Complexes of platinum(II) containing ferrocenylethynyl ligands: synthesis, characterization and spectroscopic and electrochemical properties†

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A series of homoleptic and heteroleptic platinum(II) complexes $[Pt(C{\equiv}CFc)_2(L\text{-}L)]$ (L-L = COD **1**, 1,1′-bis(diphenylphosphino)ferrocene (dppf) **2**), $Q_2[cis/trans\text{-}Pt(C_6F_5)_2(C{\equiv}CFc)_2]$ (cis, Q = $PMePh_3$, **3**; $trans$, Q = NBu_4, **4**), $(NBu_4)[Pt(bzq)(C{\equiv}CFc)_2]$ **5** (Hbzq = 7,8-benzoquinoline) and $(NBu_4)_2[Pt(C{\equiv}CFc)_4]$ **6** has been synthesized and characterized spectroscopically and the structures of **1**·2CHCl₃, **2** and **6**·2H₂O·2CH₂Cl₂ confirmed by single-crystal X-ray studies. The anion of complex **6**, shows strong $O\text{–}H{\cdots}\pi(C{\equiv}C)$ interactions and weaker $C\text{–}Cl{\cdots}\pi(C{\equiv}C)$ contacts between the protons of two water and two CH₂Cl₂ molecules and the $C_\alpha{\equiv}C_\beta$ of mutually cis alkynyl groups. In this complex the presence of additional $O\text{–}H{\cdots}H\text{–}C(Cp)$ and $C\text{–}Cl{\cdots}H\text{–}C(Cp)$ contacts gives rise to an extended bidimensional network. The optical and electrochemical properties of all derivatives have been examined. It is remarkable that for complexes **2** and **5** a facile oxidatively induced coupling, giving rise to 1,4-diferrocenylbutadiyne, is observed, this also having been proven by chemical oxidation.

Introduction

The design of metal-based advanced materials exhibiting interesting electronic properties are currently actively investigated because of their potential application in the construction of molecular electronic devices.[1-5] In this context, the study of conjugated organometallic systems that contain redox-active terminal groups and metal centers incorporated into their structure is an intriguing area of research, since such systems provide the possibility of studying the electronic communication between the redox sites through the metal centres.[6-9] In this area, polynuclear complexes in which the metal centres are connected by π conjugated alkynyl (–C≡C–) fragments, have attracted a great deal of attention due to their potential utility as precursors of rigid-rod polymers and their remarkable electronic and optoelectronic properties.[10-17]

Due to their well-behaved redox chemistry as well as their synthetic versatility,[18] ferrocenyl-based materials with π-conjugation are among the most thoroughly investigated,[19-21] however, heteropolymetallic macromolecular materials containing a high number of ferrocenyl (Fc) units are still scarce.[22-39] Ethynylferrocene has been widely used to introduce ferrocenyl moieties in the synthesis of heteropolymetallic complexes.[40-47] In these systems, the degree of electronic communication between the ferrocenyl groups through or with the central metal is strongly dependent on the nature of the central metal ion as well as its geometry and the

type of coligands.[8,17,43,48,49] Therefore, the construction of novel ferrocenyl-containing heteropolynuclear systems and the study of their structural–property correlations are of great importance in designing functional materials. With this in mind and in line with our interest in heteropolynuclear platinum (Pt/M, M = Cu(I), Ag(I), Tl(I), Cd(II), Pb(II), Ir(I, III), Rh(I, III)) alkynyl based complexes[50-60] we consider it of interest to prepare several mononuclear neutral and anionic (ferrocenylethynyl)platinate(II) complexes which can be subsequently used as precursors of novel multiresponsive, photo and electrochemically active Pt/Fe/M (M = Tl(I), Cu(I) or Ag(I)) systems. Since Fc groups are commonly known as efficient luminescent quenchers,[61-63] it is of particular interest to us to examine their influence on photophysical properties.

In this paper we report the preparation and characterization of the neutral compound $[Pt(C{\equiv}CFc)_2(dppf)]$ **2** (dppf = 1,1′-bis(diphenylphosphino)ferrocene) and its corresponding precursor $[Pt(C{\equiv}CFc)_2(COD)]$ **1** and of the anionic $Q_2[cis/trans\text{-}Pt(C_6F_5)_2(C{\equiv}CFc)_2]$ (cis, Q = $PMePh_3$, **3**; $trans$, Q = NBu_4, **4**) $(NBu_4)[Pt(bzq)(C{\equiv}CFc)_2]$ **5** (Hbzq = 7,8-benzoquinoline) and $(NBu_4)_2[Pt(C{\equiv}CFc)_4]$ **6** respectively. In addition their optical and electrochemical properties have been examined.
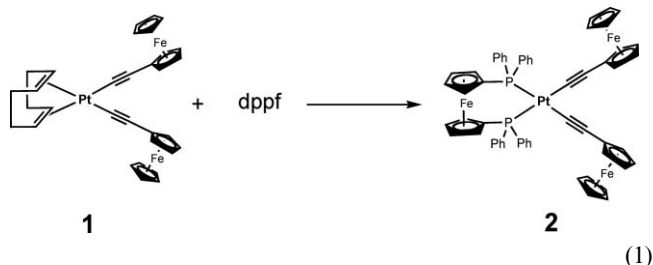
Results and discussion

Synthesis and spectroscopic properties

A series of neutral and anionic complexes **1–6** was synthesized, characterized and their electrochemical and optical properties were studied. It should be noted that complex $[Pt(C{\equiv}CFc)_2(COD)]$ **1**, which was used as a precursor of **2**, has been previously reported by Wrackmeyer et al.[64] For the purpose of comparison we report here its characterization by X-ray diffraction, and its optical, and electrochemical properties. As shown in eqn (1),

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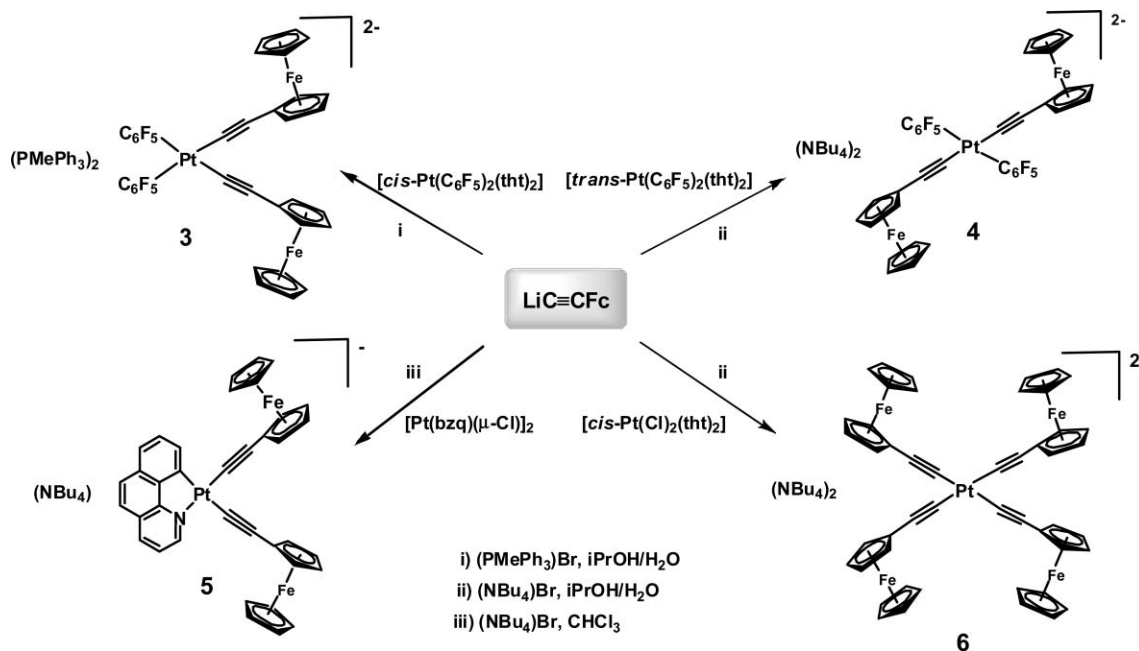
(1)

treatment of $[Pt(C{\equiv}CFc)_2(COD)]$ **1** with 1 equiv. of 1,1′-bis-(diphenylphosphino)ferrocene (dppf) affords $[Pt(C{\equiv}CFc)_2(dppf)]$ **2** due to the facile substitution of COD by donor ligands such as phosphines.

The anionic derivatives **3–6** were synthesized following similar procedures to those reported by us for related complexes.[51,65–67] Thus, treatment of the adequate platinum precursor (see Scheme 1) with an excess of ferrocenylethynyllithium generated "*in situ*" (from ^{n}BuLi and HC${\equiv}$CFc in ~ 50 cm^3 of Et$_2$O), affords the corresponding dilithium "Li$_2$[PtX$_2$(C${\equiv}$CFc)$_2$]" (X = C$_6$F$_5$ **3**, **4**; X = C${\equiv}$CFc **6**) or monolithium "Li[Pt(bzq)(C${\equiv}$CFc)$_2$]" species. The subsequent phosphonium (PMePh$_3$)$_2$[*cis*-Pt(C$_6$F$_5$)$_2$(C${\equiv}$CFc)$_2$] **3** or tetrabutylammonium salts (NBu$_4$)$_2$[*trans*-Pt(C$_6$F$_5$)$_2$(C${\equiv}$CFc)$_2$] **4** and (NBu$_4$)$_2$[Pt(C${\equiv}$CFc)$_4$] **6·2H$_2$O** were isolated in low (33% **6·2H$_2$O**) or moderate (60% **3**, 72% **4**) yield by removing the diethyl ether from the reaction mixture, dissolving the corresponding lithium species in a cold deoxygenated mixture of H$_2$O and isopropyl alcohol (iPrOH) (~ 1 : 1), filtering through Celite and treating the filtrate with (PMePh$_3$)Br (**3**) or (NBu$_4$)Br (**4**, **6**) salts. For the synthesis of the orthometallate complex **5**, the lithium compound Li[Pt(bzq)(C${\equiv}$CFc)$_2$] was extracted with CHCl$_3$. Subsequent treatment with (NBu$_4$)Br and usual work up afforded (NBu$_4$)[Pt(bzq)(C${\equiv}$CFc)$_2$] **5** in 37% yield. We have previously noted the tendency of some homoleptic complexes (NBu$_4$)$_2$[Pt(C${\equiv}$CR)$_4$] to retain molecules of H$_2$O in

their crystallization.[66] Similarly, complex **6** crystallizes as **6·2H$_2$O** as confirmed by analytical, IR, ^{1}H NMR and even X-ray crystallography (see below). Finally, it should be noted that all attempts to crystallize the anion [*cis*-Pt(C$_6$F$_5$)$_2$(C${\equiv}$CFc)$_2$]$^{2-}$ with NBu$_4^+$ as countercation failed. With this cation the complex is always obtained as an oily residue.

All complexes **1–6** were isolated as air and moisture stable orange solids and were fully characterized by usual analytical and spectroscopic means as well as single crystal X-ray crystallography for **1**, **2** and **6**. Crystals of complex **5** were also easily obtained in different solvents and subjected to several crystallographic studies. However, the data obtained have not been of an adequate quality. Conductivity measurements for **3–6** in nitromethane are in agreement with the expected 1 : 2 or 1 : 1 (**5**) electrolyte behaviour.[68] The IR spectra show the expected one (**4**, **6**) or two (**2**, **3**, **5**) characteristic ν_{max}(C${\equiv}$C) absorptions bands (2129–2074 cm^{-1}), in the typical range of terminal alkynyl ligands.[65,66] These bands are observed at lower frequencies in the anionic derivatives (2100–2074 cm^{-1}) than in the neutral complex $[Pt(C{\equiv}CFc)_2(dppf)]$ **2** (2129, 2116 cm^{-1}), thus reflecting the negative charge at Pt(II) which increases the π-back donor component (Pt$\cdots$π*C${\equiv}$CFc) decreasing the corresponding strength of the ν(C${\equiv}$C) vibration. The presence of two strong bands at 3480 and 1635 cm^{-1} in complex **6·2H$_2$O** is in agreement with the presence of H$_2$O, which is also confirmed by proton NMR spectroscopy (δ 3.02) and X-ray crystallography. The ^{1}H NMR spectra confirm the presence of the corresponding ferrocenyl and remaining organic groups in the expected molar ratio (see Experimental section for details), while the ^{31}P{^{1}H} spectrum of **2** exhibits a singlet at δ 13.15 ppm with a $^1J_{P-Pt}$ of 2363 Hz typical of *cis*-bis(phosphine)bis(alkynyl)platinum(II) complexes.[16,69–72]

Complexes **3** and **4** are not soluble enough in common solvents, which precludes their characterization by ^{13}C{^{1}H} NMR spectroscopy. For complex **6**, the resonances of the C$_\alpha$ and C$_\beta$ alkynyl carbons are seen at δ 112.4 and 97.2 ppm and are easily identified


i) (PMePh$_3$)Br, iPrOH/H$_2$O
ii) (NBu$_4$)Br, iPrOH/H$_2$O
iii) (NBu$_4$)Br, CHCl$_3$

Scheme 1

Table 1 Selected bond distances (Å) and angles (°) for **1**, **2** and **6**

1·2CHCl$_3$

Pt–C(9)	1.990(5)	Pt–C(21)	1.988(6)
Pt–C(1)	2.201(6)	Pt–C(2)	2.221(5)
Pt–C(5)	2.226(5)	Pt–C(6)	2.225(6)
C(9)–C(10)	1.190(8)	C(21)–C(22)	1.187(8)
C(9)–Pt–C(21)	88.6(2)	Pt–C(9)–C(10)	178.5(5)
C(9)–C(10)–C(11)	176.5(6)	C(21)–C(22)–C(26)	176.4(6)
Pt–C(21)–C(22)	173.7(5)		

2

Pt–C(35)	2.021(4)	Pt–C(47)	2.014(5)
Pt–P(1)	2.307(1)	Pt–P(2)	2.305(1)
C(35)–C(36)	1.174(6)	C(47)–C(48)	1.187(6)
C(35)–Pt–C(47)	86.06(18)	P(1)–Pt–P(2)	98.81(4)
C(35)–C(36)–C(37)	173.3(5)	C(47)–C(48)–C(49)	176.8(6)
C(1)–P(1)–Pt	123.30(15)	C(6)–P(2)–Pt	115.59(16)
Pt–C(47)–C(48)	174.8(4)	Pt–C(35)–C–(36)	176.0(4)

6·2H$_2$O·2CH$_2$Cl$_2$

Pt–C(1)	2.013(4)	Pt–C(13)	2.016(4)
C(1)–C(2)	1.200(5)	C(13)–C(14)	1.206(6)
H(1)···C(1)	2.55(6)	H(1)···C(2)	2.42(6)
H(2)···C(13)	2.49(8)	H(2)···C(14)	2.34(10)
C(1)–Pt–C(13)	89.57(15)	Pt–C(1)–C(2)	177.0(4)
Pt–C(13)–C(14)	176.4(4)	C(1)–C(2)–C(3)	173.5(5)
C(13)–C(14)–C(15)	171.7(4)		

due to the strongly different coupling constants to the ^{195}Pt nucleus ($J_{Pt–C\alpha} = 990$; $J_{Pt–C\beta} = 292$ Hz). In the diphenylphosphinoferrocene complex **2**, these resonances appear as the A part of an AXX′ (X = P) spin system (5 lines pattern) at δ 98.4 (C$_\alpha$, $|^2J_{(C–Ptrans)} + {}^2J_{(C–Pcis)}| = 176.5$ Hz) and 105.9 ppm (C$_\beta$, $|^3J_{(C–Ptrans)} + {}^3J_{(C–Pcis)}| = 35.9$ Hz), respectively, due to the presence of chemically but magnetically non-equivalent ^{31}P nuclei. In the orthometallate derivative, the four expected C≡C resonances due to the non-equivalent C≡CFc (*trans* to N and *trans* to C) are seen (δ 124.3, 101.0, 97.4 and 92.1 ppm). ^{195}Pt satellites are only observed for signals at δ 101.0 ($^2J_{Pt–C\beta} = 245$ Hz) and 97.4 ppm ($^2J_{Pt–C\beta} = 450$ Hz) and are therefore assigned to the acetylenic C$_\beta$ *trans* to metallated C and N atoms, respectively.

The identity of **1**, **2**, and **6** has been confirmed by single crystal X-ray diffraction (Fig. 1, 2, 3 and Table 1). Complex **1·2CHCl$_3$** (Fig. 1) shows an approximately square planar environment formed by the two C$_\alpha$ of the alkynyl carbons and the two olefinic bonds (η^2-bonded) of one cyclooctadiene ligand. To the best of
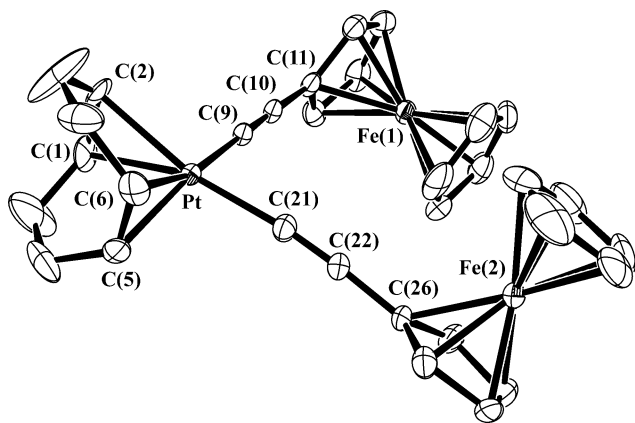

Fig. 1 ORTEP plot (50% probability level) of the molecular structure of complex **1·2CHCl$_3$**. Hydrogen atoms and CHCl$_3$ molecules are omitted for clarity.

our knowledge this is the first structural characterization of a [Pt(C≡CR)$_2$(COD)] derivative. In this complex, the two olefinic bonds of the COD ligand are approximately perpendicular to the coordination plane. The Pt–C(COD) bond distances (2.201(6)–2.226(5) Å) are slightly larger than those seen in [PtCl$_2$(COD)][73] (2.154(5)–2.178(6) Å) in accordance with the higher *trans* influence of C(sp) in relation to the chlorine atom. The Pt–C$_\alpha$ (1.988(6), 1.990(5) Å), C≡C distances (1.190(8), 1.187(8) Å) and angles at C$_\alpha$ (173.7(5), 178.5(5)°) and C$_\beta$ (~ 176.5 °) are not unusual, and are similar to those reported in other platinum alkynyl complexes.[50,66,69,74,75] Finally, it is worth noting that both ferrocenyl groups adopt an almost staggered conformation and they are not coplanar with the platinum coordination plane (dihedral angles 24.1° and 85.0°), suggesting a very low delocalization through the "Pt(C≡C)$_2$" framework.

The molecule of complex **2** (Fig. 2) also shows the expected *cis* arrangement for both ferrocenylethynyl ligands (C(35)–Pt(1)–C(47) = 86.06(18)°) as imposed by the presence of the chelating dppf ligand. The observed Pt–P distances (Pt–P(1) 2.307(1), Pt–P(2) 2.305(1) Å) and angle (P(1)–Pt–P(2) 98.81(4)°) are comparable to other reported crystal structures containing the "Pt(dppf)" unit.[69,76,77] The ferrocenyl group of the chelating dppf ligand deviates from the local D_{5d} point symmetry demonstrated by the torsional angle P(1)–C(1)–C(6)–P(2) of 30.84° and the observed angle of 35.7° between both cyclopentadienyl groups, which means that the dppf in **2** is very close to having an ideal 'synclinar staggered' conformation.[76] The two alkynyl ligands show slight deviation from linearity (see Table 1). Curiously, both ferrocenyl substituents of the alkynyl groups are oriented in a cisoidal disposition (Fig. 2b) and make small angles (11.96 and 36.42 °) with the PtP$_2$C$_2$ square plane, pointing to a certain degree of delocalization through the carbon π alkynyls and the platinum centre. This geometry contrasts with the nearly orthogonal orientations found in the related complex [*cis*-Pt(C≡CFc)$_2$(PPh$_3$)$_2$].[78]

Complex **6** crystallizes as **6·2H$_2$O·2CH$_2$Cl$_2$** in the triclinic $P\bar{1}$ space group with one molecule each of H$_2$O and CH$_2$Cl$_2$ in the asymmetric unit. The Pt atom lies on a crystallographic inversion centre, which implies a totally planar coordination symmetry (Fig. 3a), with bond lengths Pt–C$_\alpha$ (2.013(4), 2.016(4) Å) and C$_\alpha$≡C$_\beta$ (1.200(5), 1.206(6) Å) comparable to those found in the anions [Pt(C≡CR)$_4$]$^{2-}$ (R = C$_6$H$_4$CF$_3$, C$_5$H$_4$N-4).[66] The relative orientation of both Fc moieties in the asymmetric unit is nearly cisoidal (dihedral angle Fe–C$_w$···C$_w$′–Fe′ = 5.82°) and as a consequence, in the anion they adopt a transoidal conformation with their corresponding mutually *trans* Fc moieties. It is remarkable that the cyclopentadienyl rings η^5-C$_5$H$_4$ are nearly coplanar with the platinum coordination plane, the dihedral angles being 13.80° and 11.60°, respectively. This fact is probably suggestive of significant π conjugation of the alkynyl groups through the Pt centre.

Another relevant structural feature is the presence of two molecules of water associated with the anion through very short O–H···π(C≡C) (2.330–2.550 Å) interactions and two additional CH$_2$Cl$_2$ molecules that contact more weakly (C–H···π(C≡C), 2.548–2.686 Å). This kind of interaction (X–H···π) with the π electron density of the C≡C bonds seems to be a fairly common feature in the crystal structures of organic alkynes.[79] Short C–H···π(C≡C) interactions in platinum alkynyl complexes have also been observed especially with CHCl$_3$[66,75,80] and CH$_2$Cl$_2$[81] as solvents and, in some cases, these interactions have even
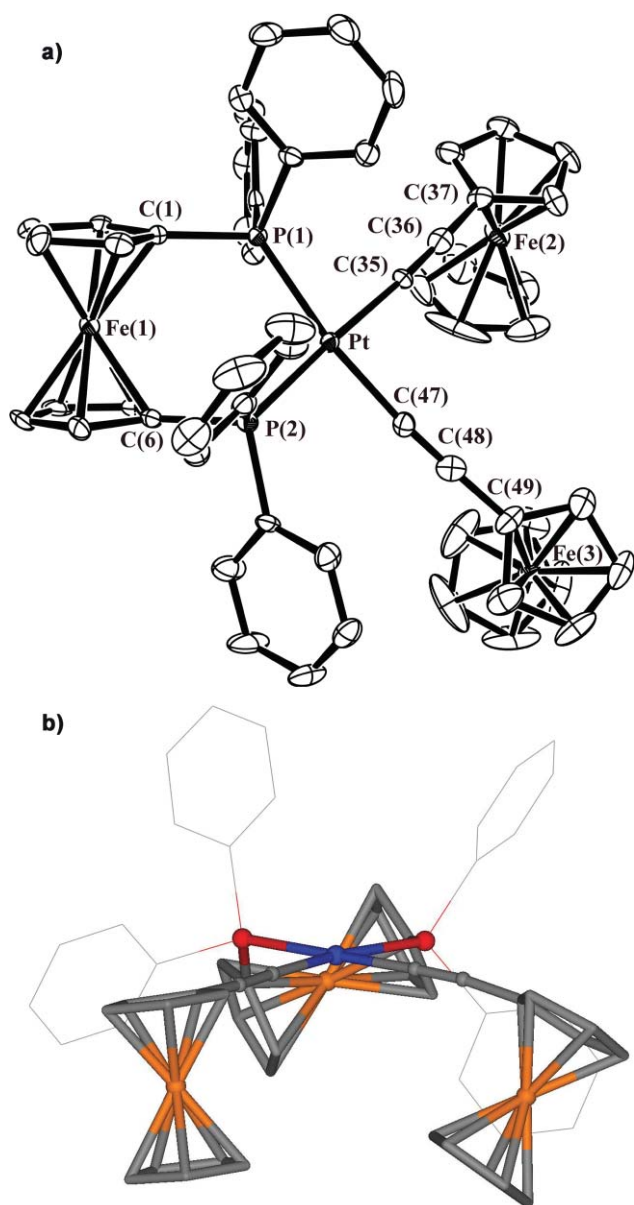
Fig. 2 (**a**) Molecular structure of complex **2**. Ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. (**b**) Frontal view of complex **2**.

been found to be responsible for the vapoluminescent behaviour of the complexes.[81] However, to the best of our knowledge, weak interactions between H_2O and the electron density of the alkynyl bonds of an organometallic complex "[M]–C≡CR" have never been reported. In the aquo solvate complex {[*cis*-Pt(C≡CC(OH)Me$_2$)$_2$(PPh$_3$)$_2$]·H$_2$O},[82] the water molecule was found to interact with both hydroxy groups of the alkynyl substituents, C(OH)Me$_2$. The hydrogen atoms of the H_2O molecule in **6**·2H_2O were located from difference maps and refined isotropically. As shown in Fig. 3(a), the water molecules lie below and above the platinum coordination plane [H(1)H(2)O] and interact with C_α and C_β of two mutually *cis* alkynyl groups [H(1)···C(1) 2.55(6), H(1)···C(2) 2.42(6), H(2)···C(13) 2.49(8), H(2)···C(14) 2.34(10) Å]. These contacts are far shorter than the sum of the van der Waals radii ($r_H + r_C = 2.9$ Å),[83] which is indicative of a
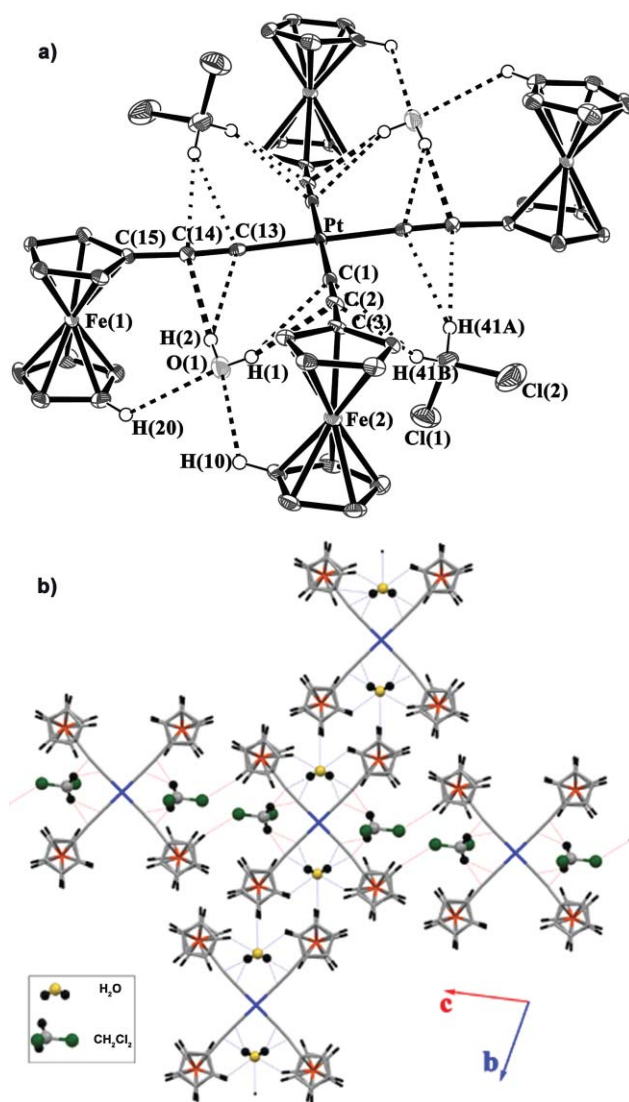
Fig. 3 (**a**) ORTEP plot (50% probability level) of the anion [Pt(C≡CFc)$_4$]$^{2-}$ in complex **6**·2H_2O·2CH_2Cl_2. (**b**) Schematic front view of a layer projected down the crystallographic *a* axis showing the interactions between the anions [Pt(C≡CFc)$_4$]$^{2-}$ and the solvents.

strong interaction. Interestingly, the oxygen atoms of the water molecules are also acting as H acceptors contacting with two C–H protons (H(10) and H(20)) of both η-C$_5$H$_5$ of the same mutually *cis* ferrocenylethynyl groups. Although the observed C–H···O(1) distance of 2.648 Å is only slightly shorter than the sum of the van der Waals radii ($r_H + r_O = 2.72$ Å),[83] both H_2O molecules are well "embedded" in the resulting anion [Pt(C≡CFc)$_4$·2H_2O]$^{2-}$ and surely play an important role in stabilizing the final complex. In fact, the crystals used for this study were grown by slow evaporation of a saturated CH_2Cl_2 solution of the crude solid **6**·2H_2O, thus indicating that the water molecules are retained in the crystallization process. Inspection of the crystal packing reveals that the lattice organisation is governed by additional contacts involving the H_2O and CH_2Cl_2 molecules. As can be seen in Fig. 3(b), the CH_2Cl_2 molecules contact weakly with the alkynyl fragments C–H···π(C≡C) (2.548–2.686 Å) and connect the anions through C–Cl···H–C(Cp) interactions (Cl(2)···H(22) = 2.783 Å) along the *c* axis. Similar weak hydrogen bonding

interaction between protons of neighboring ferrocenyl groups (C(5)–H(5)) and the oxygen atoms of the H_2O molecules along the b axis give rise to a bidimensional network. As has been previously observed in the crystal structures of related alkynyl platinate complexes such as $(NBu_4)[Pt(C^\wedge N^\wedge C)(C\equiv CR)_2]$[84] (H–C^∧N^∧C–H = 2,6-diphenylpyridine), the NBu_4^+ cations fit in the space between the layers of anions giving an interesting final stacking pattern (Fig. S1, ESI†).

As previously commented on, because of the poor quality of the crystals, the structural analysis of $(NBu_4)[Pt(bzq)(C\equiv CFc)_2]$ **5** is not of high accuracy. Nevertheless, the connectivity shown in Scheme 1 was unequivocally established (see Fig. S2, ESI†).

Optical properties

The UV-vis absorption spectra of all complexes **1–6** were recorded in CH_2Cl_2 (see Fig. 4 for selected regions) and the data are summarized in Table 2. The absorption bands of ethynylferrocene and 1,1′-bis(diphenylphosphino)ferrocene are also included for reference purposes. The weak absorption bands of ferrocene at 325 ($\varepsilon = 0.051$ M^{-1} cm^{-1}) and 440 nm ($\varepsilon = 0.087$ M^{-1} cm^{-1}) have been previously assigned to $^1A_{2g} \rightarrow {}^1E_{2g}$ and $^1A_{1g} \rightarrow {}^1E_{2g}$ ligand field transitions of D_{5d} symmetry.[85] In accordance with the electron-withdrawing effect of the acetylene group, these bands

Fig. 4 Electronic spectra of complexes **1–6** in CH_2Cl_2 at room temperature.

appear slightly red-shifted in HC≡CFc (336, 443 nm) and have a greater intensity due to increased mixing of metal and ligand orbitals.[86] According to previous assignments, the lowest energy band (443 nm) is attributed to MLCT transition with some d–d character and the one at 336 nm to ligand centred π–π* also mixed with some d–d character.[86,87] Attachment of the two PPh_2 fragments to ferrocene also has a similar effect in the dppf ligand (445 nm, $\varepsilon = 460$ M^{-1} cm^{-1}). As shown in Fig. 4, the corresponding absorption associated with the ferrocenyl groups is seen in all platinum complexes with a remarkable increase in molar absorptivity scale. The slight red shift observed (445 **2**–490 nm **5**) relative to ethynylferrocene could be attributed to further enhancement in the extent of the π delocalization of the acetylenic moieties through the platinum centre. All complexes also display high-energy bands ($\lambda < 300$ nm) ascribable to π–π* ligand-centred transitions of the different ligands (and $PMePh_3^+$ in **3**, see Table 2).[51,66,67,88]

The anionic complexes $(NBu_4)_2[Pt(C\equiv CFc)_4]\cdot 2H_2O$ **6**·$2H_2O$ and $(NBu_4)_2[trans\text{-}Pt(C_6F_5)_2(C\equiv CFc)_2]$ **4** exhibit two low energy bands (326, 344 nm **6**·$2H_2O$; 316, 343 nm **4**), which, on the basis of previous assignments in related complexes are attributed to one admixture of π→π*(C≡CFc) IL/dπ(Pt)→π*(C≡CFc) MLCT.[66] For comparative purposes, these bands are seen at 335 and 347 nm in $(NBu_4)_2[Pt(C\equiv CPh)_4]$[66] and at 334 and 342 nm in $(NBu_4)_2[trans\text{-}Pt(C_6F_5)_2(C\equiv CPh)_2]$ suggesting a predominant π–π*(C≡C) intraligand character. The corresponding *cis*-bis(pentafluorophenyl)platinate derivative $(PMePh_3)_2[cis\text{-}Pt(C_6F_5)_2(C\equiv CFc)_2]$ **3** displays, in the same region, a broad absorption profile with lower molar absorptivity slightly blue-shifted (290–360 nm). This fact is in agreement with previous observations in related *cis* and *trans* configured bis(alkynyl)platinate complexes, suggesting that the extent of π delocalization through Pt is more efficient when the alkynyl groups are mutually *trans*.[71,89]

As shown in Fig. 4, complex $[Pt(C\equiv CFc)_2(COD)]$ **1** shows two bands at 321 and 388 nm. The low energy band at 388 nm is remarkably intense ($\varepsilon = 10\,100$ M^{-1} cm^{-1}) and red-shifted relative to that reported for $[Pt(C\equiv CPh)_2(COD)]$[90] (325, 359 nm). On the basis of theoretical calculations, in this latter complex the intense band at 325 nm ($\varepsilon = 3170$ M^{-1} cm^{-1}) has been assigned to a LL′CT (π C≡CPh → π* COD) transition while the low intensity shoulder at 359 nm ($\varepsilon = 580$ M^{-1} cm^{-1}) was ascribed to the corresponding triplet absorption. In complex **1** the band at 321 nm could be similarly ascribed to a LL′CT transition. The band at 388 nm, with
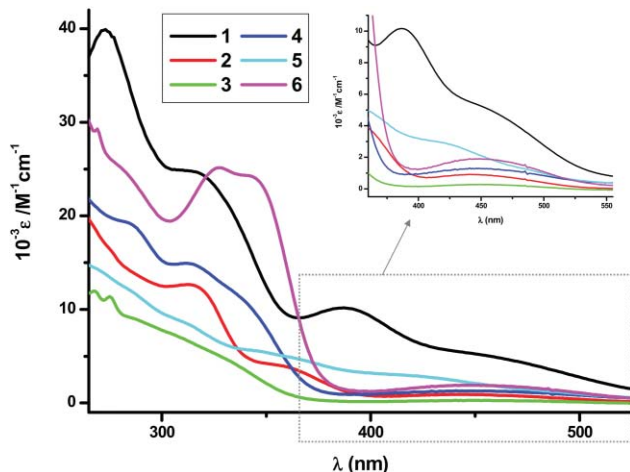
Table 2 UV-vis absorption data[a]

| Compound	λ_{max}/nm (10^3 ε/$M^{-1}cm^{-1}$)
HC≡CFc	236 (49.4), 262 (8.60), 270 (7.77), 336 (0.29), 443 (0.33)
dppf	234 (47.4), 253 (36.0), 445 (0.46)
1	237 (47.5), 272 (39.8), 321 (24.2), 388 (10.1), 468 (4.53)
2	230 (45.9), 257 (22.6), 315 (12.5), 363 (3.65), 445 (0.89)
3	231 (32.3), 267 (11.9), 275 (11.4), 290–360 (br), 455 (0.26)
4	231 (42.9), 287 (18.8), 316 (14.7), 343 (9.48), 455 (1.26)
5	236 (52.4), 269 (33.1), 287 (27.2), 313 (19.6), 358 (11.1),[b] 424 (6.06), 490 (sh, 1.91)
	269 (31.8), 287 (25.6), 313 (18.0), 358 (11.1), 410 (7.05), 490 (sh, 1.70)[c]
	269 (34.1), 287 (26.7), 313 (20.8), 358 (13.0), 412 (7.68), 492 (sh, 1.99)[d]
6	232 (64.1), 263 (31.0), 268 (29.2), 285 (23.9), 326 (25.1),[e] 344 (23.9), 456 (1.86)

[a] CH_2Cl_2 at room temperature, ∼ 5 × 10^{-5} M. [b] With tail to 380 nm. [c] CH_3CN at room temperature (5 × 10^{-5} M). [d] DMF at room temperature (5 × 10^{-5} M). [e] With tail to 390 nm.

a high molar absorptivity, and the analogous band at 363 nm (ε = 3650 M^{-1} cm^{-1}) in the diphosphine complex [Pt(C≡CFc)$_2$(dppf)] **2** are tentatively assigned, as in other neutral phosphine stabilized platinum ethynyl complexes, to a π(C≡C)→π*(C≡C) transition with a remarkable LMCT character.[8,71] In these complexes overlap between the π*(C≡C) and the platinum p orbital has been invoked and, in particular, recent theoretical calculations on [*trans*-Pt(C≡CFc)$_2$(PEt$_3$)$_2$][25] have shown the existence of a significant overlap between the iron 3d orbital and the two orthogonal π systems on the conjugated alkyne units.[25]

The benzoquinolinate complex (NBu$_4$)[Pt(bzq)(C≡CFc)$_2$] **5** exhibits, in this range, two maxima at 313 and 358 nm that are insensitive to solvent polarity, attributable to ligand-centred transitions (^{1}IL π–π*) of the alkynyl and cyclometalated C^N ligands, together with a solvent-dependent low energy absorption. As is noted in Table 2, this band exhibits a small negative solvatochromism (CH$_2$Cl$_2$ 424; DMF 412; CH$_3$CN 410 nm) effect, suggesting its charge-transfer nature.[91] With reference to previous assignments and theoretical studies,[67] we assign this band to a mixed MLCT (Pt(d)→bzq)/LL′CT (C≡CFc→bzq). In accordance with this assignment and the electron rich nature of the ferrocenylethynyl group, this band is red-shifted in relation to other bis(alkynyl)(benzoquinolinate)platinate(II) complexes (NBu$_4$)[Pt(bzq)(C≡CR)$_2$] (R = Ph, 397; R = C$_6$H$_4$CF$_3$-4, 392 nm).[67] Not unexpectedly, none of the complexes have detectable luminescence either in rigid matrix (solid at 298 and 77 K, glass CH$_2$Cl$_2$ 77 K) or in room temperature CH$_2$Cl$_2$ solution. This fact is presumably due to the presence of the ferrocenyl groups, which provide efficient channels for excited-state deactivation.[61–63]

Electrochemistry

The electrochemical properties of **1–6** were investigated by cyclic voltammetry (CV) and differential pulse voltrammetry (DPV) (Fig. 5, 6, 7 and Table 3). As shown in Fig. 5(b), complex [Pt(C≡CFc)$_2$(COD)] **1** displays a reversible two electron redox couple at 0.45 V on sweeping at anodic potential, which is attributed to the concomitant oxidation of the two ferrocenyl units (measured by coulommetry at controlled potential). No appreciable wave splitting was observed by recording the corresponding differential pulse voltammogram (Fig. 5(a)) suggesting a nil or a very low interaction between the iron centres ($\Delta E_p' = 0.09$ V, $\Delta E_{1/2} < 0.07$ V).[92,93] For comparison, a value of $\Delta E_{1/2}$ of 0.07 V has
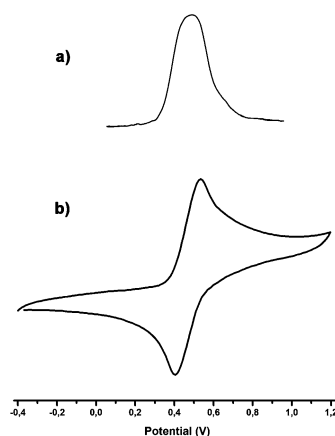
Fig. 5 (a) Differential pulse voltammogram of **1** in CH$_2$Cl$_2$; scan rate = 10 mV s^{-1}, pulse amplitude = 10 mV, pulse width = 50 ms, pulse period = 20 ms. (b) Cyclic voltammogram of complex **1** in CH$_2$Cl$_2$ at a scan rate of 50 mV s^{-1}.

been reported in related [*cis*-Pt(C≡CFc)$_2$L$_2$] (L = PPh$_3$, 1/2dppe) complexes.[94] Compared to the redox potentials found in other phosphine complexes such as [*cis*-Pt(C≡CFc)$_2$(dppe)][94] ($E_{1/2}$ = 0.35 V *vs* SCE) or even in **2** ($E_{1/2}$ = 0.34 V), the Fc oxidation potential in **1** is anodically shifted (0.45 V), which would indicate that the "Pt(COD)" framework makes oxidation of the Fc groups more difficult. Notwithstanding, the oxidation of **1** is still ∼ 0.16 V less positive than free ethynylferrocene ($E_{1/2}$ = 0.61 V), indicating the existence of some transference of electron density from the Pt centre that would lower the potential of the oxidation *via* π-conjugation and an inductive effect.[26,46,95–98] It must be noted that this complex does not undergo any oxidation or reduction of the platinum atom in dichloromethane from −1.8 V to +1.6 V, pointing to the significant redox stability of this centre.

The voltammograms of complexes **2–6** are more complicated. Thus, complex [Pt(C≡CFc)$_2$(dppf)] **2** (Fig. 6) displays two ill resolved one-electron oxidations (0.34, 0.42 V) due to the sequential oxidation of both Fc groups, with an electronic communication ($\Delta E_{1/2} = 0.08$ V) similar to that found in related [*cis*-Pt(C≡CFc)$_2$L$_2$][94] complexes. At higher anodic potential more additional oxidation and reduction peaks than would be expected are observed, due to electrochemically generated decomposition products. By comparison with reported values,[69,99] the reversible wave ($E_{1/2}$ = 1.03 V) could be tentatively ascribed to oxidation of the dppf ligand. In order to further elucidate the possible

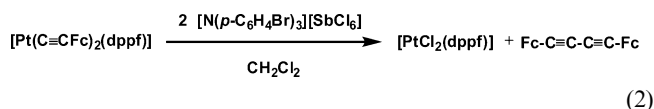**Table 3** $E_{1/2}$ oxidations for the couple Fc/Fc$^+$ for complexes **1–6**[a]

Compounds	$E_{1/2}$/V	E_{pa}/V	E_{pc}/V
Fc/Fc$^+$	0.46	0.49	0.43
HC≡CFc/HC≡CFc$^+$	0.61	0.65	0.56
dppf/dppf$^+$	0.66	0.72	0.60
1	0.45	0.50	0.41
2	0.34, 0.42, 0.59, 0.69 1.03, 1.22	0.38, 0.46, 0.64, 0.73, 1.07, 1.27	0.27, 0.36, 0.55, 0.64, 0.99, 1.17
3	0.11, 0.22[b]		
4	0.08, 0.22[b]		
5	0.18, 0.28, 0.59, 0.69	0.25, 0.35, 0.63, 0.75	0.11, 0.22, 0.55, 0.63
6		0.09	

[a] All measurements were carried out in CH$_2$Cl$_2$ at 25 °C with NBu$_4$PF$_6$ 0.1 M. Scan rate of 100 mV s^{-1} and *vs* Ag/AgCl reference electrode. [b] Measured in the differential pulse voltammogram.
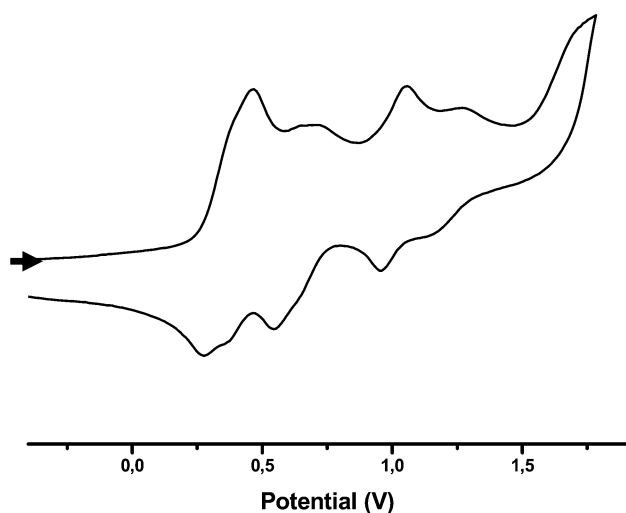
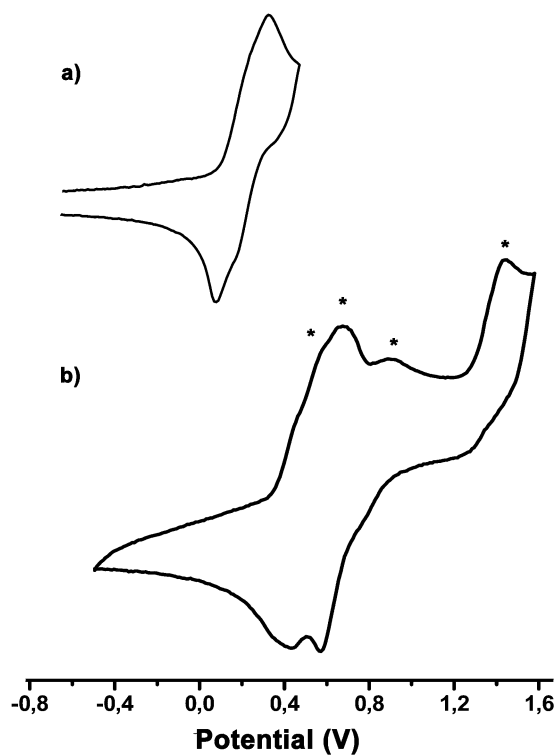**Fig. 6** Cyclic voltammogram of complex **2** in CH₂Cl₂ at a scan rate of 100 mV s⁻¹.

electrochemically generated compounds, complex **2** was subjected to chemical oxidation with 2 equiv. of [N(p-C₆H₄Br)₃][SbCl₆]. Under these conditions the reaction was found to proceed with formation of the coupling product [Fc-C≡C–C≡C–Fc] and [PtCl₂(dppf)] (eqn (2)),

$$[Pt(C≡CFc)_2(dppf)] \xrightarrow[CH_2Cl_2]{2\ [N(p\text{-}C_6H_4Br)_3][SbCl_6]} [PtCl_2(dppf)] + Fc\text{-}C≡C\text{-}C≡C\text{-}Fc$$

(2)

the latter presumably formed by further interaction of the generated [Pt(dppf)]²⁺ fragment with Cl⁻ ligands of the [SbCl₆]⁻ anion present in the medium. This result is not unexpected since easy reductive elimination of ferrocenylethynyl units has been previously observed in titanocene–ferrocenyl derivatives.[100–103] In this context it should be noted that the reaction between [Pt(C≡CPh)₂(dppf)] with an excess of [Au(PPh₃)]⁺ has been shown to give [Pt(η²-Ph–C≡C–C≡C–Ph)(dppf)] after the coupling reduction of the phenylalkynide groups.[104] On the basis of this behaviour, the peaks observed at 0.59 and 0.69 V for complex **2** are tentatively attributed to the oxidation of the probably electrochemically generated by-product [Fc(C≡C)₂Fc].

Complexes **3** and **4** show two ill resolved waves due to the Fc groups, which are cathodically shifted ($E_{1/2} = 0.11$, 0.22 V **3**; $E_{1/2} = 0.08$, 0.22 V **4**) in comparison to the neutral complexes (**1**, **2**), as was expected, due to the greater electron density in these compounds. The electronic interaction between both Fc groups is stronger in the *trans* derivative **4** ($\Delta E_{1/2} = 0.14$ V) than in the *cis* isomer **3** ($\Delta E_{1/2} = 0.11$ V). However, both complexes show also in their voltammograms additional peaks (see Fig. S3 and S4, ESI†), which increase in successive scans. Complex **5** shows clearly the oxidation of the Fc groups as two partially overlapped waves at higher potential than the dianionic **3** and **4** ($E_{1/2} = 0.18$, 0.28 V), being completely reversible when the scan is turned back at 0.40 V (Fig. 7(a)). However, in the complete scan (−1.2 to 1.5 V) the voltammogram also shows additional anodic waves. By comparison with pure [Fc–C≡C–C≡C–Fc], the two first reversible partially overlapped waves (0.59, 0.69 V) could be tentatively assigned to the successive oxidation of both Fc in

Fig. 7 (a) Cyclic voltammogram of **5** in CH₂Cl₂ shows the reversibility of the waves with a scan from −0.6 to 0.4 V. (b) 5th scan of complex **5**, taken without pause, which shows only the waves due to by-products (*), since the two first waves (shown in Fig 7(a)) have vanished.

electrochemically generated [Fc(C≡C)₂Fc]. As can be observed in Fig. 7(b), after several scans the waves due to ferrocenyl groups in complex **5** vanish while the ones ascribed to [Fc(C≡C)₂Fc] and the remaining products increase, pointing to a relatively facile oxidative-induced coupling, as was observed in complex **2**. Finally, the cyclic voltammogram of complex **6** (see Fig. S5, ESI†) shows an irreversible oxidation peak at 0.09 V, together with an additional oxidation (0.65 V) and a reduction peak (0.50 V). The irreversibility of the first wave indicates that **6** decomposes instantaneously after initial oxidation.

In order to obtain further insight into the electronic communication in the neutral complexes **1** and **2**, their chemical oxidation with [N(p-C₆H₄Br)₃][SbCl₆] has been studied by UV-vis spectroscopy. Oxidation was achieved by stepwise addition of oxidant to dichloromethane solutions of both complexes. The electronic spectra do not display the characteristic band of the radical cation [N(p-C₆H₄Br)₃]˙⁺ (700 nm),[105] implying that the radical cation is reduced to the aromatic amine while **1** and **2** are oxidized. As is seen in Fig. 8 for complex **1**, in both cases the spectra of the oxidised species exhibit a new, broad low-energy band (855 nm, **1**; 925 nm **2**), which increases in intensity with successive addition of oxidant (a straight line is obtained from a Beer plot of the absorbance against the equiv. of oxidant, Fig. S6†). This band compares to previous observations in [*trans*-Pt(C≡CFc)₂(PEt₃)₂] (1000 nm) and FcC≡C–C≡CFc (760 nm)[25] after oxidation of the complexes, which have been ascribed to an LMCT transition of ferrocenium groups, thus a similar assignment is proposed. Within the limits of our equipment (to 1100 nm), no IVCT transition has been observed.
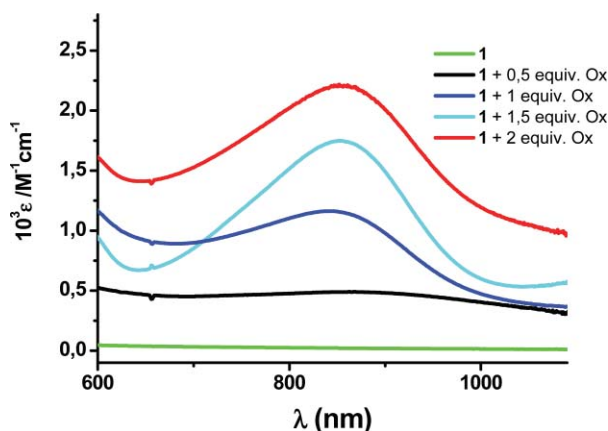
Fig. 8 UV-vis spectra in CH_2Cl_2 of **1** and the oxidized species upon chemical oxidation with $[N(p\text{-}C_6H_4Br)_3][SbCl_6]$ (Ox).

Conclusions

In summary we have described the synthesis, characterization, electronic absorption and electrochemical properties of a series of neutral and anionic bis(ferrocenylethynyl)platinum(II) complexes (**1–6**). In the crystal structure of **6** several hydrogen interactions between the anions and solvent (H_2O, CH_2Cl_2) molecules were found, giving rise to a bidimensional network. The NBu_4^+ cations fit between the layers forming an interesting three-dimensional network. The UV-vis and electrochemical properties of all complexes have been studied. The oxidation of the Fc groups has been found to be easier in the anionic complexes (**3–6**) than in the neutral ones (**1**, **2**), a fact which can be attributed to the higher electronic density in the anionic compounds. In the heteroleptic complexes (**1–5**), a weak electronic interaction between the ferrocenyl moieties has been detected, depending on the charge of the complex and its geometry (dianionic (**4 > 3**) > monoanionic **5** > neutral (**2 > 1**)). In complexes **2** and **5** a facile oxidatively induced coupling has been observed, giving rise to 1,4-diferrocenylbutadiyne, as was also proved by chemical oxidation with $[N(p\text{-}C_6H_4Br)_3][SbCl_6]$ in dichloromethane. Due to the η^2 coordination ability of the alkynyl ligands and the strong basicity of the Pt(II) centre in the anionic complexes, these compounds are potential precursors for preparing interesting, high nuclearity, heterotrimetallic (Pt, Fe, M) systems which are currently under investigation.

Experimental section

All reactions were carried out under Ar using dried solvents purified by known procedures and distilled prior use. IR spectra were recorded on a FT-IR Nicolet Nexus spectrometer as Nujol mulls between polyethylene sheets and NMR spectra were recorded on a Bruker ARX 300 spectrometer and on a Bruker Avance 400. Chemical shifts are reported in ppm relative to external standards ($SiMe_4$, $CFCl_3$ and 85% H_3PO_4). Elemental analyses were carried out with a Perkin-Elmer 2400 CHNS/O microanalyzer and MALDI-TOF spectra on a Microflex MALDI-TOF Bruker spectrometer operating in the linear and reflector modes using dithranol as matrix. Conductivities were measured in nitromethane solutions (*ca.* 5×10^{-4} mol L^{-1}) using a Crison GLP31 conductimeter. Cyclic and pulse differential voltammetry

were carried out in 0.1 M NBu_4PF_6 solutions as supporting electrolyte, using a three-electrode configuration (Pt disk as working electrode, Pt-wire counter electrode, Ag/AgCl reference electrode) and a Voltalab PST 050. The ferrocene/ferrocenium couple served as internal reference (+ 0.46 V *vs* Ag/AgCl). UV-vis absorption spectra were recorded on a Hewlet-Packard 8453 spectrometer. Literature methods were used to prepare the starting materials $[Pt(C\equiv CFc)_2(COD)]$,[64] *cis/trans*-$[Pt(C_6F_5)_2(tht)_2]$[106] and $[Pt(bzq)(\mu\text{-}Cl)]_2$.[107]

Synthesis of $[Pt(C\equiv CFc)_2(dppf)]$ 2

To a solution of $[Pt(COD)(C\equiv CFc)_2]$ (0.2 g, 0.27 mmol) in CH_2Cl_2 (20 cm³) was added dppf (0.15 g, 0.27 mmol) and the mixture was stirred for 1 h. The solution was concentrated to small volume (5 cm³) under vacuum and the addition of EtOH ($\sim$3 cm³) afforded **2** as an orange solid (0.26 g, 80%) (Found: C, 59.38; H, 3.88 $C_{58}H_{46}Fe_3P_2Pt$ requires C, 59.67; H, 3.97%); IR ν_{max}(Nujol)/cm^{-1} 2129 (m), 2116 (m) ν(C≡C); δ_H (300.1 MHz; CDCl₃; 20 °C) 7.87 (m, 8H, Ph), 7.37 (m, 12H, Ph), 4.28 (s, 4H$_\alpha$, dppf), 4.18 (s, 4H$_\beta$, dppf), 3.94 (s, 10H, Cp, Fc), 3.88 (s, 4H, C_5H_4, Fc), 3.83 (s, 4H, C_5H_4, Fc); δ_P (121.5 MHz; CDCl₃; 20 °C) 13.15 (s, $^1J_{Pt\text{-}P}$ = 2363 Hz); δ_C (100.62 MHz; CDCl₃; 20 °C) 135.1 (pt, $J_{C\text{-}P}$ 11.5 Hz, *o*-C, Ph), 133.4 (AXX′, 5 lines pattern, $|^1J_{(C\text{-}P)} + ^3J_{(C\text{-}P)}|$ 57.3 Hz, *i*-C, Ph), 130.4 (s, *p*-C, Ph), 127.8 (pt, $J_{C\text{-}P}$ 10.7 Hz, *m*-Ph), 105.9 (AXX′, 5 lines pattern, $|^3J_{(C\text{-}Ptrans)} + ^3J_{(C\text{-}Pcis)}|$ 35.9 Hz, ≡C$_\beta$), 98.4 (AXX′, dd, $|^2J_{(C\text{-}Ptrans)} + ^2J_{(C\text{-}Pcis)}|$ 176.5 Hz, C$_a$≡), $\sim$75.8 (AXX′, $|^3J_{(C\text{-}P)} + ^3J_{(C\text{-}P)}|$ ∼ 59 Hz, C–P, C_5H_4, dppf), 75.4 (pt, $J_{C\text{-}P}$ 10 Hz, C$_a$, dppf), 72.7 (pt, $J_{C\text{-}P}$ 6.4 Hz, C$_\beta$, dppf), 71.9 (s, *i*-C, C–P, C_5H_4, Fc), 70.6 (s, $C^{2/5}$, Fc), 69.4 (s, Cp, Fc), 66.6 (s, $C^{3/4}$, Fc); *m/z* (MALDI-TOF +) 1168 [M$^+$] (67%), 958 [Pt(dppf)(C≡CFc)] (27%), 749 [Pt(dppf)] (100%).

Synthesis of $(PMePh_3)_2[cis\text{-}Pt(C_6F_5)_2(C\equiv CFc)_2]$ 3

To a solution of $LiC\equiv CFc$ (2.83 mmol) in Et_2O (40 cm³) at −78 °C, prepared from $HC\equiv CFc$ (0.59 g, 2.83 mmol) and *n*-BuLi (1.77 mL, 2.83 mmol), *cis*-$[Pt(C_6F_5)_2(tht)_2]$ (0.39 g, 0.566 mmol) was added. The mixture was stirred at low temperature for 30 min and then allowed to reach room temperature ($\sim$1 h). The solvent was then evaporated to dryness under vacuum. The residue was treated with H_2O/iPrOH (40:60), filtered through Celite and treated with $(PMePh_3)Br$ (2.5 equiv.) to afford **3** as an orange solid (0.51 g, 60%) (Found: C, 59.07; H, 3.71 $C_{74}H_{54}F_{10}Fe_2P_2Pt$ requires C, 59.18; H, 3.62%); Λ_M (CH_3NO_2) 148 Ω^{-1} cm^2 mol^{-1}; IR ν_{max}(Nujol)/cm^{-1} 2090 (sh), 2081 (m) ν(C≡C), 801, 781 $\nu(C_6F_5$ Xsensible); δ_H (300.1 MHz; CDCl₃; 20 °C) 7.85 (m, 12H, *o*-Ph), 7.67 (m, 6H, *p*-Ph), 7.57 (m, 12H, *m*-Ph), 3.88 (s, 4H, C_5H_4), 3.86 (s, 10H, Cp), 3.84 (s, 4H, C_5H_4), 3.73 (d, 6H, $^2J_{P\text{-}H}$ 12.7 Hz, Me, PMePh₃); δ_P (121.5 MHz; CDCl₃; 20 °C) 21.7 (s, PMePh₃); δ_F (282.4 MHz; CD₃Cl₃; 20 °C) −114.5 (dm, $^3J_{Pt\text{-}Fo}$ 388 Hz, 4 F$_o$), −167.9 (m, 4F$_m$), −168.8 (t, 2F$_p$). *m/z* (MALDI-TOF −) 948 [Pt(C₆F₅)₂(C≡CFc)₂] (44%), 780 [Pt(C₆F₅)(C≡CFc)₂] (100%), 529 [Pt(C₆F₅)₂] (80%).

Synthesis of $(NBu_4)_2[trans\text{-}Pt(C_6F_5)_2(C\equiv CFc)_2]$ 4

This complex was prepared in a similar way to **3** starting from $LiC\equiv CFc$ (1.41 mmol) and *trans*-$[Pt(C_6F_5)_2(tht)_2]$ (0.2 g, 0.28 mmol). In this case the reaction time at room temperature

was 5 h and the filtrate was treated with an aqueous solution of $(NBu_4)Br$ (0.23 g, 0.7 mmol) to give **4** as an orange solid (0.29 g, 72%) (Found: C, 56.98; H, 6.41; N 1.95 $PtC_{68}H_{90}N_2Fe_2F_{10}$ requires C, 57.03; H, 6.33; N, 1.96%); Λ_M (CH_3NO_2) 135 Ω^{-1} cm^2 mol^{-1}; IR ν_{max}(Nujol)/cm^{-1} 2093 (m) ν(C≡C); 759 ν($C_6F_{5\ Xsensible}$); δ_H (300.1 MHz; CDCl$_3$; 20 °C) 4.08 (s, 10H, Cp), 3.88 (s, 4H, C_5H_4), 3.80 (s, 4H, C_5H_4), 3.34 (m, 16H, NCH$_2$-, NBu$_4$), 1.54 (m, 16H, -CH$_2$-, NBu$_4$), 1.30 (m, 16H, -CH$_2$-, NBu$_4$), 0.86 (t, 24H, -CH$_3$, NBu$_4$); δ_C (75.5 MHz; CD$_2$Cl$_2$; 20 °C) Only signals due to Fc and NBu$_4$$^+$ are observed, 69.6 (s, Cp, Fc), 65.8 (s, *i*-C, C_5H_4), 65.6 (s, $C^{2/5}$, C_5H_4), 64.3 (s, $C^{3/4}$, C_5H_4), 59.4 (s, N-CH$_2$, NBu$_4$), 24.8 (s, -CH$_2$-), 19.8 (s, -CH$_2$-), 14.1 (s, -CH$_3$, NBu$_4$); δ_F (282.4 MHz; CDCl$_3$; 20 °C) −112.0 (dm, $^3J_{Pt-Fo}$ 390 Hz, 4 F$_o$), −168.7 (m, 4F$_m$), −169.5 (t, 2F$_p$); *m/z* (MALDI-TOF −) 738 [Pt(C$_6$F$_5$)$_2$(C≡CFc)] (100%), 529 [Pt(C$_6$F$_5$)$_2$] (12%).

Synthesis of (NBu$_4$)[Pt(bzq)(C≡CFc)$_2$] 5

To a low temperature (−70 °C) solution of LiC≡CFc (3.42 mmol) prepared from HC≡CFc (0.723 g, 3.42 mmol) and *n*-BuLi 1.6 N (2.15 ml, 3.42 mmol) in Et$_2$O (30 cm^3), [Pt(bzq)(μ-Cl)]$_2$ (0.400 g, 0.489 mmol) was added. The mixture was then allowed to warm to 25 °C and then stirred for 1.5 h. The solvent was removed *in vacuo* and the resulting brown residue was extracted with CHCl$_3$, filtered and treated with 0.237 g (0.73 mmol) of (NBu$_4$)Br. The solution was concentrated again to dryness and the addition of cold acetone (∼ 5 mL) caused the precipitation of **5** as an orange solid (0.372 g, 37%) (Found: C, 61.20; H 5.91, N 2.65. $C_{53}H_{62}Fe_2N_2Pt$ requires C, 61.57; H 6.04, N 2.71%); Λ_M (CH_3NO_2) 79.2 Ω^{-1} cm^2 mol^{-1}; IR ν_{max}(Nujol)/cm^{-1} 2100 (vs), 2083 (s) ν(C≡C); δ_H (300.1 MHz; CDCl$_3$; 20 °C) 10.22 (d, J_{H-H} 5.5 Hz, $^3J_{Pt-H}$ 26.3 Hz, H^2, bzq), 8.72 (d, J_{H-H} 7.4 Hz, $^3J_{Pt-H}$ 41.1 Hz, H^9, bzq), 8.24 (d, J_{H-H} = 7.4 Hz,

H^4, bzq), 7.73 (d, J_{H-H} = 9.8 Hz, 1H, bzq), 7.60–7.44 (m, 4H, bzq), 4.35 (s br, 4H, C_5H_4), 4.28 (s, 5H, Cp), 4.26 (s, 5H, Cp), 4.03 (s, 2H, C_5H_4), 4.01 (s, 2H, C_5H_4), 3.26 (m, 8H, -CH$_2$-, NBu$_4$), 1.39 (m. 8H, -CH$_2$-, NBu$_4$), 1.19 (m, 8H, -CH$_2$-, NBu$_4$), 0.78 (t, 12H, -CH$_3$, NBu$_4$); δ_C (75.5 MHz; CDCl$_3$; −40 °C) 163.4 (s, C^{10}), 157.7 (s, C^{12}), 150.1 (s, C^2), 143.6 (s, C^{11}), 135.6 (s, C^4), 134.7 (s, C^9), 132.9 (s, C$^{13/14}$), 129.3 (s, C^7), 129.2 (s, C^8), 126.0 (s, C$^{13/14}$), 124.3 (s, C$_a$≡), 122.4 (s, C$^{5/6}$), 120.9 (s, C^3), 119.7 (s, C$^{5/6}$), 101.0 (s, $J_{Pt-Cβ}$ 245 Hz, ≡C$_β$, *trans*-C), 97.4 (s, $J_{Pt-Cβ}$ 450 Hz, ≡C$_β$, *trans*-N), 92.1 (s, C$_a$≡), 70.2 (s, C$^{2/5}$, Fc), 70.0 (s, C$^{2/5}$, Fc), 69.9 (s, *i*-C, C_5H_4, Fc), 69.4 (s, Cp, Fc), 69.2 (s, *i*-C, C_5H_4, Fc), 66.5 (s, C$^{3/4}$, Fc), 66.2 (s, C$^{3/4}$, Fc), 57.7 (s, N-CH$_2$, NBu$_4$), 23.5 (s, -CH$_2$-), 19.2 (s, -CH$_2$-), 13.8 (s, -CH$_3$, NBu$_4$). *m/z* (MALDI-TOF −) 1373.1 [Pt$_2$(bzq)$_2$(C≡CFc)$_3$]$^-$ (5%), 791 [Pt(bzq)(C≡CFc)$_2$]$^-$ (36%).

Synthesis of (NBu$_4$)$_2$[Pt(C≡CFc)$_4$]·2H$_2$O 6·2H$_2$O

[PtCl$_2$(tht)$_2$] (0.35 g, 0.79 mmol) was added to a fresh (−78 °C) solution of LiC≡CFc (4.73 mmol) in Et$_2$O (50 mL). The mixture was stirred at low temperature for 5 min, and then allowed to reach room temperature (*ca.* 2 h). The solvent was removed under vacuum, and the residue extracted with a cold mixture of i-PrOH and H$_2$O (50 : 50) and filtered through Celite. Treatment of the filtrate with (NBu$_4$)Br (0.64 g, 1.98 mmol) caused the precipitation of **6** as an orange solid (0.40 g, 33%) (Found: C, 61.82; H 7.17, N 1.78. $C_{80}H_{112}N_2Fe_4O_2Pt$ requires C, 61.90; H 7.27, N 1.80%); Λ_M (CH_3NO_2) 138 Ω^{-1} cm^2 mol^{-1}; IR ν_{max}(Nujol)/cm^{-1} 2074 (vs) ν(C≡C), bands at 3480 (s) and 1635 due to H$_2$O are also seen; δ_H (300.1 MHz; CDCl$_3$; 20 °C) 4.19 (s, 28H, Fc), 3.94 (st, 8H, C_5H_4), 3.65 (m, 16H, -CH$_2$-, NBu$_4$), 1.74 (m. 16H, -CH$_2$-, NBu$_4$), 1.61 (m, 16H, -CH$_2$-, NBu$_4$), 1.01 (t, 24H, -CH$_3$, NBu$_4$); δ_C (100.62 MHz; CDCl$_3$; 20 °C) 112.4 (pt, J_{C-Pt} 990 Hz, C$_a$≡), 97.2 (pt, J_{C-Pt} 292 Hz,

Table 4 Crystal data and structure refinement parameters for complex **1**·2CHCl$_3$, **2** and **6**·2H$_2$O·2CH$_2$Cl$_2$

	1·2CHCl$_3$	**2**	**6**·2H$_2$O·2CH$_2$Cl$_2$
Empirical formula	C$_{34}$H$_{32}$Cl$_6$Fe$_2$Pt	C$_{58}$H$_{46}$Fe$_3$P$_2$Pt	C$_{82}$H$_{116}$Cl$_4$Fe$_4$N$_2$O$_2$Pt
Formula weight	960.09	1167.53	1722.06
Temperature/K	173(1)	173(1)	100(1)
Wavelength/Å	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	P 2(1)/c	P 2(1)/n	P$\bar{1}$
Crystal dimensions/mm	0.20 × 0.175 × 0.10	0.225 × 0.10 × 0.075	0.10 × 0.10 × 0.05
a/Å	11.6163(3)	10.0422(1)	12.6320(7)
b/Å	16.9063(6)	18.2488(5)	13.2780(5)
c/Å	17.7695(4)	25.2322(7)	13.5760(8)
a/°	90	90	81.272(3)
β/°	104.500(2)	98.312(2)	63.866(2)
γ/°	90	90	70.778(3)
V/Å^3	3378.57(17)	4575.43(18)	1930.2(1)
D$_{calc}$/Mg m^{-3}	1.887	1.695	1.481
Z value	4	4	1
μ(Mo-Kα)/mm^{-1}	5.477	4.090	2.725
F(000)	1872	2320	888
θ range/°	2.37–27.49	3.95–27.49	1.92–27.54
No. of reflns measd	50545	74239	29742
No. of obsd reflns	7724 [R(int) = 0.0830]	10 405 [R(int) = 0.0992]	8828 [R(int) = 0.0733]
Goodness of fit on F^2 ^{a}	1.099	1.098	1.057
Final R indices [I > 2σ(I)]^a	R1 = 0.0433, wR2 = 0.0810	R1 = 0.0432, wR2 = 0.0662	R1 = 0.0453, wR2 = 0.0728
R indices (all data)	R1 = 0.0674, wR2 = 0.0894	R1 = 0.0726, wR2 = 0.0740	R1 = 0.0649, wR2 = 0.0809

^{a} $R1 = \sum(|F_o| - |F_c|)/\sum|F_o|$; $wR2 = [\sum[w(F_o^2 - F_c^2)^2/\sum wF_o^2]]^{1/2}$; goodness of fit = $\{\sum[w(F_o^2 - F_c^2)^2]/(N_{obs} - N_{param})\}^{1/2}$; $w = [\sigma^2(F_o^2) + (g_1P)^2 + g_2P]^{-1}$; $P = [max(F_o^2;0) + 2F_c^2]/3$.

$\equiv C_\beta$), 75.5 (s, *i*-C, C_5H_4, Fc), 70.1 (s, $C^{2/5}$, C_5H_4, Fc), 66.5 (s, Cp, Fc), 66.3 (s, $C^{3/4}$, C_5H_4, Fc), 59.4 (s, N-CH_2, NBu_4), 24.8 (s, -CH_2-), 20.0 (s, -CH_2-), 14.2 (s, -CH_3, NBu_4); *m/z* (MALDI-TOF −): Molecular peak not observed.

X-Ray crystal structure determinations

Table 1 reports details of the structural analyses and Table 4 crystal data and structure refinement parameters for complexes **1**, **2** and **6**. Red (**1**, **6**) or orange (**2**) crystals were grown by diffusion of *n*-hexane into a solution of $CHCl_3$ (**1**) or CH_2Cl_2 (**2**) at −30 °C or by slow evaporation of a CH_2Cl_2 saturated solution of the compound at room temperature (**6**). For complex **1**, two molecules of $CHCl_3$ and for complex **6**, one molecule of H_2O and one of CH_2Cl_2 were found in the asymmetric unit. X-Ray studies were performed with a NONIUS-κCCD area-detector diffractometer, using graphite-monochromated Mo-K_α radiation. The data were processed using the DENZO[108] and SCALEPACK[108] software. Structures **1** and **6** were solved by Patterson and **2** by direct methods, and refined by full-matrix least squares on F^2 using SHELXL-97.[109] For all complexes, absorption corrections were carried out using MULTISCAN.[110] In **6**, the positions of both H_2O hydrogen atoms were found in the density maps. They were refined with no positional constraints and a common thermal isotropic parameter. The rest of the hydrogen atoms (and all hydrogen atoms in **1** and **2**) were constrained to idealized geometries fixing isotropic displacement parameters 1.2 times the U_{iso} value of their attached carbon for the aromatic and CH_2 hydrogen atoms and 1.5 times for the methyl groups (in NBu_4 molecules of **6**). Non-hydrogen atoms were refined with anisotropic displacement parameters. Finally, **1** and **6** present some residual peaks greater than 1 e Å^{-3} in the vicinity of the platinum atoms, but with no chemical meaning.

References

1 I. Manners, in *Synthetic Metal Containing Polymers*, Wiley-VCH, Weinheim, 2004.
2 P. J. Low, *Dalton Trans.*, 2005, **17**, 2821.
3 J. Otsuki, T. Akasaka and K. Araki, *Coord. Chem. Rev.*, 2008, **252**, 32.
4 R. Sakamoto, M. Murata and H. Nishihara, *Angew. Chem., Int. Ed.*, 2006, **45**, 4793.
5 R. A. Wassel and C. B. Gorman, *Angew. Chem., Int. Ed.*, 2004, **43**, 5120.
6 S. C. Jones, V. Coropceanu, S. Barlow, T. Kinnibrugh, T. Timofeeva, J. L. Brédas and S. R. Marder, *J. Am. Chem. Soc.*, 2004, **126**, 11782.
7 L. Kondrachova, K. E. Paris, P. C. Sanchez, A. M. Vega, R. Pyati and C. D. Rithner, *J. Electroanal. Chem.*, 2005, **576**, 287.
8 T. L. Schull, J. G. Kushmerick, C. H. Patterson, C. George, M. H. Moore, S. K. Pollack and R. Shashidhar, *J. Am. Chem. Soc.*, 2003, **125**, 3202.
9 S. Rigaut, D. Touchard and P. H. Dixneuf, *Coord. Chem. Rev.*, 2004, **248**, 1585.
10 P. Leoni, L. Marchetti, S. K. Mohapatra, G. Ruggeri and L. Ricci, *Organometallics*, 2006, **25**, 4226.
11 T. M. Cooper, in *Encyclopedia of Nanoscience and Nanotechnology*, ed. H. S. Nalwa, American Scientific Publishers, Valencia, CA, 2004.
12 K. Venkatesan, O. Blacque and H. Berke, *Dalton Trans.*, 2007, 1091.
13 S. Rigaut, *Chem. Commun.*, 2007, 3100.
14 S. Szafert and J. A. Gladysz, *Chem. Rev.*, 2006, **106**, PR1.
15 K. Osakada, in *Comprehensive Organometallic Chemistry III*, ed. A. Canty, Elsevier, Oxford, 2007, vol. 8, pp. 445–609.
16 R. D'amato, A. Furlani, M. Colapietro, G. Portalone, M. Casalboni, M. Falconieri and M. V. Russo, *J. Organomet. Chem.*, 2001, **627**, 13.
17 M. Mayor, C. von Hänisch, H. B. Weber, J. Reichert and D. Beckmann, *Angew. Chem., Int. Ed.*, 2002, **41**, 1183.
18 Special issue on the "50th Anniversary of the Discovery of Ferrocene", *J. Organomet. Chem.*, 2001, **637–639**.
19 T. Y. Dong, S. W. Chang, S. F. Lin, M. C. Lin, Y. S. Wen and L. Lee, *Organometallics*, 2006, **25**, 2018.
20 E. Peris, *Coord. Chem. Rev.*, 2004, **248**, 279.
21 S. Creager, C. J. Yu, C. Bamdad, S. O'Connor, T. MacLean, E. Lam, Y. Chong, G. T. Olsen, J. Luo, M. Gozin and J. F. Kayyem, *J. Am. Chem. Soc.*, 1999, **121**, 1059.
22 T. Y. Dong, M. C. Lin, S. W. Chang, C. C. Ho, S. F. Lin and L. Lee, *J. Organomet. Chem.*, 2007, **692**, 2324.
23 T. Y. Dong, K. Chen, M. C. Lin and L. Lee, *Organometallics*, 2005, **24**, 4198.
24 G. Vives, A. Gonzalez, J. Jaud, J. P. Launay and G. Rapenne, *Chem.–Eur. J.*, 2007, **13**, 5622.
25 G. Vives, A. Carella, S. Sistach, J. P. Launay and G. Rapenne, *New J. Chem.*, 2006, **30**, 1429.
26 N. J. Long, A. J. Martin, R. Vilar, A. J. P. White, D. J. Williams and M. Younus, *Organometallics*, 1999, **18**, 4261.
27 O. Crespo, M. C. Gimeno, P. G. Jones, A. Laguna and C. Sarroca, *Chem. Commun.*, 1998, 1481.
28 H. W. Shih and T. Y. Dong, *Inorg. Chem. Commun.*, 2004, **7**, 646.
29 K. W. Poon, Y. Yan, X. Y. Li and D. K. P. Ng, *Organometallics*, 1999, **18**, 3528.
30 M. W. Cooke, T. S. Cameron, K. N. Robertson, J. C. Swarts and M. A. S. Aquino, *Organometallics*, 2002, **21**, 5962.
31 N. Prokopuk and D. F. Shriver, *Inorg. Chem.*, 1997, **36**, 5609.
32 S. Achar, C. E. Immoos, M. G. Hill and V. J. Catalano, *Inorg. Chem.*, 1997, **36**, 2314.
33 Q. H. Wei, G. Q. Yin, L. Y. Zhang and Z. N. Chen, *Organometallics*, 2006, **25**, 4941.
34 Q. H. Wei, L. Y. Zhang, L. X. Shi and Z. N. Chen, *Inorg. Chem. Commun.*, 2004, **7**, 286.
35 D. Salazar-Mendoza, S. A. Baudron, M. W. Hosseini, N. Kyritsakas and A. De Cian, *Dalton Trans.*, 2007, 565.
36 V. Chandrasekhar, S. Nagendran, S. Bansal, A. W. Cordes and A. Vij, *Organometallics*, 2002, **21**, 3297.
37 M. V. Barybin, T. C. Holovics, S. F. Deplazes, G. H. Lushington, D. R. Powell and M. Toriyama, *J. Am. Chem. Soc.*, 2002, **124**, 13668.
38 R. Horikoshi, C. Nambu and T. Mochida, *Inorg. Chem.*, 2003, **42**, 6868.
39 Y. N. Liu, G. Orlowski, G. Schatte and H. B. Kraatz, *Inorg. Chim. Acta*, 2005, **358**, 1151.
40 U. Siemeling, J. Vor der Brüggen, U. Vorfeld, B. Neumann, A. Stammler, H. G. Stammler, A. Brockhinke, R. Plessow, P. Zanello, F. Laschi, F. Fabrizi de Biani, M. Fontani, S. Steenken, M. Stapper and G. Gurzadyan, *Chem.–Eur. J.*, 2003, **9**, 2819.
41 M. J. L. Tschan, B. Therrien, J. Ludvík, P. Stepnicka and G. Süss-Fink, *J. Organomet. Chem.*, 2006, **691**, 4304.
42 Z. Li, A. M. Beatty and T. P. Fehlner, *Inorg. Chem.*, 2003, **42**, 5707.
43 G. L. Xu, M. C. DeRosa, R. J. Crutchley and T. Ren, *J. Am. Chem. Soc.*, 2004, **126**, 3728.
44 G. L. Xu, R. J. Crutchley, M. C. DeRosa, Q. J. Pan, H. X. Zhang, X. Wang and T. Ren, *J. Am. Chem. Soc.*, 2005, **127**, 13354.
45 J. H. K. Yip, J. Wu, K. Y. Wong, K. W. Yeung and J. J. Vittal, *Organometallics*, 2002, **21**, 1612.
46 A. Albinati, F. Fabrizi de Biani, P. Leoni, L. Marchetti, M. Pasquali, S. Rizzato and P. Zanello, *Angew. Chem., Int. Ed.*, 2005, **44**, 5701.
47 N. D. Jones, M. O. Wolf and D. M. Giaquinta, *Organometallics*, 1997, **16**, 1352.
48 M. Mayor, H. B. Weber, J. Reichert, M. Elbing, C. von Hänisch, D. Beckmann and M. Fischer, *Angew. Chem., Int. Ed.*, 2003, **42**, 5834.

49 S. N. Yalikari and M. A. Ratner, *Ann. N. Y. Acad. Sci.*, 2002, **960**, 153.
50 J. Forniés, S. Fuertes, A. Martín, V. Sicilia, E. Lalinde and M. T. Moreno, *Chem.–Eur. J.*, 2006, **12**, 8253.
51 J. Fernández, J. Forniés, B. Gil, J. Gómez, E. Lalinde and M. T. Moreno, *Organometallics*, 2006, **25**, 2274.
52 I. Ara, J. R. Berenguer, E. Eguizábal, J. Forniés, J. Gómez and E. Lalinde, *J. Organomet. Chem.*, 2003, **670**, 221.
53 J. R. Berenguer, J. Forniés, J. Gómez, E. Lalinde and M. T. Moreno, *Organometallics*, 2001, **20**, 4847.
54 J. Forniés, J. Gómez, E. Lalinde and M. T. Moreno, *Inorg. Chem.*, 2001, **40**, 5415.
55 B. Gil, J. Forniés, J. Gómez, E. Lalinde, A. Martín and M. T. Moreno, *Inorg. Chem.*, 2006, **45**, 7788.
56 I. Ara, J. Forniés, J. Gómez, E. Lalinde and M. T. Moreno, *Organometallics*, 2000, **19**, 3137.
57 J. Forniés, S. Ibáñez, A. Martín, B. Gil, E. Lalinde and M. T. Moreno, *Organometallics*, 2004, **23**, 3963.
58 I. Ara, J. R. Berenguer, J. Forniés, J. Gómez, E. Lalinde, A. Martín and R. Merino, *Inorg. Chem.*, 1997, **36**, 6461.
59 J. P. H. Charmant, J. Forniés, J. Gómez, E. Lalinde, R. I. Merino, M. T. Moreno and A. G. Orpen, *Organometallics*, 2003, **22**, 652.
60 J. R. Berenguer, J. Forniés, B. Gil and E. Lalinde, *Chem.–Eur. J.*, 2006, **12**, 785.
61 S. Fery-Forgues, B. Delavaux-Nicot, D. Lavabre and K. Rurack, *J. Photochem. Photobiol., A*, 2003, **155**, 107.
62 S. Fery-Forgues and B. Delavaux-Nicot, *J. Photochem. Photobiol., A*, 2000, **132**, 137.
63 E. J. Lee and M. S. Wrighton, *J. Am. Chem. Soc.*, 1991, **113**, 8562.
64 M. Herberhold, T. Schmalz, W. Milius and B. Wrackmeyer, *J. Organomet. Chem.*, 2002, **641**, 173.
65 P. Espinet, J. Forniés, F. Martínez, M. Sotés, E. Lalinde, M. T. Moreno, A. Ruiz and A. J. Welch, *J. Organomet. Chem.*, 1991, **403**, 253.
66 J. Benito, J. R. Berenguer, J. Forniés, B. Gil, J. Gómez and E. Lalinde, *Dalton Trans.*, 2003, 4331 and references therein.
67 S. Fernández, J. Forniés, B. Gil, J. Gómez and E. Lalinde, *Dalton Trans.*, 2003, 822.
68 W. J. Geary, *Coord. Chem. Rev.*, 1971, **7**, 81.
69 W. Y. Wong, G. L. Lu and K. H. Choi, *J. Organomet. Chem.*, 2002, **659**, 107.
70 J. D. Bradshaw, L. Guo, C. A. Tessier and W. J. Youngs, *Organometallics*, 1996, **15**, 2582.
71 R. Saha, M. A. Qaium, D. Debnath, M. Younus, N. Chawdhury, N. Sultana, G. Kociok-Köhn, L. L. Ooi, P. R. Raithby and M. Kijima, *Dalton Trans.*, 2005, 2760.
72 K. Campbell, R. McDonald, M. J. Ferguson and R. R. Tykwinski, *J. Organomet. Chem.*, 2003, **683**, 379.
73 A. B. Goel, S. Goel and D. Van Der Veer, *Inorg. Chim. Acta*, 1982, **65**, L205.
74 J. Manna and K. D. Hopkins, *Adv. Organomet. Chem.*, 1995, **38**, 79.
75 U. Siemeling, K. Bausch, H. Fink, C. Bruhn, M. Baldus, B. Angerstein, R. Plessow and A. Brockhinke, *Dalton Trans.*, 2005, 2365.
76 G. Bandoli and A. Dolmella, *Coord. Chem. Rev.*, 2000, **209**, 161.
77 S. S. Sun, J. A. Anspach, A. J. Lees and P. Y. Zavalij, *Organometallics*, 2002, **21**, 685.
78 W. Weigand and C. Robl, *Chem. Ber.*, 1993, **126**, 1807.
79 H. C. Weiss, R. Boese, H. L. Smith and M. M. Haley, *Chem. Commun.*, 1997, 2403.
80 M. S. Khan, M. R. A. Al-Mandhary, M. K. Al-Suti, F. R. Al-Battashi, S. Al-Saadi, B. Ahrens, J. K. Bjernemose, M. F. Mahon, P. R. Raithby, M. Younus, N. Chawdhury, A. Köhler, E. A. Marseglia, E. Tedesco, N. Feeder and S. J. Teat, *Dalton Trans.*, 2004, 2377.
81 W. Lu, M. C. W. Chan, N. Zhu, C. M. Che, Z. He and K. Y. Wong, *Chem.–Eur. J.*, 2003, **9**, 6155.
82 A. Furlani, S. Licoccia, M. V. Russo, A. C. Villa and C. Guastini, *J. Chem. Soc., Dalton Trans.*, 1984, 2197.
83 A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441.
84 J. R. Berenguer, E. Lalinde and J. Torroba, *Inorg. Chem.*, 2007, **46**, 9919.
85 H. B. Gray, Y. S. Sohn and N. Hendrickson, *J. Am. Chem. Soc.*, 1971, **93**, 3603.
86 M. M. Bhadbhade, A. Das, J. C. Jeffery, J. A. McCleverty, J. A. Navas Badiola and M. D. Ward, *J. Chem. Soc., Dalton Trans.*, 1995, 2769.
87 S. Barlow, H. E. Bunting, C. Ringham, J. C. Green, G. U. Bublitz, S. G. Boxer, J. W. Perry and S. R. Marder, *J. Am. Chem. Soc.*, 1999, **121**, 3715.
88 J. Forniés, S. Ibáñez, A. Martín, B. Gil, E. Lalinde and M. T. Moreno, *Organometallics*, 2004, **23**, 3963.
89 K. Haskins-Glusac, I. Ghiviriga, K. A. Abboud and K. S. Schanze, *J. Phys. Chem. B*, 2004, **108**, 4969.
90 A. Klein, J. van Slageren and S. Záliš, *J. Organomet. Chem.*, 2001, **620**, 202.
91 X. Han, L. Z. Wu, G. Si, J. Pan, Q. Z. Yang, L. P. Zhang and C. H. Tung, *Chem.–Eur. J.*, 2007, **13**, 1231.
92 D. Astruc, in *Electron Tranfer and Radical Processes in Transition-Metal Chemistry*, VCH, New York, 1995.
93 P. Zanello, in *Inorganic Electrochemistry. Theory, Practice and Application*, The Royal Society of Chemistry, Cambridge, 2003.
94 D. Osella, R. Gobetto, C. Nervi, M. Ravera, R. D'amato and M. V. Russo, *Inorg. Chem. Commun.*, 1998, **1**, 239.
95 W. Y. Wong, G. L. Lu, K. F. Ng, K. H. Choi and Z. Lin, *J. Chem. Soc., Dalton Trans.*, 2001, 3250.
96 K. R. Justin Thomas, J. T. Lin and K. J. Lin, *Organometallics*, 1999, **18**, 5285.
97 M. Sato, E. Mogi and M. Katada, *Organometallics*, 1995, **14**, 4837.
98 M. Younus, N. J. Long, P. R. Raithby and J. Lewis, *J. Organomet. Chem.*, 1998, **570**, 55.
99 J. Granifo, M. E. Vargas, M. T. Garland and R. Baggio, *Inorg. Chim. Acta*, 2000, **305**, 143.
100 H. Lang and T. Stein, *J. Organomet. Chem.*, 2002, **641**, 41.
101 S. Back, H. Pritzkow and H. Lang, *Organometallics*, 1998, **17**, 41.
102 Y. Hayashi, M. Osawa, K. Kobayashi, T. Sato, M. Sato and Y. Wakatsuki, *J. Organomet. Chem.*, 1998, **569**, 169.
103 Y. Hayashi, M. Osawa and Y. Wakatsuki, *J. Organomet. Chem.*, 1997, **542**, 241.
104 C. V. Ursini, G. H. M. Dias, M. Hörner, A. J. Bortoluzzi and M. K. Morigaki, *Polyhedron*, 2000, **19**, 2261.
105 N. G. Connelly and W. E. Geiger, *Chem. Rev.*, 1996, **96**, 877.
106 R. Usón, J. Forniés, F. Martinez and M. Tomás, *J. Chem. Soc., Dalton Trans.*, 1980, 888.
107 P. S. Pregosin and F. Wombacher, *J. Organomet. Chem.*, 1991, **418**, 249.
108 Z. Otwinowski and W. Minor, *Methods Enzymol.*, 1997, **276**, 307.
109 G. M. Sheldrick, *SHELX-97, a program for the refinement of crystal structures*, University of Göttingen, Germany, 1997.
110 R. H. Blessing, *Acta Crystallogr., Sect. A*, 1995, **51**, 33.