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Note

Redox behavior of boronato-functionalized 1,1′-bis(diphenylphosphino)ferrocenes

Piero Zanello [a,*], Arnaldo Cinquantini [a], Marco Fontani [a], Marco Giardiello [a,1], Gianluca Giorgi [a], Clark R. Landis [b], Barbara F.M. Kimmich [b]

[a] *Dipartimento di Chimica dell'Università di Siena, Via Aldo Moro, 53100 Siena, Italy*

[b] *Department of Chemistry, University of Winsconsin–Madison, 1101 University Avenue, Madison, WI 53706, USA*

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Abstract

The one-electron oxidation of 1,1′-bis(diphenylphosphino)-2-[1-((boronato-functionalised)amino)ethyl)]ferrocenes leads to ferrocenium congeners which are generally more stable than the unsubstituted 1,1′-bis(diphenylphosphino)ferrocenium ion. 1,1′-bis-(Diphenylphosphino)ferrocenes bearing in position 2 different bulky substituents also tend to improve the chemical stability of the respective ferrocenium congeners, without affecting the localization of the ferrocene/ferrocenium electrode potential. It is hence assumed that, independently from their inductive effects, sterically encumbering X substituents in 1,1′-bis(diphenylphosphino)-2-[1-((X)amino)ethyl]ferrocenes attenuate the well known instability of the 1,1′-bis(diphenylphosphino)ferrocenium cation. Mass spectrometric techniques have however proved that, as it happens for solutions of 1,1′-bis(diphenylphosphino)ferrocenium ion, the ultimate fate of the highly reactive 1,1′-bis(diphenylphosphino)-2-[1-((X)amino)ethyl]ferrocenium ions is the rearrangement to 1,1′-bis(oxodiphenylphosphoranyl)-2-[1-((X)amino)ethyl]ferrocenes, a reaction which is likely triggered by traces of water. © 2001 Published by Elsevier Science B.V.

Keywords: 1,1′-bis(Diphenylphosphino)-2-[1-((boronato-functionalised)amino)ethyl)]ferrocenes; Electrochemistry; Mass spectrometry; Ferrocenium ion rearrangement

1. Introduction

A few years ago some of us reported the synthesis and the structural characterization of the boron-containing 1,1′-bis(diphenylphosphino)ferrocenes illustrated in Chart 1, which proved to be able to form stable metal adducts effective in asymmetric catalysis [1].

In order to evaluate the electronic effects that these boronate substituents can play also with respect to their catalytic activity, we have studied the electrochemical behavior of these novel ligands. All the species undergo the expected ferrocene-centred oxidation, but the electrogenerated ferrocenium congeners do not appear to be stable species. The nature of the chemical complication following the electron removal has been studied by mass spectrometric techniques.

2. Results and discussion

2.1. Electrochemistry

It is well known that 1,1′-bis(diphenylphosphino)-ferrocene undergoes a ferrocene-centred one-electron oxidation accompanied by relatively fast chemical complications, which generate ferrocene-bis(phosphine) oxides, which in turn undergo further oxidation processes at higher potential values [2–4]. As a matter of fact, in cyclic voltammetry the i_{pc}/i_{pa} current ratio for the first electron removal is lower than unity even at relatively

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* Corresponding author. Tel.: + 39-0577-234-262; fax: + 39-0577-234-233.

E-mail address: zanello@unisi.it (P. Zanello).

[1] On leave from the University of Leicester, UK.

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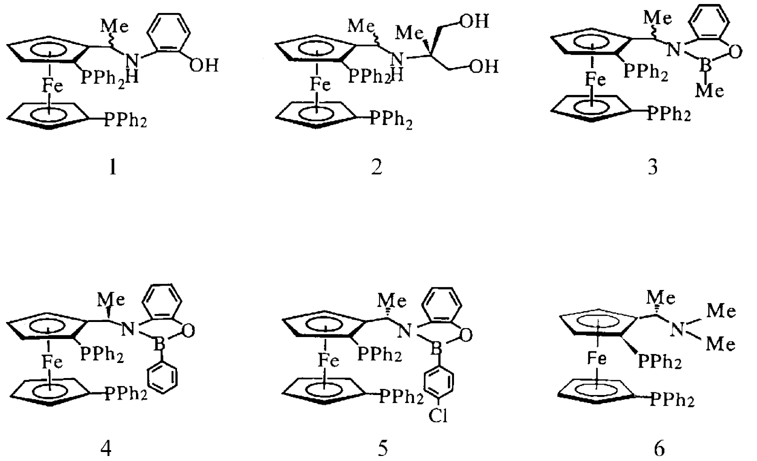


Chart 1.

fast scan rates. For instance, under the present experimental conditions, the i_{pc}/i_{pa} ratio resulted equal to 0.6 at 0.5 V s^{-1}. As Fig. 1a shows, the insertion of one 1-((1-hydroxy-2-phenyl)amino)ethyl substituent in 1,1′-bis(diphenylphosphino)ferrocene to give **1** further decreases the stability of the corresponding ferrocenium cation, as proved by the fact that the first ferrocene-based oxidation does not display any associated reduction peak in the reverse scan, even at the scan rate of 10.2 V s^{-1}. Quite different is the electrochemical response of the borylated species **3**, in that, as illustrated in Fig. 1b, it exhibits an oxidation process possessing features of marked chemical reversibility in the cyclic voltammetric time scale.

As expected from a ferrocene-centred oxidation, controlled potential coulometry ($E_w = +0.8$ V) consumes one electron per molecule, but a cyclic voltammogram recorded on the exhaustively oxidized solution no more reveals the presence of the original ferrocene-centred peaks-system. In addition, the exhaustive electron removal does not cause appreciable colour changes with respect to the original pale yellow solution. These data prelude that in the long times of macroelectrolysis, the ferrocenium cation $[\mathbf{3}]^+$ is not indefinitely stable.

Confirming the results from exhaustive electrolysis, analysis of the cyclic voltammograms of **3** with scan rate varying from 0.02 to 5.12 V s^{-1} shows that: (i) the current ratio i_{pc}/i_{pa} is equal to 0.6 at the lowest scan rate and progressively increases up to reach the unity value at 2.00 V s^{-1}; (ii) the current function $i_{pa} \cdot v^{-1/2}$ tends to decrease by about 10% for a tenfold increase in the scan rate; (iii) the peak-to-peak separation progressively increases from 79 to 290 mV. All these data are diagnostic for a quasireversible one-electron step complicated by slow chemical reactions [5]. In order to ascertain if such a complication involves a first- or a second-order reaction, voltammetric tests have been performed on solutions of **3** in concentrations varying from 2×10^{-4} to 2×10^{-3} mol dm^{-3}. No appreciable variation of the cited trend of the current ratio i_{pc}/i_{pa} with concentration was obtained. Assuming hence the occurrence of a first-order (or pseudo-first-order) chemical complication in the cyclic voltammetric time scale, a lifetime ($t_{1/2}$) of about 6 s was calculated for the ferrocenium monocation $[\mathbf{3}]^+$ [5].

Essentially the same behaviour is exhibited by the boron-containing species **4** and **5**, thus supporting that the presence of the boronate substituents increase the kinetic stability of the ferrocenium species with respect to either 1,1′-bis(diphenylphosphino)ferrocene, or 1,1′-

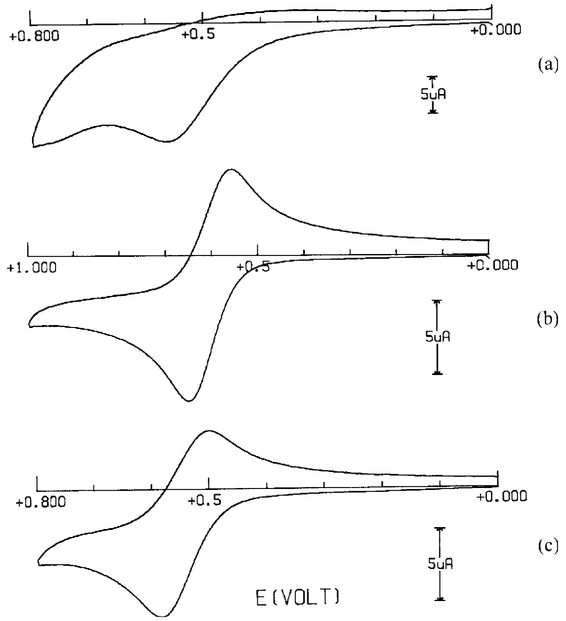


Fig. 1. Cyclic voltammograms recorded at a platinum electrode on CH_2Cl_2 solutions containing $[NBu_4][PF_6]$ (0.2 mol dm^{-3}) and: (a) **1** (0.6×10^{-3} mol dm^{-3}), scan rate 1.0 V s^{-1}; (b) **3** (0.9×10^{-3} mol dm^{-3}), scan rate 0.2 V s^{-1}; (c) **2** (0.8×10^{-3} mol dm^{-3}), scan rate 0.2 V s^{-1}.

Table 1
Formal electrode potentials (V vs. SCE) and peak-to-peak separations (mV) for the one-electron oxidation of the complexes illustrated in Chart 1, together with the half-life (s) of the corresponding monocations

Complex	$E^{\circ\prime}$	ΔE_p [a]	$t_{1/2}$
1	+0.52 [a,b]	–	<0.03
2	+0.58	86	≈3
3	+0.65	96	≈6
4	+0.64	87	≈3
5	+0.65	85	≈3
6	+0.55	95	≈1
$Fe(C_5H_4PPh_2)_2$	+0.59	66	≈1
$Fe(C_5H_5)_2$	+0.39	98	Stable

Dichloromethane solvent; $[NBu_4]PF_6$ (0.2 mol dm^{-3}) supporting electrolyte.

[a] Measured at 0.2 V s^{-1}.

[b] Peak potential value for irreversible processes.

bis(diphenylphosphino)-2-[1-((1-hydroxy-2-phenyl)-amino)ethyl]ferrocene (**1**). The relevant electrochemical data are compiled in Table 1.

It is interesting to note that, independently from the quite different inductive effects of the different boron substituents, complexes **3**–**5** oxidize at essentially the same potential values. This preliminarily points out that there is no flow of electron density between the boronate group and the ferrocene unit. Such result makes difficult to account for the stabilization of the corresponding ferrocenium monocations. This ambiguity is further enhanced by the fact that complex **2**, although lacking the boronate group, also affords a relatively stable monocation (Fig. 1c). The same happens for complex **6**. Based on the approximate similarity of the oxidation potentials of complexes **1**, **2**, **6** with complexes **3**–**5**, it does not seem ventured to state more precisely that no electronic communication exists between the ferrocene unit and the groups placed beyond the amino nitrogen atom.

Coming back to the stabilization of the ferrocenium species, the only conceivable reason could be thus ascribed to the steric effects of the bulky substituents present in position proximal to the diphenylphosphino group, which likely attenuates the rate of the chemical complications responsible for the instability of 1,1′-bis(-diphenylphosphino)ferrocenium species.

2.2. Mass spectrometry

Mass spectrometric measurements have been carried out to account for the instability of the present ferrocenium species. The electron mass spectra of the neutral derivatives **3**–**5** have been preliminarily recorded. As illustrated in Scheme 1, all the compounds show a common path consisting either in the elimination of the substituents bound to the boron atom (ions at *m*/*z* 698) or the cleavage of the exocyclic C–N bond (ions at *m*/*z* 581) followed in turn by the loss of a diphenylphosphino radical (ions at *m*/*z* 396). Each complex also exhibits a specific pattern eliminating the $P(C_6H_5)_2^{\bullet}$ radical directly from the respective molecular ion (ions at *m*/*z* 528, 590 and 624, respectively, for **3**, **4** and **5**), followed by the release of a methyl radical (ions at *m*/*z* 513, 575 and 609, respectively).

It is noted that electrospray mass spectrometry affords quite different results, yielding exclusively the monoprotonated species, without the occurrence of the possible oxidation processes triggered by the source itself. The most abundant ions occur at *m*/*z* 581, also in this case due to the cleavage of the exocyclic C–N bond, which occurs even at low capillary voltage (3 V). The MS/MS ESI spectra further confirm the occurrence of the only exocyclic C–N bond cleavage (as a typical example, Figure S1 in Section 5 shows the ESI MS^n spectra of **4**).

Let us now pass to the mass spectrometric experiments carried out on the product obtained from the electrochemical oxidation of **3**, which, among the here studied complexes, proved to afford the relatively more stable ferrocenium congener. A comparison between the mass spectrum of **3** and that of the species electrogenerated by its exhaustive oxidation is reported in Fig. 2.

It is evident that as a consequence of the electrode process, new peaks appear at *m*/*z* 714, 729 and 745, respectively, in addition to the molecular ion at *m*/*z* 713. Since the last two ions differ by 16 and 32 u, respectively, from **3**, it is conceivable that they arise from species containing one/two more oxygen atoms, respectively, with respect to the original frame. As it happens for the neutral precursor, these oxygenated species show a prominent fragmentation pattern involving the primarily loss of a methyl radical (*m*/z 730 $[3-O]^+$ and 714 $[3-O_2]^+$, respectively). MS/MS experiments carried out on these ions show the subsequent elimination of 132 u, corresponding to fragmentation of the boron-containing substituent.

3. Conclusions

The electrochemical investigation of the widely substituted 1,1′-bis(diphenylphosphino)-2-[1-((X)amino)-ethyl]ferrocenes here studied suggests that the corresponding ferrocenium ions are fairly stable, their lifetimes ranging roughly from 0.01 to 10 s. Mass spectrometry allowed us to disregard that the electrochemical experiments might trigger fragmentation of the original molecular frame, and in particular, in the case of the borylated species (which constitute the main target of the present study), the release of the boronate fragment. As a matter of fact, the final product is constituted by 1,1′-bis(oxodiphenylphosphoranyl)-2-[1-((X)amino)ethyl]ferrocenes. In agreement with previous findings [6], the addition of oxygen atoms can be reliably triggered by reaction of the electrogenerated monocations with traces of water present in the nominally anhydrous solvent which cause oxygenation of one or both the diphenylphosphine moieties accompanied by the concomitant reduction of the oxygenated ferrocenium ion to the corresponding ferrocene. As a consequence it could be speculated that the different lifetimes of the actual ferrocenium species depend upon the steric encumbrance of the substituents, which potentially governs the degree of interaction with the traces of water. The marked anodic shift of the redox potential of 1,1′-bis(oxodiphenylphosphoranyl)ferrocene with respect to 1,1′-bis(diphenylphosphino)ferrocene (by about 0.3 V) [7], well accounts for the disappearance of the ferrocene/ferrocenium step after exhaustive electrolysis.

It is finally noted that in spite of the fact that side reactions involving 1,1′-bis(diphenylphosphino)ferrocenium ion seem to be triggered by dimerization processes [4], in the present 2-substituted analogs the chemical complications look like a first-order (or pseudo-first-order) chemical reaction (at least in the cyclic voltammetric time scale).

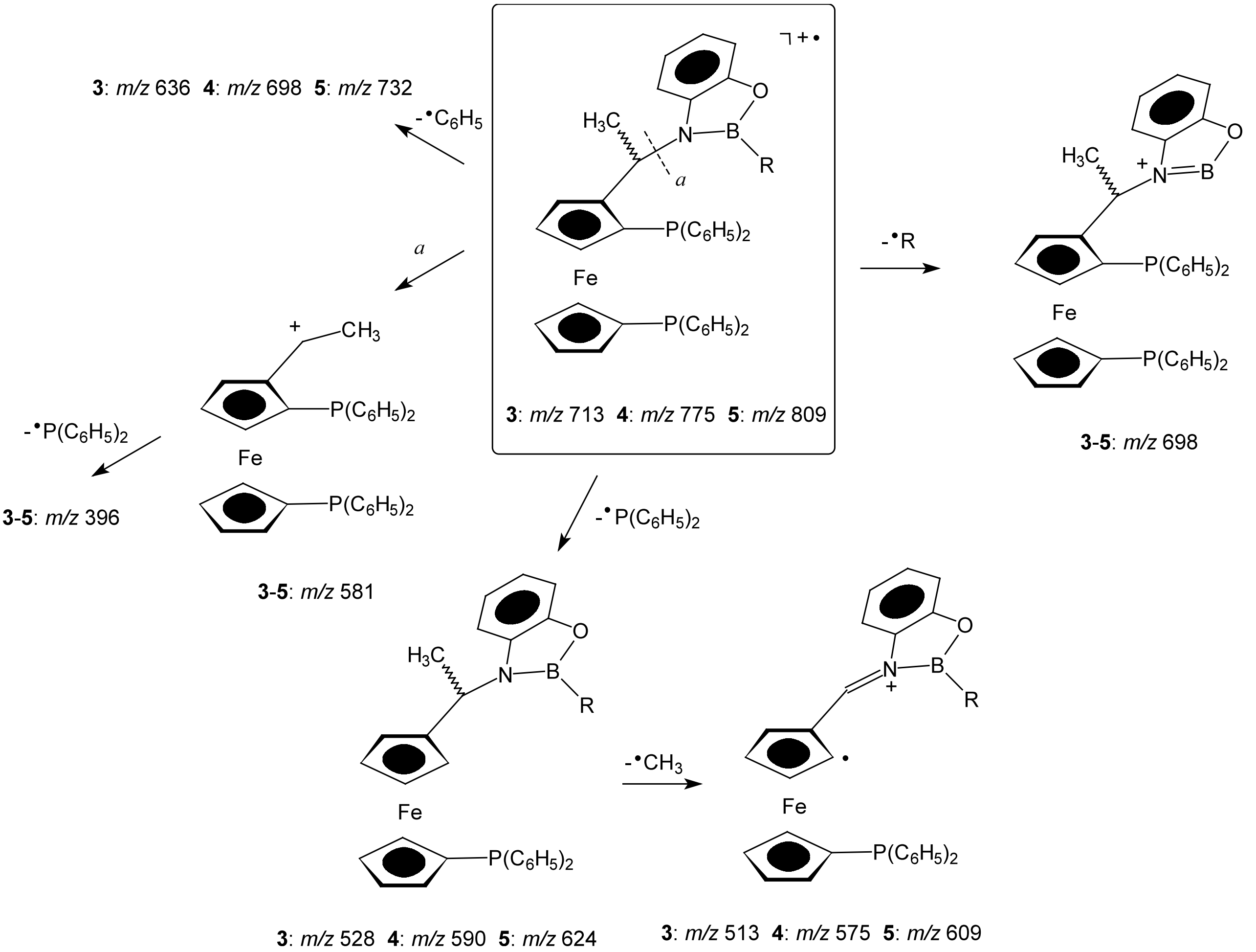
4. Experimental

Complexes **1**–**5** have been prepared according to literature procedures [1]. 1,1′-bis(diphenylphosphino)ferrocene and *N*,*N*-dimethyl-1-[1′,2-bis(diphenylphosphino)ferrocenyl]ethylamine (**6**) were Aldrich products.

Material and apparatus for electrochemistry have been described elsewhere [8]. Potential values are referred to the saturated calomel electrode (SCE).

Electron ionization mass spectrometry experiments were carried out on a VG70-250S double-focusing instrument under the following experimental conditions: acceleration voltage 8 kV, source temperature 200 °C, electron energy 70 eV, current emission 100 mA, resolution 1000 M/ΔM (10% of valley).

Powders of the original ferrocene derivatives were dissolved in chloroform, whereas those of the species



Scheme 1.

Fig. 2. Comparison between the electron ionization mass spectra of compound **3** (top) and that obtained from its exhaustive electrochemical oxidation (bottom).

derived by solvent evaporation of the oxidized solution were dissolved in toluene (in order to minimize the content of the supporting electrolyte). A drop of such solutions was put on the quartz tip of the direct inlet probe and heated to about 200 °C. Collision induced dissociation experiments were carried out in the first field-free region by linked scans according to the law $B/E=k$. Argon was introduced in the collision cell until the intensity of the main beam was reduced to 50% of its original value.

A ThermoFinnigan LCQ Deca ion trap was used for electrospray (ESI) measurements operating in the positive mode. Successive mass spectrometry separations were obtained till MS [4].

Repetitive MS and MS^n measurements gave good reproducibility of the data.

5. Supplementary material

The electrospray MS^n ($n=2$–4) spectra of **4** may be obtained from the corresponding author.

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References

[1] B.F.M. Kimmich, C.R. Landis, D.R. Powell, Organometallics 15 (1996) 4141.

[2] T.M. Miller, K.J. Ahmed, M.S. Wrighton, Inorg. Chem. 28 (1989) 2347.

[3] B. Corain, B. Longato, G. Favero, D. Ajò, G. Pilloni, U. Russo, F.R. Kreissl, Inorg. Chim. Acta 157 (1989) 259.

[4] G. Pilloni, B. Longato, B. Corain, J. Organomet. Chem. 420 (1991) 57.

[5] E.R. Brown, J.R. Sandifer, in: B.W. Rossiter, J.F. Hamilton (Eds.), Physical Methods of Chemistry, Electrochemical Methods, Ch. 4, vol. 2, Wiley, New York, 1986.

[6] P. Zanello, G. Opromolla, G. Giorgi, G. Sasso, A. Togni, J. Organomet. Chem. 506 (1996) 61.

[7] G. Pilloni, B. Corain, M. Degano, B. Longato, G. Zanotti, J. Chem. Soc. Dalton Trans. (1993) 1777.

[8] M. Hobi, G. Rihs, G. Rist, A. Albinati, P. Zanello, D. Zech, H. Keller, Organometallics 13 (1994) 1224.