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Oxidized Fe^{II} ferrocenylacetylide complexes. A novel type of mixed-valence complex

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Abstract

Reaction of lithium ferrocenylacetylide with $(\eta\text{-}C_5H_5)LL'FeI$ ($L = L' = CO$, $L = L' = P(OMe)_3$, and $L = CO$, $L' = PPh_3$) gave the corresponding Fe^{II} ferrocenylacetylide complexes, $(\eta\text{-}C_5H_5)LL'FeCCFc$, in moderate yields. $(\eta\text{-}C_5Me_5)(CO)_2FeCCFc$ was similarly prepared. In their cyclic voltammograms, all the complexes gave two irreversible waves in acetonitrile. The complexes, when oxidized with various oxidants, showed a broad absorption in the near-infrared region and low frequency-shift of the acetylide group in the IR spectrum. The spectral data suggest that the oxidized complexes are a novel Class II type of mixed-valence complex.

Key words: Iron; Mixed-valence complex; Ferrocenylacetylide; Metallocenes

1. Introduction

Mixed-valence complexes currently attract much attention because of the possibility of using them to produce high temperature and novel superconducting materials and of elucidating mixed-valence compounds of biological origin [1]. Considering organometallic mixed-valence complexes, oxidized binuclear ferrocene derivatives are typical and have been extensively investigated [2–6]. Mixed-valence complexes of bis$[(\eta\text{-}C_5H_5)L_2Fe]$ were recently reported [7,8], and interesting dinuclear iron complexes [9–11]. However, only a few binuclear complexes containing different types of iron atoms have been investigated [12]. These may give more insight into the electronic structure of mixed-valence complexes, the extent of delocalization of electrons, and the factors which affect this in the complex (the mode of coordination to a metal, the kind of coordinated ligands, and so on). We now report the synthesis and some properties of four Fe^{II} ferrocenylacetylide complexes and the corresponding oxidized species.

2. Results and discussion

Lithium ferrocenylacetylide reacted with $(\eta\text{-}C_5H_5)(CO)_2FeI$ in THF at low temperature to give $(\eta\text{-}C_5H_5)(CO)_2FeCCFc$ (Fc = ferrocenyl) (**1**) as yellow crystals in good yield. $(\eta\text{-}C_5Me_5)(CO)_2FeCCFc$ (**2**) and $(\eta\text{-}C_5H_5)[(MeO)_3P]_2FeCCFc$ (**4**) were similarly obtained from the reaction of lithium ferrocenylacetylide with $(\eta\text{-}C_5Me_5)(CO)_2FeI$ and $(\eta\text{-}C_5H_5)[(MeO)_3P]_2FeI$, respectively. $(\eta\text{-}C_5H_5)(CO)(Ph_3P)FeCCFc$ (**3**) was obtained as red-orange crystals in moderate yield from the reaction of **1** with triphenylphosphine under photoirradiation. Structures of the new complexes were assigned by elemental analysis, IR, ^1H, and ^{13}C NMR spectra. For example, complex **3** showed the C≡C stretching vibration at 2088 cm^{-1} and the CO stretching at 1932 cm^{-1} in the IR spectrum. The ^1H NMR spectrum of **3** showed the proton signals of the ferro-

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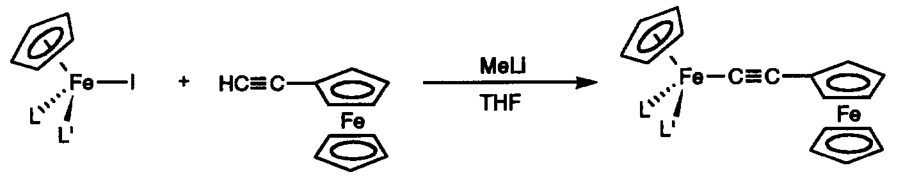
cenyl ring at δ 3.97 (2H), 3.88 (2H), and 3.84 (5H), the proton signal of the η-C_5H_5 ring at δ 4.49 (5H), and the phenyl protons of PPh_3 at δ 7.72 and 7.43 (15H) as broad multiplets. In the ^{13}C NMR spectrum of **3**, the carbon signals of the ferrocenyl nucleus appeared at 66.21, 68.93, 69.90, and 74.00 ppm, the carbon signal of the η-C_5H_5 ring coordinating to the Fe atom at 84.33 ppm, acetylenic carbon signals at 98.25 and 114.40 ppm, and the carbonyl carbon signal at 219.73 ppm.

The results of the cyclic voltammetry for complexes **1**–**4** are summarized in Table 1. The cyclic voltammogram of **1** showed two irreversible waves at $E_{pa} = -0.07$ V and $E_{pa} = +0.86$ V (*vs.* FcH/FcH$^+$) in CH_3CN. Complexes **2** and **3** also showed behaviour similar to that of complex **1**. The lower-potential wave in the voltammogram of complexes **1**–**3** is assigned to the redox wave of the ferrocenyl moiety and the other one to that of the (η-C_5R_5)LL′Fe-moiety, because the redox potential of ferrocenylacetylene, (η-C_5H_5)(Ph_3P)-

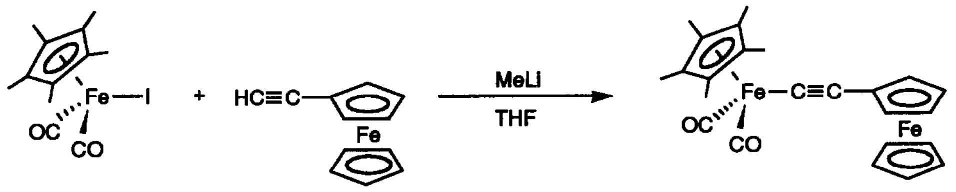
TABLE 1. Redox potentials (V *vs.* FcH/FcH$^+$) of Fe^{II} ferrocenylacetylide and the related compounds in CH_3CN (0.1 M Bu_4NClO_4)

Compound	$E_{pa}(1)$	$E_{pa}(2)$
1	−0.07	+0.86
2	−0.10	+0.71
3	−0.13	+0.45
4	−0.30	+0.23
FcC≡CH	+0.17 [a]	
Fp*C≡CPh		+0.55 [a]
Cp(Ph$_3$P) (CO) FeBr		+0.28 [a]
Cp[(MeO)$_3$P]$_2$FeI	−0.18 [a]	

[a] Value of $E_{1/2}$ (reversible)



1 L, L' = 2CO
3 L = CO, L' = PPh$_3$
4 L, L' = 2 P(OMe)$_3$



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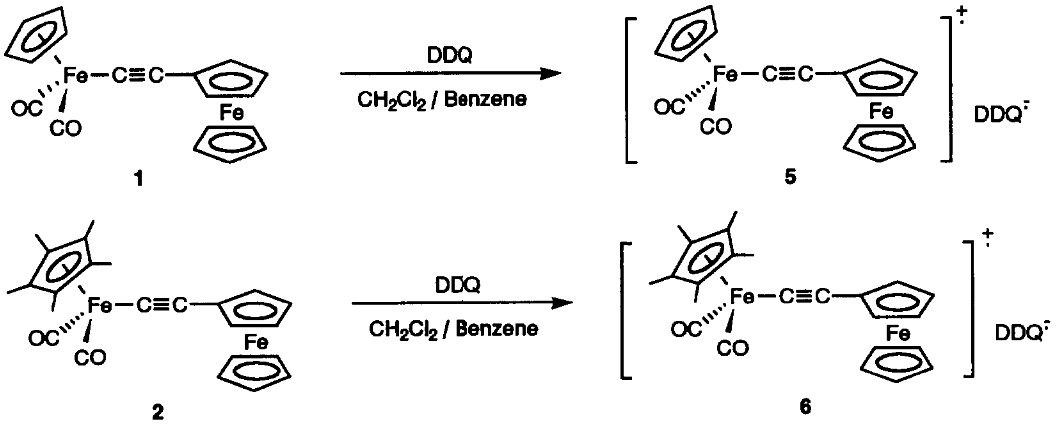


(CO)FeBr, and (η-C_5Me_5)(CO)$_2$FeCCPh were +0.17 V ($E_{1/2}$), +0.28 V ($E_{1/2}$) and +0.55 V (E_{pa}), respectively. The redox potentials of **2** and **3** are lower than those of **1**. This is probably because the η-C_5Me_5 and PPh_3 ligands have more electron-donating capability than the η-C_5H_5 and CO ligands. The first oxidation potentials of **1–3** are lower than that of ferrocenylacetylene ($\Delta = \sim 0.2$ V). This is probably due to the increase in electron density which accompanies the change of the acetylene group to the Fe^{II} acetylide group. The second oxidation potentials are higher than those of the reference compounds, (η-C_5Me_5)(CO)$_2$FeCCPh and (η-C_5H_5)(Ph_3P)(CO)FeBr ($\Delta = \sim 0.3$ V), being due to the electrostatic effect of the oxidized ferrocenyl group. This suggests that the one electron-oxidized state of complexes **1–3** is stabilized by electrons being delocalized between two Fe atoms. Next, the cyclic voltammogram of **4** showed two irreversible waves at $E_{pa} = -0.30$ and $+0.23$ V in CH_3CN. In contrast to the other complexes **1–3**, the lower-potential wave at −0.30 V in **4** is assigned to the (η-C_5H_5)[(MeO)$_3$P]$_2$Fe-moiety because the redox potential of (η-C_5H_5)[(MeO)$_3$P]$_2$FeI is $E_{1/2} = -0.18$ V; the higher-potential wave is then assigned to the ferrocenyl. The higher oxidation-potential of **4** is also a little higher ($\Delta = 0.06$ V) than that of the reference compound, ferrocenylacetylene. Some electron delocalization would therefore be expected between the two Fe atoms in the one electron-oxidized state of **4**, as occurs in **1–3**. However, the potential difference between the lower and higher waves in **3** and **4** is smaller than that in **1** or **2**, which probably indicates that their one electron-oxidized states are less stable.

Complexes **1** and **2** were oxidized with dichlorodicyanobenzoquinone (DDQ) in dichloromethane/benzene under nitrogen to give the brown oxidized complexes **5** and **6**, respectively. However, oxidation of **1** and **2** with $FcH^+PF_6^-$ or $AgPF_6$ gave no stable oxidized product. Complex **4** could be oxidized with $AgPF_6$ in dichloromethane, but no stable oxidized complex could be isolated. Complex **3** gave only an intractable product in a similar reaction. Oxidation of **1–4** with iodine produced no definite product. Complexes **5** and **6** were relatively stable in the solid state, but unstable in solution. In the IR spectrum, **5** and **6** showed the stretching vibration of the terminal carbonyl at 2050–1980 cm^{-1}, whose position is similar to those observed in the neutral complexes **1** and **2**. This suggests that there is little positive charge on the Fe atom of the (η-C_5R_5)Fe(CO)$_2$ moiety (R = H or Me) in **1** and **2**, because the carbonyl stretching vibrations in the cation complexes were observed at a wavenumber higher by 30–70 cm^{-1} than in the neutral complexes {*e.g.* 2065 and 2019 cm^{-1} in [(η-C_5H_5)Fe(CO)$_2$(THF)]BF_4 [13] and 2085 and 2005 cm^{-1} in [(η-C_5Me_5)Fe(CO)$_2$(THF)]BF_4 [14]}.

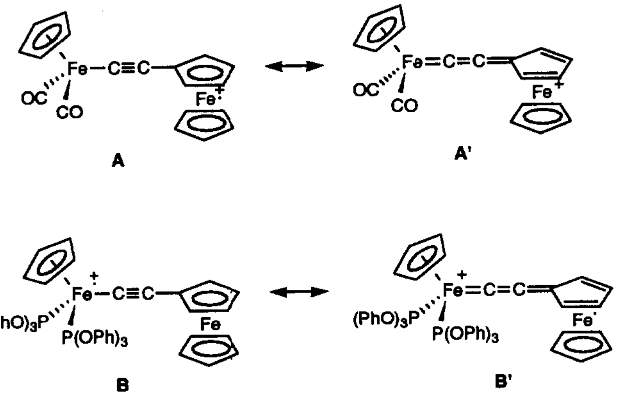
In contrast the C≡C stretching vibration of **5** (2090 cm^{-1}) and **6** (2072 cm^{-1}) were observed at a wavenumber lower by 20–30 cm^{-1} than in the neutral complexes **1** (2109 cm^{-1}) and **2** (2099 cm^{-1}). Also, in the IR spectrum of the solution of complex **4** and $AgPF_6$ in dichloromethane, the C≡C stretching vibration observed at 2074 cm^{-1} in the neutral complex **4** disappeared to be replaced by a new strong absorption at 1964 cm^{-1}. Thus, the C≡C stretching vibration in the oxidized complex of **4** is just intermediate between the C≡C stretching vibration of the neutral acetylide complexes (2072–2100 cm^{-1}) and the =C=C= stretching vibration of allenylidene complexes (1926 cm^{-1}) [15]. These suggest that the triple bond character of the acetylide bond is decreased, slightly in **5** and **6** and considerably in the oxidized complexes of **4**, and a partial electron-delocalization is then observable between the two Fe atoms in these oxidized complexes. The structures A′ and B′, which are a type of allenylidene complex, are an addition to the limiting structures A and B, and this seems to contribute to the structures of **5**, **6**, and the oxidized complex of **4** to some extent.

In the electronic spectra of **5** and **6**, a broad absorption was observed in the near infrared region (Table 2). The solvent effect for the absorption maximum in the near infrared region was examined. As shown in Fig. 1, ν_{max} for the absorption maximum varied almost linearly

TABLE 2. Spectral data of the IT bands for **5** and **6**

Complex	Solvent	$(1/n^2 - 1/D_s)$	λ_{max}	ν_{max}	ϵ_{max}
5	acetone	0.496	990	10100	1132
	acetonitrile	0.526	1000	9990	1403
	nitromethane	0.489	1005	9950	1385
	dichloromethane	0.380	1060	9430	679 [a]
6	acetonitrile	0.526	1130	8850	1875
	dichloromethane	0.380	1250	8000	1472

[a] Complex **5** is very unstable in CH_2Cl_2.



with $(1/n^2 - 1/D_s)$, where n^2 and D_s are the optical and static dielectric constants of the solvent involved [16]. Meyer observed the linearity between ν_{max} and $(1/n^2 - 1/D_s)$ in oxidized biferrocenyl systems on the basis of the Hush treatment for a localized mixed-valence compound [4d]. The absorption band observed in the near infrared region can therefore be assigned as an intervalence transfer (IT) band caused by an electron transfer between two metal atoms.

It is interesting to apply the Hush theoretical analysis of the IT transition to **5** and **6**. In the treatment [16], the halfwidth $(\Delta\nu_{1/2})$ is related to the energy of the IT transition (ν_{max}) by the equation

$$\nu_{max} - \nu_0 = (\Delta\nu_{1/2})^2/2310\ \mathrm{cm}^{-1}$$

where ν_0 is the internal energy difference between the two oxidation state isomers. According to the Taube treatment in the study of oxidized $FcCNRu(NH_3)_5$ [17], an upper limit for ν_0 can be approximated by the difference in the redox potentials between the two metal centres in the complex. For **5** and **6**, the differences in potentials are found to be 0.93 V ($\nu_0 = 7.5 \times 10^3$ cm^{-1}) and 0.81 V ($\nu_0 = 6.5 \times 10^3$ cm^{-1}) from the cyclic voltammograms (Table 1), respectively. The lower limits for $\Delta\nu_{1/2}$ calculated as above are 2.4×10^3 (**5**) and 2.3×10^3 (**6**) cm^{-1}. The observed halfwidths were 3.90×10^3 (**5**) and 3.74×10^3 (**6**) in the IT band in CH_3CN. The ratio, 1.6, between observed and calculated $\Delta\nu_{1/2}$ for the oxidized carbonyl complexes **5** and **6** are near to the value (1.1–1.3) reported for mixed-valence compounds of the weakly interacted type (class II). Hush further proposed an expression for the interaction parameter α^2 which gives an approximate measure for the degree of ground-state delocalization in a mixed-valence complex, where d is the distance between the metal centres.

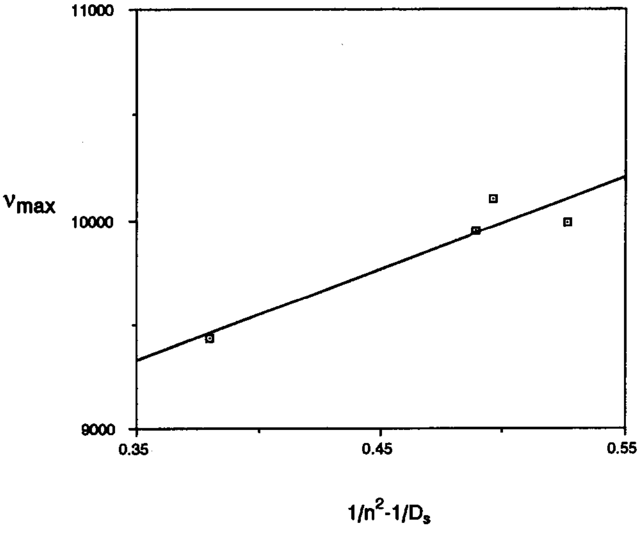


Fig. 1. Relationship of ν_{max} with $(1/n^2 - 1/D_s)$.

$$\alpha^2 = \left[(4.2 \times 10^{-4})\epsilon_{max}\Delta\nu_{1/2}\right]/\nu_{max}d^2$$

If the internuclear distance (6.01 Å) obtained for the analogous Ru complex is used as the value of d [18], α^2 for the oxidized complexes **5** and **6** is calculated as 6.37×10^{-3} and 9.21×10^{-3}, respectively. The value for the oxidized carbonyl complexes **5** is somewhat larger than α^2 for several class II mixed-valence ions having a similar internuclear distance: diferrocenylacetylene monocation (2.4×10^{-3}) [4c], $[FcCNRu(NH_3)_5]^+$ (2.3×10^{-3}) [17], $[FcCCo(CO)_6L_3]^+$ (2.7×10^{-3}) [19]. This suggests that complex **5** is to be classified as a class II type of a mixed-valence complex. The α^2 value for complex **6** having η-C_5Me_5 ligand (9.21×10^{-3}) is somewhat larger than that for **5** and close to that of biferrocenyl monocation ($9 \times 10^{-3} \sim 1.4 \times 10^{-2}$) [2c]. Considering the effect of the distance between the two redox sites [for example, $\alpha^2(FcC{\equiv}CFc+)/\alpha^2(Fc\text{–}Fc) = ca.\ 0.3$], the value observed for complex **6** indicates that there is a moderate electron-delocalization between the metal centres in spite of the long metal–metal distance in **6**. This suggests that increasing electron density on metal centres leads to moderate electron-delocalization between them, since the η-C_5Me_5 ligand has more electron donating effect than the η-C_5H_5 ligand.

In the Mössbauer spectrum at 78 K, the carbonyl complex **1** showed two doublets (QS = 1.88, IS = −0.04 and QS = 2.32, IS = 0.42 mm s^{-1}). The doublet of QS = 2.32 mm s^{-1} is assigned to the Fe atom of the ferrocenyl moiety, since the QS value is typical for the substituted ferrocene. The other doublet is therefore assigned to the signal due to the Fe atom of the $[(\eta\text{-}C_5H_5)Fe(CO)_2]$ moiety. The QS value (1.88 mm s^{-1}) is in accordance with that (1.88 mm s^{-1}) reported for $(\eta\text{-}C_5H_5)\text{-}Fe(CO)_2Cl$ [20]. The oxidized complex **5** also afforded one doublet (QS = 1.89, IS = −0.06 mm

s^{-1}) and a broad singlet (IS = 0.59 mm s^{-1}). On the oxidation of **1** to **5**, the doublet of QS = 1.88 mm s^{-1} remains intact, but the doublet of QS = 2.32 mm s^{-1} disappears and a broad singlet newly appears at IS = 0.59 mm s^{-1} [21]. This suggests that the oxidation of complex **1** takes place at the Fe atom of the ferrocene moiety, the cation-radical site remains to localize on the original Fe site, and there is only slight electron-delocalization, if any, between two Fe atoms. No averaged spectrum was observed even on warming to room temperature.

The ESR spectrum of complex **5** was recorded at 58 K for the powdered sample and showed a polycrystalline line shape which could be fitted with an axial g tensor. The observed values $g_{\parallel} = 3.81$ and $g_{\perp} = 1.68$ are in the range of 3.2–4.35 of the $g_{\parallel}$ value and 1.91–1.26 of the $g_{\perp}$ value for ferrocenium and biferrocenium ions, respectively [22,23]. This suggests that the ferrocenyl moiety was oxidized in oxidation of complex **1**. Curiously, on cooling of the sample to an even lower temperature an additional pair of signals appeared, which showed g = 3.55 and g = 1.30 at 5.5 K. We cannot yet explain this phenomenon, because other spectral data indicate that the unpaired electron generated by the oxidation is localized on the Fe atom of the ferrocenyl moiety and that there is little, if any, electron-delocalization between the two Fe atoms in **5**.

In summary, the cyclic voltammograms of new Fe^{II} ferrocenylacetylide complexes suggested the stabilization of the one electron-oxidized species. The oxidation of **1** and **2** with DDQ gave the stable complexes **5** and **6**. The α^2 value calculated from the IT band observed in the NIR region suggested that the one electron-oxidized complexes **5** and **6** are a class II type of the mixed-valence complex with a partial electron-delocalization. The IR, ESR, and Mössbauer spectra of **5** suggested localization of the unpaired-electron at the Fe atom of the ferrocenyl moiety.

3. Experimental section

3.1. General

Visible and near-IR spectra were recorded with a Shimadzu 365 spectrometer and IR spectra with a Hitachi 270-50 spectrometer. ^{1}H and ^{13}C NMR spectra were measured with a Bruker AM400 instrument. Electrochemical measurements were by cyclic voltammetry in a solution of 0.1 M tetrabutylammonium perchlorate in acetonitrile under nitrogen at 25°C, using a standard three-electrode cell on a BAS CV-27 analyzer. All potentials were measured *vs.* a $Ag/AgNO_3$ (0.05 M) electrode and the scan rate was 100 mV s^{-1}. Mössbauer spectra were measured with a constant acceleration-type spectrometer and the velocity scale was calibrated on the spectrum of metallic iron at room temperature. Spectra were fitted with Lorenzian-line shapes by least-squares. The isomer shifts were reported with respect to α-Fe foil at room temperature. The error of the values of isomer shift and quadrupole splitting was estimated as within ± 0.02 mm s^{-1}.

Ferrocenylacetylene [24,25], $(\eta\text{-}C_5H_5)(CO)_2FeI$ [26], $(\eta\text{-}C_5Me_5)(CO)_2FeI$ [27] and $(\eta\text{-}C_5H_5)[P(OMe)_3]_2FeI$ [28] were prepared according to the methods described in the literature. All experiments were undertaken in a nitrogen-saturated solvent under nitrogen.

3.2. $(\eta\text{-}C_5H_5)(CO)_2FeCCFc$ (1)

Ferrocenylacetylene (168 mg, 0.8 mmol) was dissolved in dry THF (3.5 ml) and cooled at −78°C. To the solution was added methyllithium (1.3 ml of 1.4 M solution in diethylether, 2.1 mmol). After stirring for 1 h, a solution of $(\eta\text{-}C_5H_5)(CO)_2FeI$ (200 mg, 0.66 mmol) in dry THF (6 ml) below −30°C was added dropwise. After the solution had been stirred for 45 min at −30°C, it was poured into the water and the mixture was extracted with dichloromethane. The extract was dried over $MgSO_4$ and evaporated. The residue was chromatographed on deactivated alumina to give the title compound (213 mg, 84%) as yellow crystals after recrystallization from dichloromethane/hexane. M.p. 143°C. (Found: C, 58.85; H, 3.57. $C_{19}H_{14}O_2Fe_2$ calcd.: C, 59.12; H, 3.66%). IR (CH_2Cl_2): 2109 (C≡C), 2040, 1991 (CO) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.03 (s, 5H, $\eta\text{-}C_5H_5$), 4.26 (t, J = 1.7 Hz, 2H), 4.01 (t, J = 1.7 Hz, 2H) and 4.13 (s, 5H) (Fc). ^{13}C NMR ($CDCl_3$): δ 66.69 (Fc-β), 69.99 (Fc-unsub.), 70.83 (Fc-α), 71.89 (Fc-*ipso*), 85.12 ($\eta\text{-}C_5H_5$), 79.58, 111.73 (C≡C), 212.66 (CO) ppm.

3.3. $(C_5Me_5)(CO)_2FeCCFc$ (2)

This complex was prepared by a method similar to that for **1**. Orange crystals (60%). M.p. 143°C. (Found: C, 62.84; H, 5.28. $C_{24}H_{29}O_2Fe_2$ calcd.: C, 63.19; H, 5.30%). IR (CH_2Cl_2): 2099 (C≡C), 2016, and 1966 cm^{-1} (CO). ^{1}H NMR ($CDCl_3$): δ 1.89 ($\eta\text{-}C_5Me_5$), 4.26 (t, J = 1.7 Hz, 2H), 4.00 (t, J = 1.7 Hz, 2H), and 4.13 (s, 5H) (Fc). ^{13}C NMR ($CDCl_3$): δ 9.93 ($\eta\text{-}C_5Me_5$), 66.61 (Fc-β), 69.48 (Fc-unsub.), 70.63 (Fc-α), 73.18 (Fc-*ipso*), 96.77 ($\eta\text{-}C_5Me_5$), 98.03, 107.26 (C≡C) and 214.66 (CO) ppm.

3.4. $(\eta\text{-}C_5H_5)(Ph_3P)(CO)FeCCFc$ (3)

A solution of complex **1** (50 mg, 0.13 mmol) and PPh_3 (34 mg, 0.13 mmol) in ether (15 ml) and hexane (15 ml) was irradiated by a 100 W high-pressure Hg lamp for 20 min under bubbling of nitrogen. After the solution had been condensed, it was filtered. The filtrate was evaporated and the residue was crystallized from dichloromethane/hexane. Orange crystals (32.2 mg, 40.1%). M.p. 155°C (dec) (Found: C, 67.61; H, 4.48. $C_{36}H_{29}OPFe_2 \cdot 1/3CH_2Cl_2$ calcd. C, 67.28; H, 4.61%). IR (CH_2Cl_2): 2092 (C≡C), 1943 cm^{-1} (CO). ^1H NMR ($CDCl_3$) δ 3.97 (bs, 2H, Fc), 3.88 (bs, 2H, Fc), 3.84 (s, 5H, Fc), 4.49 (s, 5H, η-C_5H_5), and 7.72–7.43 (m, 15H, Ph). ^{13}C NMR ($CDCl_3$) δ 66.22 (Fc), 68.93 (Fc-unsub.), 69.90 (Fc), 74.00 (Fc-*ipso*), 84.33 (η-C_5H_5), 98.45, 114.40 (each, C≡C), 127.96–136.50 (Ph), 219.74 (CO).

3.5. $(\eta\text{-}C_5H_5)[(CH_3O)_3P]_2FeCCFc$ (4)

This complex was prepared by a similar method to that described in 3.2. Orange crystals (170 mg, 74%). M.p. 143°C. (Found: C, 47.52; H, 5.35. $C_{23}H_{32}O_6P_2Fe_2$ calcd.: C, 47.78; H, 5.58%). IR (CH_2Cl_2): 2074 cm^{-1} (C≡C). ^1H NMR ($CDCl_3$): δ 3.77 (t, 9H, OCH_3), 3.93 (bs, 2H, Fc), 4.04 (bs, 2H, Fc), 4.07 (s, 5H, Fc-unsub.), 4.29 (s, 5H, η-C_5H_5). ^{13}C NMR ($CDCl_3$): δ 52.41 (OCH_3), 66.07 (Fc), 68.92 (Fc-unsub.), 69.49 (Fc), 75.37 (Fc-*ipso*) and 79.95 ppm (η-C_5H_5).

3.6. $[(\eta\text{-}C_5H_5)(CO)_2FeCCFc]^+[C_6O_2Cl_2(CN)_2]^-$ (5)

To a solution of complex 1 (50 mg, 0.13 mmol) in CH_2Cl_2 (1 ml) and benzene (12 ml) was slowly added a solution of dichlorodicyanobenzoquinone (34.1 mg, 0.15 mmol), freshly recrystallized from dichloromethane, on an ice-water bath under nitrogen. After stirring for 15 min, the resulting red-brown precipitates were filtered. Yield: 75 mg (94%). M.p. *ca.* 150°C (dec). (Found: C, 52.86; H, 2.33; N, 4.77. $C_{27}H_{14}C_{12}N_2O_4Fe_2$ calcd.: C, 52.90; H, 2.30; N, 4.56%). IR (CH_2Cl_2): 2217 (CN), 2090 (C≡C), 2041 and 2009 cm^{-1} (CO). Vis-NIR (CH_2Cl_2): 450 (ε 4240), 575 (2270) and 1060 nm (680).

3.7. $[(\eta\text{-}C_5Me_5)(CO)_2FeCCFc]^+[C_6H_4Cl_2(CN)_2]^-$ (6)

This complex was similarly prepared from complex 2 according to the method described above. Yield: 58 mg (78%). M.p. *ca.* 135°C (dec). (Found: C, 55.91; H, 3.63; N, 3.92%. $C_{32}H_{24}Cl_2N_2O_4Fe$ calcd.: C, 56.26; H, 3.54; N, 4.10%). IR (CH_2Cl_2) 2211 (CN), 2072 (C≡C), 2016 and 1982 cm^{-1} (CO). Vis-NIR (CH_2Cl_2): 460 (ε 6430), 525 (6690) and 1250 nm (1470).

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