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Synthesis, reactivity, and some photochemistry of *ortho*-*N*,*N*-dimethylaminomethyl substituted aryl and ferrocenyl pentamethylcyclopentadienyl dicarbonyl iron complexes

Guillaume Grelaud [a,b], Thierry Roisnel [c], Vincent Dorcet [c], Mark G. Humphrey [b], Frédéric Paul [a], Gilles Argouarch [a,*]

[a] Institut des Sciences Chimiques de Rennes, Organométalliques: Matériaux et Catalyse, UMR CNRS 6226, Université de Rennes 1, Campus de Beaulieu, 35042 Rennes Cedex, France
[b] Research School of Chemistry, Australian National University, Canberra, ACT 0200, Australia
[c] Institut des Sciences Chimiques de Rennes, Centre de Diffractométrie X, UMR CNRS 6226, Université de Rennes 1, Campus de Beaulieu, 35042 Rennes Cedex, France

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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.

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] is particularly noteworthy (Fig. 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 $[CpFe(CO)_2]^+$ 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].

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 (Fig. 2).

* Corresponding author. Tel.: +33 (0)223235961.
E-mail address: gilles.argouarch@univ-rennes1.fr (G. Argouarch).

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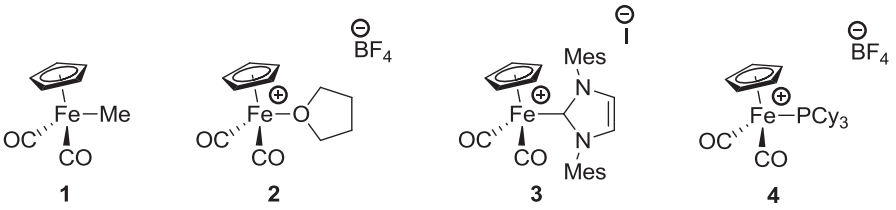

Fig. 1. Selected catalysts incorporating the [CpFe(CO)$_2$] fragment.

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 analoganalog **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.

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 analog 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** toward 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

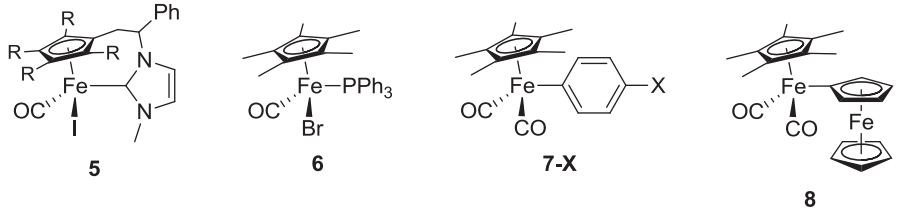

Fig. 2. Selected Cp-modified or Cp* iron carbonyl catalysts. R = H, Me; X = H, Me, OMe.