂X substituent being substantially wider (91.31 – 99.91°) than those on the other side (88.36 – 89.93°). This feature allows to accommodate the steric bulk of the CH₂X substituent. As a consequence, the geometries around the iron centre are deformed in 10, 13-R and 14 compared than in their unsubstituted parents 7-H and 8, which are almost perfectly symmetrical. This effect is even more marked for 14, as the aryl ring brings the substituent closer to the iron center than is the case with a 1,2-substituted ferrocene. In complexes 10 and 13-R the cyclopentadienyl ligands of the ferrocenic fragment are in an eclipsed conformation, with a barely discernible tilt angle as revealed by the Cp_{subst}-Fe-Cp angles ranging from 177.0 to 179.9°. In most cases the value of the tilt angle is higher than is the case for 8, the increased steric hindrance of the substituted Cp ring displacing the entire ferrocenyl unit towards the iron center in a disfavored conformation, the tilt angle being increased as a consequence. Overall, the ferrocenyl moieties in 10 and 13-R are very similar (in term of bond lengths) to ferrocene itself [60]. In 14 the iodine atom is closer to the nitrogen (4.344 Å) than the iron atom (7.112 Å) [61], confirming the presence of the positive charge on the former. These electrostatic attractions result in an arrangement of the nitrogen and iodide of two anion/cation pairs in an almost square fashion (side length: 4.344 and 5.055 Å, angles: 88.83 and 91.97°). Lastly, an explanation of the unsuccessful reaction of 10 (via 12) with triphenylmethanol due to steric limitations can be deduced from the molecular structure of 13-CHPh₂. The hydrogen atom of the benzhydrid substituent is located within a pocket formed by the Cp*Fe(CO₂) and one phenyl of the benzhydrid, the C-H bond being on an axis parallel to that one of the Fe-C_{ipso} bond and pointing toward the bulky Cp* substituent. In the case of a hypothetical 13-CPh₃, it then become apparent that the additional phenyl ring could not be accommodated in that available space, explaining thereby the absence of reaction between 12 and
triphenylmethanol. With steric repulsion preventing the approach of triphenylmethanol to \( \textbf{12} \), no substitution reaction could take place, and only decomposition of \( \textbf{12} \) occurred.

Figure 5: ORTEP representations of complexes \( \textbf{10} \) (left, racemic twins) and \( \textbf{14} \) (right) with 50\% thermal ellipsoids. Hydrogen atoms and CH\(_2\)Cl\(_2\) solvate (\( \textbf{14} \)) have been omitted for clarity.
Figure 6: ORTEP representation of the $R_{fc}$ enantiomer of complexes 13-Ph (A), 13-Bz (B), 13-CHPh$_2$ (C) and 13-Menthy (D) with 50% thermal ellipsoids. Hydrogen atoms have been omitted for clarity.
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Table 2. Selected crystallographic data and collection parameters for 10, 13-R and 14. <sup>a</sup> Two molecules in the asymmetric unit. <sup>b</sup> R1 = ∑ ||F<sub>o</sub>|| - |F<sub>c</sub>|| / ∑ |F<sub>o</sub>|. <sup>c</sup> wR2 = { ∑ [w(F<sub>o</sub><sup>2</sup> -F<sub>c</sub><sup>2</sup>)<sup>2</sup>] / ∑ [w(F<sub>o</sub><sup>2</sup>)<sup>2</sup>]}<sup>1/2</sup>.
Table 3. Selected bond lengths and angles for 10, 13-R and 14.
3. Conclusion

Syntheses of Cp*Fe(CO)$_2$ ferrocenyl and aryl complexes bearing a dimethylaminomethyl substituent at their ortho position was achieved by reaction between the iodo precursor 9 and the corresponding ortho-lithiated $N,N$-dimethylaminomethylferrocene and benzylidimethylaniline. Upon reaction with methyl iodide in methanol, the expected corresponding ammonium salt was obtained in the case of the aryl complex 11. In contrast for the ferrocenyl complex 10, etherification of the elusive ammonium 12 readily takes place by methanolysis and the methoxy-substituted complex 13-Me is isolated instead. Alcoholysis of 12 also occurs in ethanol, isopropanol and in acetonitrile in the presence of an excess of alcohol, permitting access to a variety of alkoxy-substituted complexes. However, the reaction shows a dependence on the steric bulk of the alcohol, with decreased yields (or no reaction at all) when spatially demanding alcohols are employed. The same reaction occurs with $N,N$-dimethylaminomethyl ferrocene methiodide, but at a much slower rate, which demonstrates that the presence of the electron-rich [Cp*Fe(CO)$_2$] moiety induces an increase in the reactivity of the ferrocenyl substrate. Finally, photolysis of complexes 10 and 15 leads to the formation of unstable complexes, decomposition products or incomplete chelate formation. However, in the case of 11 photolysis in toluene proceed cleanly and selectively and allows the isolation of the chelate 20 in pure form. With the confirmation that this type of complex can be accessed by photolabilization of one of the carbonyl ligands, further work is now required to obtain chelates of the other complexes reported herein and to assess their catalytic behavior.

4. Experimental Section

4.1. General comments

Air and/or moisture sensitive reactions were performed under an atmosphere of argon in distilled and deoxygenated solvents using standard Schlenk techniques. Photolyses were performed
with a Heraeus UV lamp (TQ150, 150 W, medium pressure) equipped with a water-cooled quartz jacket. Standard work-up consists of extraction of the reaction mixtures / solid residues with Et₂O (with filtration if necessary), washing of the organic extracts with water and saturated aqueous NaCl, drying over MgSO₄, filtration, and removal of the solvent under reduced pressure. Flash column chromatography was performed using silica gel (Merck Kieselgel 60, 230 – 400 mesh) in glass columns of various sizes (indicated as diameter × length). For ferrocenyl and amino-substituted complexes, 1% Et₃N was added in the eluent. R_f values were measured on silica plates.

4.2. Instruments

¹H and ¹³C NMR spectra were recorded on a Bruker Ascend 400 MHz NMR spectrometer, chemical shifts being referenced to the residual chloroform signal (δ 7.26 ppm for ¹H, 77.0 ppm for ¹³C) [62]. Infrared spectra were obtained as KBr pellets [63], CH₂Cl₂ solution or liquid film between NaCl windows, as indicated, on a Bruker IFS28 FT-IR spectrometer (400-4000 cm⁻¹). UV-visible spectra were measured as CH₂Cl₂ solutions, using a 1 cm long quartz cell in a Cary 5 spectrometer. Cyclic voltammograms were recorded using a PAR 263 instrument in dry and degassed CH₂Cl₂ containing 0.1 M [n-Bu₄N][PF₆] at 20 °C with 100 mV/s scan rate at a platinum disk (1 mm diameter), using a SCE reference electrode and ferrocene as internal calibrant (0.46 V vs SCE) [64]. Melting points were measured on a Kofler hot stage calibrated against a reference compound of similar melting point. High resolution mass spectra and elemental analyses were performed at the “Centre Regional de Mesures Physiques de l’Ouest” (CRMPO), Université de Rennes 1, France.

4.3. Reagents

Cp*Fe(CO)₂I [38], (o-(N,N-dimethylaminomethyl)phenyl)lithium [41, 42], and o-bromo(methoxymethyl)benzene [65] were prepared according to the literature methods, while other chemicals were obtained commercially and used without further purification.
4.3.1. General procedure for the syntheses of dicarbonyl(pentamethylcyclopentadienyl)iron complexes from iododicarbonyl(pentamethylcyclopentadienyl)iron and lithium reagents

A Et₂O or THF solution of the appropriate lithium reagent (1.20 – 1.25 eq.) was added dropwise via a cannula to iododicarbonyl(pentamethylcyclopentadienyl)iron (1.0 eq.) dissolved in the same solvent at 0°C. After 5 min of stirring at 0°C, the cooling bath was removed, stirring was maintained for 1 h at room temperature, and the reaction mixture was slowly hydrolyzed with water (25 mL). The crude oil or solid obtained after standard work-up was adsorbed onto elite and chromatographed (silica gel). A red band of dicarbonyl(pentamethylcyclopentadienyl)iron dimer was eluted (preceded by a yellow band of an unidentified volatile carbonyl iron complex) with hexanes/Et₂O 98:2, followed by a yellow or orange band of the desired complex which was eluted with hexanes/Et₂O (95:5 to 4:1). The residue obtained after removal of solvents was recrystallized from aqueous ethanol, and the crystals obtained after 16 h of standing at -18°C were collected on a fine porosity glass sintered funnel, washed with 50 % aqueous ethanol (10 mL), and dried in vacuo.

4.3.1.1. rac-1-(dicarbonyl(pentamethylcyclopentadienyl)iron)-2-(N,N-dimethylaminomethyl)ferrocene (10)

From rac-2-lithio(dimethylaminomethyl)ferrocene (prepared from N,N-dimethylaminomethylferrocene (0.97 g, 4.0 mmol) and n-BuLi (2.75 mL, 1.60 M in hexanes, 4.40 mmol) in Et₂O (25 mL) at room temperature for 16 h) [39] and iododicarbonyl(pentamethylcyclopentadienyl)iron (1.20 g, 3.20 mmol) in Et₂O (10 mL), 0.67 g (43 %) of orange needles were obtained. Column size: 5 × 20 cm. Recrystallization: EtOH/water 3:1, 40 mL. R_f (hexanes/ethyl acetate 1:1): 0.39. mp: 128°C. Elemental analysis: calcd for C₂₅H₃₁Fe₂N₂O₂: C: 61.38 %, H: 6.39 %, N: 2.86 %; found: C: 61.47 %, H: 6.48 %, N: 2.79 %. HRMS (ESI,
CH$_3$OH/CH$_2$Cl$_2$ 9:1): calc: 489.1054 [M]$^+$, found: 489.1052. IR (CH$_2$Cl$_2$, cm$^{-1}$): 1989 and 1932 (s, C=O), 813 (s, δC-H Cp Fc). UV-Visible (CH$_2$Cl$_2$): $\lambda_{\text{max}}$, nm (ε, 10$^3$ M$^{-1}$·cm$^{-1}$): 366 (1.9); 280 (8.8). Cyclic voltammetry (CH$_2$Cl$_2$, 0.10 M [n-Bu$_4$N][PF$_6$], V vs. SCE): E$_{1/2}$: 0.16 (ΔE$_{1/2}$ = 0.072 V; $i_{\text{pa}}$/i$_{\text{pc}}$ = 1.0) 1.26 and 1.47 (irreversible processes).

$^1$H NMR (400 MHz, CDCl$_3$, ppm): 7.44 (t, 2H, $^3$J$_{\text{H,H}}$ = 7 Hz, C$_6$H$_4$), 6.96 (t, 1H, $^3$J$_{\text{H,H}}$ = 7 Hz, C$_6$H$_4$), 6.84 (t, 1H, $^3$J$_{\text{H,H}}$ = 7 Hz, C$_6$H$_4$), 3.49 (s, 2H, CH$_2$), 2.34 (s, 6H, NMe$_2$), 1.67 (s, 15H, Cp*). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$, ppm): δ 219.2 and 218.3 (2× s, C=O), 96.3 (s, Cp$^*$), 92.1 (s, Cp$^*$), 90.2 (s, C$_{\text{ipso}}$ CH$_2$NMe$_2$), 79.0, 71.5 and 68.1 (3× s, C$_{\text{aromatics}}$), 61.8 (s, CH$_2$), 46.0 (s, NMe$_2$), 9.6 (s, CH$_3$ Cp$^*$). X-ray quality crystals were grown by slow cooling of a saturated EtOH solution to -18°C.

4.3.1.2. dicarbonyl(pentamethylcyclopentadienyl)(o-(N,N-dimethylaminomethyl)phenyl)iron (II)

From (o-(N,N-dimethylaminomethyl)phenyl)lithium (0.85 g, 6.0 mmol) in THF (10 mL) and iododicarbonyl(pentamethylcyclopentadienyl)iron (1.87 g, 5.0 mmol) in THF (25 mL), 1.10 g (58 %) of yellow flakes were obtained. Column size: 5 × 15 cm. Recrystallization: EtOH/water 5:3, 80 mL. R$_f$ (ethyl acetate): 0.11. mp: 114°C. Elemental analysis: calcd for C$_{21}$H$_{27}$FeNO$_2$: C: 66.15 %, H: 7.14 %, N: 3.67 %. found: C: 66.53 %, H: 7.19 %, N: 3.52 %. HRMS (ESI, CH$_3$OH/CH$_2$Cl$_2$ 9:1): calc: 382.1469 [M+H]$^+$, found: 382.1467. IR (CH$_2$Cl$_2$, cm$^{-1}$): 1992 and 1935 (vs, C=O). UV-Visible (CH$_2$Cl$_2$): $\lambda_{\text{max}}$, nm (ε, 10$^3$ M$^{-1}$·cm$^{-1}$): 360 (1.2), 294 (5.2). Cyclic voltammetry (CH$_2$Cl$_2$, 0.10 M [n-Bu$_4$N][PF$_6$], V vs. SCE): E$_{1/2}$: 0.97 and 1.24 (irreversible processes).

$^1$H NMR (400 MHz, CDCl$_3$, ppm): 7.44 (t, 2H, $^3$J$_{\text{H,H}}$ = 7 Hz, C$_6$H$_4$), 6.96 (t, 1H, $^3$J$_{\text{H,H}}$ = 7 Hz, C$_6$H$_4$), 6.84 (t, 1H, $^3$J$_{\text{H,H}}$ = 7 Hz, C$_6$H$_4$), 3.49 (s, 2H, CH$_2$), 2.34 (s, 6H, NMe$_2$), 1.67 (s, 15H, Cp$^*$). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$, ppm): δ 218.1 (s, C=O), 156.7 and 148.2 (2× s, C$_{\text{quat}}$ C$_3$H$_4$), 144.7, 128.5, 124.9, and 122.9 (4× s, C$_{\text{aromatics}}$), 96.6 (s, C$_{\text{quat}}$ Cp$^*$), 68.3 (s, CH$_2$), 45.8 (s, NMe$_2$), 9.8 (s, CH$_3$ Cp$^*$).
4.3.1.3. dicarbonyl(pentamethylcyclopentadienyl)(o-(methoxymethyl)phenyl)iron (15)

From o-lithio benzyl methyl ether (prepared from o-bromo(methoxymethyl)benzene (0.80 g, 4.0 mmol)[66] and n-BuLi (2.5 mL, 1.60 M in hexane, 4.0 mmol) in THF (10 mL) at –90°C for 30 min) and iododicarbonyl(pentamethylcyclopentadienyl)iron (1.20 g, 3.20 mmol). 0.63 g (53 %) of yellow fluffy crystals were obtained. Column size: 4 × 25 cm. Recrystallization: EtOH/water 2:1, 30 mL. R_f (hexanes/ethyl acetate 95:5): 0.34. mp: 150°C. Elemental analysis: calcd for C_{20}H_{24}FeO_3: C: 65.23 %, H: 6.57 %; found: C: 65.71 %, H: 6.81 %. HRMS (ESI, CH_3OH/CH_2Cl_2 9:1): calc: 391.0973 [M+Na]^+, found: 391.0972. IR (CH_2Cl_2, cm⁻¹): 1994 and 1937 (s, /2/C=O). UV-Visible (CH_2Cl_2): /7 max, nm (e, 10^3 M⁻¹·cm⁻¹): 358 (1.0), 290 (4.9). Cyclic voltammetry (CH_2Cl_2, 0.10 M [n-Bu_4N][PF_6], V vs SCE): E_{1/2}: 1.09 and 1.35 (irreversible processes). ^1H NMR (400 MHz, CDCl_3, ppm): δ 7.46 (d, 1H, ^3J_{H,H} = 8 Hz, H_\text{aromatics}), 7.34 (d, 1H, ^3J_{H,H} = 8 Hz, H_\text{aromatics}), 7.00 (t, 1H, ^3J_{H,H} = 8 Hz, H_\text{aromatics}), 6.89 (t, 1H, ^3J_{H,H} = 8 Hz, H_\text{aromatics}), 4.44 (s, 2H, CH_2), 3.51 (s, 3H, OMe), 1.69 (s, 15H, Cp*). ^13C{^1H} NMR (100 MHz, CDCl_3, ppm): δ 217.6 (s, C=O), 156.1 and 147.7 (2 × s, C_\text{quat aromatics}), 144.6, 128.3, 125.7, and 123.0 (4 × s, C_\text{aromatics}), 96.6 (s, C_\text{quat Cp*}), 79.2 (s, CH_2), 58.4 (s, OMe), 9.6 (s, CH_3 Cp*).

4.3.2. dicarbonyl(pentamethylcyclopentadienyl)(o-dimethylaminomethylphenyl)iron methiodide (14)

To a MeOH solution (25 mL) of dicarbonyl(pentamethylcyclopentadienyl)(o-dimethylaminomethylphenyl)iron (0.191 g, 0.50 mmol) at 0°C, methyl iodide (0.31 mL, 5.0 mmol) was added. The yellow solution was stirred at 0°C for 10 min, the cooling bath was removed, and stirring was maintained for 16 h at room temperature. The reaction mixture was taken to dryness, the yellow residue triturated in Et_2O (25 mL), rapidly stirred for 5 min, and the solid collected on a sintered glass funnel. The crude yellow ammonium salt was taken up in CH_2Cl_2 (10 mL) and filtered
into 100 mL of stirred Et₂O. The precipitate was collected on a sintered glass funnel, washed with Et₂O (3 × 25 mL), and dried *in vacuo* (0.24 g, 92 %). mp: 200°C (decomp.). Elemental analysis: calcd for C₂₂H₃₀FeINO₂: C: 50.50 %, H: 5.78 %, N: 2.68 %; found: C: 50.47 %, H: 5.67 %, N: 2.68 %.

HRMS (ESI, CH₃OH/CH₂Cl₂ 9:1): calc: 396.1626 [M-I]⁺, found: 396.1625. IR (CH₂Cl₂, cm⁻¹): 1996 and 1928 (2 vs, νC=O). ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.55 and 7.42 (2 × m, 2 × 1H, C₆H₄), 6.95 (m, 2H C₆H₄), 4.93 (s, 2H, CH₂), 3.26 (s, 9H, NMe₃), 1.51 (s, 15H, Cp*). ¹³C{¹H} NMR (100 MHz, CDCl₃, ppm): δ 218.7 (s, C=O), 165.3 and 145.8 (2 × s, C-quat aromatics), 137.7, 132.4, 128.1 and 123.4 (4 × s, C aromatics), 98.0 (s, Cp*), 74.7 (s, CH₂), 53.2 (s, NMe₃), 9.5 (s, CH₃ Cp*).

Crystals suitable for a X-ray diffraction study were grown by slow diffusion of a CH₂Cl₂ solution layered with *n*-hexane.

### 4.3.3. General procedures for the syntheses of 1-(dicarbonyl(pentamethylcyclopentadienyl)iron)-2-(alkoxymethyl)ferrocene from rac-1-(dicarbonyl(pentamethylcyclopentadienyl)iron)-2-(N,N-dimethylaminomethyl)ferrocene

*By solvolysis:* rac-1-(dicarbonyl(pentamethylcyclopentadienyl)iron)-2-(dimethylaminomethyl)ferrocene (0.245 g, 0.50 mmol) was dissolved in the appropriate alcohol (25 mL) and cooled to 0°C. Methyl iodide (0.31 mL, 5.0 mmol) was added in one portion, and the reaction mixture was stirred for 1 h at 0°C and then 16 h at room temperature, and was finally refluxed for 1 h. The solvent and volatiles were removed under reduced pressure and the residue was treated with water (25 mL). Et₂O (25 mL) was added and the biphasic system vigorously stirred for 5 min and then subjected to standard work-up. The crude oil was adsorbed onto celite and loaded on the top of a chromatographic column (silica gel, 3 × 20 cm). Elution with hexanes/Et₂O mixtures afforded the desired complex as the main yellow band, which was collected and taken to dryness.
Recrystallization of the residue from aqueous ethanol and standing for 16 h at -18°C yielded the corresponding complexes as yellow crystalline solids, which were collected on a fine porosity glass sintered funnel, washed with 50% aqueous ethanol (5 mL) and dried in vacuo.

4.3.3.1. rac-1-(dicarbonyl(pentamethylcyclopentadieny)iron)-2-(methoxymethyl)ferrocene (13-Me)

Using methanol as the solvent, 0.17 g (71%) of the complex was obtained. Eluent: hexanes/Et₂O 95:5. Recrystallization: EtOH/water 2:1, 30 mL. Rf (hexanes/Et₂O 95:5): 0.29. mp: 112°C. Elemental analysis: calcéd for C₂₄H₂₈Fe₂O₃: C: 60.54 %, H: 5.93 %; found: C: 61.09 %, H: 6.16 %. HRMS (ESI, CH₃OH): calc: 476.0737 [M]+, found: 476.0737. IR (CH₂Cl₂, cm⁻¹): 2918 (m, H-CCH₂), 2815 (m, H-COMe), 1990 and 1934 (vs, C=O), 1031 (s, O-C), 820 (m, H-C₅H₅). Cyclic voltammetry (CH₂Cl₂, 0.10 M [n-Bu₄N][PF₆], V vs SCE): E½: 0.13 (ΔE½ = 0.068 V; iₚa/iₚc = 1.0), 1.50 (irreversible process). ¹H NMR (400 MHz, CDCl₃, ppm): δ 4.50 and 4.30 (2×s, 2×1H, C₅H₃), 4.04 (m, 8H, C₅H₃+C₅H₅+CH₂), 3.35 (s, 3H, OMe), 1.71 (s, 15H, Cp*). ¹³C{¹H} NMR (100 MHz, CDCl₃, ppm): δ 219.0 and 218.1 (2×s, C=O), 96.4 (s, Cquat Cp*), 89.2 (s, Fe-C), 79.3, 73.9, 71.1 and 70.1 (4×s, C₅H₅), 69.8 (m, C₅H₅+CH₂), 58.1 (s, OMe), 9.6 (s, CH₃ Cp*).

4.3.3.2. rac-1-(dicarbonyl(pentamethylcyclopentadieny)iron)-2-(ethoxymethyl)ferrocene (13-Et)

Using ethanol as the solvent, 0.14 g (57%) of the complex was obtained. Eluent: gradient from hexanes/Et₂O 95:5 to 9:1. Recrystallization: EtOH/water 2:1, 30 mL. Rf (hexanes/Et₂O 95:5): 0.45. mp: 120°C. Elemental analysis: calcéd for C₂₅H₃₀Fe₂O₃: C: 61.25 %, H: 6.17 %; found: C: 61.62 %, H: 6.17 %. HRMS (ESI, CH₃OH/CH₂Cl₂ 95:5): calc: 490.0894 [M]+, found: 490.0893. IR (CH₂Cl₂, cm⁻¹): 2870 (m, νH-C CH₂), 1990 and 1934 (2×s, νC=O), 1083 (s, νO-C), 820 (m, δH-C C₅H₅). ¹H NMR (400 MHz, CDCl₃, ppm): δ 4.23 – 4.13 (3×s overlapped, 3H, C₅H₃), 3.59 (s, 2H, CH₂CH₃), 3.59 (s, 2H, CH₂CH₃) 1.72 (s, 15H, Cp*), 1.26 (s, 3H, CH₂CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃, ppm): δ 219.0 and 218.2 (2×s,C=O), 96.4 (s, Cquat Cp*), 94.2, 79.2, 71.7, 71.0 and 65.8 (5×
s, C₅H₅ + CH₂, possibly overlapped signals), 89.6 (s, Fe-C), 69.5 (s, C₅H₅), 15.5 (s, CH₃), 9.6 (s, CH₃ Cp*).

4.3.2.3. rac-1-(dicarbonyl(pentamethylcyclopentadienyl)iron)-2-(isopropoxymethyl)ferrocene (13-iPr)

Using isopropanol as the solvent, 0.17 g (68 %) of the complex was obtained. Eluent: gradient from hexanes/Et₂O 95:5 to 9:1. Recrystallization: EtOH/water 2:1, 30 mL. Rf (hexanes/Et₂O 95:5): 0.51. mp: 88°C. Elemental analysis: calcd for C₂₆H₃₂Fe₂O₃: C: 61.93 %, H: 6.40 %; found: C: 62.44 %, H: 6.50 %. HRMS (ESI, CH₃OH/CH₂Cl₂ 95:5): calc: 504.1050 [M]+, found: 504.1049. IR (CH₂Cl₂, cm⁻¹): 2870 (m, v_H-C(CH₃)₂), 1990 and 1934 (s, v_C=O), 1034 (s, v_O-C), 820 (m, δ_H-C₅H₅).

¹H NMR (400 MHz, CDCl₃, ppm): δ 4.66, 4.44, 3.99 and 3.97 (4 × s, 4 × 1H, C₅H₅ + CH(CH₃)₂), 4.15 (s, 5H, C₅H₅), 3.63 (s, 2H, CH₂), 1.75 (s, 15H, Cp*), 1.13 (s, 6H, CH(CH₃)₂). ¹³C{¹H} NMR (100 MHz, CDCl₃, ppm): δ 219.0 and 218.2 (2 × s, C=O), 96.4 (s, C_quat Cp*), 94.8, 90.6 (s, Fe-C), 79.0, 70.8, and 68.9 (5 × s, C₅H₅ + CH₂, possibly overlapped signals), 70.0 (s, C₅H₅), 22.3 (s, iPr), 9.7 (s, CH₃ Cp*).

By alcoholysis in CH₂CN: Methyl iodide (0.31 mL, 5.0 mmol) was added in one portion to a solution of rac-1-(dicarbonyl(pentamethylcyclopentadienyl)iron)-2-(dimethylaminomethyl)ferrocene (0.245 g, 0.50 mmol) and the appropriate alcohol or phenol (5.0 mmol) in acetonitrile (25 mL) at 0°C. Reaction time, temperatures, work-up and purification were identical to those of the solvolytic method. Unless otherwise specified, the complexes were obtained as yellow crystalline solids.

4.3.3.4. rac-1-(dicarbonyl(pentamethylcyclopentadienyl)iron)-2-(phenoxymethyl)ferrocene (13-Ph)

Using phenol (0.470 g), 0.14 g (57 %) of the complex was obtained. Elution: hexanes/Et₂O 95:5. Recrystallization: EtOH/water 5:3, 80 mL. Rf (hexanes/Et₂O 95:5): 0.41. mp: 192°C. HRMS
(ESI, CH₃OH/CH₂Cl₂ 95:5): calc: 538.0894 [M]⁺, found: 538.0887. IR (CH₂Cl₂, cm⁻¹): 2857 (m, νH-C CH₂), 1991 and 1935 (s, νC=O), 1029 (s, νO-C), 821 (m, δH-C C₅H₅). ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.31 (m, 2H, Ph), 6.96 (m, 3H, Ph), 4.74 (s, 2H, CH₂), 4.53, 4.32 and 3.94 (3 × s, 3 × 1H, C₅H₅), 4.06 (s, 5H, C₅H₅), 1.68 (s, 15H, Cp*).

¹³C{¹H} NMR (100 MHz, CDCl₃, ppm): δ 218.8 and 218.1 (2 × s, C=O), 159.3 (s, Cquat Ph), 129.6, 120.4 and 114.6 (3 × s, Ph), 96.5 (s, Cquat Cp*), 88.2 (s, Fe-C), 79.4, 71.0, 70.5 and 69.1 (4 × s, C₅H₃ + CH₂), 69.8 (s, C₅H₅), 9.7 (s, CH₃ Cp*). Crystals suitable for a X-ray structural study were grown from EtOH.

4.3.3.5. rac-1-(dicarbonyl(pentamethylcyclopentadienyl)iron)-2-(benzyloxymethyl)ferrocene (13-Bz)

Using benzyl alcohol (0.52 mL), 0.160 g (58 %) of the complex was obtained. Elution: gradient from hexanes/Et₂O 98:2 to 95:5. Recrystallization: EtOH/water 2:1, 75 mL. Rf (hexanes/Et₂O 95:5): 0.63. mp: 130°C. Elemental analysis: calcd for C₃₀H₃₂Fe₂O₃: C: 65.24 %, H: 5.84 %; found: C: 65.66 %, H: 6.11 %. HRMS (ESI, CH₃OH/CH₂Cl₂ 9:1): calc: 552.1050 [M]⁺, found: 552.1046. IR (CH₂Cl₂, cm⁻¹): 2857 (m, νH-C CH₂), 1990 and 1934 (s, C=O), 1028 (s, νO-C), 819 (m, δH-C C₅H₅). ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.28 (m, 5H, Ph), 4.50, 4.40 and 3.80 (3 × s, 3 × 1H, C₅H₅), 4.19 (s, 2H, CH₂), 3.91 (s, 7H, C₅H₅ + CH₂), 1.60 (s, 15H, Cp*). ¹³C{¹H} NMR (100 MHz, CDCl₃, ppm): δ 219.0 and 218.2 (2 × s, C=O), 139.2 (s, Cquat Ph), 128.4, 127.6 and 127.4 (3 × s, Ph), 96.4 (s, Cquat Cp*), 89.6 (s, Fe-C), 79.2, 72.5, 71.7 and 71.0 (4 × s, C₅H₃ + CH₂, possible overlaps), 69.8 (s, C₅H₅), 9.7 (s, CH₃ Cp*). Crystals suitable for a X-ray structural study were grown by slow cooling of a saturated EtOH solution to -18°C.

4.3.3.6. I-(dicarbonyl(pentamethylcyclopentadienyl)iron)-2-(a-phenylethoxymethyl)ferrocene (13-CHMePh)

Using rac-1-phenylethanol (0.60 mL), 0.15 g (53 %) of the complex was obtained as an orange gum. Elution: hexanes/Et₂O 95:5. Rf (hexanes/Et₂O 95:5): 0.42. HRMS (ESI, CH₃OH/CH₂Cl₂...
95:5); calc: 566.1207 [M]+, found: 566.1203. IR (CH$_2$Cl$_2$, cm$^{-1}$): 2861 (m, ν$_{\text{C}-\text{H}}$ CH$_2$), 1990 and 1935 (2 × s, ν$_{\text{C}=\text{O}}$), 1033 (s, ν$_{\text{O}-\text{C}}$), 820 (m, δ$_{\text{H}-\text{C}}$ C$_5$H$_3$). $^1$H NMR (400 MHz, CDCl$_3$, ppm): δ for the mixture of diastereomers 7.37 (m, 2 × 4H, Ph), 7.28 (m, 2 × 1H, Ph), 4.59 (dd, 1H, $J_{\text{H-H}}$ = 6 and 6 Hz, C$_5$H$_3$), 4.46 (dd, 1H, $J_{\text{H-H}}$ = 6 and 6 Hz, C$_5$H$_3$), 4.42 and 4.37 (2 × s, 2 × 1H, C$_5$H$_3$), 4.21 (s, 2H, CH$_2$), 4.15 (s, 1H, O-CH), 4.07 (s, 3H, CH$_2$ + O-CH), 4.01 and 3.82 (2 × s, 2 × 1H, C$_5$H$_3$), 3.97 and 3.89 (2 × s, 2 × 5H, C$_5$H$_5$), 1.70 and 1.63 (2 × s, 2 × 15H, Cp*), 1.43 and 1.42 (2 × s, 2 × 3H, Me). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$, ppm): δ for the mixture of diastereomers 218.7, 218.7, 218.1 and 218.0 (2 × pseudo d, C=O), 144.6 and 144.6 (pseudo d, C$_{\text{quat}}$ Ph), 128.4, 128.3, 127.2, 127.2, 126.5 and 126.2 (6 × s, Ph), 96.2 and 96.2 (pseudo d, C$_{\text{quat}}$ Cp*), 90.5 and 90.4 (2 × s, Fe-C), 79.1, 78.9, 77.7, 77.4, 70.5, 70.3, 69.6, 69.2, 69.1 and 69.0 (10 × s, C$_5$H$_3$ + CH$_2$), 70.0 and 69.8 (2 × s, C$_5$H$_5$), 31.5 and 30.2 (2 × s, CH), 24.5 and 24.1 (2 × s, Me), 9.6 and 9.5 (pseudo d, CH$_3$ Cp*).

4.3.3.7. rac-1-(dicarbonyl(pentamethylcyclopentadienyl)iron)-2-(benzhydryloxy)methyl)ferrocene (13-CHPh$_2$)

Using benzhydrol (0.921 mL), 0.09 g (29 %) of the complex was obtained. Elution: gradient from hexanes/Et$_2$O 98:2 to 95:5. Recrystallization: EtOH/water 2:1, 30 mL. $R_f$ (hexanes/Et$_2$O 95:5): 0.72. mp: <45°C. Elemental analysis: calcd for C$_{36}$H$_{36}$Fe$_2$O$_3$: C: 68.81 %, H: 5.77 %; found: C: 68.29 %, H: 6.08 %. HRMS (ESI, CH$_3$OH/CH$_2$Cl$_2$ 9:1): calc: 628.1363 [M]$^+$, found: 628.1366. IR (CH$_2$Cl$_2$, cm$^{-1}$): 2859 (m, ν$_{\text{H}-\text{C}}$ CH$_2$), 1990 and 1935 (2 × s, ν$_{\text{C}=\text{O}}$), 1029 (s, ν$_{\text{O}-\text{C}}$), 820 (m, δ$_{\text{H}-\text{C}}$ C$_5$H$_3$). $^1$H NMR (400 MHz, CDCl$_3$, ppm): δ 7.38 (m, 4H, Ph), 7.30 (m, 4H, Ph), 7.23 (m, 2H, Ph), 5.42 (s, 1H, CH), 4.59, 4.34 and 4.13 (3 × s, C$_5$H$_3$), 4.02 (s, 7H, C$_5$H$_5$ + CH$_2$), 1.61 (s, 15H, Cp*). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$, ppm): δ 218.8 and 218.1 (2 × s, C=O), 143.2 (s, C$_{\text{quat}}$ Ph), 128.4, 128.4, 127.4, 127.3, 127.1 and 127.0 (6 × s, Ph), 96.3 (s, C$_{\text{quat}}$ Cp*), 90.5 (s, Fe-C), 83.3 (s, CH), 79.2, 74.0, 71.6, 70.6,
70.0 and 69.2 (6 × s, C₅H₅ + C₅H₅ + CH₂), 9.6 (s, CH₃ Cp*). Crystals suitable for a X-ray diffraction study were grown by slow cooling of a saturated EtOH solution to -18°C.

4.3.3.8. 1-(dicarbonyl(pentamethylcyclopentadienyl)iron)-2-(d-menthyloxymethyl)ferrocene (13-Menthyl)

Using d-menthol (0.781 g), 0.12 g (40 %) of the complex was obtained. Elution: gradient from hexanes/Et₂O 99:1 to 98:2. Recrystallization: EtOH/water 4:3, 35 mL. R₇ (hexanes/Et₂O 99:1): 0.37. mp: 174°C. Elemental analysis: calcd for C₃₃H₄₄Fe₂O₃: C: 66.02 %, H: 7.39 %; found: C: 66.06 %, H: 7.48 %. HRMS (ESI, CH₃OH/CH₂Cl₂ 9:1): calc: 600.1989 [M]+, found: 600.1986. IR (CH₂Cl₂, cm⁻¹): 2870 (m, /2H-C₇H₇CH₂), 1991 and 1935 (2 × s, /2C=O), 820 (m, δH-C₅H₅). ¹H NMR (400 MHz, CDCl₃, ppm): δ 4.72, 3.70 and 3.07 (3 × s, 3 × 1H, C₅H₃), 4.44 (s, 2H, CH₂), 4.15 (s, 5H, C₅H₅), 2.17 (s, 2H, menthyl), 1.75 (s, 17H, Cp* + menthyl), 1.28 (s, 4H, menthyl), 0.86 (s, 11H, menthyl). ¹³C{¹H} NMR (100 MHz, CDCl₃, ppm): δ 219.1 and 218.1 (2 × s, C=O), 96.5 (s, C_quat Cp*), 91.7 (s, Fe-C), 80.5, 79.1, 73.8, 71.5 and 70.5 (5 × s, C₅H₅ + C₅H₅ + CH₂, possible overlaps), 48.6, 40.8, 34.9, 31.7, 25.8, 25.5, 23.6, 22.6, 21.1 and 16.5 (10 × s, menthyl), 9.8 (s, CH₃ Cp*). Crystals suitable for a X-ray diffraction study were grown by slow cooling of a saturated EtOH solution to -18°C.

4.3.4. N,N-dimethylaminomethylferrocene methiodide (17)[52, 67]

N,N-dimethylaminomethylferrocene (0.73 g, 3.0 mmol) was dissolved in MeOH (50 mL), cooled to 0°C and methyl iodide (1.90 mL, 30.0 mmol) was added in one portion. The reaction mixture was allowed to warm to room temperature slowly with the cold bath in place, stirred for 16 h at room temperature, and finally heated to reflux and refluxed for 1 h. After removal of solvent and volatiles under reduced pressure, the light brown residue was triturated with Et₂O (25 mL), rapidly
stirred for 5 min, and the suspension filtered on a glass frit. The solid was washed with additional Et$_2$O (3 × 10 mL) and dried in vacuo to give the desired compound (0.98 g, 84 %) as a light brown solid. mp: 220°C (decomp., darkening above 175°C.). HRMS (ESI, CH$_3$OH): calc: 258.0945 [M-I]$^+$, found: 258.0943. IR (KBr, cm$^{-1}$): 2965 (m, $\nu_{\text{H-C}}$ CH$_3$), 2939 (m, $\nu_{\text{H-C}}$ CH$_2$), 1470 (s, $\delta_{\text{H-C}}$ CH$_2$), 1408 and 1382 (m, $\delta_{\text{H-C}}$ CH$_3$), 819 (s, $\delta_{\text{H-C}}$ Fc). $^1$H NMR (400 MHz, CDCl$_3$, ppm): δ 4.81 (m, 2H, C$_5$H$_4$), 4.51 (m, 2H, C$_5$H$_4$), 4.23 and 4.21 (m, 7H, CH$_2$ + C$_5$H$_5$), 3.20 (s, 9H, NMe$_3$). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$, ppm): δ 72.1 (superimposed s, CH$_2$ and C$_5$H$_4$), 70.5 (s, C$_5$H$_4$), 69.9 (s, C$_5$H$_5$), 66.9 (s, C$_\text{quat}$ C$_5$H$_4$), 52.5 (s, NMe$_3$).

From the combined filtrates, methoxymethylferrocene (0.10 g, 14%) was obtained as an orange oil after evaporation of the solvents and purification of the residue by column chromatography (silica gel, 2.5 × 15 cm). The yellow band, eluting with hexanes/Et$_2$O 95:5, was collected and taken to dryness to give the title compound.

4.3.5. methoxymethylferrocene (18)[68]

$N,N$-dimethylaminomethylferrocene methiodide (0.385 g, 1.0 mmol) was refluxed in MeOH (25 mL) for 24 h, cooled to room temperature and evaporated under reduced pressure. The resulting residue was triturated with Et$_2$O (25 mL), rapidly stirred for 5 min, and the suspension was filtered on a sintered glass funnel. The solid was washed with Et$_2$O (50 mL) and the solvent removed from the combined filtrates. The crude orange oil was chromatographed (silica gel, 3 × 20 cm) using a gradient elution with hexanes/Et$_2$O 95:5 to 9:1. The yellow band was collected, the solvent evaporated, and the orange oil (0.18 g, 78 %) dried in vacuo. The compound is best stored in the solid state at -18°C to prevent decomposition. R$_f$ (hexanes/Et$_2$O 95:5): 0.29. HRMS (ESI, CH$_3$OH): calc: 230.0394 [M]$^+$, found: 230.0392. IR (liquid film, cm$^{-1}$): 2922 and 2852 (2 × m, $\nu_{\text{H-C}}$ CH$_2$), 2815 (m,
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\( \nu_{\text{H-C OCH}_3} \), 1090 (s, \( \nu_{\text{O-C OCH}_3} \)), 818 (s, \( \delta_{\text{H-C Fc}} \)). \(^1\)H NMR (400 MHz, CDCl\(_3\), ppm): \( \delta \) 4.25 and 4.23 (2 × m, 2 × 2H, C\(_5\)H\(_4\)), 4.16 (superimposed s, 7H, CH\(_2\) + C\(_5\)H\(_3\)), 3.32 (s, 3H, OCH\(_3\)). \(^{13}\)C\{\(^1\)H\} NMR (100 MHz, CDCl\(_3\), ppm): \( \delta \) 83.3 (s, C\(_\text{quat C}_5\)H\(_4\)), 70.9, 69.5 and 68.6 (3 × s, CH\(_2\) + C\(_5\)H\(_4\)), 68.5 (s, C\(_5\)H\(_5\)), 57.7 (s, OCH\(_3\)).

4.3.6. benzhydrol oxymethyl ferrocene (19)

\( N,N\)-dimethylaminomethylferrocene methiodide (0.383 g, 1.0 mmol) and benzhydrol (0.921 g, 5.0 mmol) were refluxed in acetonitrile (25 mL) for 24 h. After cooling to room temperature and evaporation under reduced pressure, the resulting residue was triturated in Et\(_2\)O (25 mL), stirred rapidly for 5 min, and the solid removed by filtration on a sintered glass funnel. The solid was washed with additional Et\(_2\)O (50 mL) and the combined filtrates taken to dryness on a rotary evaporator. The crude yellow oil was adsorbed onto celite and subjected to column chromatography (silica gel, 3 × 20 cm). Elution with hexanes/Et\(_2\)O 9:1 developed a yellow band, which was collected and the solvent evaporated. The residue was dissolved in the minimum amount of 50% aqueous ethanol (10 mL); after standing for 16 h at -18°C, pale yellow crystals were obtained (0.060 g, 16%), which were collected on a sintered glass funnel and dried in vacuo. \( R_f \) (hexanes/Et\(_2\)O 9:1): 0.58. mp: 80°C. Elemental analysis: calcd for C\(_{24}\)H\(_{22}\)FeO: C: 75.41 %, H: 5.80 %; found: C: 76.01 %, H: 6.13 %.

HRMS (ESI, CH\(_3\)OH/CH\(_2\)Cl\(_2\) 9:1): calc: 382.1020 [M]\(^+\), found: 382.1020. IR (KBr, cm\(^{-1}\)): 3082 and 3024 (2 × m, \( \nu_{\text{H-C Ph + Fc}} \)), 2857 (m, \( \nu_{\text{H-C CH}_2} \)), 1341 (m, \( \delta_{\text{H-C CH}} \)), 1092 (s, \( \nu_{\text{O-C}} \)), 818 (s, \( \delta_{\text{H-C Fc}} \)), 738 and 700 (s, \( \delta_{\text{H-C Ph}} \)). CV (CH\(_2\)Cl\(_2\), 0.10 M \([n\text{-Bu}_4\text{N}][\text{PF}_6]\), V vs SCE): \( E_{1/2} \): 0.46 (\( \Delta E_{1/2} = 0.068 \) V; \( i_{\text{pa}}/i_{\text{pc}} = 0.95 \)). \(^1\)H NMR (400 MHz, CDCl\(_3\), ppm): \( \delta \) 7.36-7.32 (m, 8H, Ph), 7.28-7.25 (m, 2H, Ph), 5.46 (s, 1H, CH), 4.32 (s, 2H, CH\(_2\)), 4.28 and 4.19 (2 × s, 2 × 2H, C\(_5\)H\(_4\)), 4.14 (s, 5H C\(_5\)H\(_5\)). \(^{13}\)C\{\(^1\)H\} NMR (100 MHz, CDCl\(_3\), ppm): \( \delta \) 142.3 (s, C\(_\text{quat Ph}\)), 128.5, 127.5 and 127.5 (3 × s, Ph), 82.1 (s, CH), 69.6, 68.9, 68.7, 68.7 and 67.0 (5 × s, Fc + CH\(_2\)).
4.3.7. rac- carbonyl(pentamethylcyclopentadienyl)(κ²C,N-o-(dimethylaminomethyl)phenyl) iron (20)

A toluene solution (25 mL) of dicarbonyl(pentamethylcyclopentadienyl)(o-dimethylaminomethylphenyl)iron (0.191 g, 0.50 mmol) under 1 atm of argon was irradiated overnight with a medium pressure quartz lamp. The solvent and volatiles were removed in vacuo, and the brown residue was taken up in n-pentane (10 mL) and cooled to -90°C, inducing the precipitation of a brown solid. After decantation, the supernatant was removed using a filter-paper tipped cannula and the precipitate washed with additional n-pentane (10 mL) at the same temperature and finally dried in vacuo (0.125 g, 71 %). mp: 98°C[69]. HRMS (ESI, CH₂Cl₂): calc: 353.1442 [M]+, found: 353.1439. IR (CH₂Cl₂, cm⁻¹): 1886 (s, /2C=O). Cyclic voltammetry (CH₂Cl₂, 0.10 M [N-n-Bu₄][PF₆], V vs SCE): E½: -0.03 (ΔEp = 0.074 V; iₚa/iₚc = 1), 1.00 and 1.39 (irreversible processes). ¹H NMR (400 MHz, C₆D₆, ppm): δ 7.84 (d, 1H, JHH = 7 Hz, Haromatic), 7.24 (t, 1H, JHH = 7 Hz, Haromatic), 7.10 (t, 1H, JHH = 7 Hz, Haromatic), 7.01 (d, 1H, JHH = 7 Hz, Haromatic), 3.48 (d, 1H, JHH = 12 Hz, CH₂), 2.62 (d, 1H, JHH = 12 Hz, CH₂), 1.86 (s, 3H, NMe₂), 1.74 (s, 3H, NMe₂), 1.45 (s, 15H, Cp*). ¹³C{¹H} NMR (100 MHz, C₆D₆, ppm): δ 224.3 (s, C=O), 179.3 (s, Fe–C), 147.7 (s, Cipso CH₂NMe₂), 141.5, 125.4, 121.7 and 121.1 (4 x s, Caromatics), 89.1 (s, Cquat Cp*), 74.1 (s, CH₂), 57.6 and 53.9 (2 x s, NMe₂), 10.4 (s, CH₃ Cp*).

4.2. Crystallography

Data collection was carried out in a Bruker Apex-II CCD diffractometer at 150 K. The structure was solved by direct methods using the SIR97 program[70], and then refined with full-matrix least-square methods based on F² (SHELXL-97)[71] with the aid of the WINGX program[72]. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included.
in their calculated positions. Details of the data collection, cell dimensions, and structure refinements are given in Table 1, selected bond distances and angles in Table 2 while molecular structures for 10, 14 and for 13-Ph (A), 13-Bz (B), 13-CHPh₂ (C) and 13-Menthy1 (D) are depicted in Figure 5 and 6 respectively.

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Appendix A. Supplementary materials

CCDC 928736 (10), 928273 (13-Ph), 928738 (13-Bz), 928275 (13-CH₂Ph), 928274 (13-Menthy1) and 928737 (14) contain the supplementary crystallographic data for compounds 10, 13-R (R = Ph, Bz, CH₂Ph and Menthy1) and 14. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

References


During this investigation it was found that sodium borohydride reduction of formylferrocene in methanol result in the formation of methoxymethylferrocene and not hydroxymethylferrocene: sodium borohydride (0.61 g, 15.60 mmol) was added by small portion to ferrocenecarboxaldehyde (2.59 g 12.0 mmol) in MeOH (50 mL) at 0°C. After 1 h of stirring, the gas evolution had subsided, the cold bath was removed and stirring continued for 2 h at room temperature. The reaction mixture was poured into 100 mL of ice/water containing 10 mL of concentrated HCl. After standard work-up and purification by column chromatography (silica gel, 4.5 x 20 cm) gave 2.47 g (95 %) of methoxymethylferrocene as identified by comparison with an authentic sample.