Accepted Manuscript

Synthesis, Reactivity, and Some Photochemistry of *Ortho*-*N*,*N*-dimethylaminomethyl Substituted Aryl and Ferrocenyl Pentamethylcyclopentadienyl Dicarbonyl Iron Complexes

Grelaud Guillaume, Thierry Roisnel, Vincent Dorcet, Mark G. Humphrey, Fr^{o} d^{o} ric Paul, Gilles Argouarch

PII: S0022-328X(13)00418-X

DOI: 10.1016/j.jorganchem.2013.05.031

Reference: JOM 18053

To appear in: *Journal of Organometallic Chemistry*

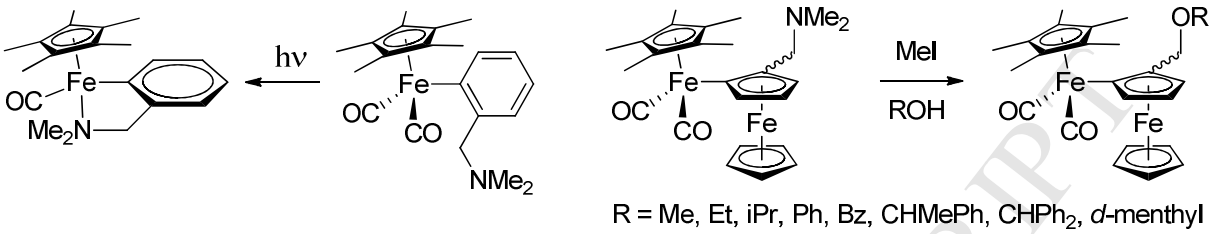
Received Date: 25 March 2013

Revised Date: 15 May 2013

Accepted Date: 23 May 2013

Please cite this article as: G. Guillaume, T. Roisnel, V. Dorcet, M.G. Humphrey, F. Paul, G. Argouarch, Synthesis, Reactivity, and Some Photochemistry of *Ortho*-*N*,*N*-dimethylaminomethyl Substituted Aryl and Ferrocenyl Pentamethylcyclopentadienyl Dicarbonyl Iron Complexes, *Journal of Organometallic Chemistry* (2013), doi: 10.1016/j.jorganchem.2013.05.031.

Graphical Abstract



R = Me, Et, iPr, Ph, Bz, CHMePh, $CHPh_2$, *d*-menthyl

Highlights

- New pentamethylcyclopentadienyl dicarbonyl iron complexes are synthesized
- The parent alkoxy-substituted complexes are obtained by quaternization/alcoholysis
- Photolytic displacement of carbonyl ligands is achieved to form chelated complexes

Synthesis, Reactivity, and Some Photochemistry of *Ortho*-*N*,*N*-dimethylaminomethyl Substituted Aryl and Ferrocenyl Pentamethylcyclopentadienyl Dicarbonyl Iron Complexes

Grelaud Guillaume,[†,‡] *Thierry Roisnel,*[§] *Vincent Dorcet,*[§] *Mark G. Humphrey,*[‡] *Frédéric Paul,*[†] *and Gilles Argouarch*[†,*]

[†] Institut des Sciences Chimiques de Rennes, Organométalliques: Matériaux et Catalyse, UMR CNRS 6226, Université de Rennes 1, Campus de Beaulieu, 35042 Rennes Cedex, France.

[‡] Research School of Chemistry, Australian National University, Canberra, ACT 0200, Australia.

[§] Institut des Sciences Chimiques de Rennes, Centre de Diffractométrie X, UMR CNRS 6226, Université de Rennes 1, Campus de Beaulieu, 35042 Rennes Cedex, France.

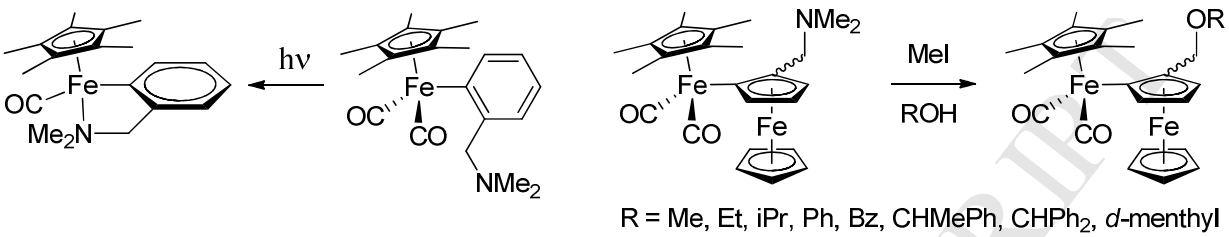
E-mail: gilles.argouarch@univ-rennes1.fr

Keywords: Iron complexes, Piano-stool structures, Ferrocenes, Alcoholysis.

Abstract:

Ortho-lithiated *N*,*N*-dimethylaminomethyl ferrocene and benzyldimethylamine react with $Cp^*Fe(CO)_2I$ to give the new complexes $((Cp^*Fe(CO)_2)$-2-$(CH_2NMe_2)C_5H_3)Fe(Cp)$ and $Cp^*Fe(CO)_2$-C_6H_4(*o*-CH_2NMe_2). Access to a wide variety of alkoxy-substituted complexes $((Cp^*Fe(CO)_2)$-2-$(CH_2OR)C_5H_3)Fe(Cp)$ can be easily achieved by tandem quaternization/alcoholysis of $((Cp^*Fe(CO)_2)$-2-$(CH_2NMe_2)C_5H_3)Fe(Cp)$. Preliminary results show that chelated complexes can be obtained by displacement of one of the carbonyl ligands by photolysis. Crystal structures of $((Cp^*Fe(CO)_2)$-2-$(CH_2NMe_2)C_5H_3)Fe(Cp)$, $((Cp^*Fe(CO)_2)$-2-$(CH_2OR)C_5H_3)Fe(Cp)$ (R = Ph, Bz, $CHPh_2$ and *d*-menthyl) and $[Cp^*Fe(CO)_2$-C_6H_4(*o*-$CH_2NMe_2)][I]$ are reported.

Graphical Abstract



Highlights

- ((Cp*Fe(CO)$_2$)-2-(CH$_2$NMe$_2$)C$_5$H$_3$)Fe(Cp) and Cp*Fe(CO)$_2$-C$_6$H$_4$(*o*-CH$_2$NMe$_2$) are synthesized from Cp*Fe(CO)$_2$I and ortho-lithiated *N*,*N*-dimethylaminomethyl ferrocene or benzyldimethylamine
- alkoxy-substituted complexes ((Cp*Fe(CO)$_2$)-2-(CH$_2$OR)C$_5$H$_3$)Fe(Cp) can be easily obtained by tandem quaternization/alcoholysis of ((Cp*Fe(CO)$_2$)-2-(CH$_2$NMe$_2$)C$_5$H$_3$)Fe(Cp).
- Photolytic displacement of one of the carbonyl ligands of Cp*Fe(CO)$_2$-C$_6$H$_4$(*o*-CH$_2$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 = η^5-C_5H_5)[14-20] and the cationic complex $[CpFe(CO)_2(THF)][BF_4]$ (**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 andh hydrosilanes to form thiosilanes was reported.[15] The commercially available THF adduct **2** of the 16-electron complex $[CpFe(CO)_2]^+$ 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].

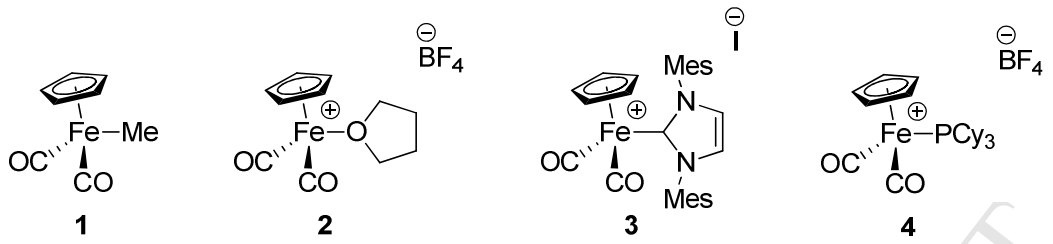


Figure 1. Selected catalysts incorporating the [CpFe(CO)$_2$] fragment.

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 = η^5-C_5Me_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).

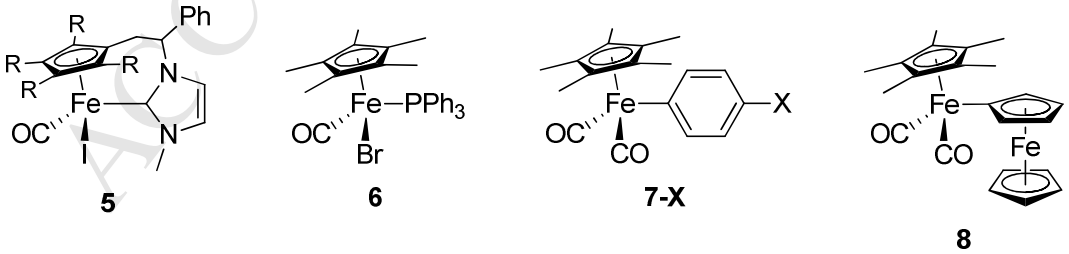


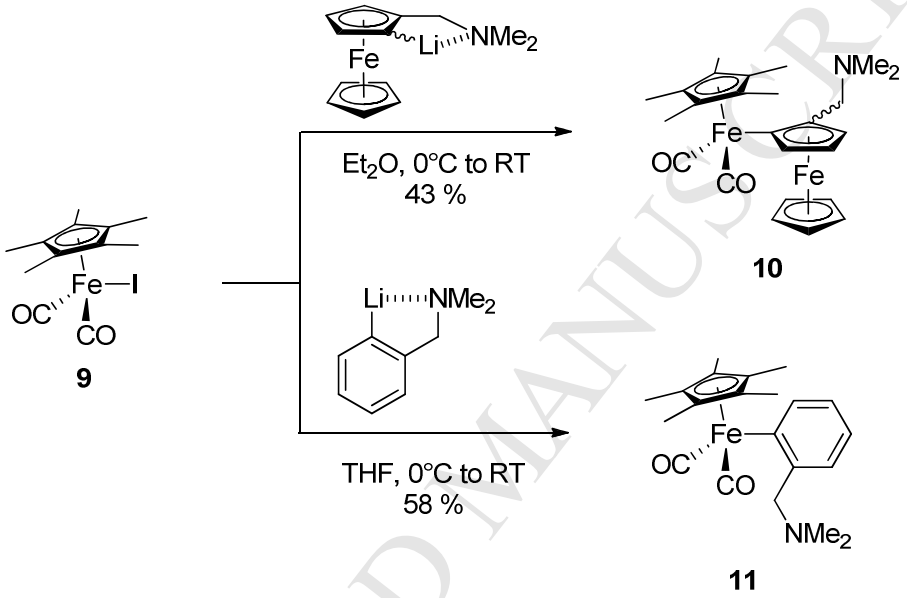
Figure 2: Selected Cp-modified or Cp* iron carbonyl catalysts. R = H, Me; X = H, Me, OMe.

In a previous communication,[36] we have reported the synthesis of a series of piano-stool iron(II) σ–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)$_2$I **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.



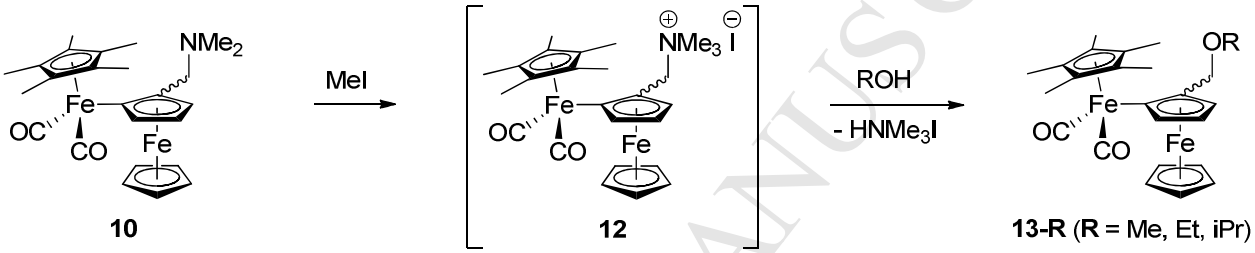
Scheme 1: Synthesis of complexes **10** and **11**.

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)$_2$] moiety in these complexes is evidenced by two strong $\nu_{C\equiv O}$ bands at *ca*. 1990 and 1930 cm^{-1} in the IR spectra. The Cp* ligand gives typical NMR resonances at δ_H *ca*. 1.70 ppm and δ_C *ca*. 96 and 10 ppm. The carbonyl ligands are also visible by ^{13}C NMR spectroscopy, with two signals at δ_C 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 δ_H 2.20 – 2.30 ppm and δ_C *ca*. 46 ppm are related to the dimethylamino moieties whereas the ferrocenyl (**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_2Cl_2 at 0.16 V (vs. SCE in CH_2Cl_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 $CpFe(CO)_2Fc$,[44-47] and for their ruthenium counterparts $CpRu(CO)_2Fc$ and $Cp^*Ru(CO)_2Fc$.[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.

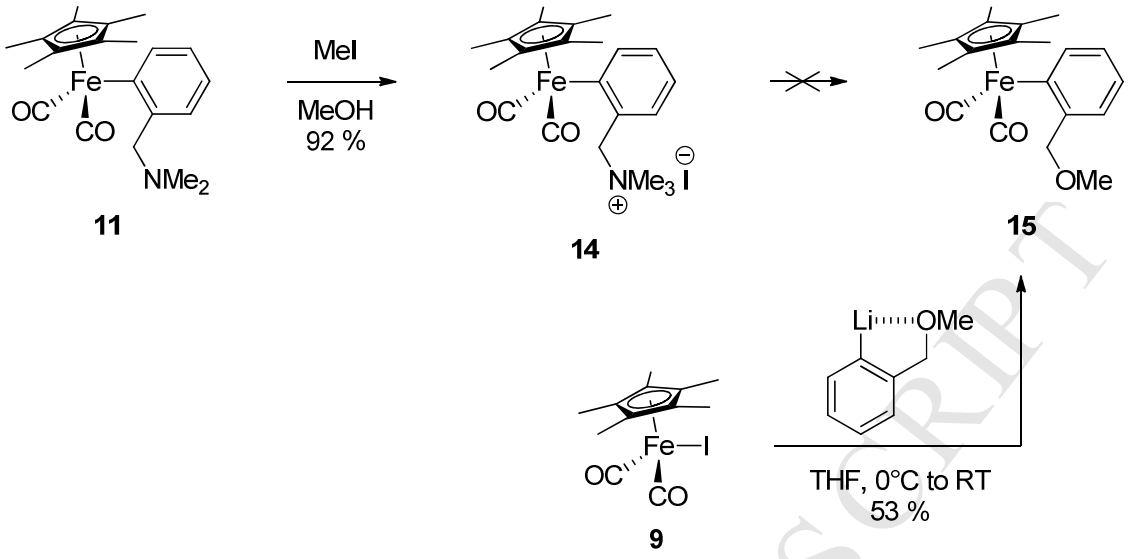
Displacement of trimethylammonium groups by nucleophiles such as cyanide or hydroxyl anion is a known reaction at α-dimethylaminomethyl ferrocene methiodide substrates [49-51]. Thus, in order to introduce other functional groups at **10**, its quaternization with methyl iodide was attempted. However, 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 ($\nu_{C\equiv O}$ 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_2Cl_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.



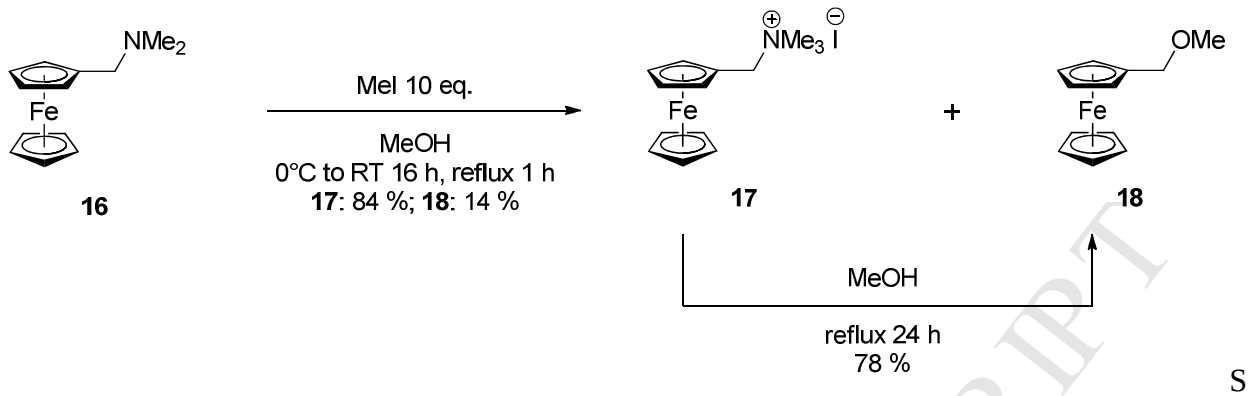
Scheme 2: Solvolysis of **10** in the presence of iodomethane.

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.



Scheme 3: Synthesis of **14** and **15**.

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.

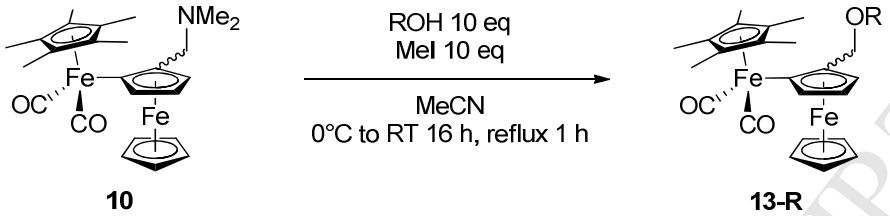


Scheme 4: Syntheses of **17** and **18**.

It can be concluded that the stabilization of the carbocation formed by the loss of the trimethylamino group, *via* coordination of the cyclopentadienyl-methylidene ligand (in a η^6-fulvenic fashion) by the iron atom [55], is favored by the presence of the electron-rich [Cp*Fe(CO)$_2$] synthon in **10**, which increases the electron density at the iron center of the ferrocene. This is supported by the lower value of the oxidation potential of the ferrocenyl in **10** compared to that of *N*,*N*-dimethylaminomethylferrocene (**16**) (0.16 and 0.66 V vs. SCE in CH_2Cl_2, respectively) [56]. The release of the trimethylammonium group in **12** may occur spontaneously at room temperature in polar solvents, preventing its isolation and giving only decomposition products in the absence of nucleophiles.. Although the electron-rich [Cp*Fe(CO)$_2$] synthon is also present on **14**, the lower stabilization of the "benzylic" carbocation probably makes the displacement of the ammonium more difficult at **14**. As a result, **14** retains the same inertness toward methanolysis as benzyltrimethylammonium iodide [57].

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).



10 **13-R**

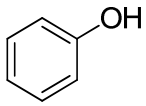
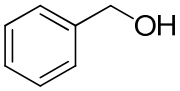
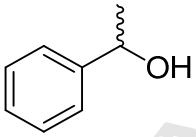
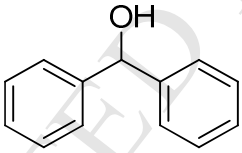
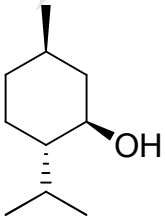
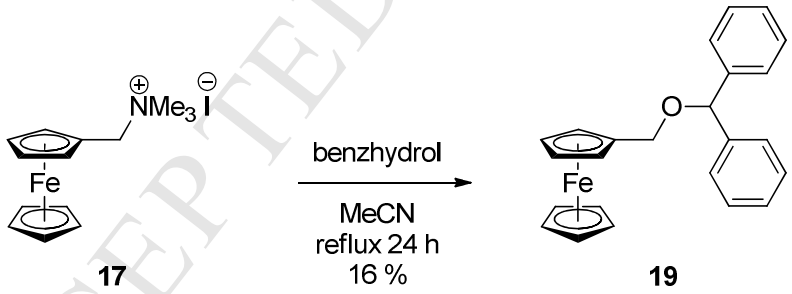
Entry	Alcohol	Complex	Yield
1		**13-Ph**	57 %
2		**13-Bz**	58 %
3		**13-CHMePh**	53 %
4		**13-CHPh$_2$**	29 %
5		**13-Menthyl**	40 %

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, $CHPh_2$, Menthyl) were obtained (Figure 6).

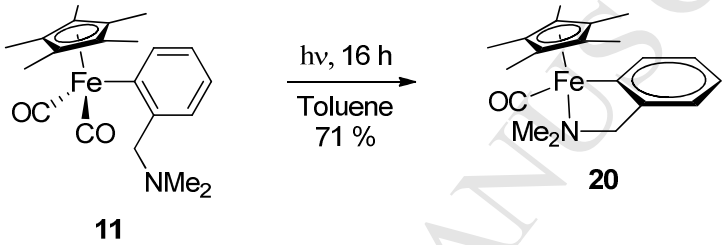
The excess of methyl iodide required in this procedure precluded extending the scope to embrace N-, S- and P-nucleophiles. Indeed, these are likely to be quaternized and thereby becoming unreactive toward **12**. Nevertheless, this method could also be applied to the trimethylammonium derivative **17**.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



Scheme 5: Alcoholysis of **17** with benzhydrol.

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 $[Cp^*Fe(CO)_2]_2$ 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.

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 $\nu_{C\equiv O}$ 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 [Cp*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 metallacycle can still be seen by ^{1}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 $^2J_{H,H}$ = 9 Hz), respectively. The signals found at higher field can be assigned to the protons closest to the Cp* ligand, the ring current deshielding the signals (Figure 3).

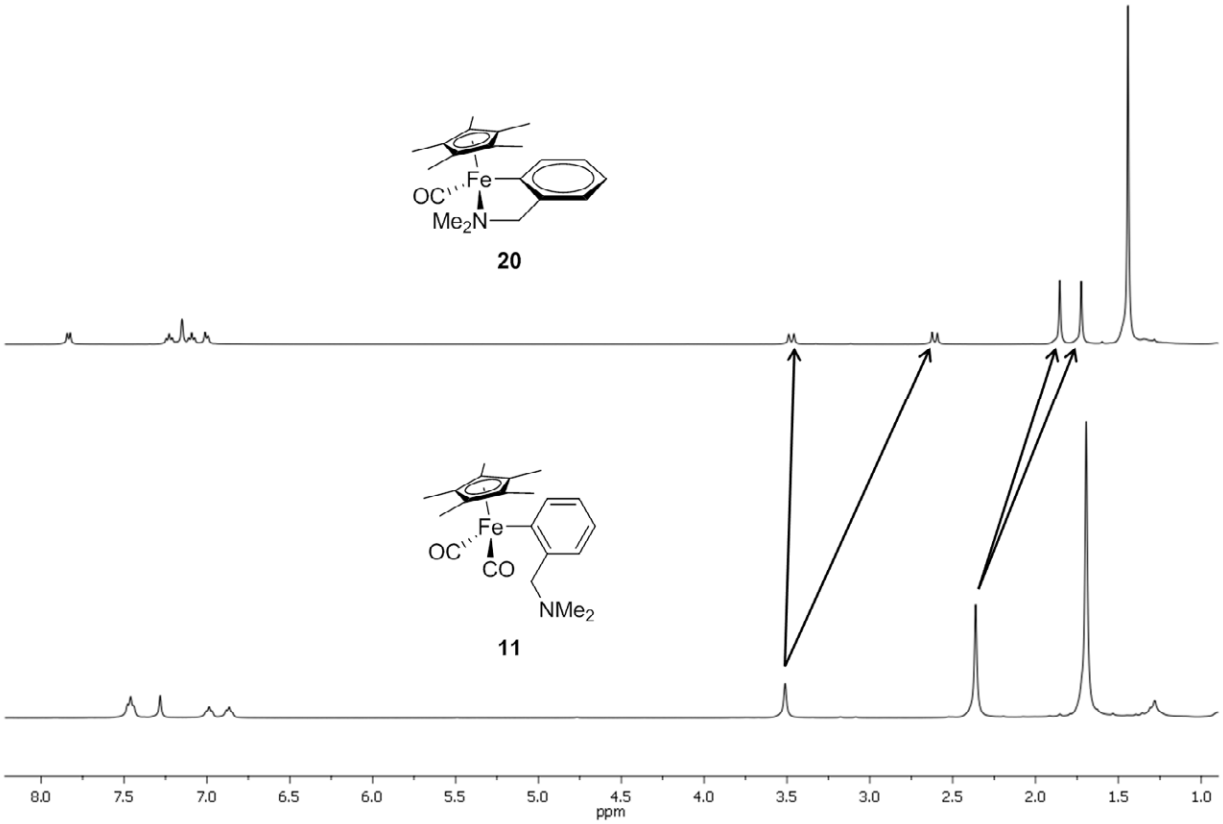


Figure 3: Comparison of the ^{1}H NMR spectra of **11** (in $CDCl_3$) and **20** (in C_6D_6).

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 σ-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_2Cl_2/0.10 M [*n*-Bu_4N][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, $CHPh_2$, menthyl) 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-Menthyl** 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_{ispo} angles, with the OC-Fe-C_{ispo} angle on the same side of the CH_2X 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 CH_2X 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-$CHPh_2$**. The hydrogen atom of the benzhydril substituent is located within a pocket formed by the Cp*Fe(CO_2) and one phenyl of the benzhydril, 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-CPh_3**, 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 **12**, no substitution reaction could take place, and only decomposition of **12** occurred.

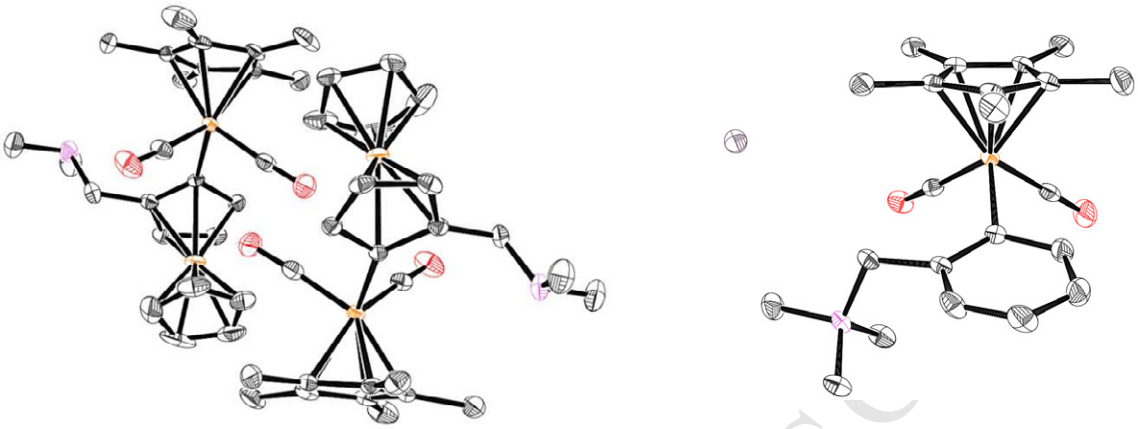


Figure 5: ORTEP representations of complexes **10** (left, racemic twins) and **14** (right) with 50% thermal ellipsoids. Hydrogen atoms and CH_2Cl_2 solvate (**14**) have been omitted for clarity.

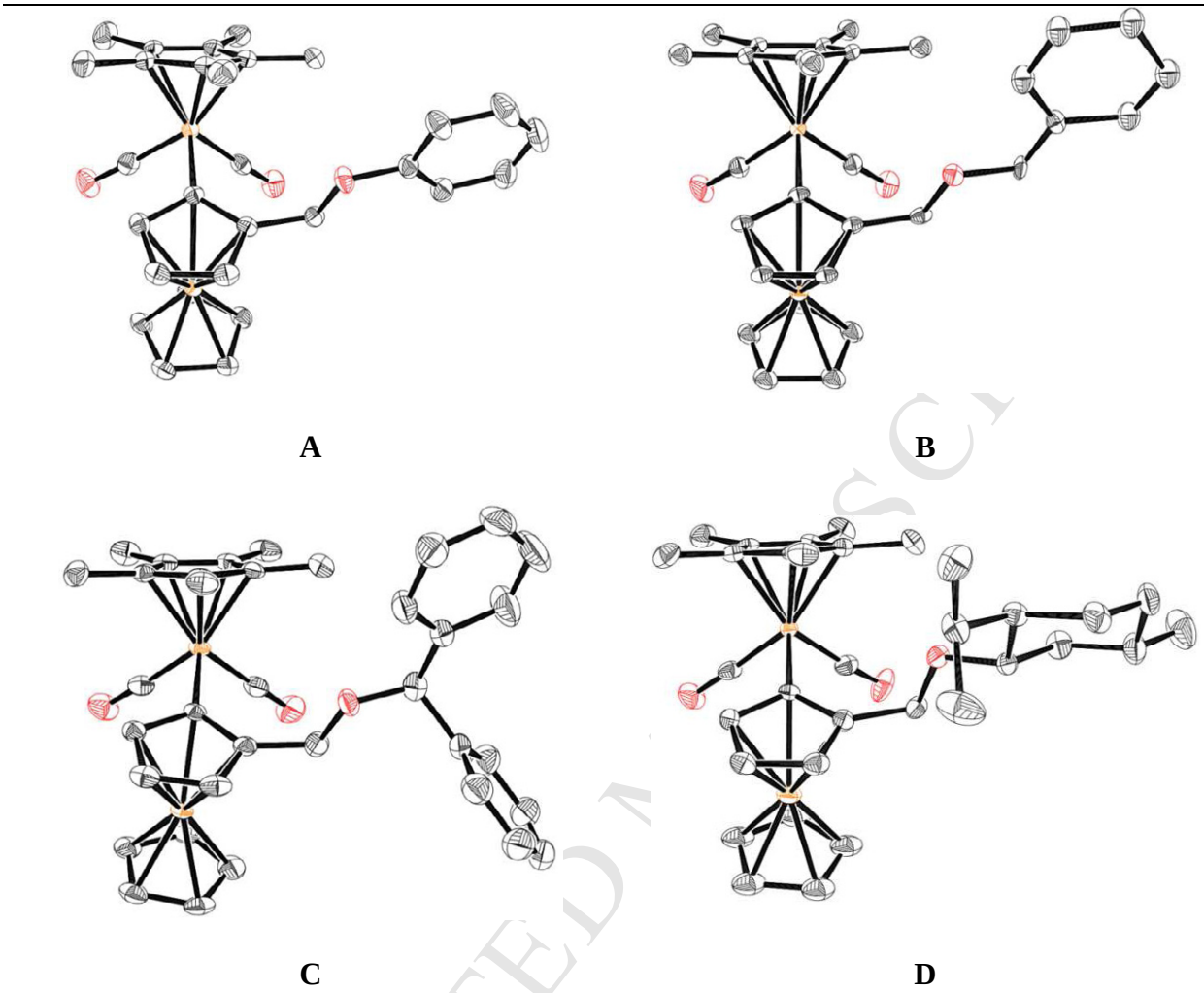


Figure 6: ORTEP representation of the R_{Fc} enantiomer of complexes **13-Ph** (**A**), **13-Bz** (**B**), **13-$CHPh_2$** (**C**) and **13-Menthyl** (**D**) with 50% thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

Compound	**10**[a]	**13-Ph**[a]	**13-Bz**[a]	**13-CHPh$_2$**	**13-Menthyl**	**14**
Formula	$C_{25}H_{31}Fe_2NO_2$	$C_{29}H_{30}Fe_2O_3$	$C_{30}H_{32}Fe_2O_3$	$C_{36}H_{36}Fe_2O_3$	$C_{33}H_{44}Fe_2O_3$	$C_{22}H_{30}FeINO_2$
Fw, g/mol	978.42	1076.46	1104.51	628.35	600.38	1131.37
Crystal size, mm	$0.52 \times 0.37 \times 0.32$	$0.6 \times 0.34 \times 0.28$	$0.54 \times 0.48 \times 0.4$	$0.4 \times 0.2 \times 0.1$	$0.6 \times 0.1 \times 0.08$	$0.46 \times 0.07 \times 0.04$
Color	Orange	Orange	Orange	Orange	Red	Yellow
space group	P b c 2_1	P -1	C c	P -1	P 2_1 2_1 2_1	C 2/c
a, Å	9.0778(3)	13.3551(5)	16.7845(4)	10.0067(4)	10.4735(11)	33.5797(8)
b, Å	16.9803(7)	13.3642(4)	14.5218(5)	10.9900(4)	11.9525(12)	7.6772(2)
c, Å	29.9753(13)	14.4993(5)	21.1350(6)	14.3062(6)	24.381(3)	25.3776(5)
α, deg	90	98.5850(10)	90	89.180(2)	90	90
β, deg	90	100.1160(10)	94.3760(10)	81.398(2)	90	132.7030(10)
γ, deg	90	99.4890(10)	90	78.149(2)	90	90
V, Å^3	4620.5(3)	2470.05(15)	5136.5(3)	1522.23(10)	3052.1(6)	4807.79(19)
Z	4	2	4	2	4	4
d_{calcd}, g/cm^3	1.407	1.447	1.428	1.371	1.307	1.563
θ range, deg	3.15 to 27.41	3.01 to 27.48	2.97 to 27.48	3.04 to 27.48	3.08 to 27.47	3.52 to 27.48
μ, mm^{-1}	1.276	1.203	1.159	0.987	0.981	2.040
no. of obsd data, I > 2σ (I)	8637	8549	9101	5704	5170	4504
data / restraints / parameters	9925 / 1 / 555	11145 / 0 / 623	10983 / 20 / 390	6903 / 0 / 375	6661 / 0 / 343	5428 / 0 / 266
R1 (all data)[b]	0.0464	0.0564	0.0488	0.0476	0.0697	0.0447
wR2 (all data)[c]	0.0847	0.0902	0.0864	0.1042	0.0886	0.0687
$(\Delta\rho)_{min}$, e.Å^{-3}	-0.542	-0.345	-0.435	-0.477	-0.421	-0.72
$(\Delta\rho)_{max}$, e.Å^{-3}	0.448	0.341	0.457	0.773	0.514	0.723

Table 2.Selected crystallographic data and collection parameters for **10**, **13-R** and **14**. [a] Two molecules in the asymmetric unit. [b] R1 = $\sum$ | $|F_o|$ - $|F_c|$ | / $\sum$ $|F_o|$.[c] wR2 = $\{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$.

Compound	**10**: R_{Fc}; S_{Fc}	**13-Ph**: R_{Fc}; R'_{Fc}	**13-Bz**: R_{Fc}; S_{Fc}	**13-CHPh$_2$**	**13-Menthyl**	**14**
Bond lengths (Å)						
Fe-Cp*	1.739; 1.737	1.727; 1.721	1.720; 1.735	1.735	1.733	1.747
Fe-C	2.013(3); 2.019(3)	1.997(2); 2.004(2)	2.003(8); 2.000(9)	2.005(2)	2.005(3)	2.031(3)
Fe-CO	1.150 (5); 1.764(4)	1.749(2); 1.755(3)	1.751(9); 1.746(9)	1.752(2)	1.746(4)	1.755(3)
	1.50(4); 1.760(4)	1.755(3); 1.757(3)	1.770(9); 1.745(9)	1.754(2)	1.757(4)	1.755(3)
C-O	1.150(5); 1.154(5)	1.155(3); 1.150(3)	1.144(10); 1.163(11)	1.149(3)	1.161(4)	1.146(3)
	1.150(4); 1.159(4)	1.149(3); 1.147(3)	1.124(11); 1.173(11)	1.153(3)	1.160(4)	1.151(3)
Fe_{Fc}-Cp_{subst}	1.656; 1.655	1.646; 1.646	1.655; 1.631	1.644	1.651	/
Fe_{Fc}-Cp	1.661; 1.666	1.651; 1.655	1.653; 1.644	1.648	1.649	/
$C_{Cp/Ar}$-CH_2	1.517(5); 1.509(5)	1.484(3); 1.492(3)	1.467(11); 1.512(10)	1.495(3)	1.502(5)	1.505(3)
CH_2-N/O	1.475(5); 1.466(5)	1.449(2); 1.446(2)	1.455(9); 1.422(9)	1.443(2)	1.442(4)	1.538(3)
N/O-C	1.465(5); 1.463(5)	1.372(3); 1.377(3)	1.407(9); 1.421(8)	1.429(3)	1.422(4)	1.494(3); 1.496(3)
	1.463(6); 1.464(6)					1.500(3)
Angles (°)						
Cp*-Fe-CO	122.31; 122.85	123.89; 123.45	123.87; 123.91	123.36	124.22	123.46
	124.59; 124.59	126.14; 124.48	124.78; 123.73	126.20	124.36	125.31
Cp*-Fe-C	121.54; 121.33	120.86; 122.10	121.69; 122.49	120.33	120.89	118.97
OC-Fe-C	88.61(16);88.58(15)	88.56(10); 88.36(10)	88.9(4); 89.3(4)	89.96(9)	89.14(15)	89.93(12)
	94.19(16); 94.49(15)	91.31(10); 92.07(10)	93.4(4); 92.6(4)	94.10(9)	94.60(16)	99.91(11)
OC-Fe-CO	96.42(18); 96.57(17)	96.14(11); 97.04(11)	95.0(4); 95.7(4)	93.72(10)	94.74(17)	91.29(12)
Fe-Cp_{subst}-Fe_{Fc}	93.52; 93.2	93.20; 91.43	91.61; 92.63	94.48	94.16	/
Cp_{subst}-Fe_{Fc}-Cp	179.93; 178.7	178.83; 179.58	178.70; 178.12	178.90	177.0	/
Fe-$C_{Cp/Ar}$-CH_2	89.25; 89.70	89.77; 89.00	88.90; 89.51	89.96	91.20	/
$C_{Cp/Ar}$-CH_2-N/O	113.70; 113.55	108.06(17);	111.3(6); 109.4(6)	107.70(18)	107.7(3)	115.0(2)
CH_2-N/O-C	108.6(3); 109.5(3)	116.96(17);	111.3(6); 109.5(5)	113.09(17)	116.5(3)	107.2(2); 110.85(19)
	112.8(3); 112.9(3)					113.0(2)

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 benzyldimethylamine. 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 Et_2O (with filtration if necessary), washing of the organic extracts with water and saturated aqueous NaCl, drying over $MgSO_4$, 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% Et_3N was added in the eluent. R_f values were measured on silica plates.

4.2. Instruments

^1H and ^{13}C 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 ^{13}C) [62]. Infrared spectra were obtained as KBr pellets [63], CH_2Cl_2 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 CH_2Cl_2 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 CH_2Cl_2 containing 0.1 M [*n*-Bu_4N][PF_6] 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 Et_2O 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/Et_2O 98:2, followed by a yellow or orange band of the desired complex which was eluted with hexanes/Et_2O (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 Et_2O (25 mL) at room temperature for 16 h) [39] and iododicarbonyl(pentamethylcyclopentadienyl)iron (1.20 g, 3.20 mmol) in Et_2O (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 $C_{25}H_{31}Fe_2NO_2$: C: 61.38 %, H: 6.39 %, N: 2.86 %; found: C: 61.47 %, H: 6.48 %, N: 2.79 %. HRMS (ESI,

CH_3OH/CH_2Cl_2 9:1): calc: 489.1054 $[M]^+$, found: 489.1052. IR (CH_2Cl_2, cm^{-1}): 1989 and 1932 (s, $\nu_{C\equiv O}$), 813 (s, $\delta_{C\text{-}H}$ Cp Fc). UV-Visible (CH_2Cl_2): λ_{max}, nm (ε, 10^3 $M^{-1}\cdot cm^{-1}$): 366 (1.9); 280 (8.8). Cyclic voltammetry (CH_2Cl_2, 0.10 M [*n*-Bu_4N][PF_6], V vs. SCE): $E_{1/2}$: 0.16 ($\Delta E_{1/2}$ = 0.072 V; i_{pa}/i_{pc} = 1.0) 1.26 and 1.47 (irreversible processes). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 4.27, 4.10 and 3.75 (3 × s, 3 × 1H, Fc), 3.93 (s, 5H, Fc), 3.44 and 3.01 (2 × d, $^2J_{H,H}$ = 13 Hz, CH_2), 2.23 (s, 6H, NMe_2), 1.70 (s, 15H, Cp*). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm): δ 219.2 and 218.3 (2 × s, C≡O), 96.3 (s, C_{quat} Cp*), 93.2 (s, Fe-C), 90.2 (s, C_{ipso} CH_2NMe_2), 79.0, 71.5 and 68.1 (3 × s, Cp), 71.5 (s, C_5H_5), 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 (**11**)*

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_3OH/CH_2Cl_2 9:1): calc: 382.1469 $[M+H]^+$, found: 382.1467. IR (CH_2Cl_2, cm^{-1}): 1992 and 1935 (vs, $\nu_{C\equiv O}$). UV-Visible (CH_2Cl_2): λ_{max}, nm (ε, $10^3\cdot M^{-1}\cdot cm^{-1}$): 360 (1.2), 294 (5.2). Cyclic voltammetry (CH_2Cl_2, 0.10 M [*n*-Bu_4N][PF_6], V vs. SCE): $E_{1/2}$: 0.97 and 1.24 (irreversible processes). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.44 (t, 2H, $^3J_{H,H}$ = 7 Hz, C_6H_4), 6.96 (t, 1H, $^3J_{H,H}$ = 7 Hz, C_6H_4), 6.84 (t, 1H, $^3J_{H,H}$ = 7 Hz, C_6H_4), 3.49 (s, 2H, CH_2), 2.34 (s, 6H, NMe_2), 1.67 (s, 15H, Cp*). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm): δ 218.1 (s, C≡O), 156.7 and 148.2 (2 × s, C_{quat} C_6H_4), 144.7, 128.5, 124.9, and 122.9 (4 × s, $C_{aromatics}$), 96.6 (s, C_{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, $\nu_{C\equiv O}$). UV-Visible (CH_2Cl_2): λ_{max}, nm (ε, 10^3 $M^{-1}\cdot cm^{-1}$): 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). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.46 (d, 1H, $^3J_{H,H}$ = 8 Hz, $H_{aromatics}$), 7.34 (d, 1H, $^3J_{H,H}$ = 8 Hz, $H_{aromatics}$), 7.00 (t, 1H, $^3J_{H,H}$ = 8 Hz, $H_{aromatics}$), 6.89 (t, 1H, $^3J_{H,H}$ = 8 Hz, $H_{aromatics}$), 4.44 (s, 2H, CH_2), 3.51 (s, 3H, OMe), 1.69 (s, 15H, Cp*). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm): δ 217.6 (s, C≡O), 156.1 and 147.7 (2 × s, C_{quat} aromatics), 144.6, 128.3, 125.7, and 123.0 (4 × s, $C_{aromatics}$), 96.6 (s, C_{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 Et_2O. The precipitate was collected on a sintered glass funnel, washed with Et_2O (3 × 25 mL), and dried *in vacuo* (0.24 g, 92 %). mp: 200°C (decomp.). Elemental analysis: calcd for $C_{22}H_{30}FeINO_2$: C: 50.50 %, H: 5.78 %, N: 2.68 %; found: C: 50.47 %, H: 5.67 %, N: 2.68 %. HRMS (ESI, CH_3OH/CH_2Cl_2 9:1): calc: 396.1626 $[M\text{-}I]^+$, found: 396.1625. IR (CH_2Cl_2, cm^{-1}): 1996 and 1928 (2 × vs, $\nu_{C\equiv O}$). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 7.55 and 7.42 (2 × m, 2 × 1H, C_6H_4), 6.95 (m, 2H C_6H_4), 4.93 (s, 2H, CH_2), 3.26 (s, 9H, NMe_3), 1.51 (s, 15H, Cp*). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 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, CH_2), 53.2 (s, NMe_3), 9.5 (s, CH_3 Cp*). Crystals suitable for a X-ray diffraction study were grown by slow diffusion of a CH_2Cl_2 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). Et_2O (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/Et_2O 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(pentamethylcyclopentadienyl)iron)-2-(methoxymethyl)ferrocene (**13-Me**)*

Using methanol as the solvent, 0.17 g (71 %) of the complex was obtained. Eluent: hexanes/Et_2O 95:5. Recrystallization: EtOH/water 2:1, 30 mL. R_f (hexanes/Et_2O 95:5): 0.29. mp: 112°C. Elemental analysis: calcd for $C_{24}H_{28}Fe_2O_3$: C: 60.54 %, H: 5.93 %; found: C: 61.09 %, H: 6.16 %. HRMS (ESI, CH_3OH): calc: 476.0737 $[M]^+$, found: 476.0737. IR (CH_2Cl_2, cm^{-1}): 2918 (m, $\nu_{H\text{-}C}$ CH_2), 2815 (m, $\nu_{H\text{-}C}$ OMe), 1990 and 1934 (vs, C≡O), 1031 (s, $\nu_{O\text{-}C}$), 820 (m, $\delta_{H\text{-}C}$ C_5H_5). Cyclic voltammetry (CH_2Cl_2, 0.10 M [*n*-Bu_4N][PF_6], V vs SCE): $E_{1/2}$: 0.13 ($\Delta E_{1/2}$ = 0.068 V; i_{pa}/i_{pc} = 1.0), 1.50 (irreversible process). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 4.50 and 4.30 (2 × s, 2 × 1H, C_5H_3), 4.04 (m, 8H, C_5H_3 + C_5H_5 + CH_2), 3.35 (s, 3H, OMe), 1.71 (s, 15H, Cp*). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm): δ 219.0 and 218.1 (2 × s, C≡O), 96.4 (s, C_{quat} Cp*), 89.2 (s, Fe-C), 79.3, 73.9, 71.1 and 70.1 (4 × s, C_5H_3), 69.8 (m, C_5H_5 + CH_2), 58.1 (s, OMe), 9.6 (s, CH_3 Cp*).

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

Using ethanol as the solvent, 0.14 g (57 %) of the complex was obtained. Eluent: gradient from hexanes/Et_2O 95:5 to 9:1. Recrystallization: EtOH/water 2:1, 30 mL. R_f (hexanes/Et_2O 95:5): 0.45. mp: 120°C. Elemental analysis: calcd for $C_{25}H_{30}Fe_2O_3$: C: 61.25 %, H: 6.17 %; found: C: 61.62 %, H: 6.17 %. HRMS (ESI, CH_3OH/CH_2Cl_2 95:5): calc: 490.0894 $[M]^+$, found: 490.0893. IR (CH_2Cl_2, cm^{-1}): 2870 (m, $\nu_{H\text{-}C}$ CH_2), 1990 and 1934 (2 × s, $\nu_{C\equiv O}$), 1083 (s, $\nu_{O\text{-}C}$), 820 (m, $\delta_{H\text{-}C}$ C_5H_5). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 4.23 – 4.13 (3 × s overlapped, 3H, C_5H_3), 3.97 (s, 7H, C_5H_5 + CH_2), 3.59 (s, 2H, CH_2CH_3) 1.72 (s, 15H, Cp*), 1.26 (s, 3H, CH_2CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm): δ 219.0 and 218.2 (2 × s,C≡O), 96.4 (s, C_{quat} Cp*), 94.2, 79.2, 71.7, 71.0 and 65.8 (5 ×

s, C_5H_3 + CH_2, possibly overlapped signals), 89.6 (s, Fe-C), 69.5 (s, C_5H_5), 15.5 (s, CH_3), 9.6 (s, CH_3 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/Et_2O 95:5 to 9:1. Recrystallization: EtOH/water 2:1, 30 mL. R_f (hexanes/Et_2O 95:5): 0.51. mp: 88°C. Elemental analysis: calcd for $C_{26}H_{32}Fe_2O_3$: C: 61.93 %, H: 6.40 %; found: C: 62.44 %, H: 6.50 %. HRMS (ESI, CH_3OH/CH_2Cl_2 95:5): calc: 504.1050 $[M]^+$, found: 504.1049. IR (CH_2Cl_2, cm^{-1}): 2870 (m, ν_{H-C} CH_2), 1990 and 1934 (s, $\nu_{C\equiv O}$), 1034 (s, ν_{O-C}), 820 (m, δ_{H-C} C_5H_5). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 4.66, 4.44, 3.99 and 3.97 (4 × s, 4 × 1H, C_5H_3 + C*H*$(CH_3)_2$), 4.15 (s, 5H, C_5H_5), 3.63 (s, 2H, CH_2), 1.75 (s, 15H, Cp*), 1.13 (s, 6H, CH(C*H*$_3)_2$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 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, C_5H_3 + CH_2, possibly overlapped signals), 70.0 (s, C_5H_5), 22.3 (s, iPr), 9.7 (s, CH_3 Cp*).

By alcoholysis in CH_3CN: 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/Et_2O 95:5. Recrystallization: EtOH/water 5:3, 80 mL. R_f (hexanes/Et_2O 95:5): 0.41. mp: 192°C. HRMS

(ESI, CH_3OH/CH_2Cl_2 95:5): calc: 538.0894 $[M]^+$, found: 538.0887. IR (CH_2Cl_2, cm^{-1}): 2857 (m, ν_{H-C} CH_2), 1991 and 1935 (s, $\nu_{C\equiv O}$), 1029 (s, ν_{O-C}), 821 (m, δ_{H-C} C_5H_5). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 7.31 (m, 2H, Ph), 6.96 (m, 3H, Ph), 4.74 (s, 2H, CH_2), 4.53, 4.32 and 3.94 (3 × s, 3 × 1H, C_5H_3), 4.06 (s, 5H, C_5H_5), 1.68 (s, 15H, Cp*). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm): δ 218.8 and 218.1 (2 × s, C≡O), 159.3 (s, C_{quat} Ph), 129.6, 120.4 and 114.6 (3 × s, Ph), 96.5 (s, C_{quat} Cp*), 88.2 (s, Fe-C), 79.4, 71.0, 70.5 and 69.1 (4 × s, C_5H_3 + CH_2), 69.8 (s, C_5H_5), 9.7 (s, CH_3 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/Et_2O 98:2 to 95:5. Recrystallization: EtOH/water 2:1, 75 mL. R_f (hexanes/Et_2O 95:5): 0.63. mp: 130°C. Elemental analysis: calcd for $C_{30}H_{32}Fe_2O_3$: C: 65.24 %, H: 5.84 %; found: C: 65.66 %, H: 6.11 %. HRMS (ESI, CH_3OH/CH_2Cl_2 9:1): calc: 552.1050 $[M]^+$, found: 552.1046. IR (CH_2Cl_2, cm^{-1}): 2857 (m, ν_{H-C} CH_2), 1990 and 1934 (s, $\nu_{C\equiv O}$), 1028 (s, ν_{O-C}), 819 (m, δ_{H-C} C_5H_5). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 7.28 (m, 5H, Ph), 4.50, 4.40 and 3.80 (3 × s, 3 × 1H, C_5H_3), 4.19 (s, 2H, CH_2), 3.91 (s, 7H, C_5H_5 + CH_2), 1.60 (s, 15H, Cp*). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm): δ 219.0 and 218.2 (2 × s, C≡O), 139.2 (s, C_{quat} Ph), 128.4, 127.6 and 127.4 (3 × s, Ph), 96.4 (s, C_{quat} Cp*), 89.6 (s, Fe-C), 79.2, 72.5, 71.7 and 71.0 (4 × s, C_5H_3 + CH_2, possible overlaps), 69.8 (s, C_5H_5), 9.7 (s, CH_3 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. 1-(dicarbonyl(pentamethylcyclopentadienyl)iron)-2-(á-phenylethyloxymethyl)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/Et_2O 95:5. R_f (hexanes/Et_2O 95:5): 0.42. HRMS (ESI, CH_3OH/CH_2Cl_2

95:5): calc: 566.1207 $[M]^+$, found: 566.1203. IR (CH_2Cl_2, cm^{-1}): 2861 (m, $\nu_{H\text{-}C}$ CH_2), 1990 and 1934 (2 × s, $\nu_{C\equiv O}$), 1033 (s, $\nu_{O\text{-}C}$), 820 (m, $\delta_{H\text{-}C}$ C_5H_5). ^1H 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, $J_{H,H}$ = 6 and 6 Hz, C_5H_3), 4.46 (dd, 1H, $J_{H,H}$ = 6 and 6 Hz, C_5H_3), 4.42 and 4.37 (2 × s, 2 × 1H, C_5H_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_5H_3), 3.97 and 3.89 (2 × s, 2 × 5H, C_5H_5), 1.70 and 1.63 (2 × s, 2 × 15H, Cp*), 1.43 and 1.42 (2 × s, 2 × 3H, Me). $^{13}C\{^1H\}$ 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_{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_{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_5H_3 + CH_2), 70.0 and 69.8 (2 × s, C_5H_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-(benzhydriloxymethyl)ferrocene (**13-CHPh$_2$**)*

Using benzhydrol (0.921 mL), 0.09 g (29 %) of the complex was obtained. Elution: gradient from hexanes/Et_2O 98:2 to 95:5. Recrystallization: EtOH/water 2:1, 30 mL. R_f (hexanes/Et_2O 95:5): 0.72. mp: <45°C. Elemental analysis: calcd for $C_{36}H_{36}Fe_2O_3$: C: 68.81 %, H: 5.77 %; found: C: 68.29 %, H: 6.08 %. HRMS (ESI, CH_3OH/CH_2Cl_2 9:1): calc: 628.1363 $[M]^+$, found: 628.1366. IR (CH_2Cl_2, cm^{-1}): 2859 (m, $\nu_{H\text{-}C}$ CH_2), 1990 and 1935 (2 × s, $\nu_{C\equiv O}$), 1029 (s, $\nu_{O\text{-}C}$), 820 (m, $\delta_{H\text{-}C}$ C_5H_5). ^1H 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_5H_3), 4.02 (s, 7H, C_5H_5 + CH_2), 1.61 (s, 15H, Cp*). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm): δ 218.8 and 218.1 (2 × s, C≡O), 143.2 (s, C_{quat} Ph), 128.4, 128.4, 127.4, 127.3, 127.1 and 127.0 (6 × s, Ph), 96.3 (s, C_{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, C_5H_3 + C_5H_5 + CH_2), 9.6 (s, CH_3 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/Et_2O 99:1 to 98:2. Recrystallization: EtOH/water 4:3, 35 mL. R_f (hexanes/Et_2O 99:1): 0.37. mp: 174°C. Elemental analysis: calcd for $C_{33}H_{44}Fe_2O_3$: C: 66.02 %, H: 7.39 %; found: C: 66.06 %, H: 7.48 %. HRMS (ESI, CH_3OH/CH_2Cl_2 9:1): calc: 600.1989 $[M]^+$, found: 600.1986. IR (CH_2Cl_2, cm^{-1}): 2870 (m, $\nu_{H\text{-}C}$ CH_2), 1991 and 1935 (2 × s, $\nu_{C\equiv O}$), 1067 (s, $\nu_{O\text{-}C}$), 820 (m, $\delta_{H\text{-}C}$ C_5H_5). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 4.72, 3.70 and 3.07 (3 × s, 3 × 1H, C_5H_3), 4.44 (s, 2H, CH_2), 4.15 (s, 5H, C_5H_5), 2.17 (s, 2H, menthyl), 1.75 (s, 17H, Cp* + menthyl), 1.28 (s, 4H, menthyl), 0.86 (s, 11H, menthyl). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 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, C_5H_3 + C_5H_5 + CH_2, 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, CH_3 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 Et_2O (25 mL), rapidly

stirred for 5 min, and the suspension filtered on a glass frit. The solid was washed with additional Et_2O (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_3OH): calc: 258.0945 $[M\text{-}I]^+$, found: 258.0943. IR (KBr, cm^{-1}): 2965 (m, $\nu_{H\text{-}C}$ CH_3), 2939 (m, $\nu_{H\text{-}C}$ CH_2), 1470 (s, $\delta_{H\text{-}C}$ CH_2), 1408 and 1382 (m, $\delta_{H\text{-}C}$ CH_3), 819 (s, $\delta_{H\text{-}C}$ Fc). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 4.81 (m, 2H, C_5H_4), 4.51 (m, 2H, C_5H_4), 4.23 and 4.21 (m, 7H, CH_2 + C_5H_5), 3.20 (s, 9H, NMe_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm): δ 72.1 (superimposed s, CH_2 and C_5H_4), 70.5 (s, C_5H_4), 69.9 (s, C_5H_5), 66.9 (s, C_{quat} C_5H_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_2O 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_2O (25 mL), rapidly stirred for 5 min, and the suspension was filtered on a sintered glass funnel. The solid was washed with Et_2O (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_2O 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_2O 95:5): 0.29. HRMS (ESI, CH_3OH): calc: 230.0394 $[M]^+$, found: 230.0392. IR (liquid film, cm^{-1}): 2922 and 2852 (2 × m, $\nu_{H\text{-}C}$ CH_2), 2815 (m,

$\nu_{H\text{-}C}$ OCH_3), 1090 (s, $\nu_{O\text{-}C}$ OCH_3), 818 (s, $\delta_{H\text{-}C}$ Fc). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 4.25 and 4.23 (2 × m, 2 × 2H, C_5H_4), 4.16 (superimposed s, 7H, CH_2 + C_5H_5), 3.32 (s, 3H, OCH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm): δ 83.3 (s, C_{quat} C_5H_4), 70.9, 69.5 and 68.6 (3 × s, CH_2 + C_5H_4), 68.5 (s, C_5H_5), 57.7 (s, OCH_3).

*4.3.6. benzhydriloxymethyl 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_2O (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_2O (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_2O 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_2O 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_3OH/CH_2Cl_2 9:1): calc: 382.1020 $[M]^+$, found: 382.1020. IR (KBr, cm^{-1}): 3082 and 3024 (2 × m, $\nu_{H\text{-}C}$ Ph + Fc), 2857 (m, $\nu_{H\text{-}C}$ CH_2), 1341 (m, $\delta_{H\text{-}C}$ CH), 1092 (s, $\nu_{O\text{-}C}$), 818 (s, $\delta_{H\text{-}C}$ Fc), 738 and 700 (s, $\delta_{H\text{-}C}$ Ph). CV (CH_2Cl_2, 0.10 M [*n*-Bu_4N][PF_6], V vs SCE): $E_{1/2}$: 0.46 ($\Delta E_{1/2}$ = 0.068 V; i_{pa}/i_{pc} = 0.95). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 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_5H_4), 4.14 (s, 5H C_5H_5). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm): δ 142.3 (s, C_{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, CH_2Cl_2): calc: 353.1442 $[M]^+$, found: 353.1439. IR (CH_2Cl_2, cm^{-1}): 1886 (s, $\nu_{C\equiv O}$). Cyclic voltammetry (CH_2Cl_2, 0.10 M [N-*n*-Bu_4][PF_6], V vs SCE): $E_{1/2}$: -0.03 (ΔEp = 0.074 V; i_{pa}/i_{pc} = 1), 1.00 and 1.39 (irreversible processes). ^{1}H NMR (400 MHz, C_6D_6, ppm): δ 7.84 (d, 1H, $^3J_{H,H}$ = 7 Hz, $H_{aromatic}$), 7.24 (t, 1H, $^3J_{H,H}$ = 7 Hz, $H_{aromatic}$), 7.10 (t, 1H, $^3J_{H,H}$ = 7 Hz, $H_{aromatic}$), 7.01 (d, 1H, $^3J_{H,H}$ = 7 Hz, $H_{aromatic}$), 3.48 (d, 1H, $^2J_{H,H}$ = 12 Hz, CH_2), 2.62 (d, 1H, $^2J_{H,H}$ = 12 Hz, CH_2), 1.86 (s, 3H, NMe_2), 1.74 (s, 3H, NMe_2), 1.45 (s, 15H, Cp*). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6, ppm): δ 224.3 (s, C≡O), 179.3 (s, Fe-C), 147.7 (s, C_{ipso} CH_2NMe_2), 141.5, 125.4, 121.7 and 121.1 (4 × s, $C_{aromatics}$), 89.1 (s, C_{quat} Cp*), 74.1 (s, CH_2), 57.6 and 53.9 (2 × s, NMe_2), 10.4 (s, CH_3 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 F^2 (*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-CHPh$_2$** (**C**) and **13-Menthyl** (**D**)are depicted in Figure 5 and 6 respectively.

Acknowledgements: G.G. thanks *Region Bretagne* for a scholarship. The *CNRS*, the *Université de Rennes 1* and the ANR Blanc program (*ANR 2010 BLAN 719*) are acknowledged for financial support. M.G.H. thanks the *Australian Research Council* for an ARC Australian Professorial Fellowship. The authors are grateful to M.-C. Hautbois (IUT Rennes) for assistance in melting points measurements and for a gift of benzhydrol.

Appendix A. Supplementary materials

CCDC 928736 (**10**), 928273 (**13-Ph**), 928738 (**13-Bz**), 928275 (**13-CH$_2$Ph**), 928274 (**13-Menthyl**) and 928737 (**14**) contain the supplementary crystallographic data for compounds **10**, **13-R** (**R** = Ph, Bz, CH_2Ph and Menthyl) 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

[1] C. Bolm, J. Legros, J. Le Paih, L. Zani, Chem. Rev., 104 (2004) 6217-6254.
[2] B. Plietker, Iron Catalysis in Organic Chemistry, Wiley CH, Weinhem, 2008.
[3] A. Correa, O. Garcia Mancheno, C. Bolm, Chem. Soc. Rev., 37 (2008) 1108-1117.
[4] S. Enthaler, K. Junge, M. Beller, Angew. Chem., Int. Ed., 47 (2008) 3317-3321.
[5] B.D. Sherry, A. Fürstner, Acc. Chem. Res., 41 (2008) 1500-1511.
[6] W.M. Czaplik, M. Mayer, J. Cvengroš, A.J. Von Wangelin, ChemSusChem, 2 (2009) 396-417.
[7] R.H. Morris, Chem. Soc. Rev., 38 (2009) 2282-2291.
[8] C.-L. Sun, B.-J. Li, Z.-J. Shi, Chem. Rev., 111 (2011) 1293-1314.
[9] M. Zhanga, A. Zhang, Appl. Organometal. Chem., 24 (2010) 751-757.

[10] T.W.-S. Chow, G.-Q. Chen, Y. Liu, C.-Y. Zhou, C.-M. Che, Pure Appl. Chem., 84 (2012) 1685-1704.
[11] D. Bezier, J.-B. Sortais, C. Darcel, Adv. Synth. Catal., 355 (2013) 19-33.
[12] T. Bach, D.N.A. Fox, M.T. Reetz, J. Chem. Soc., Chem. Commun., (1992) 1634-1636.
[13] M. Ishio, T. Terashima, M. Ouchi, M. Sawamoto, Polym. J., 42 (2010) 17-24.
[14] K.H. Pannell, H.K. Sharma, Organometallics, 29 (2010) 4741-4745.
[15] K. Fukumoto, M. Kasa, T. Oya, M. Itazaki, H. Nakazawa, Organometallics, 30 (2011) 3461-3463.
[16] H.K. Sharma, R. Arias-Ugarte, A.J. Metta-Magana, K.H. Pannell, Angew. Chem., Int. Ed., 48 (2009) 6309-6312.
[17] M.F. Mayer, M.M. Hossain, J. Organomet. Chem., 654 (2002) 202-209.
[18] M.E. Bruin, E.P. Kundig, Chem. Commun., (1998) 2635-2636.
[19] E.P. Kündig, C.M. Saudan, F. Viton, Adv. Synth. Catal., 343 (2001) 51-56.
[20] A. Bãdoiu, G. Bernardinelli, J. Mareda, E.P. Kündig, F. Viton, Chem. Asian J., 3 (2008) 1298-1311.
[21] D. Benito-Garagorri, J. Wiedermann, M. Pollak, K. Mereiter, K. Kirchner, Organometallics, 26 (2006) 217-222.
[22] D.J. Casper, A.V. Sklyarov, S. Hardcastle, T.L. Barr, F.H. Försterling, K.F. Surerus, M.M. Hossain, Inorg. Chim. Acta, 359 (2006) 3129-3138.
[23] M.E. Dudley, M.M. Morshed, C.L. Brennan, M.S. Islam, M.S. Ahmad, M.-R. Atuu, B. Branstetter, M.M. Hossain, J. Org. Chem., 69 (2004) 7599-7608.
[24] M.D. Redlich, M.F. Mayer, M.M. Hossain, Aldrichimica Acta, 36 (2003) 3-13.
[25] F. Jiang, D. Bézier, J.-B. Sortais, C. Darcel, Adv. Synth. Catal., 353 (2011) 239-244.
[26] D. Bézier, G.T. Venkanna, J.-B. Sortais, C. Darcel, ChemCatChem, 3 (2011) 1747-1750.
[27] L.C.M. Castro, J.-B. Sortais, C. Darcel, Chem. Commun., 48 (2012) 151-153.
[28] D. Bézier, G.T. Venkanna, L.C. Misal Castro, J. Zheng, T. Roisnel, J.-B. Sortais, C. Darcel, Adv. Synth. Catal., 354 (2012) 1879-1884.
[29] D. Bézier, F. Jiang, T. Roisnel, J.-B. Sortais, C. Darcel, Eur. J. Inorg. Chem., (2012) 1333-1337.
[30] J. Zheng, L.C. Misal Castro, T. Roisnel, C. Darcel, J.-B. Sortais, Inorg. Chim. Acta, 380 (2012) 301-307.
[31] C.P. Casey, H. Guan, J. Am. Chem. Soc., 129 (2007) 5816-5817.
[32] C.P. Casey, H. Guan, J. Am. Chem. Soc., 131 (2009) 2499-2507.
[33] V.V.K.M. Kandepi, J.M.S. Cardoso, E. Peris, B. Royo, Organometallics, 29 (2010) 2777-2782.
[34] J.M.S. Cardoso, B. Royo, Chem. Commun., 48 (2012) 4944-4946.
[35] M. Ishio, T. Terashima, M. Ouchi, M. Sawamoto, Macromolecules, 43 (2010) 920-926.
[36] G. Argouarch, G. Grelaud, T. Roisnel, M.G. Humphrey, F. Paul, Tetrahedron Lett., 53 (2012) 5015-5018.
[37] For application of related $CpFe(CO)_2Ar$ complexes in organic synthesis see: Y. Shiego, Y. Hideki, K. Oshima, Organometallics, 29 (2010), 2634-2636 and references therein.
[38] M. Akita, M. Terada, M. Tanaka, Y. Morooka, J. Organomet. Chem., 510 (1996) 255-261.
[39] I.R. Butler, B. Woldt, M.-Z. Oh, D.J. Williams, Inorg. Chem. Commun., 9 (2006) 1255-1258.
[40] D.W. Slocum, B.W. Rockett, C.R. Hauser, J. Am. Chem. Soc., 87 (1965) 1241-1246.
[41] F.N. Jones, R.L. Vaulx, C.R. Hauser, J. Org. Chem., 28 (1963) 3461-3465.
[42] J.Y. Wu, B.N. Stanzl, T. Ritter, J. Am. Chem. Soc., 132 (2010) 13214-13216
[43] G. Grelaud, G. Argouarch, unpublished results.
[44] A.N. Nesmeyanov, L.G. Makarova, V.N. Vinogradova, Russ. Chem. Bull., 21 (1972) 1541-1544.
[45] L.I. Denisovich, S.P. Gubin, J. Organomet. Chem., 57 (1973) 109-119.
[46] K.H. Pannell, J.B. Cassias, G.M. Crawford, A. Flores, Inorg. Chem., 15 (1976) 2671-2675.
[47] M. Kumar, F. Cervantes-Lee, K.H. Pannell, J. Shao, Organometallics, 27 (2008) 4739-4748.

[48] M. Herberhold, W. Feger, U. Kölle, J. Organomet. Chem., 436 (1992) 333-350.
[49] D. Lednicer, C.R. Hauser, Org. Synth., 40 (1960) 45-46.
[50] D. Lednicer, J. Mashburn, T. Arthur, C.R. Hauser, Org. Synth., 40 (1960) 52-53.
[51] D. Marquarding, H. Klusacek, G. Gokel, P. Hoffmann, I. Ugi, J. Am. Chem. Soc., 92 (1970) 5389-5393.
[52] D. Lednicer, C.R. Hauser, Org. Synth., 40 (1960) 31-34.
[53] O. Riant, O. Samuel, T. Flessner, S. Taudien, H.B. Kagan, J. Org. Chem., 62 (1997) 6733-6745.
[54] 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.
[55] A.A. Koridze, Russ. Chem. Rev., 55 (1986) 277-302.
[56] Ž. Petrovski, M.R.P. Norton de Matos, S.S. Braga, C.C.L. Pereira, M.L. Matos, I.S. Gonçalves, M. Pillinger, P.M. Alves, C.C. Romão, J. Organomet. Chem., 693 (2008) 675-684.
[57] No trace of methoxymethylbenzene were detected when benzyltrimethylammonium iodide was refluxed in methanol for 24h.
[58] J. Morrow, D. Catheline, M.H. Desbois, J.M. Manriquez, J. Ruiz, D. Astruc, Organometallics, 6 (1987) 2605-2607.
[59] R. T. Aplin, J. Booth, R. G. Compton, S. G. Davies, S. Jones, J. P. McNally, M. R. Metzler, W. Carl Watkins, J. Chem. Soc., Perkin Trans. 2, (1999) 913-922.
[60] P. Seiler, J.D. Dunitz, Acta Crystallogr., Sect. B: Struct. Sci., 35 (1979) 1068-1074.
[61] A closer iodine atom can be found in the crystal packing at 5.690 Å.
[62] G.R. Fulmer, A.J.M. Miller, N.H. Sherden, H.E. Gottlieb, A. Nudelman, B.M. Stoltz, J.E. Bercaw, K.I. Goldberg, Organometallics, 29 (2010) 2176-2179.
[63] M.M. Stimson, M.J. O'Donnell, J. Am. Chem. Soc., 74 (1952) 1805-1808.
[64] N.G. Connelly, W.E. Geiger, Chem. Rev., 96 (1996) 877-910.
[65] K. Miyawaki, F. Ueno, I. Ueda, Heterocycles, 54 (2001) 887-900.
[66] H.J. Reich, W.S. Goldenberg, A.W. Sanders, K.L. Jantzi, C.C. Tzschucke, J. Am. Chem. Soc., 125 (2003) 3509-3521.
[67] G. Ghini, L. Lascialfari, C. Vinattieri, S. Cicchi, A. Brandi, D. Berti, F. Betti, P. Baglioni, M. Mannini, Soft Matter, 5 (2009) 1863-1869.
[68] R. Jiang, Y. Zhang, Y.-C. Shen, X. Zhu, X.-P. Xu, S.-J. Ji, Tetrahedron, 66 (2010) 4073-4078.
[69] 20, when progessively heated on the Kofler hot stage, did not showany melting point probably due to thermal decomposition. The present reported melting point was determined by deposing minute amount of the complex at various temperature points on the hot stage and then narrowed down to the exact melting point temperature.
[70] A. Altomare, M.C. Burla, M. Camalli, G.L. Cascarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, G. Polidori, R. Spagna, J. Appl. Crystallogr., 32 (1999) 115-119.
[71] G. Sheldrick, Acta Crystallogr., Sect. A: Found. Crystallogr., 64 (2008) 112-122.
[72] L. Farrugia, J. Appl. Crystallogr., 32 (1999) 837-838.