Convenient routes to mono- and dinuclear (C$_5$Me$_5$)iron(II) complexes bearing acyl, alkynyl, aryl and thienyl ligands

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Abstract

Treatment of the cations [Fe(C$_5$Me$_5$)(CO)$_2$(L)][PF$_6$] (**1a**, L = CO; **1c**, L = PPh$_3$) with LiC≡CSiMe$_3$ gives the corresponding acyl derivatives [Fe(C$_5$Me$_5$)(CO)$_2${C(O)C≡CSiMe$_3$}] (**2**) and [Fe(C$_5$Me$_5$)(CO)(PPh$_3$){C(O)C≡CSiMe$_3$}] (**4**), respectively. The nucleophile adds at the carbonyl ligand, but in the case of **1a**, competitive attack occurs at the metal centre leading to the formation of the alkynyl complex [Fe(C$_5$Me$_5$)(CO)$_2${C≡CSiMe$_3$}] (**3**). The latter species is formed as the only product from the acetonitrile complex [Fe(C$_5$Me$_5$)(CO)$_2$(CH$_3$CN)][PF$_6$] (**1b**), under the same conditions. Similarly, the dinuclear bis(acyl) complex [Fe(C$_5$Me$_5$)(CO)$_2${μ-η^1,η$^{1'}$-C(O)-]$_2$(2,2'-C$_4$H$_2$S) (**6**) is obtained from **1a** by using 0.5 equivalents of the dilithium salt 2,2'-Li$_2$C$_4$H$_2$S/TMEDA. Complete decarbonylation by UV irradiation of **3** or **6** in the presence of dppe affords the corresponding disubstituted complexes [Fe(C$_5$Me$_5$)(dppe){C≡CSiMe$_3$}] (**5**) and [Fe(C$_5$Me$_5$)(dppe)]$_2${μ-η^1,η$^{1'}$-2,2'-C$_4$H$_2$S} (**7**), respectively. Complexes [Fe(C$_5$Me$_5$)-(CO)$_2${CH(OMe)C$_6$H$_4$-p-Br}] (**9**) and [Fe(C$_5$Me$_5$)(CO)$_2${CH(OMe)-2-C$_4$H$_3$S}] (**10**) are synthesised from the methoxycarbene complex [Fe(C$_5$Me$_5$)(CO)$_2$(=CHOMe)][PF$_6$] (**8**); the nucleophilic addition of the organolithium reagents occurs at the carbene ligand. Dinuclear complexes such as the thiophene derivative [Fe(C$_5$Me$_5$)(CO)$_2${μ-η^1,η$^{1'}$-CHOMe-]$_2$(2,2'-C$_4$H$_2$S) (**11**) and the biphenylene complex [Fe(C$_5$Me$_5$)(CO)$_2${μ-η^1,η$^{1'}$-CHOMe-]$_2$(p-C$_6$H$_4$-C$_6$H$_4$) (**12**) are obtained by using the appropriate dilithiated nucleophiles. Protonolysis of **12** gives the bis(carbene) complex [Fe(C$_5$Me$_5$)(CO)$_2${μ-η^1,η$^{1'}$-CH-]$_2$(p-C$_6$H$_4$-C$_6$H$_4$) (**13**), which is stable at −50°C. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Iron; Unsaturated ligand; Dinuclear; Carbene; Aromatic bridge

1. Introduction

Complexes containing an unsaturated ligand such as a vinyl, an alkynyl or an aromatic group constitute an important class of compounds, especially as building blocks for the synthesis of di- or polymetallic complexes linked by a π-conjugated system. Unsaturated bridges can provide a facile pathway for electron delocalisation between metal centres, and in this context, the [Fe(C$_5$Me$_5$)] fragment is very promising [1]. However, the preparation of complexes with hydrocarbon ligands having sp^2 and sp-carbon bonded to the iron are not straightforward [1,2]. We have previously shown that activation of 2-alkyn-1-ols by [Fe(C$_5$Me$_5$)(CO)$_2$(H$_2$O)]$^+$ opens a route to α,β-unsaturated acyl complexes [Fe(C$_5$Me$_5$)(CO)$_2${C(O)CH=CR^{1}R^2}], and subsequent decarbonylation affords the vinyl complexes [Fe(C$_5$Me$_5$)(CO)$_2${CH=CR^{1}R^2}] [3]. However, activation of terminal alkynes is only effective for [Fe(C$_5$Me$_5$)(dppe)(Cl)], since no reaction is observed in the case of the dicarbonyl analogue [4]. This led us to develop synthetic routes to [Fe(C$_5$Me$_5$)(L)$_2$] (L = CO, or L$_2$ = dppe) organo-iron derivatives possessing different unsaturated ligands such as acyl, alkynyl, aryl and thienyl groups. We report here the reactivity of the cations [Fe(C$_5$Me$_5$)(CO)$_2$(L)][PF$_6$] (L = CO [5]; L = PPh$_3$ [5]; L = CH$_3$CN [5]; L = CHOMe [6]) towards organolithium reagents. This strategy gives access to dinuclear complexes, and in particular complexes containing a bis(carbene) and a thiophene bridge. The electron-rich dppe-substituted analogues are then accessible by photochemical decarbonylation in the presence of dppe. These compounds are not available directly, since the reaction of [Fe(C$_5$Me$_5$)(dppe)(L)]$^+$ complexes

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with organolithium reagents leads to electron-transfer reactions [1].

2. Results and discussion

2.1. Reactivity of the cations [Fe(C₅Me₅)(CO)₂(L)][PF₆] (L = CO, PPh₃, CH₃CN)

2.1. Reactivity of the cations $[Fe(C_5Me_5)(CO)_2(L)][PF_6]$ (L = CO, PPh₃, CH₃CN)

Treatment of complex $[Fe(C_5Me_5)(CO)_3][PF_6]$ (**1a**) at $-80°C$ (THF) with LiC≡CSiMe₃ affords a mixture of the acyl complex $[Fe(C_5Me_5)(CO)_2\{C(O)C≡CSiMe_3\}]$

Scheme 1.

Scheme 2.

Scheme 3.

(**2**) and the alkynyl derivative $[Fe(C_5Me_5)(CO)_2\{C≡CSiMe_3\}]$ (**3**) in a 60:40 ratio (Scheme 1). These two compounds are readily separated by column chromatography. These products can be well-differentiated by NMR spectroscopy. The resonances of the alkynyl substituent appear at δ 106.20 ($C≡CSiMe_3$) and 100.00 ($C≡CSiMe_3$) for **2**, whereas they are located at δ 131.32 ($C≡CSiMe_3$) and 118.57 ($C≡CSiMe_3$) for **3** in the ^{13}C-NMR spectra. Moreover, the acyl group of **2** gives rise to a characteristic low-field signal at δ 252.78. The formation of **2** and **3** results from nucleophilic attack at the carbonyl ligand or at the metal centre of **1a**, respectively. Complex **3** is readily obtained as the only product from the acetonitrile complex $[Fe(C_5Me_5)(CO)_2(CH_3CN)][PF_6]$ (**1b**) (Scheme 1). The phosphine-substituted complex $[Fe(C_5Me_5)(CO)(PPh_3)\{C(O)C≡CSiMe_3\}]$ (**4**), formed under the same reaction conditions from $[Fe(C_5Me_5)(CO)_2(PPh_3)][PF_6]$ (**1c**), is isolated as an orange powder in 51% yield after purification by chromatography (Scheme 1). The ^{13}C-NMR spectrum exhibits two signals at δ 106.53 (d, $^2J(C–P) = 7$ Hz, $C≡CSiMe_3$) and 96.31 (s, $C≡CSiMe_3$), in agreement with the proposed structure.

The dppe complex $[Fe(C_5Me_5)(dppe)\{C≡CSiMe_3\}]$ (**5**) is then obtained from the dicarbonyl derivative **3**, under UV irradiation (95:5 toluene–acetonitrile) in the presence of one equivalent of dppe (Scheme 2). The two carbon atoms of the alkynyl ligand are located at δ 162.89 (t, $^2J(C–P) = 37$ Hz, Cα) and δ 123.71 (Cβ) in the ^{13}C-NMR spectrum. The $\nu(C≡C)$ absorption band is observed at 1981 cm^{-1} in the IR spectrum (CH₂Cl₂).

This strategy can be extended to the preparation of dinuclear complexes. Addition of 0.5 equivalents of 2,2'-Li₂C₄H₂S/TMEDA to **1a** leads to the formation of the bis(acyl) derivative $[Fe(C_5Me_5)(CO)_2\{\mu-\eta^1,\eta^{1'}-C(O)-\}]_2(2,2'-C_4H_2S)$ (**6**), which is isolated as a yellow powder in 68% yield. The dppe-substituted complex $[Fe(C_5Me_5)(dppe)]_2\{\mu-\eta^1,\eta^{1'}-2,2'-C_4H_2S\}$ (**7**) is then obtained after decarbonylation of **6** by UV irradiation in the presence of dppe (Scheme 3). Compound **7** is obtained as a thermally stable black solid in 80% yield.

The cyclic voltammogram (Pt electrode, THF, 0.1 M $[nBu_4N][PF_6]$, 0.1 V s^{-1}) of **7** (Fig. 1) exhibits two reversible one-electron processes at $E_1° = -0.592$ V versus SCE and $E_2° = -0.038$ V versus SCE with $i_p^a/i_p^c = 1$. The calculated comproportionation constant $K_c = 2.36 \times 10^9$ (from $|E_1° - E_2°| = 0.554$) is quite large compared with that of the octatetraynediyl derivative $[Fe(C_5Me_5)(dppe)]_2\{\mu-C_8\}$ ($K_c = 2 \times 10^7$) [7]. These preliminary studies indicate that the mixed-valence Fe(II)–Fe(III) complex should be isolable, and its electronic properties deserve to be examined [8]. No such example has been studied so far for thiophene-bridged dinuclear complexes.
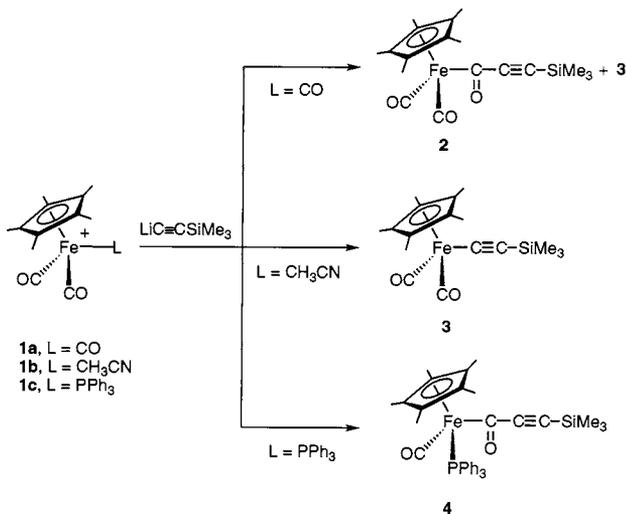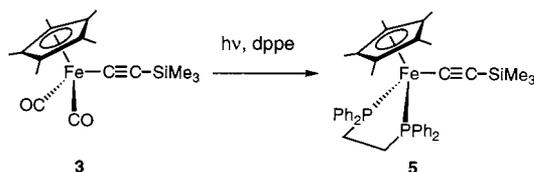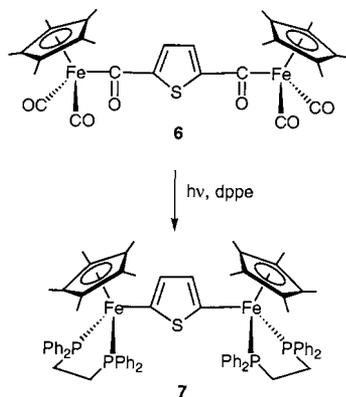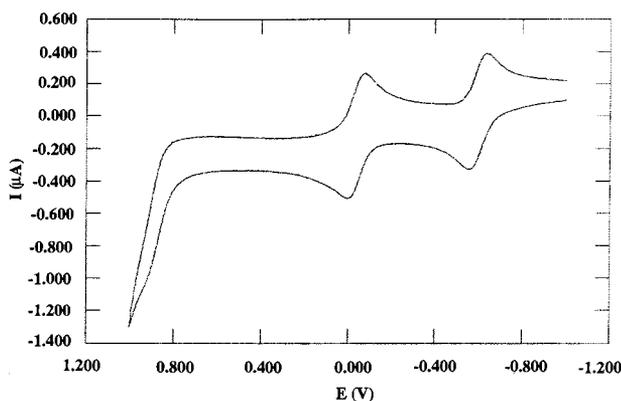
Fig. 1. Cyclic voltammogram of $[Fe(C_5Me_5)(dppe)]_2\{\mu\text{-}\eta^1,\eta^{1'}\text{-}2,2'\text{-}C_4H_2S\}$ (**7**) (Pt electrode, THF, 0.1 M $[nBu_4N][PF_6]$, 0.1 V s^{-1}).
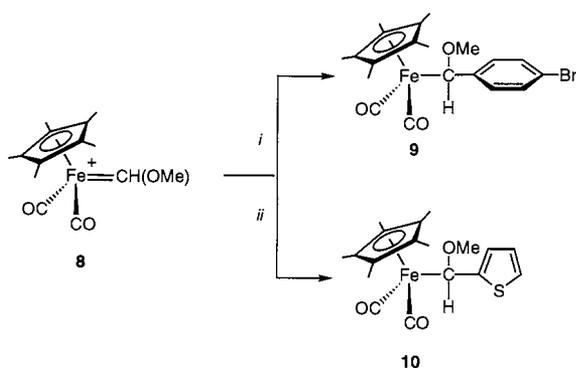
Scheme 4.
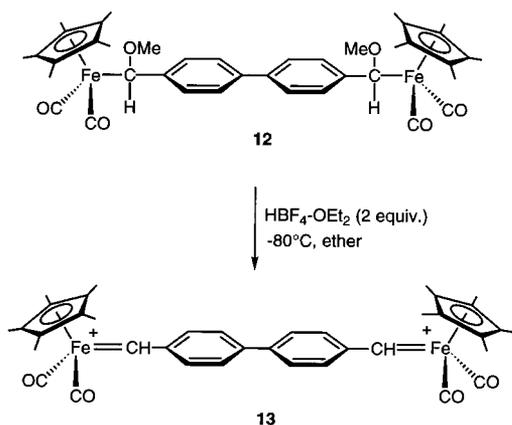
Scheme 5.

2.2. Reactivity of the methoxycarbene complex

The methoxycarbene complex $[Fe(C_5Me_5)(CO)_2(=CHOMe)][PF_6]$ (**8**) cleanly reacts with organolithium reagents [9]. For instance, complexes $[Fe(C_5Me_5)$-

$(CO)_2\{CH(OMe)C_6H_4\text{-}p\text{-}Br\}]$ (**9**) and $[Fe(C_5Me_5)$-$(CO)_2\{CH(OMe)\text{-}2\text{-}C_4H_3S\}]$ (**10**) are obtained from **6** by using the appropriate nucleophiles $LiC_6H_4\text{-}p\text{-}Br$ and $2\text{-}LiC_4H_3S$ (Scheme 4). Both compounds have been fully characterised by NMR spectroscopy. The ^{13}C-NMR spectra clearly show two diastereotopic carbonyl ligands, caused by the presence of the stereogenic α-carbon. Such derivatives are potential precursors of non-heteroatom-stabilised carbene complexes [10]. In addition, the presence of a bromide substituent on the C_6 ring or the lithiation of the thienyl substituent may give access to dinuclear species. For instance, Maiorona et al. have used this synthetic approach to prepare the heterobimetallic complex $[(CO)_5Cr\{\mu\text{-}C(OEt)\text{-}(2,2'\text{-}C_4H_2S)_2\text{-}C(OEt)\}W(CO)_5]$ [11].

Treatment of the methoxycarbene complex **8** with dilithiated nucleophiles provides a route to symmetrical dinuclear α,α'-methoxy complexes. Addition of $2,2'\text{-}Li_2C_4H_2S/TMEDA$ to two equivalents of **8** at $-80°C$ gives the thiophene derivative $[Fe(C_5Me_5)(CO)_2\{\mu\text{-}\eta^1,\eta^{1'}\text{-}CHOMe\text{-}]_2(2,2'\text{-}C_4H_3S)$ (**11**). The biphenylene complex $[Fe(C_5Me_5)(CO)_2\{\mu\text{-}\eta^1,\eta^{1'}\text{-}CHOMe\text{-}]_2(p\text{-}C_6H_4\text{-}C_6H_4)$ (**12**) is obtained as a yellow powder in 75% yield by using p-dilithiobiphenylene. Since there are two stereogenic carbon centres (Cα) in **11** and **12**, they are formed as a mixture of *meso* and *dl* diastereoisomers. This is clearly established by the NMR spectra, where two sets of signals are seen. For example, the NMR spectra of **11** exhibit two signals for the CH groups at $\delta(^1H)$ 5.36 and 5.33 and $\delta(^{13}C)$ 81.8 and 81.6.

The conversion of **12** into the corresponding bis(carbene) complex $[Fe(C_5Me_5)(CO)_2\{\mu\text{-}\eta^1,\eta^{1'}\text{-}CH\text{-}]_2(p\text{-}C_6H_4\text{-}C_6H_4)$ (**13**) is achieved by elimination of both methoxide groups by using two equivalents of HBF_4–OEt_2 (Scheme 5), a procedure described for analogous mononuclear species [12]. The reaction, when carried out in ether at $-80°C$, gives a dark purple solid which is stable at temperatures below $-50°C$. The key spectroscopic feature of **13** is the carbene fragment resonances located at characteristic chemical shifts $\delta(^1H)$ 15.63 and $\delta(^{13}C)$ 341.9 [12]. Examples of di-iron bis-(carbene) complexes have been previously reported and are generally formed by ligand–ligand coupling reactions [13,14].

The above reactions are convenient routes to a wide variety of $[Fe(C_5Me_5)(CO)_2]$ complexes and their phosphine derivatives, these latter species not being directly accessible. This opens an entry to novel bimetallic complexes. The mononuclear species can serve as building blocks for the preparation of intramolecular charge-transfer compounds having both electron-donating and electron-accepting organometallic fragments. We are currently studying the synthesis of disymmetric π-conjugated bridged complexes.

3. Experimental

3.1. General data

All manipulations were carried out under an argon atmosphere with Schlenk techniques. Solvents were dried and distilled under nitrogen before use by standard methods. Complexes $[Fe(C_5Me_5)(CO)_2(L)][PF_6]$ (**1**; **a**, L = CO; **b**, L = CH_3CN; **c**, L = PPh_3) [5] and $[Fe(C_5Me_5)(CO)_2(\equiv CHOMe)][PF_6]$ (**8**) [6] were prepared according to the literature procedures. Photolysis experiments were carried out by using an Original Hanau 150 W (Hg, high pressure) lamp. NMR spectra were recorded on Bruker DPX-200 and Bruker AC 300 (by S. Sinbandhit, CRMPO, Université de Rennes 1) spectrometers. Infrared spectra were obtained with a Bruker IFS28 FT-IR spectrometer. Mass spectra were recorded on a Varian MAT 311 (70 eV) instrument and FAB mass spectra on a Micromass ZABSpec TOF spectrometer at the CRMPO. Cyclic voltammetry was performed on a PAR potentiostat model 263. Microanalyses were performed by the 'Centre de Microanalyse du CNRS' at Vernaison, France.

3.2. $[Fe(C_5Me_5)(CO)_2\{C(O)C\equiv CSiMe_3\}]$ (2)

A suspension of 1 mmol (420 mg) of **1a** in THF (20 ml) was treated at $-80°C$ with a freshly prepared solution of $LiC\equiv CSiMe_3$ (1.1 mmol) in THF (10 ml). After stirring overnight, the solution was warmed up to room temperature (r.t.) and evaporated to dryness. The residue was extracted with diethylether. Chromatography on silica gel (eluent: 50:50 pentane–ether) gave 100 mg (50%) of yellow microcrystals of **2**. Elution with 75:25 pentane–ether afforded 100 mg of complex **3**. Complex **2**, ^{1}H-NMR (200 MHz, CDCl$_3$) δ 1.84 (s, 15H, C$_5$Me$_5$), 0.23 (s, 9H, SiMe$_3$); ^{13}C-NMR $\{^1$H$\}$ (50.3 MHz, CDCl$_3$) δ 252.78 (C=O), 215.12 (CO), 106.20 ($C\equiv CSiMe_3$), 100.00 (C$\equiv C$SiMe$_3$), 97.47 (C_5Me$_5$), 9.76 (C_5Me_5), -0.06 (SiMe$_3$); IR (CH$_2$Cl$_2$, cm^{-1}) 2003 (νCO)), 1952 (ν(CO)), 1614 (ν(C=O)). The ν(C$\equiv$C) band was not observed, but may be masked by the strong ν(CO) absorption bands. Anal. Calc. for C$_{18}$H$_{24}$O$_3$FeSi: C, 58.07; H, 6.55. Found: C, 58.10; H, 6.55.

3.3. $[Fe(C_5Me_5)(CO)_2(C\equiv CSiMe_3)]$ (3)

The title compound was prepared by the procedure described above, by using 3 mmol (1.3 g) of **1b** and $LiC\equiv CSiMe_3$ (3.5 mmol) in THF (30 ml). Chromatography on silica gel (eluent: 75:25 pentane–ether) gave brown yellow microcrystals (876 mg, 84.8%). ^{1}H-NMR (300 MHz, CDCl$_3$) δ 1.83 (s, 15H, C$_5$Me$_5$), 0.10 (s, 9H, SiMe$_3$); ^{13}C-NMR $\{^1$H$\}$ (75.5 MHz, CDCl$_3$) δ 214.57 (CO), 131.32 ($C\equiv CSiMe_3$), 118.57 (C$\equiv C$SiMe$_3$), 96.97 (C_5Me$_5$), 9.86 (C_5Me_5), 1.76 (SiMe$_3$); IR (CH$_2$Cl$_2$, cm^{-1}) 2036 (ν(C$\equiv$C)), 2007 (ν(CO)), 1966 (ν(CO)).

Anal. Calc. for C$_{17}$H$_{24}$O$_2$FeSi: C, 59.30; H, 7.03. Found: C, 59.01; H, 7.08.

3.4. $[Fe(C_5Me_5)(CO)(PPh_3)\{C(O)C\equiv CSiMe_3\}]$ (4)

As described above, 0.5 mmol (330 mg) of **1c** was treated with $LiC\equiv CSiMe_3$ (0.65 mmol) in THF (20 ml). Work-up gave after chromatography on silica gel (eluent: 75:25 pentane–ether) orange microcrystals (155 mg, 50.8%). ^{1}H-NMR (300 MHz, CDCl$_3$) δ 7.51 (m, PPh$_3$), 7.33 (m, PPh$_3$), 1.48 (s, 15H, C$_5$Me$_5$), 0.19 (s, 9H, SiMe$_3$); ^{31}P-NMR $\{^1$H$\}$ (121.5 MHz, CDCl$_3$) δ 73.47 (s, PPh$_3$); ^{13}C-NMR $\{^1$H$\}$ (50.3 MHz, CDCl$_3$) δ 269.45 (d, ^2J(C–P) = 28 Hz, C=O), 221.72 (d, ^2J(C–P) = 28 Hz, CO), 134.0 (v. br. s, Ph$_{ortho}$), 133.74 (d, ^1J(C–P) = 20 Hz, Ph$_{ipso}$), 129.45 (br.s, Ph$_{para}$), 127.74 (d, ^3J(C–P) = 8 Hz, Ph$_{meta}$), 106.53 (d, ^2J(C–P) = 7 Hz, $C\equiv CSiMe_3$), 96.31 (C$\equiv C$SiMe$_3$), 93.83 (C_5Me$_5$), 9.32 (C_5Me_5), -0.24 (SiMe$_3$); IR (CH$_2$Cl$_2$, cm^{-1}) 1915 (ν(CO)), the ν(C$\equiv$C) absorption band was not observed. Anal. Calc. for C$_{35}$H$_{39}$O$_2$FeSiP: C, 69.30; H, 6.48. Found: C, 69.56; H, 6.31.

3.5. $[Fe(C_5Me_5)(dppe)\{C\equiv CSiMe_3\}]$ (5)

Complex **3** (1.2 mmol, 406 mg) and 1.77 mmol (705 mg) of dppe were dissolved in 200 ml of a mixture of 95:5 toluene–acetonitrile. The solution was irradiated for 4 h. After evaporation to dryness, the residue was extracted with pentane. Crystallisation gave red microcrystals (590 mg, 72% yield). ^{1}H-NMR (300 MHz, CDCl$_3$) δ 7.95 (m, 4H, Ph$_{ortho}$), 7.28 (m, 16H, Ph), 2.76 (m, 2H, CH$_2$), 1.99 (m, 2H, CH$_2$), 1.38 (s, 15H, C$_5$Me$_5$), -0.11 (s, 9H, SiMe$_3$); ^{31}P-NMR $\{^1$H$\}$ (121.5 MHz, CDCl$_3$) δ 100.56 (s, dppe); ^{13}C-NMR $\{^1$H$\}$ (50.3 MHz, CDCl$_3$) δ 162.89 (t, ^2J(C–P) = 37 Hz, Cα), 139.07–137.48 (2 × m, Ph$_{ipso}$), 134.42–133.95 (2 × m, Ph$_{ortho}$), 128.69–128.44 (2 × m, Ph$_{para}$), 127.10–126.77 (2 × m, Ph$_{meta}$), 123.71 (Cβ), 87.45 (C_5Me$_5$), 30.66 (CH$_2$), 9.95 (C_5Me_5), 1.34 (SiMe$_3$); IR (CH$_2$Cl$_2$, cm^{-1}) 1981 (ν(C$\equiv$C)). Anal. Calc. for C$_{41}$H$_{48}$FeSiP$_2$: C, 71.71; H, 7.05. Found: C, 71.92; H, 7.10.

3.6. $[Fe(C_5Me_5)(CO)_2\{\mu-\eta^1,\eta^{1\prime}-C(O)-]_2(2,2'-C_4H_2S)$ (6)

A suspension of 2 mmol (840 mg) of **1a** in 20 ml of THF was transferred by a canula at $-80°C$ to a freshly prepared suspension of 1 mmol of 2,2'-Li$_2$C$_4$H$_2$S–TMEDA in heptane. The reaction mixture was allowed to warm up to r.t. overnight, and the solvent removed in vacuo. The residue was extracted with ether, crystallisation in a CH$_2$Cl$_2$–pentane mixture gave 430 mg of yellow crystals (68%). ^{1}H-NMR (300 MHz, CDCl$_3$) δ 7.40 (s, 2H, H$_{3/3'}$), 1.77 (s, 30H, C$_5$Me$_5$); ^{13}C-NMR $\{^1$H$\}$ (50.3 MHz, CDCl$_3$) δ 253.4 (C=O), 215.9 (CO), 156.2 (C$_{2/2'}$), 128.4 (C$_{3/3'}$), 97.4

(C_5Me_5), 9.6 (C_5Me_5); IR (CH_2Cl_2, cm^{-1}) 2006 (ν(CO)), 1946 (ν(CO)), 1563 (ν(C=O)). Anal. Calc. for $C_{30}H_{32}O_6SFe_2$: C, 56.98; H, 5.10. Found: C, 57.87; H, 5.05.

3.7. [Fe(C$_5$Me$_5$)(dppe)]$_2$\{μ-η^1,η$^{1'}$-2,2'-C$_4$H$_2$S\} (7)

A solution of 0.3 mmol (220 mg) of **6** and 1 mmol (398 mg) of dppe in 200 ml of a mixture of 95:5 toluene–acetonitrile was irradiated under UV for 2 h. The yellow solution became black. After evaporation to dryness, the residue was washed with pentane. Crystallisation in a THF–pentane mixture gave 346 mg of a black powder (80%). ^{1}H-NMR (300 MHz, C$_6$D$_6$) δ 7.69–7.02 (m, 40H, Ph), 6.43 (s, 2H, H$_{3/3'}$), 1.85 (m, 8H, CH$_2$PPh$_2$), 1.54 (s, 30H, C$_5$Me$_5$); ^{13}C-NMR \{^{1}H\} (75.5 MHz, C$_6$D$_6$) δ 150.4 (m, C$_{2/2'}$), 143.9 (C$_{3/3'}$), 143.8 (m, Ph), 140.1 (m, Ph), 135.2 (m, Ph), 128.8 (m, Ph), 87.0 (C$_5$Me$_5$), 30.3 (m, CH$_2$), 11.7 (C$_5$Me$_5$); ^{31}P-NMR \{^{1}H\} (121.5 MHz, C$_6$D$_6$) δ 105.2 (dppe). HRM mass FAB m/z 1260.3624 [M$^+$] calc. for $C_{76}H_{80}P_4SFe_2$ 126.3635 [M$^+$]. Cyclic voltammetry (Pt, THF, [nBu$_4$N][PF$_6$] 0.1 M, 0.1 V s^{-1}): $E°$(Fe^{II}/Fe^{III}) = − 0.592 V vs. SCE, $E°$(Fe^{III}/Fe^{III}) = − 0.038 V vs. SCE.

3.8. [Fe(C$_5$Me$_5$)(CO)$_2$\{CH(OMe)C$_6$H$_4$-p-Br\}] (9)

To a suspension of 0.41 mmol (179 mg) of **8** in 15 ml of diethyl ether were added at − 80°C, 1.5 equivalents of freshly prepared LiC$_6$H$_4$-p-Br. The reaction mixture was allowed to warm up to r.t., and several drops of methanol were added to quench the excess of lithium salt. After evaporation of the solvent at reduced pressure, the residue was extracted with pentane. Crystallisation gave 100 mg (55% yield) of orange microcrystals. ^{1}H-NMR (300 MHz, CD$_2$Cl$_2$) δ 7.24 (d, ^3J(H−H) = 8.2 Hz, 2H, Ar), 6.95 (d, ^3J(H−H) = 8.2 Hz, 2H, Ar), 4.93 (s, 1H, CH), 3.14 (s, 3H, OMe), 1.77 (s, 15H, C$_5$Me$_5$); ^{13}C-NMR \{^{1}H\} (75.5 MHz, CD$_2$Cl$_2$) δ 219.4 (CO), 217.7 (CO), 153.9 (Ar$_{ipso}$), 131.1 (Ar), 125.6 (Ar), 116.4 (Ar$_{Br}$), 96.6 (C$_5$Me$_5$), 86.1 (CH), 60.8 (OMe), 9.6 (C$_5$Me$_5$); IR (pentane, cm^{-1}) 1999.3 (ν(CO)), 1948.5 (ν(CO)). Anal. Calc. for $C_{20}H_{23}O_3BrFe$: C, 53.72; H, 5.18. Found: C, 53.68; H, 5.03.

3.9. [Fe(C$_5$Me$_5$)(CO)$_2$\{CH(OMe)(2-C$_4$H$_3$S)\}] (10)

Complex **10** was prepared according to the procedure described for **7**, starting from 2 mmol (872 mg) of **8** and 2 mmol of 2-LiC$_4$H$_3$S. Extraction with pentane (2 × 10 ml) and crystallisation gave a yellow brown oil (377 mg, 65%). ^{1}H-NMR (300 MHz, CDCl$_3$) δ 7.01 (dd, ^3J(H−H) = 5.0 Hz, ^4J(H−H) = 1.2 Hz, 1H, H$_{2'}$), 6.80 (dd, ^3J(H−H) = 3.5 Hz, ^3J(H−H) = 5.0 Hz, 1H, H$_{3'}$), 6.66 (dd, ^3J(H−H) = 3.5 Hz, ^4J(H−H) = 1.2 Hz, 1H, H$_3$), 5.27 (s, 1H, CH), 3.25 (s, 3H, OMe), 1.77 (s, 15H,

C$_5$Me$_5$); ^{13}C-NMR \{^{1}H\} (75.5 MHz, C$_6$D$_6$) δ 219.3 (CO), 217.3 (CO), 160.6 (C$_2$), 126.3 (C$_{3'}$), 121.6 (C$_{2'}$), 118.9 (C$_3$), 95.8 (C$_5$Me$_5$), 81.3 (CH), 60.2 (OMe), 9.2 (C$_5$Me$_5$); IR (CH$_2$Cl$_2$, cm^{-1}) 1991 (ν(CO)), 1934 (ν(CO)). Anal. Calc. for $C_{18}H_{22}O_3SFe$: C, 57.76; H, 5.92. Found: C, 57.62; H, 5.80.

3.10. [Fe(C$_5$Me$_5$)(CO)$_2$\{μ-η^1,η$^{1'}$-CHOMe-]$_2$(2,2'-C$_4$H$_2$S) (11)

A suspension of 1.7 mmol (742 mg) of **8** in 15 ml of THF was transferred by a canula at − 80°C to a freshly prepared suspension of 0.8 mmol of 2,2'-Li$_2$C$_4$H$_2$S–TMEDA in heptane. The reaction mixture was allowed to warm up to r.t. overnight, and the solvent removed in vacuo. Compound **11** was extracted with pentane (2 × 10 ml), a yellow powder (225 mg, 40%) precipitated by concentration of pentane. ^{1}H-NMR (300 MHz, C$_6$D$_6$) δ 6.79–6.78 (2 × s, 2H, H$_{3,3'}$), 5.36–5.33 (2 × s, 2H, CH), 3.39–3.38 (2 × s, 6H, OMe), 1.49–1.48 (2 × s, 30H, C$_5$Me$_5$), ratio of integration, 1:1; ^{13}C-NMR \{^{1}H\} (75.5 MHz, C$_6$D$_6$) δ 219.4–219.3 (CO), 217.4–217.3 (CO), 156.43–156.37 (C$_2$), 118.6–118.5 (C$_3$), 95.6–95.5 (C$_5$Me$_5$), 81.8–81.6 (CH), 60.0 (OMe), 9.2 (C$_5$Me$_5$); IR (CH$_2$Cl$_2$, cm^{-1}) 1989 (ν(CO)), 1933.6 (ν(CO)). Anal. Calc. for $C_{32}H_{40}O_6SFe_2$: C, 57.85; H, 6.07. Found: C, 57.67; H, 6.01.

3.11. [Fe(C$_5$Me$_5$)(CO)$_2$\{μ-η^1,η$^{1'}$-CHOMe-]$_2$(p-C$_6$H$_4$-C$_6$H$_4$) (12)

A solution of 2 mmol (872 mg) of **8** in 25 ml of THF was treated with 1 mmol of p-Li-C$_6$H$_4$-C$_6$H$_4$-Li (freshly prepared from 1 mmol (312 mg) of 4,4'-dibromophenylene and 2 mmol (1.25 ml) of nBuLi (1.6 M in hexane) in THF (15 ml). After warming up to r.t., the solution was evaporated under vacuum and the residue extracted with toluene. Crystallisation in CH$_2$Cl$_2$–hexane gave 555 mg (75% yield) of a yellow powder. ^{1}H-NMR (300 MHz, C$_6$D$_6$) δ 7.63–7.62 (2 × d, ^3J(H−H) = 8 Hz, 2H, Ar), 7.45 (d, ^3J(H−H) = 8 Hz, 2H, Ar), 5.15 (s, 1H, CH), 3.27–3.26 (2 × s, 3H, OMe), 1.53 (s, 15H, C$_5$Me$_5$), ratio of integration, 1:1; ^{13}C-NMR \{^{1}H\} (75.5 MHz, C$_6$D$_6$) δ 219.5 (C=O), 217.5 (CO), 152.7 (Ar$_{ipso}$), 137.7–137.6 (2 × s, Ar$_{para}$), 126.9 (Ar$_{meta}$), 124.5 (Ar$_{ortho}$), 95.8 (C$_5$Me$_5$), 86.9 (CH), 60.6 (OMe), 9.3 (C$_5$Me$_5$); IR (CH$_2$Cl$_2$, cm^{-1}) 1989 (ν(CO)), 1932 (ν(CO)). Anal. Calc. for $C_{40}H_{46}O_6Fe_2$: C, 65.41; H, 6.31. Found: C, 65.45; H, 6.11.

3.12. [Fe(C$_5$Me$_5$)(CO)$_2$\{μ-η^1,η$^{1'}$-CH-]$_2$(p-C$_6$H$_4$-C$_6$H$_4$) (13)

A suspension of 176 mg (0.24 mmol) of **11** in 10 ml of Et$_2$O was treated at − 80°C with 95 μl (0.5 mmol) of HBF$_4$–OEt$_2$. The colour became purple. The ether was

removed by canula and the dark purple solid dried under vacuum. ^{1}H-NMR (300 MHz, CD_2Cl_2, 25°C) δ 15.63 (s, 1H, =CH), 8.16 (d, ^3J(H–H) = 8 Hz, 2H, Ar), 8.09 (d, ^3J(H–H) = 8 Hz, 2H, Ar), 2.02 (s, 15H, C_5Me_5); ^{13}C-NMR {[1]H} (75.5 MHz, CD_2Cl_2, −50°C) δ 341.9 (=C), 210.3 (CO), 153.2 ($Ar_{ipso/para}$), 148.6 ($Ar_{ipso/para}$), 135.9 (Ar), 129.9 (Ar), 107.8 (C_5Me_5), 10.1 (C_5Me_5).

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