ELSEVIER

Journal of Organometallic Chemistry 637–639 (2001) 258–265

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Characterization and electrochemical study of bis(ferrocenes) with a furan spacer and ferrocenophanes prepared from α-bromoacetyl substituted ferrocenes

P. Molina *, A. Tárraga *, D. Curiel, M.D. Velasco

Departamento de Química Orgánica, Facultad de Química, Universidad de Murcia, Campus de Espinardo, Espinardo 30071, Murcia, Spain

Received 2 January 2001; received in revised form 20 February 2001; accepted 21 February 2001

Abstract

The bis(ferrocene) derivative 3-bromo-2,4-bis(ferrocenyl)furan (**3**) was prepared from α-bromoacetylferrocene (**1**) by basic treatment. The heterotrimetallic complex **7** containing two ferrocene moieties and Pd(II) was synthesized by oxidative addition of **3** with a zerovalent palladium precursor. These stable solids were characterized throroughly by spectroscopic means and electrochemical methods (CV and DPV). The new [4]-ferrocenophane (**8**), with all sp^{2}C bridges was prepared easily from 1,1′-bis(α-bromoacetyl)ferrocene (**2**) by treatment with K^{t}BuO whereas the reaction with Na_2S provides a mixture of 3-thia-[5]ferrocenophane (**9**), as the major product, and [5,5]ferrocenophane (**10**), as the minor product.

Keywords: α-Bromoacetyl substituted ferrocenes; Bis(ferrocenes); Ferrocenophanes; Palladium; Electrochemistry

---

1. Introduction

The concept of ferrocene acting as a three-dimensional metal-containing equivalent of benzene has prompted the synthesis of a various kind of ferrocene-based compounds which have found many applications in synthetic organic chemistry and material sciences, owing to stable coordination of the cyclopentadienyl ligands, possible induction of chirality in the molecules and reversible redox behaviour of the metal center [1]. Fundamental to their success has been the development of simple and viable synthetic methods, which allow the functionalization of the ferrocene nucleous either at the cyclopentadienyl ring or at the side chain. In this context, the α-chloroacetyl ferrocene has recently been used as starting material for the preparation of chiral ferrocenyl substituted β-aminocyclopentadienes [2]. However, the only method reported for its preparation [3], which is based on the Friedel–Crafts acylation of ferrocene with acetyl chloride in the presence of aluminium chloride, affords the desired α-chloroacetylferrocene in 26% yield together with acetylferrocene.

During the course of a recent project aimed at the preparation of ferrocenyl-substituted azaheterocycles [4], we reported the preparation of α-bromoacetylferrocene (**1**) [5] and 1,1′-bis(α-bromoacetyl)ferrocene (**2**) [6] in yields higher than 80%. Compounds **1** and **2** are converted easily into the corresponding azide derivatives, which have proven to be useful building blocks for the preparation of a number of homobi and homotrimetallic oxazolo-ferrocene complexes.

Structurally, compounds **1** and **2** can be considered as phenacyl bromides in which the benzene ring has been replaced by a ferrocene unit. We wish to report now that compounds **1** and **2** may themselves be valuable starting materials for further elaboration taking into account that α-halocarbonyl compounds exhibit a rich chemistry [7].

It is well known that base induced reactions as well as electrochemical reduction of phenacyl halides lead to rearranged and unrearranged products. Although a considerable amount of work has been done with the reactions of various phenacyl halides in the presence of base [8], the product(s) obtained seemingly depend

---

* Corresponding authors. Tel.: +34-968-367-496; fax: +34-968-364-149.

E-mail address: pmolina@um.es (P. Molina).

0022-328X/01/$ - see front matter © 2001 Elsevier Science B.V. All rights reserved.
PII: S0022-328X(01)00913-5

upon the base used as well as the solvent, with no apparent correlation.

In this context, we have found that α-bromoacetylferrocene (**1**) is a useful building block for the preparation of a novel kind of homobi- and heterotrimetallic ferrocene complexes, whereas the 1,1′-bis(α-bromoacetyl)ferrocene (**2**) allows the preparation of new kinds of ferrocenephanes.

2. Results and discussion

2.1. Preparation of homobi- and heterotrimetallic ferrocene derivatives

When a solution of α-bromoacetylferrocene (**1**) in dry THF was treated with an excess of LDA (1:5) at − 78 °C under N_2, 3-bromo-2,4-bis(ferrocenyl)furan (**3**) was isolated as an orange air stable solid in 26% yield after chromatographic separation. However, when compound **1** was treated with a slight excess of K^{t}BuO (1:1.6) in THF from 0 °C to room temperature, *trans*-1,2,3-tris(ferrocenecarbonyl)cyclopropane (**4**) was obtained in 15% yield as an orange precipitated solid. From the crude mixture compound **3** was also isolated in 22% yield after chromatographic separation (Scheme 1).

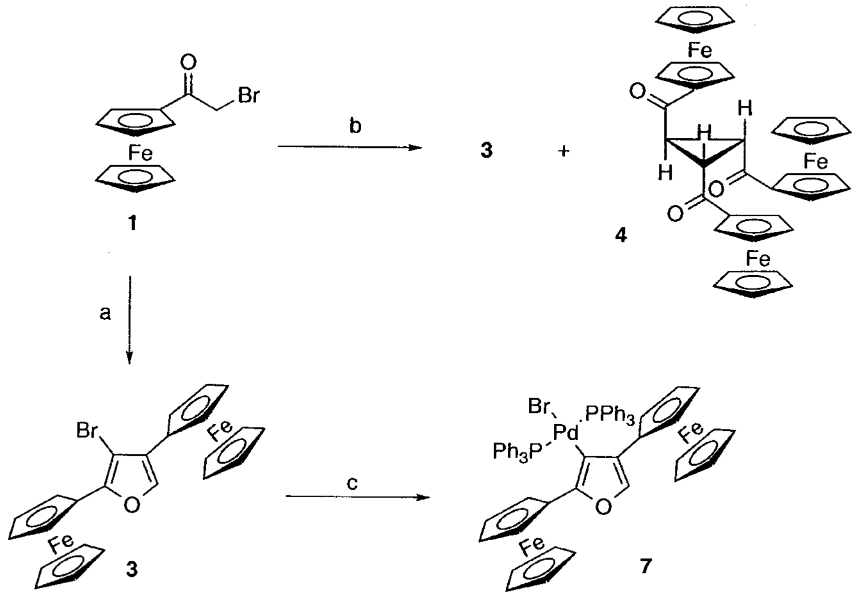
Compounds **3** and **4** were characterized by ^{1}H-, ^{13}C-NMR spectroscopy, EI MS and elemental analyses. The results are in accordance with the proposed molecular formulations. In the ^{1}H-NMR spectrum of compound **3**, the ferrocenyl groups show clearly two sets of three well-separated signals This non-equivalence of the two ferrocenyl groups in compound **3** is also showed in the ^{13}C-NMR spectrum.

The ^{1}H-NMR spectrum of the tris(ferrocene) compound **4** shows two sets of three well-separated signals in 2:1 ratio, characteristics of mono-substituted ferrocenes indicating that two ferrocenyl groups are magnetically equivalents. The ^{13}C-NMR spectrum also reveals the existence in the molecule of two different types of monosubstituted ferrocene, carbonyl groups, and cyclopropane carbon atoms.

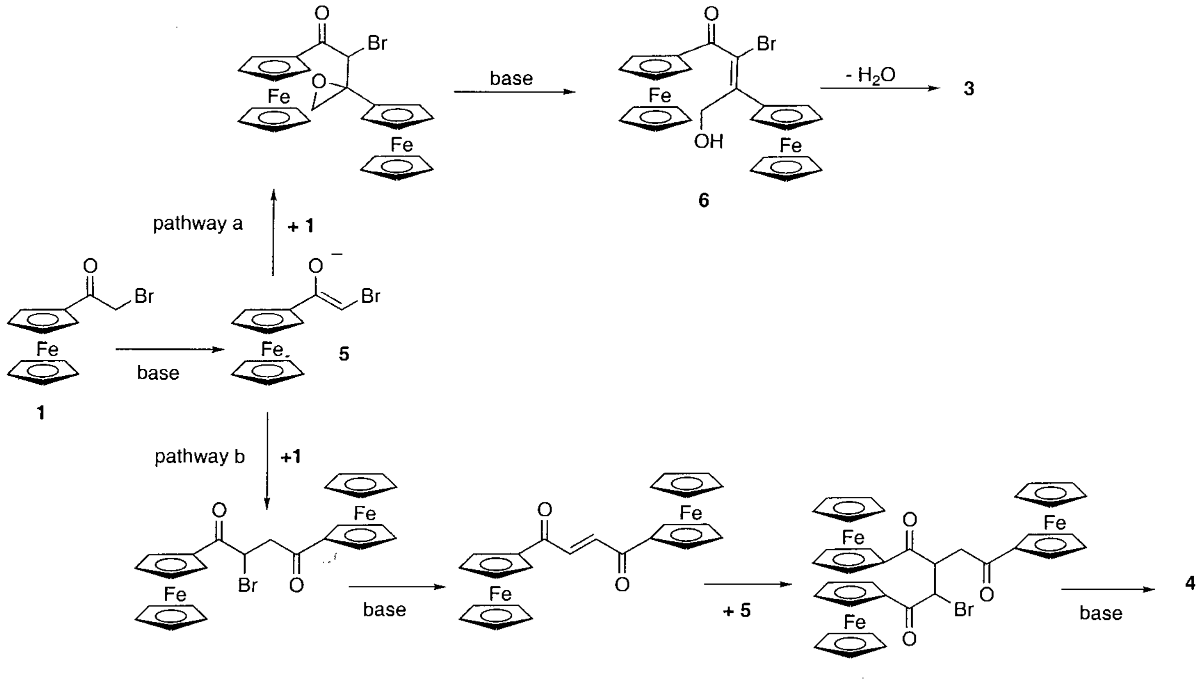
In Scheme 2 we address the question of how compounds **3** and **4** are formed. A tentative mechanism could involve initial formation of the enolate **5** in the basic medium, which reacts with one equivalent of **1** across the carbonyl group (pathway a) to give a ketoepoxide. This compound undergoes ring-opening of the oxirane ring under basic conditions to give the allylic alcohol **6**, which by cyclization and further dehydration affords **3**. Isolation of compound **6** in 22% yield as well as its conversion into **3** by heating, strongly support this mechanisms.

Enolate **5** can also reacts with one equivalent of starting material **1** by displacement of the bromide atom (pathway b) to give a bromodiketone, which under the basic conditions undergoes elimination of HBr to give an enediketone. Michael addition of a second equivalent of enolate **5** on the enediketone yields a tris(ferrocene) compound which leads to the cyclopropane derivative **4** under basic conditions.

In spite of the low yields for the conversion **1** → **3** and **1** → **4** considering the number of steps involved and the relatively complex structures formed they may be considered as good. Although a number of ferrocene complexes containing thiophene and furan in the conjugation chain have been prepared [9], compound **3** represents the first example reported of a bis(ferrocene)



Scheme 1. (a) LDA, THF, − 78 °C → r.t. (b) K^{t}BuO, THF, 0 °C → r.t. (c) $Pd(PPh_3)_4$, C_6H_6, r.t.



Scheme 2.

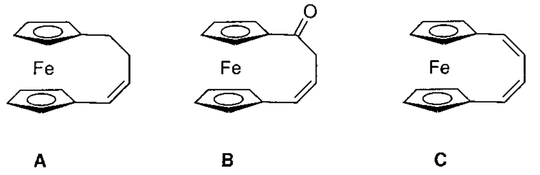
bearing a furan spacer. This compound can be considered as relatively electron rich, since the furan ring is linked directly to two ferrocene moieties, an electron donating organometallic group. An additional structural feature of compound **3** is the presence of a bromine-substituted furan ring, which pave the way to the preparation of a novel kind of bis(ferrocene)end-capped palladium (II) complex with a furan spacer.

The utility of zerovalent $Pd(PPh_3)_4$ in the preparation of *trans*-$Pd(PPh_3)_2(R)X$ complexes (X = halide and R = aryl, heteroaryl) is well documented [10]. It is that electron-withdrawing groups *para* to the C–X bond of the aryl derivative activate the aryl–X bond for oxidative addition of $Pd(PPh_3)_4$. Conversely, electron-donating groups suppress the reactivity of aryl halides. Owing to the electron-donating nature of ferrocene as well as the presence of two sterically bulky ferrocene units at the adjacent positions, it was expected that bromofuran **3** would exhibit reduced reactivity towards $Pd(PPh_3)_4$. It was found, however, that the reactivity is very similar to that observed for bromothiophenes [11]. Thus, reaction of one equivalent of $Pd(PPh_3)_4$ with **3** in benzene at reflux temperature generates the orange *trans*-$Pd(PPh_3)_2$(f)Br [f = 2,4-bis(ferrocenyl)furan] complex **7** in 55% yield after chromatographic purification. This heterotrimetallic complex is air- and moisture-stable solid.

Complex **7** was characterized by ^{1}H-, ^{13}C- and ^{31}P-NMR spectroscopy, MS in FAB^{+} mode and elemental analysis. Both ^{1}H- and ^{13}C-NMR spectra show the non-equivalence of the two ferrocene units. The ^{31}P-NMR spectrum displays a downfield signal at 19.4 ppm, referenced to 85% polyphosphoric (δ 0 ppm) and which is consistent with what is observed for the *trans*-oriented phosphines found in *trans*-$Pd(PPh_3)_2(R)X$ (X = bromine, R = thiophene) [9b]. The MS in FAB^{+} mode shows a peak at 1146 due to the $[M^{+} + 1]$.

2.2. Preparation of ferrocenophanes

The most prevalent organometallic analogs of cyclophanes are the ferrocenophanes with bivalve-like structure, in which the two cyclopentadienyl groups of ferrocene are joined by an atomic or a molecular bridge. Many of the desirable characteristics of the parent ferrocene are retained in the ferrocenophanes and they are expected to show unique chemical properties owing to functionality of the side arm [12]. Indeed, there have been many different classes of ferrocenophanes described, most of them possessing carbon-based bridges exclusively [13], while others contain heteroaromatic atoms. In particular, ferrocenophanes with an unsaturated bridge have been exploited in ring-opening methatesis polymerization (ROMP) [14]. This approach is particularly attractive for generating conjugated polymers because the unsaturation in the monomer is retained in the resulting polymer. Unsaturated [4]ferrocenophanes represent attractive candidates for the generation of conjugated organometallic polymers via ROMP. Only three types of unsaturated [4]ferrocenophanes have been described: type **A** with a mono-olefinic bridge, type **B** with a keto mono-olefinic bridge [15] and type **C**, having a di-olefinic bridge [14,16] (block).



Block

We now report here the preparation of a novel type of unsaturated [4]ferrocenophane (**8**) having a benzoquinone-like structure. This compound was easily prepared from 1,1′-bis(α-bromoacetyl)ferrocene (**2**) by treatment with an excess of K^{t}BuO (1:2.2) in THF at room temperature. Compound **8** was isolated in 30% yield after chromatographic separation as a red air-stable solid (Scheme 3). TLC of the reaction mixture revealed that compound **8** was formed as the only soluble product. The conversion **2** → **8** involves an intramolecular cyclization reaction between α-bromoacetyl groups on the opposing cyclopentadienyl rings followed by HBr elimination.

The IR spectrum shows a strong absorption band at 1626 cm^{-1} due to the carbonyl group. The ^{1}H-NMR spectrum displays only three signals: two pseudotriplets at 4.57 and 4.69 ppm, corresponding to the ferrocene hydrogen atoms and one singlet at 6.67 ppm, due to the olefinic hydrogen atoms. In the ^{13}C-NMR spectrum the ferrocene carbon atoms appeat at 75.4, 75.6 and 78.4 ppm, respectively, whereas the olefinic and carbonyl carbon atoms appear at 136.0 and 192.7 ppm, respectively. The MS in FAB$^+$ mode shows the corresponding [M$^+$ + 1] peak.

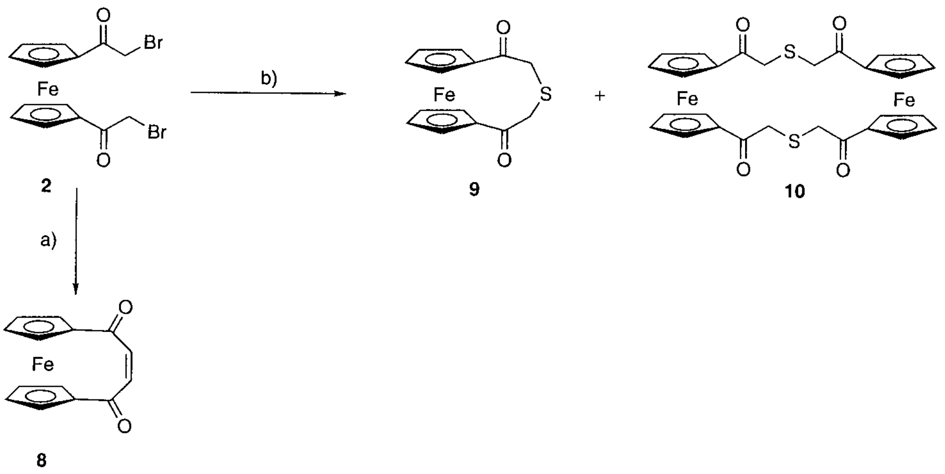
On the other hand, compound **2** undergoes intra- and intermolecular cyclizations when it was treated with Na_2S in THF–H_2O giving rise to a mixture of 3-thia[5]ferrocenophane (**9**) and [5,5]ferrocenophane (**10**), respectively. Compounds **9** and **10** were separated easily by colum chromatography in 33 and 11% yield, respectively, and were characterized by ^{1}H-, ^{13}C-NMR spectroscopy, MS and elemental analyses (see Section 3).

2.3. Electrochemistry

The electrochemical behaviour of bis(ferrocene) (**3**), tris(ferrocene) (**4**) and the palladium(II) complex **7** has been studied by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) to investigate the possibility of electronic communication between the metal centers. Significant metal–metal interaction would be indicated by two or three distinct oxidation waves in either CV or DPV.

Despite the fact that the tris(ferrocene) ligand **4** contains three ferrocenyl units, cyclic voltammetry responses of **4** with scan rate increasing from 0.02 to 1.00 V s^{-1} displays a single anodic process with features of chemical reversibility. The oxidation potential of **4** shows an anodic shift of the Fe(III)/Fe(II) couple compared with the ferrocene/ferrocinium ($E^{\circ\prime} = 0.696$ V vs. SCE) that is expected of the electron withdrawing effect of the carbonyl function attached to ferrocene. The cyclic voltammogram of **4** exhibits a peak-to-peak separation (116 mV at a scan rate of 200 mV s^{-1}) by which may be termed as a quasi-reversible redox process, bearing in mind that it is likely not affected by the presence of uncompensated solution resistances, as is evident from the oxidation step of ferrocene used as an internal reference (66 mV at the same voltammetric conditions).

Bis(ferrocene) (**3**) and its Pd(II) complex **7** exhibit two redox processes in either CV or DPV (Fig. 1). The peaks separation and virtually equal currents indicate two reversible one-electron oxidations. The results of



Scheme 3. (a) K^{t}BuO, THF, 0 °C → r.t. (b) Na_2S, MeOH/H_2O, 55 °C.

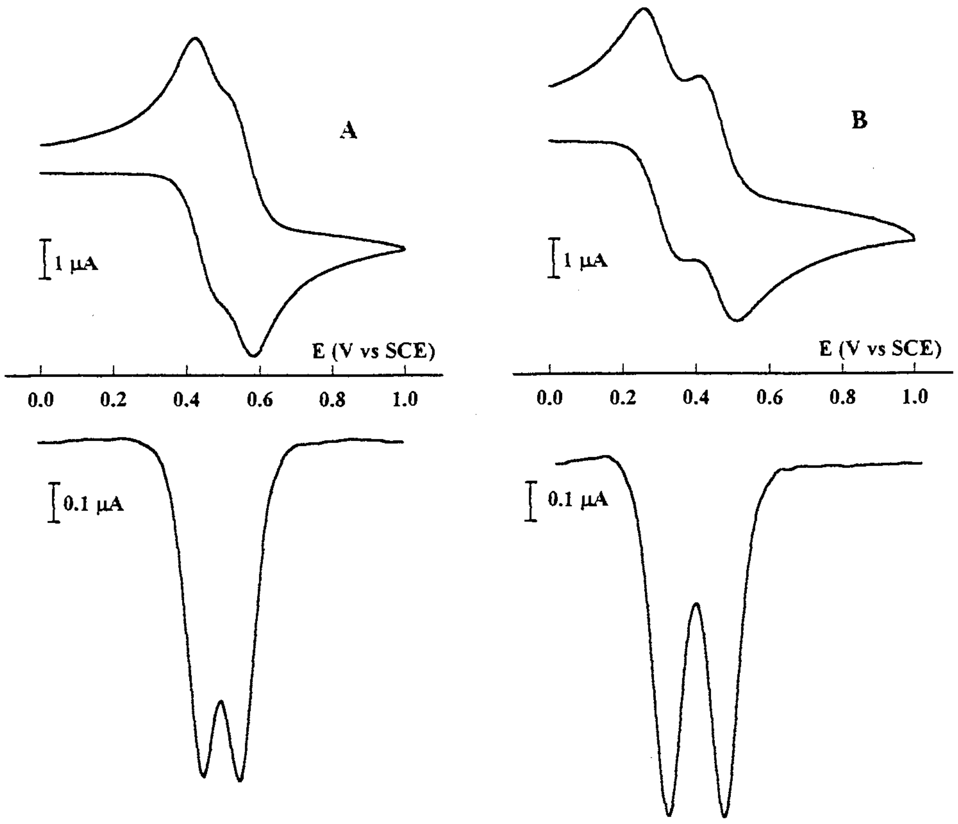


Fig. 1. Cyclic and differential pulse voltammograms of bis(ferrocenes), (A) ligand **3** and (B) complex **7**. Scan rates: cyclic voltammogram, 0.2 V s^{-1}; DPV, 0.004 V s^{-1}.

these analyses, outlined by the Richardson and Taube method [17] are presented in Table 1.

Quite interestingly, half-peak width (from DPV) between the one-electron oxidations of the two ferrocenyl groups in the complex **7** is slightly higher than in the free ligand **3**, 248 versus 204 mV.

The formal potential of **7** is lower than those for **3**, implying the presence of delocalization of Pd electron density into the spacer furan ring through a dπ–pπ interaction. The less positive oxidation process is ascribed to the Fe(III)/Fe(II) couple of the ferrocene placed at position 2 of the furan ring. The reason for this assumption is that an effective conjugation through a small length favors electron transfer from Pd to ferrocene and thus the oxidation (Scheme 4).

Finally, cyclic voltammetry measurements of ferrocene **8** carried out from 0.0 to + 1.4 V versus SCE show an essentially reversible oxidation process at scan speeds > 200 mV s^{-1} ($E^{\circ\prime} = 0.607$ V vs. Fe^{+}/Fe at 200 mV s^{-1}, $\Delta E_p = 78$ mV). At slower scan rates, however, the i_{pa}/i_{pc} ratio drops below 1 and the cyclic voltammograms show only a well-defined anodic peak ($E_{pa} =$ 618 vs. Fe/Fe^{+} at $v < 80$ mV s^{-1}). This result contrasts with that observed for ferrocene used as an internal reference for which the cyclic voltammograms display, respectively, two well-defined (one anodic and one cathodic) peaks. This behavior would indicate that the oxidative process on the electrode may be associated with a subsequent chemical reaction (EC mechanism).

3. Experimental

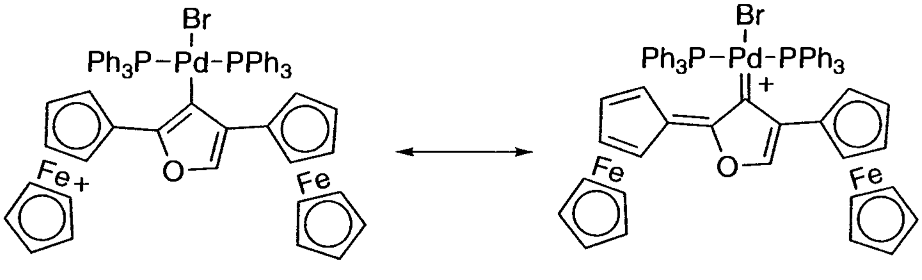
3.1. General

All melting points were determined on a Kofler hot-plate melting point apparatus and are uncorrected. IR spectra were obtained on Nujol emulsions on a Nicolet Impact 400 spectrophotometer. ^{1}H-, ^{13}C- and ^{31}P-NMR spectra were recorded at 299.95, 74.43 and 121.42 MHz, respectively, on a Varian UNITY-300 spectrometer. Chemical shifts refer to signals of tetramethylsilane

Table 1
Formal electrode potentials (V) for the compounds **3** and **7**

Compound	Width (mV)	$E^{\circ\prime}(1)$ [a]	$E^{\circ\prime}(2)$ [a]	$\Delta E^{\circ\prime}$ (mV)
3	204	+0.433	+0.549	116
7	248	+0.296	+0.453	157
FcH	92	+0.405	–	–

[a] From DPV, vs. SCE; pulse amplitude, 10 mV. Scan rate 0.004 V s^{-1}.



Scheme 4.

in the case of ^{1}H and ^{13}C spectra and to 85% aqueous phosphoric acid in the case of ^{31}P spectra. The EI and FAB$^+$ mass spectra were carried out on a VG-Autospec spectrometer. Cyclic voltammetry was perform with a conventional three-electrode configuration consisting of platinum working and auxiliary electrodes and a SCE reference electrode. A mixture of CH_2Cl_2–CH_3CN (1:1 v/v) was employed as solvent using 0.1 M $(n\text{-}C_4H_9)_4ClO_4$ as supporting electrolyte. The experiments were carried out with a 10^{-3} M solution of sample. The electrochemical solutions were bubbled with nitrogen before each experimental and through the investigation. The $E_{1/2}$ values were determined as $1/2(E_{pa}+E_{pc})$, where E_{pa} and E_{pc} are the anodic and cathodic peak potentials, respectively. Differential pulse voltammograms were recorded under a pulse amplitude of 10 mV and a pulse width of 50 ms.

3.2. 3-Bromo-2,4-bis(ferrocenyl)furan (3)

To a cooled (−78 °C) solution of LDA (4.9 mol) in anhydrous THF (10 ml) and under nitrogen, a solution of α-bromoacetylferrocene (**1**) (0.3 g, 0.98 mmol) in the same solvent (5 ml) was added dropwise. The resulting mixture was stirred at that temperature for 1 h and then allowed to warm to room temperature (r.t.) and stirred for 24 h. Then, water (10 ml) was added and the mixture was extracted with dichloromethane (2 × 25 ml). The organic layers were separated, dried ($MgSO_4$) and, after filtration, the solvent was removed under reduced pressure. The residue was then chromatographed on a silica gel column using CH_2Cl_2–ethyl acetate (20:1) as eluent to give **3**; ($R_f = 0.76$) yield 26%; m.p. 220 °C (decomposes); IR (Nujol): ν 1454, 1140, 1105, 1033, 1005, 825, cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 7.38 (s, 1H), 4.95 (t, 2H, $J=1.8$ Hz), 4.66 (t, 2H, $J=1.8$ Hz), 4.33 (t, 2H, $J=1.8$ Hz), 4.28 (t, 2H, $J=1.8$ Hz), 4.17 (s, 5H), 4.16 (s, 5H); ^{13}C-NMR ($CDCl_3$): δ 151.0 (C2), 136.6 (CH), 124.9 (C4), 95.0 (C3), 76.1 (*ipso*-Fec), 74.6 (*ipso*-Fec), 69.5 (5 × CH, C_5H_5), 69.4 (5 × CH, C_5H_5), 68.8 (2 × CH, C_5H_4), 68.3 (2 × CH, C_5H_4), 66.8 (2 × CH, C_5H_4), 66.5 (2 × CH, C_5H_4); EI mass spectrum: m/z (%) 516 ([M$^+$ + 2], 92), 514 ([M$^+$] 100), 314 (31), 286 (29), 257 (13), 165 (30), 121 (20). Anal. Calc. for $C_{24}H_{19}BrFe_2O$: C, 55.97; H, 3.72. Found: C, 55.80; H, 3.54%.

3.3. Reaction of α-bromoacetylferrocene with K^{t}BuO

To a cooled (0 °C) solution of potassium *t*-butoxide (0.18 g, 1.56 mmol) in anhydrous THF (10 ml) a solution of α-bromoacetylferrocene (**1**) (0.3 g, 0.98 mmol) in the same solvent (5 ml) was added dropwise, under nitrogen. The resultant mixture was allowed to warm to r.t. and stirred for 24 h appearing an orange solid which was separated by filtration and identified as *trans*-1,2,3-tris(ferrocenecarbonyl)cyclopropane (**4**). Then, water (10 ml) was added and the mixture was extracted with dichloromethane (2 × 25 ml). The organic layers were dried ($MgSO_4$) and the solvent was removed under reduced pressure. The resulting residue was then chromatographed on a silica gel column using ethyl acetate–*n*-hexane (1:3) as eluent to give 3-bromo-2,4-bis(ferrocenyl)furan (**3**) in 22% yield, identified as above.

3.3.1. trans-1,2,3-Tris(ferrocenecarbonyl)cyclopropane (4)

Yield 15%; m.p. 230 °C (decomposes); IR (Nujol): ν 1671, 1642, 1454, 1316, 1249, 1108, 1085, 1031, 824, 713, cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 5.01 (t, 2H, $J=1.8$ Hz), 4.85 (bs, 4H), 4.63 (t, 2H, $J=1.8$ Hz), 4.51 (bs, 4H), 4.30 (s, 5H), 4.19 (s, 10H), 3.74 (t, 1H, $J=5.5$ Hz), 3.36 (d, 2H, $J=5.5$ Hz); ^{13}C-NMR ($CDCl_3$): δ 196.8 (2 × C=O), 195.3 (C=O), 79.2 (2 × *ipso*-Fec), 78.8 (*ipso*-Fec), 73.3 (2 × CH, C_5H_4), 72.5 (4 × CH, C_5H_4), 70.3 (5 × CH, C_5H_5), 70.1 (2 × CH, C_5H_4), 69.9 (10 × CH, C_5H_5), 69.1 (4 × CH, C_5H_4), 36.9 (2 × CH), 31.3 (CH); FAB$^+$ mass spectrum: m/z (%) 679 ([M$^+$ + 1], 83), 678 ([M$^+$], 100). Anal. Calc. for $C_{36}H_{30}Fe_3O_3$: C, 63.76; H, 4.46. Found: C, 63.55; H, 4.28%.

3.4. cis-2-Bromo-1,3-bis(ferrocenyl)-4-hydroxy-2-buten-1-one (6)

To a cooled (−78 °C) solution of LDA (1.56 mmol) in anhydrous THF (10 ml) and under nitrogen, a solution of α-bromoacetylferrocene (**1**) (0.4 g, 1.3

mmol) in the same solvent (5 ml) was added dropwise. The resulting mixture was stirred at that temperature for 1 h and then allowed to warm to r.t. After stirring at that temperature for 24 h the solvent was removed under reduced pressure and the residue was then chromatographed on a silica gel column using ethyl acetate–*n*-hexane (1:2) as eluent to give **6** as a purple oil; ($R_f = 0.45$) yield 22%; IR (Nujol): ν 3432, 1644, 1445, 1377, 1264, 1107, 1036, 1006, 914, 827, 733 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 4.74 (s, 2H), 4.56 (t, 2H, $J = 1.9$ Hz), 4.41 (t, 2H, $J = 1.9$ Hz), 4.22 (s, 5H), 4.20 (t, 2H, $J = 1.75$ Hz), 4.14–4.16 (m, 7H), 2.78 (bs, 1H); ^{13}C-NMR ($CDCl_3$): δ 197.4 (C = O), 141.2 (q), 115.1 (q), 83.7 (*ipso*-Fec), 76.7 (*ipso*-Fec), 72.8 (2 × CH, C_5H_4), 70.6 (5 × CH, C_5H_5), 70.2 (2 × CH, C_5H_4), 69.7 (2 × CH, C_5H_4), 69.2 (5 × CH, C_5H_5), 68.6 (2 × CH, C_5H_4), 66.4 (CH_2); EI mass spectrum: *m*/*z* (%) 534 ([$M^+ + 2$], 5), 532 ([M^+], 5), 516 (96), 514 (100), 436 (21), 314 (53), 286 (50), 257 (21), 165 (51), 149 (44), 121 (44). Anal. Calc. for $C_{24}H_{21}BrFe_2O_2$: C, 54.08; H, 3.97. Found: C, 54.15; H, 3.78%.

3.5. Synthesis of the complex **7**

To a solution of 3-bromo-2,4-bis(ferrocenyl)furan (**3**) (0.05 g, 0.1 mol) in deoxygenated dry benzene (10 ml) $Pd(Ph_3P)_4$ (0.22 g, 0.2 mmol) was added. The reaction mixture was heated at reflux temperature for 16 h and the solvent was removed under vacuum. The residue was chromatographed on a silica gel column using CH_2Cl_2–ethyl acetate (20:1) as eluent to give **7**. Yield 55%; m.p. 187–189 °C; IR (Nujol): ν 1482, 1434, 1109, 1092, 1001, 863, 819, 740 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 8.5–6.5 (m, 31H), 4.21 (t, 2H, $J = 1.8$ Hz), 4.10 (t, 2H, $J = 1.8$ Hz), 3.92 (s, 4H), 3.77 (s, 5H), 3.66 (s, 5H); ^{13}C-NMR ($CDCl_3$): δ 147.6 (C3), 137.3 (C5), 135.1 (C_{ortho} PPh_3), 131.2 (C_{ipso} PPh_3, t, $J = 23$ Hz), 129.8 (C_{para} PPh_3), 128.9 (q), 127.5 (C_{meta} PPh_3), 124.3 (q), 81.7 (*ipso*-Fec), 81.3 (*ipso*-Fec), 69.5 (2 × CH, C_5H_4), 68.8 (5 × CH, C_5H_5), 68.1 (5 × CH, C_5H_5), 66.8 (2 × CH, C_5H_4), 66.5 (2 × CH, C_5H_4); ^{31}P-NMR ($CDCl_3$): δ 19.37; FAB$^+$ mass spectrum: *m*/*z* (%) 1146 ([$M^+ + 1$], 16). Anal. Calc. for $C_{60}H_{49}BrFe_2OP_2Pd$: C, 62.89; H, 4.31. Found: C, 62.60; H, 4.31%.

3.6. Synthesis of [4]ferrocenofane (**8**)

To a solution (0 °C) cooled of potassium *t*-butoxide (0.17 g, 1.54 mmol) in anhydrous THF (10 ml) a solution of 1,1′-bis(α-bromoacetyl)ferrocene (**2**) (0.3 g, 0.7 mmol) in the same solvent (5 ml) was added dropwise, under nitrogen. The resultant mixture was stirred for a 24-h period of time in which the formation of only one product was observed by TLC. Then, water (10 ml) was added and the mixture was extracted with dichloromethane (2 × 25 ml). The organic layers were dried ($MgSO_4$) and the solvent was removed under reduced pressure. The resulting residue was washed with diethyl ether (3 × 5 ml) and the tar formed separated by filtration. The filtrate was concentrated to dryness under vacuum and the resulting solid chromatographed on a silica gel column using dichloromethane–ethyl acetate (20:1) as eluent to give a red solid after trituration with cold ether. Yield 30%; m.p. 178–180 °C; IR (Nujol): ν 1626, 1450, 1373, 1304, 1223, 1079 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 6.67 (s, 2H), 4.69 (t, 4H, $J = 1.8$ Hz), 4.57 (t, 4H, $J = 1.8$ Hz); ^{13}C-NMR ($CDCl_3$): δ 192.7 (2 × C=O), 136.0 (2 × CH), 78.4 (2 × *ipso*-Fec), 76.5 (4 × CH, C_5H_4), 75.4 (4 × CH, C_5H_4)); FAB$^+$ mass spectrum: *m*/*z* (%) 267 ([$M^+ + 1$]). Anal. Calc. for $C_{14}H_{10}FeO_2$: C, 63.20; H, 3.79. Found: C, 63.35; H, 3.56%.

3.7. Reaction of 1,1′-bis(α-bromoacetyl)ferrocene with Na_2S

To a solution of 1,1′-bis(α-bromoacetyl)ferrocene (0.2 g, 0.46 mmol) in MeOH (10 ml), a solution of Na_2S (0.04 g, 0.52 mmol) in water (5 ml) was added. The reaction mixture was heated at 55 °C for 3 h and after cooling the solvent was removed under vacuum. The resulting crude was extracted with CH_2Cl_2 (3 × 15 ml) and the combined organic layers were dried over Na_2SO_4 filtered off and evaporated under reduced pressure. The crude product was then chromatographed on a silica gel column using dichloromethane–ethyl acetate (20:1) as eluent to give 3-thia-[5]ferrocenophane (**9**) ($R_f = 0.21$) and [5,5]-ferrocenophane (**10**) ($R_f = 0.12$) in 33 and 11%, respectively.

3.7.1. 3-Thia-[5]ferrocenophane (**9**)

M.p. 228–230 °C; IR (Nujol): ν 1667, 1380, 1293, 1152, 1087, 867 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 4.94 (s, 4H), 4.58 (s, 4H), 3.47 (s, 4H); ^{13}C-NMR ($CDCl_3$): δ 199.2 (2 × C=O), 77.9 (2 × *ipso*-Fec), 73.9 (4 × CH, C_5H_4), 71.3 (4 × CH, C_5H_4), 39.4 (2 × CH_2); EI mass spectrum: *m*/*z* (%) 300 ([M^+], 100), 254 (64), 56 (52). Anal. Calc. for $C_{14}H_{12}FeO_2S$: C, 56.02; H, 4.03. Found: C, 56.18; H, 3.95%.

3.7.2. [5,5]Ferrocenophane (**10**)

M.p. 220 °C (decomposes); IR (Nujol): ν 1669, 1652, 1382, 1290, 1070, 873 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 5.04 (s, 8H), 4.62 (s, 8H), 3.99 (s, 8H); ^{13}C-NMR ($CDCl_3$): δ 198.7 (4 × C=O), 79.1 (4 × *ipso*-Fec), 73.5 (8 × CH, C_5H_4), 71.5 (8 × CH, C_5H_4), 39.6 (4 × CH_2); FAB$^+$ mass spectrum: *m*/*z* (%) 601 ([$M^+ + 1$], 71). Anal. Calc. for $C_{28}H_{24}Fe_2O_4S_2$: C, 56.02; H, 4.03. Found: C, 55.89; H, 3.88%.

Acknowledgements

We gratefully acknowledge the financial support of the Dirección General de Investigación Científica y Técnica (project number PB95-1019).

References

[1] A. Togni, T. Hayashi, Ferrocenes. Homogeneous Catalysis. Organic Synthesis. Material Sciences, VCH, Weinheim, 1995.
[2] L. Schwink, P. Knochel, T. Ebesle, J. Okuda, Organometallics 17 (1998) 7.
[3] K. Schlögl, M. Egger, Monatsh. Chem. 95 (1962) 376.
[4] (a) P. Molina, A. Pastor, M.J. Vilaplana, M.C. Ramírez de Arellano, Tetrahedron Lett. 37 (1996) 7829;
(b) P. Molina, A. Pastor, M.J. Vilaplana, M.D. Velasco, M.C. Ramírez de Arellano, Organometallics 16 (1997) 5836;
(c) P. Molina, A. Tárraga, D. Curiel, M.C. Ramírez de Arellano, Tetrahedron 55 (1999) 1417;
(d) P. Molina, A. Tárraga, J.L. López, J.C. Martínez, J. Organomet. Chem. 584 (1999) 147.
[5] A. Tárraga, P. Molina, D. Curiel, J.L. López, M.D. Velasco, Tetrahedron 55 (1999) 14701.
[6] A. Tárraga, P. Molina, D. Curiel, M.D. Velasco, Organometallics 20 (2001) 2145.
[7] N. De Kimpe, R. Verhé, in: S. Patai, Z. Rappoport (Eds.), The Chemistry of α-Haloketones, α-Haloaldehydes and α-Haloimines, Wiley, New York, 1988.
[8] (a) R.J. De Pasquale, M. Vogel, J. Org. Chem. 35 (1970) 1057;
(b) E. Campaigne, J.H. Hutchinson, J. Heterocyclic Chem. 16 (1973) 229;
(c) J.H. Scott, T.A. Smith, J.H. Hutchinson, J. Heterocyclic Chem. 21 (1984) 903.
[9] (a) K.R. Justin Thomas, J.T. Lin, Y.S. Wen, J. Organomet. Chem. 575 (1999) 301;
(b) K.R. Justin Thomas, J.T. Lin, K.J. Lin, Organometallics 18 (1999) 5285;
(c) K.R. Justin Thomas, J.T. Lin, Y.S. Wen, Organometallics 19 (2000) 1008.
[10] (a) J.K. Stille, in: F.R. Harley, S. Patai (Eds.), The Chemistry of the Metal–Carbon Bond, Ch. 9, vol. 2, Wiley, Chichester, UK, 1985;
(b) A. Sen, J.T. Chen, W.H. Vetter, R.R. Whittle, J. Am. Chem. Soc. 109 (1987) 148.
[11] Y. Xie, B.M. Wu, F. Xue, S.C. Ng, T.C.W. Mak, T.S.A. Hor, Organometallics 17 (1998) 3988.
[12] (a) I. Manners, Adv. Organomet. Chem. 37 (1995) 131;
(b) S. Barlow, D. O'Hare, Chem. Rev. 97 (1997) 637.
[13] For a recent review see: R.W. Heo, T.R. Lee, J. Organomet. Chem. 578 (1999) 31.
[14] R.W. Heo, F.B. Somoza, T.R. Lee, J. Am. Chem. Soc. 120 (1998) 1621.
[15] J.K. Pudelski, M.R. Callstrom, Organometallics 11 (1992) 2757.
[16] M.S. Erickson, F.R. Fronczek, M.L. McLaughlin, Tetrahedron Lett. 34 (1993) 197.
[17] D.E. Richardson, H. Taube, Inorg. Chem. 20 (1981) 1278.