Electrochemistry and UV/visible spectroscopy of phosphino-substituted bis(η^5-indenyl)iron(II) complexes

Owen J. Curnow,* Glen M. Fern and Elizabeth M. Jenkins

Department of Chemistry, University of Canterbury, Private Bag 4800, Christchurch, New Zealand

Received…

* Corresponding author. Fax: +64 3 364 2110; E-mail: owen.curnow@canterbury.ac.nz

Abstract

Six phosphino-functionalized diindenyl ferrocenes have been characterized by UV/visible spectroscopy and cyclic voltammetry in dichloromethane. The complexes contain the following ligands: 1-diphenylphosphino- (**1**), 1-diphenylphosphino-2-methyl- (**2**), 1-diphenylphosphino-3-methyl- (**3**), 1-diphenylphosphino-3-trimethylsilyl- (**4**), 1-diphenylphosphino-2,3-dimethyl- (**5**), and 1-diphenylphosphino-4,7-dimethyl-indenide (**6**). The cyclic voltammetry shows an approximately additive relationship between oxidation potential and the type of substituent and its ring position, but with increasing substitution leading to lower than otherwise expected oxidation potentials. The UV/visible spectra show two absorptions with the low energy band moving to lower energy with increasing substitution on the C_5 ring.

1. Introduction

The electrochemistry of ferrocene and its derivatives have been extensively studied and the vast majority of ferrocenes have been found to exhibit a single reversible oxidative process [1]. However, the introduction of a phosphine substituent almost invariably introduces complications, whether the phosphine is directly attached to the cyclopentadienyl ring or a number of bonds away

[2,3,4]. 1,1′-bis(diphenylphosphino)ferrocene (dppf) has been intensively studied by cyclic voltammetry. Early studies reported that the complex undergoes an irreversible oxidation, however, subsequent studies have found the reversibility to be highly solvent, temperature and scan rate dependent when compared to the vast majority of ferrocenes [5]: In MeCN solvent, the electrochemistry has been reported as irreversible [6], except by Housecroft et al. who reported reversible behavior at scan rates of 20 to 200 mV s^{-1} [7]. All studies in CH_2Cl_2 have found irreversible behavior [8] whereas studies in $C_2H_4Cl_2$ show essentially reversible behavior, but are followed by a fast chemical reaction. This reaction may be a dimerization, a reaction with adventitious water, or reaction with perchlorate electrolyte [9,10]. Other ferrocenes containing a phosphine directly attached to the ring generally show unusual electrochemistry also [4,11], with notable exceptions being (diphenylphosphino)ferrocene [11–14], the highly substituted ferrocenephanes [$(C_5Me_4)CH_2PPh(C_5H_4)Fe$] [15] and [$\{(C_5Me_4)_2PPh\}Fe$] [16] and the octamethyl analogue of dppf, [$(C_5Me_4PPh_2)_2Fe$] [16]. Given the generally complicated electrochemistry of phosphine-substituted ferrocenes and the tendency of indenyl complexes to be more sensitive than their cyclopentadienyl analogues (due to their ability to undergo facile ring-slippage reactions), we expected the electrochemistry of the diindenyl analogue of dppf to be similarly complicated: at least reversible followed by a fast chemical reaction, if not irreversible—especially since a cationic oxidation product should be more susceptible to nucleophilic attack and subsequent decomposition processes via ring-slippage reactions. This paper reports on those studies. Additionally, in comparison to the analogous dicyclopentadienyliron(II) complexes, diindenyliron(II) complexes have barely been investigated [17–21]. We have recently reported systematic studies of the electrochemistry and UV/visible spectroscopy of a variety of methyl- and TMS-substituted diindenyl ferrocenes: the methyl-substituted complexes were found to be well behaved with (i) an additive relationship between the number of methyl groups and their ring position on the oxidation potential of the ferrocene and (ii) only minor effects on the UV/visible spectra [17]. The TMS derivatives, however, showed unpredictable oxidation potentials and variable UV/visible spectra [18]. Their behavior was attributed to interactions involving the π-acceptor orbitals on the TMS groups. Therefore, we sought to investigate this further by looking at the related π-acceptor phosphine derivatives to see what trends they might exhibit. In this paper, we report on the surprisingly reversible cyclic voltammetry of a series of phosphino-substituted diindenyl ferrocenes as well as their UV/visible spectra.

2. Results and Discussion

The synthesis and characterization of the ferrocenes illustrated in Scheme 1 have all been reported previously by us [22,23]. They can all be prepared by treatment of the indenide (formed by deprotonation of the indene with BuLi) with anhydrous ferrous chloride in THF. The bisplanar chiral nature of these complexes allows the possibility for the formation of *rac* and *meso* isomers. Complex **1** is the only ferrocene studied here in which we have isolated both isomers. Complex **2** is formed in a 1:1.4 isomeric ratio with the major isomer, probably *meso*, being isolated. Electrochemical and spectroscopic techniques were applied to this isomer. Complex **3** forms as a 3:1 mixture of isomers from which the major isomer (*rac*-**3**) was isolated and the electrochemical and spectroscopic techniques applied. Complex **4** is initially formed in a 3:2 ratio of isomers with one of the isomers decomposing more readily than the other and the major isomer (probably *rac*) subsequently being isolated and studied by electrochemical and spectroscopic techniques. Complexes **5** and **6** were run as mixtures of isomers (2:5 and 1:3, respectively).

	R^2	R^3	R^4	R^7
1	H	H	H	H
2	Me	H	H	H
3	H	Me	H	H
4	H	$SiMe_3$	H	H
5	Me	Me	H	H
6	H	H	Me	Me
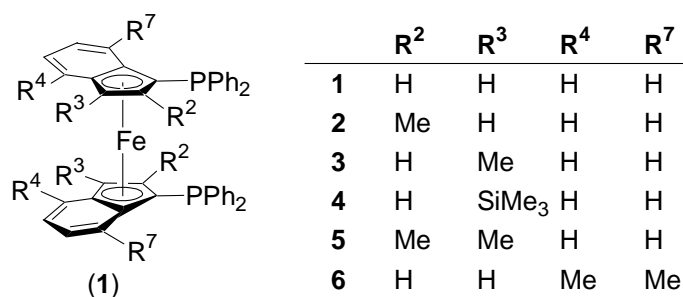
Scheme 1. Phosphino-substituted diindenyl ferrocenes

To a crude approximation, the electrochemical oxidation potential is equivalent to the energy of the HOMO, the reduction potential is equivalent to the LUMO, and the long wavelength absorption energy corresponds to the energy of the HOMO-LUMO gap [24]. However, solvent effects and transitions involving the SHOMO and SLUMO (and potentially other MOs), as well as changes in relative orbital energies and electron configurations, can significantly complicate the situation to the extent that one can generally only get meaningful information by comparing closely related compounds [25,26]. Although group 4 half-sandwich complexes have been investigated by cyclic voltammetry and UV/visible spectroscopy [26–29], the processes and orbitals involved are quite different from those observed in diindenyl ferrocene systems: Firstly, oxidation of the group 4 complexes occurs from ligand-based orbitals rather than metal-based d orbitals [26,29,30], and, secondly, although the UV/visible spectroscopy provides information on the HOMO-LUMO gap in

both systems, it is an LMCT process from the indenyl to a d^0 metal centre in the group 4 complexes [26,27,29] rather than a d-d transition of the d^6 Fe atom [19,31]. One must be careful, therefore, when making comparisons between these systems.

Diindenyl ferrocenes typically exhibit two UV/visible absorption bands (with extinction coefficients of between 300 and 900 L.mol^{-1}.cm^{-1}), one near 420 nm and the other near 555 nm [17,18,20]. These bands are likely to be d-d transitions since the HOMO is largely metal-based [19,31] and the extinction coefficients are less than 1,000 L.mol^{-1}.cm^{-1}. It has been observed that for methyl substitution the UV/visible spectra vary by only 12 nm (416–426 nm and 548–560 nm) [17,20]. For mono-TMS-substitution on the C_5 ring, we found that the UV/visible absorption peaks change by 10–22 nm whereas for disubstitution, all of the UV/visible absorption peaks shift to longer wavelength by 40–62 nm [12–14]. Apparently, the σ* orbitals of the TMS groups have a significant influence on the indenide ring MOs, thus affecting the bands in the UV/visible spectra. Table 1 gives the absorptions for the phosphino derivatives illustrated in Scheme 1 and typical UV/visible spectra (*rac*- and *meso*-**1**) are shown in Figure 1. It can be seen from Figure 1 that the *rac* and *meso* isomers both exhibit two bands in the UV/visible spectra and that these occur at similar energies. However, the band intensities for the two isomers, for **1** at least, are different: the low energy band is a little weaker for the *rac* isomer whereas the higher energy band is weaker for the *meso* isomer, even though this band also has an encroaching charge transfer band. Although some extinction coefficients for the high energy band are over 1,000 L.mol^{-1}.cm^{-1}, it should be noted that these absorptions overlap with a charge transfer band. The high energy absorptions are otherwise similar to those observed for the methyl-only derivatives. Although the low energy absorptions for **1** and **6** (566 and 546 nm, respectively) are similar to diindenyliron(II) and its methyl derivatives, somewhat curiously, further methyl or TMS substitution on the C_5 ring (**2**–**4**) shifts the absorption to longer wavelength (572, 600 and 591 nm, respectively). Unfortunately, we were unable to obtain meaningful UV/visible spectra for the sterically-congested, and consequently sensitive, complex **5**.
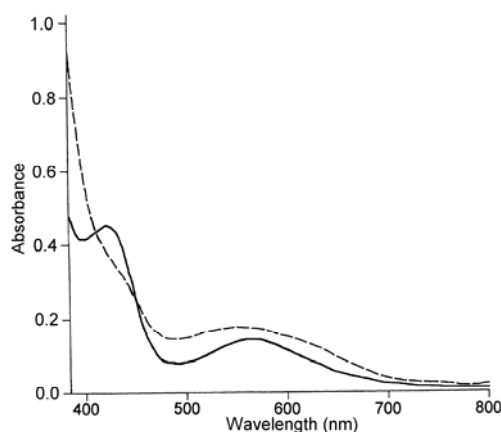
Fig. 1. Typical UV/visible spectra of phosphino-substituted diindenyl ferrocene complexes in CH$_2$Cl$_2$: Compound *rac*-**1** (solid line) and *meso*-**1** (dashed line).

Table 1

CV and UV/visible data for phosphino-substituted diindenyl ferrocenes in CH$_2$Cl$_2$

Compound	*Rac*:*meso* ratio	E_0/mV[a]	ΔE_P/mV	λ_{max}/nm (ε/L.mol^{-1}.cm^{-1})	λ_{max}/nm (ε/L.mol^{-1}.cm^{-1})
1-PPh$_2$ (*rac*-**1**)	1:0	−140	120	420 (870)	565 (265)
1-PPh$_2$ (*meso*-**1**)	0:1	−140	120	435 (660, sh)[b]	555 (330)
1-PPh$_2$-2-Me (*meso*-**2**)	0:1	−230	90	415 (1150)	570 (200)
1-PPh$_2$-3-Me (*rac*-**3**)	1:0	−235	90	420 (1340)	600 (360)
1-PPh$_2$-3-SiMe$_3$ (*rac*-**4**)	1:0	−220	90	450 (540, sh)[b]	590 (210)
1-PPh$_2$-2,3-Me$_2$ (**5**)	2:5	−350	100	—	—
1-PPh$_2$-4,7-Me$_2$ (**6**)	1:3	−230	120	435 (810, sh)[b]	545 (530)

[a] Versus the Fc/Fc$^+$ couple

[b] Data reported for the point of inflection

Cyclic voltammetry of methyl- and TMS-substituted diindenyl ferrocenes show a single-electron reversible redox process [17,18]. A typical cyclic voltammogram of a phosphino-substituted diindenyl ferrocene in CH$_2$Cl$_2$ is shown in Figure 2 and the CV data for complexes **1**–**6** are given in Table 1. Data collected at scan rates from 20 to 2000 mV s^{-1} were found to be of a similar magnitude, and to increase in a similar fashion, to ferrocene under our conditions. The large ΔE_p values are consistent with a large IR drop that is commonly observed for organic solvents such as dichloromethane. The ratios of the forward and backward currents at various scan rates were also

found to be similar to that observed for ferrocene under the same conditions, confirming that the process is reversible. Only one redox process was observed in each of the *rac*/*meso* mixtures. Like the other diindenyl ferrocenes that have been reported [17–21], the redox process is reversible. This is in stark contrast to that of dppf in CH_2Cl_2, however, for which irreversible processes are observed [8]. For complex **1**, we found that the oxidation potential has increased by 138 mV from diindenyliron(II) (–140 versus –278 mV, respectively). This compares to an increase of 140 mV for adding only one diphenylphosphino group to ferrocene in $[Cp(C_5H_4PPh_2)Fe]$ [13] and 183 mV (in dichloroethane solvent) for adding two diphenylphosphino groups to give dppf [10]. In contrast, adding a methyl group to each ring decreases the oxidation potential by about 97 mV while a single TMS group has very little nett effect on oxidation potential (+3 mV) in this solvent. The PPh_2 group is a stronger electron-withdrawing group than both Me and $SiMe_3$, and this can be attributed to both σ and π effects [4i,32,33]. Addition to **1** of a methyl group in the 2 or 3 position on each ring (**2** and **3**, respectively) decreases the oxidation potential by 90 and 95 mV, respectively. This compares to 77 and 97 mV, respectively, when going from the unsubstituted diindenyl ferrocene [11]. Addition to **1** of a TMS group in the 3 position (**4**) gives a decrease of 80 mV and, although this decrease is much larger than when adding a TMS group to each ring of diindenyliron(II) (–278 mV for $[(C_9H_7)_2Fe]$ and –275 mV for $[(1-C_9H_6SiMe_3)_2Fe]$, a difference of only 3 mV), the decrease is very similar to that found when adding a second TMS group on each ring to give $[\{1,3-C_9H_5(SiMe_3)_2\}_2Fe]$ (–358 mV, a decrease of 83 mV) [18]. This large increase in the ease of oxidation for adding a bulky TMS group to **1** or $[(1-C_9H_6SiMe_3)_2Fe]$ can be attributed to steric repulsion between the rings favoring oxidation since inter-ring separation is greater in the resultant ferrocenium [33]. A similar effect has been observed for multiple TMS additions to ferrocene [33]. In some further support of this, the oxidation potential of **5** (–350 mV) is also lower than otherwise expected: A simple additive relationship based on the oxidation potentials of diindenyliron(II) and **1**–**3** would have predicted an oxidation potential of –323 mV.
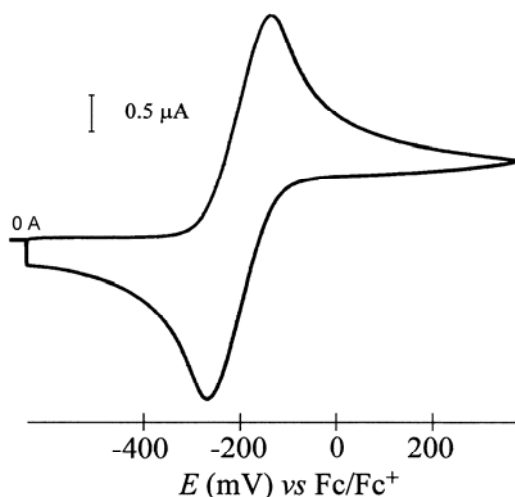
Fig. 2. Typical cyclic voltammogram of a phosphino-substituted diindenyl ferrocene—compound **2** at a scan rate of 100 mV s^{-1} is shown.

As might be expected, the influence of methyl groups in the 4 and 7 positions is smaller than for substitution on the C_5 ring and **6** is found to have an oxidation potential 90 mV less than **1**. This compares to a decrease of 65 mV on methylation of diindenyliron(II) and the difference might again be attributed to an increase in steric repulsion between the indenyl rings.

The reason for the remarkable reversibility of the redox processes for **1–6** is not obvious. A reasonable suggestion would be that the steric bulk of the ferrocenes is hindering nucleophilic attack and subsequent decomposition, however, we have previously reported the ring-flipping isomerization of *meso*-**1** to *rac*-**1** at ambient temperatures in THF via an intermediate involving coordination of THF [34], so this seems unlikely. Pilloni and coworkers have proposed a dimerization mechanism for the decomposition of dppf upon oxidation [9,10], and it may be that the steric bulk of the indenyl complexes prevents this decomposition route. Kirss and coworkers have provided good evidence that $[Cp(C_5H_4PPh_2)Fe]^+$ does not contain a ferrocenium center but may instead have a phosphorous cationic radical center [14]. The reason for the stability of this compound is also not clear.

3. Conclusions

We have characterized six phosphino-substituted bis(η^5-indenyl)iron(II) complexes by UV/visible spectroscopy and cyclic voltammetry in dichloromethane. The UV/visible spectra show two absorptions with the low energy band moving to lower energy with increasing substitution on

the C_5 ring. The cyclic voltammetry shows a surprisingly reversible oxidative process and an approximately additive relationship of oxidation potential with the type of substituent and its ring position. Increasing substitution, however, was found to give lower than otherwise expected oxidation potentials and this is attributed to steric effects. Phosphino groups were found to increase the oxidation potential of the ferrocenes in line with their electron-withdrawing ability.

4. Experimental

All manipulations and reactions were carried out under an inert atmosphere (Ar or N_2) by use of standard Schlenk line techniques. Dichloromethane was dried and distilled prior to use from CaH_2. Compounds **1**–**6** were prepared by published procedures [22]. *Meso*-**1** can be separated from *rac*-**1** by chromatography with diethyl ether on a Celite column. All other reagents were purchased from Aldrich or Sigma Chemical Companies. UV/Visible spectra were obtained on a Hewlett Packard 8452A Diode Array (2 nm resolution) spectrometer using 1 cm cuvets. Cyclic voltammetry was performed using a PAR 173 Potentiostat coupled to a PAR 175 Universal Programmer and a Graphtec WX 1200 chart recorder. All electrochemical measurements were made in CH_2Cl_2 solvent with 0.1 M [Bu_4N]PF_6 electrolyte and using a three-electrode cell comprising of a platinum-disk working electrode (1 mm diameter), a platinum-wire auxiliary electrode, and a Ag/Ag$^+$ (0.01 M $AgNO_3$, 0.1 M [Bu_4N]PF_6-CH_2Cl_2) reference electrode. Sample concentrations were 1 mM. All potentials are reported vs the ferrocene/ferrocenium (Fc/Fc$^+$) couple after referencing to *in situ* ferrocene. Before use, the electrodes were polished with 1 μm diamond paste and cleaned with acetone and distilled water. Electrochemical measurements were made at ambient temperature under an inert atmosphere. Electrochemical and UV/visible results are given in Table 1.

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