Trinuclear π-conjugated chromophores formed by a neutral ferrocenyl group and a cationic mixed ruthenium sandwich linked through an unsymmetrical Schiff-base complex spacer†

Mauricio Fuentealba,‡[a] Jean-René Hamon,*[b] David Carrillo[a] and Carolina Manzur*[a]

Received (in Montpellier, France) 24th May 2007, Accepted 27th June 2007
First published as an Advance Article on the web 18th July 2007
DOI: 10.1039/b707934f

The synthesis of neutral dinuclear unsymmetrical Schiff base complexes **1** and **2** was carried out in an one-pot two-step reaction sequence that involves the reaction of 1-ferrocenyl-1,3-butanedione with an excess of ethylenediamine in refluxing CH_2Cl_2, to generate the intermediate "half-unit" Fc–C(O)$CH_2C(CH_3)$=$NCH_2CH_2NH_2$, Fc = (η^5-Cp)Fe(η^5-C_5H_4), Cp = C_5H_5), followed by its *in situ* templated reaction with salicylaldehyde and nickel(II) or copper(II) acetate in refluxing CH_2Cl_2–EtOH (3 : 1) mixture. On the other hand, ionic trinuclear unsymmetrical complexes $>$**3**]$^+PF_6^-$ and [**4**]$^+PF_6^-$ were synthesized by reacting dinuclear precursors **1** and **2**, respectively, with [(η^5-Cp*)Ru($CH_3CN)_3]^+PF_6^-$, Cp* = C_5Me_5, in refluxing CH_2Cl_2. Both complexes contain the neutral electron-releasing ferrocenyl group and the cationic electron-withdrawal sandwich, [(η^5-Cp*)Ru(η^6-arene)]$^+$, connected by a tetradentate {M(ONNO)} chelate (M = Ni, Cu). The new unsymmetrical organometallic Schiff base compounds were characterized by elemental analysis, IR, UV-Vis, ^{1}H NMR and EPR spectroscopy. In addition, the Ni(II) containing complexes **1** and [**3**]$^+PF_6^-$ were authenticated by X-ray diffraction analysis. Solvatochromic and electrochemical properties were also studied. The organometallic–inorganic hybrid unsymmetrical Schiff base complexes [**3**]$^+PF_6^-$ and [**4**]$^+PF_6^-$ can be defined as type I non-rod-shaped dipolar chromophores.

Introduction

Unsymmetrical tetradentate Schiff bases derived from the 1 : 1 : 1 stepwise condensation of β-diketone, salicylaldehyde and a variety of alkyl- or aryldiamines and their metal(II) complexes have been known for decades.[1,2] Interests for these complexes come from the fact they can serve as synthetic models related to biological systems,[3] as catalysts in some homogeneous[4] and supported chemical processes,[5] and very recently as non-linear optical (NLO) materials.[6] Their attractiveness does also come from their preparative accessibility, their structural variability and, in addition, their tunable electronic properties allowing to carry out systematic reactivity studies based on ancillary ligand modifications. The product of monocondensation of 2,4-pentanedione with 1,2-ethanediamine (Chart 1, **A**), so-called "half-unit", first reported by Costes *et al.*,[7] and its singly condensed congeners resulting from higher aliphatic diamines[8] have widely been used as precursors for the preparation of unsymmetrical quadridentate Schiff base ligands (Chart 1, **B**) by the condensation of their free, primary, amino groups with a variety of organic reagents comprising carbonyl functionality.[2,7–9] Through the loss of the enamine and hydroxyl protons, these *cis*-N_2O_2 ligands have been used to form neutral Werner-type complexes (Chart 1 **C**) with a number of divalent metal ions. A great deal of work was therefore directed towards the spectroscopic and structural properties of such Schiff base compounds.

In all the above-mentioned work as well as in the parent salen-type series (salen = *N*,*N'*-ethylenebis(salicylideneiminato)),[10] organic groups have always been used to structurally and electronically modify the properties of the Schiff base frameworks. Recently, the ubiquitous ferrocenyl subunit, (η^5-Cp)Fe(η^5-C_5H_4) where Cp = C_5H_5, was introduced in the build-up of those acyclic chelate backbones as a symmetrical tetradentate ligand derived from the 2 : 1 condensation of 1-ferrocenyl-1,3-butanedione with 1,2-diaminoethane (Chart 1, **D**).[11] Both the copper(II) and nickel(II) complexes of this organometallic bis-enaminoketonate ligand were crystallographically characterized. Compared to organic molecules, organotransition metal complexes offer many exciting possibilities due to their diverse structural, electronic and optical properties and are, therefore, expected to possess physical properties significantly different from their organic counterparts.[12] The present contribution to this area entails the design of an unprecedented class of organometallic-inorganic hybrids (Chart 1, **E** and **F**). Ferrocene and the cationic sandwich [(η^5-Cp*)Ru(η^6-arene)]$^+$ (Cp* = C_5Me_5) were used

---

[a] *Laboratorio de Química Inorgánica, Instituto de Química, Pontificia Universidad Católica de Valparaíso, Avenida Brasil 2950, Valparaíso, Chile E-mail: cmanzur@ucv.cl*
[b] *UMR 6226 «Sciences Chimiques de Rennes», CNRS–Université de Rennes 1–Campus de Beaulieu, 35042 Rennes Cedex, France. E-mail: jean-rene.hamon@univ-rennes1.fr*

† Dedicated to the memory of Pierre Guénot.

‡ Present address: Laboratorio de Cristalografía, Departamento de Física, Facultad de Ciencias Físicas y Matemáticas, Universidad de Chile, Av. Blanco Encalada 2008, Santiago, Chile.

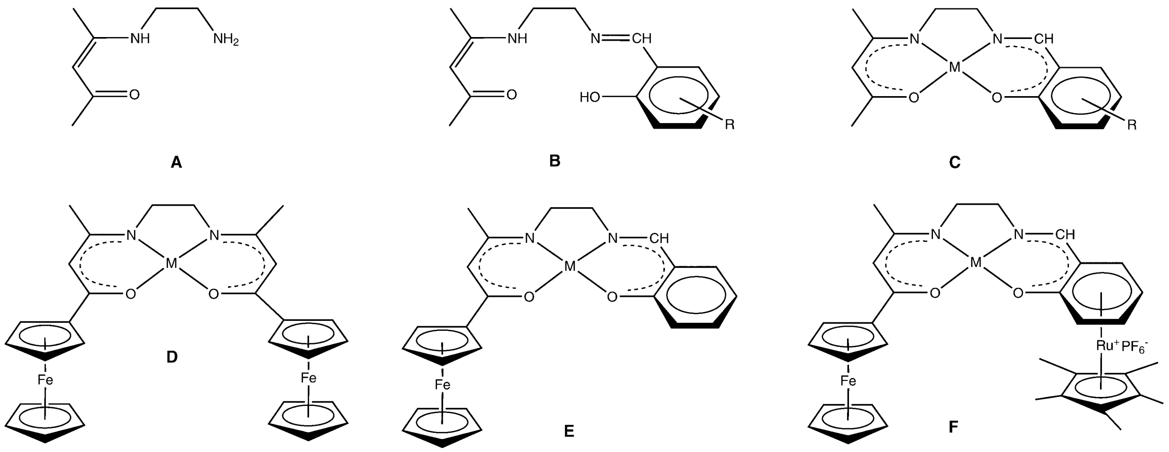


Chart 1

as donor (D) and acceptor (A) building blocks, respectively, and unsymmetrical $\{M(N_2O_2)\}$ Schiff base cores (M = Ni, Cu) were employed as conjugated linkers (π) in the construction of these novel D–π–A molecules. In branching such strong electron releasing and withdrawing organometallic end groups at the contour of the unsymmetrical Schiff base platform, one would expect some synergistic effects to occur, leading for instance to the enhancement of NLO properties of these new salen-type derivatives.[6,13] Here, we wish to report on the synthesis, the analytical and spectroscopic characterization (IR, UV-Vis, ^{1}H NMR and EPR) of these bi- and tri-heteronuclear complexes (Chart 1, **E** and **F** types, respectively). Their electronic and electrochemical properties have also been investigated and, in addition, the molecular and crystal structures of the two nickel containing derivatives, namely compounds **1** and $[\mathbf{3}]^+PF_6^-$ (see Schemes 1 and 2 below), have been determined. Detailed results and discussion are elaborated in the following sections.

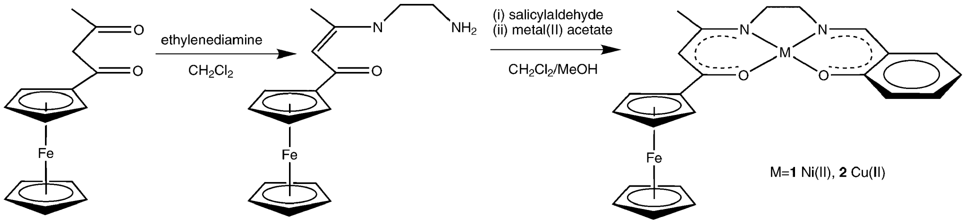
Results and discussion

Synthesis of the complexes

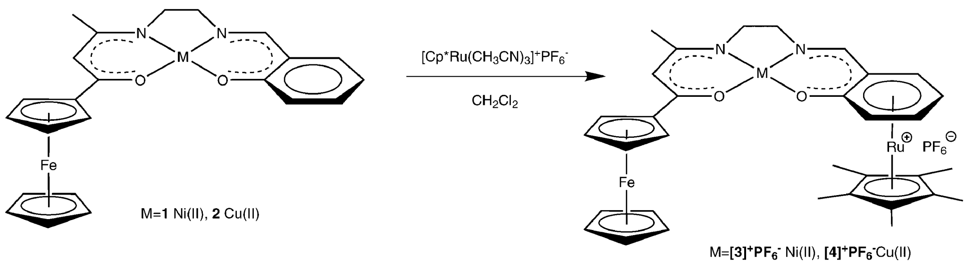
The well-known 1-ferrocenyl-1,3-butanedione, $(\eta^5\text{-}Cp)Fe(\eta^5\text{-}C_5H_4)C(O)CH_2C(O)CH_3$, was prepared in 48% yield following an improvement of the methods described earlier.[14] Indeed, our modified procedure was carried out at room temperature using the commercially available and easy to handle potassium *tert*-butoxide as basic initiator. The present one-pot method does avoid the low-temperature generation of strong bases, such metal amides (H_2N^- in liquid ammonia, $(i\text{Pr})_2N^-$) or alkoxides (MeO^-, EtO^-) needed to deprotonate the weakly acidic methyl hydrogen atoms of acetylferrocene. Moreover, the self-aldol condensation of acetylferrocene leads to the formation of side products, which in turn contributes to decrease the yield of the Claisen condensation.[15] However in 2004, Shi *et al.* reported an appealing high yield (83%), fast, large scale (72 mmol) synthesis of the 1-ferrocenyl-1,3-butanedione, using sodium ethoxide as base initiator in refluxing THF for 2 h.[16] We were unfortunately unable to reproduce this synthesis.

The neutral dinuclear Schiff base complexes **1** and **2** were prepared by a templated, one-pot two-step procedure starting from 1-ferrocenyl-1,3-butanedione, 1,2-diaminoethane, salicylaldehyde and metal acetates under mild conditions, as outlined in Scheme 1, according to an improved one-pot method for the synthesis of unsymmetrical organic salen-type nickel(II) complexes.[5a] 1-ferrocenyl-1,3-butanedione was reacted with an excess of ethylenediamine in refluxing CH_2Cl_2 for 1.5 h to generate the known "half-unit" $Fc\text{-}C(O)CH_2C(CH_3){=}NCH_2CH_2NH_2$ (Fc = ferrocenyl),[17] after excess amine was removed *in vacuo*. The metalloligand was reacted *in situ* with salicylaldehyde and then hydrated nickel(II) or copper(II) acetate in refluxing CH_2Cl_2–EtOH (3 : 1) mixture for 4 h to provide the corresponding unsymmetrical organometallic Schiff base complexes **1** and **2**, respectively. These binuclear compounds were isolated in 43 and 38% yield, respectively, as thermally air-stable orange microcrystalline solids after recrystallization from CH_2Cl_2 by slow diffusion of diethyl ether at room temperature. They are soluble in CH_2Cl_2, MeCN, Me_2CO and DMSO, and insoluble in Et_2O and hexane.

All attempts to synthesize complexes **1** and **2** through a one-step procedure by mixing all the reagents in equimolar



Scheme 1



Scheme 2

quantities at once, were unfruitful. Instead, M(salen) complexes (M = Ni, Cu),[18] and M(FcBD)$_2$ (M = Ni, Cu; FcBD = 1-ferrocenyl-1,3-butanedionate)[14c,19] were isolated. During the chromatographic separation of these symmetrical compounds on silica-gel, the desired unsymmetrical Schiff base complexes **1** and **2** were never observed.

On the other hand, the trinuclear complexes $[\mathbf{3}]^+PF_6^-$ and $[\mathbf{4}]^+PF_6^-$ were readily synthesized by reacting their respective precursors **1** and **2** with the arenophile source $[(\eta^5\text{-Cp*})Ru(NCCH_3)_3]^+PF_6^-$,[20] in refluxing CH_2Cl_2 for 15 h, as outlined in Scheme 2. These two first representatives of the unprecedented class of organometallic–inorganic hybrid unsymmetrical Schiff base complexes were isolated in 76 and 67% yield, respectively, as thermally air-stable dark red crystalline solids, after recrystallization from CH_2Cl_2–Et_2O. They are soluble in common polar organic solvents and insoluble in ethers and aliphatic solvents. Both complexes contain the neutral electron-releasing group, $(\eta^5\text{-Cp})Fe(\eta^5\text{-}C_5H_4)$–, and the cationic electron-withdrawing group, $[(\eta^5\text{-Cp*})Ru(\eta^6\text{-arene})]^+$, linked by a Ni(II) or Cu(II) classical Werner type coordination sets {M(ONNO)} (see Scheme 2). The cationic 12-electron $(\eta^5\text{-Cp*})Ru^+$ arenophile was chosen to build up the acceptor part of the targeted molecules because no convenient sources of $(\eta^5\text{-}C_5R_5)Fe^+$ (R = H, Me), as their trisolvate adducts, are practically available.[21,22] Bis-organoiron Schiff base complexes would, indeed, be of interest for purpose of comparison of their physical properties with those of our previously reported dipolar hydrazone-bridged bis-organoiron chromophores $[CpFe(\eta^6\text{-aryl})\text{-}NH\text{–}N{=}CH\text{–}Fc]^+PF_6^-$.[23] In other respects, ligand substitution reactions between a ring of ferrocene and aromatic are carried out in the presence of the strong Lewis acid $AlCl_3$,[24] which is in fact, incompatible with the functionalized aromatics **1** and **2** used here.[25]

Spectroscopic characterization

The four new complexes **1**, **2**, $[\mathbf{3}]^+PF_6^-$ and $[\mathbf{4}]^+PF_6^-$ were characterized by satisfactory elemental analyses, IR and UV-Vis spectroscopy (see Experimental section). The ^{1}H NMR and electron paramagnetic resonance (epr) spectra were also recorded for the diamagnetic nickel derivative **1** and $[\mathbf{3}]^+PF_6^-$ and the paramagnetic copper complex **2** and $[\mathbf{4}]^+PF_6^-$, respectively. Additionally, the crystal and molecular structures of **1** and $[\mathbf{3}]^+PF_6^-$ were determined by single-crystal X-ray diffraction analysis (see below). On the other hand, the ESI$^+$ mass spectra of **2** and $[\mathbf{4}]^+PF_6^-$ exhibit molecular ions (100%) corresponding to M$^+$ and the cationic fragment C$^+$, respectively, with the characteristic isotopic distribution patterns.

The more salient features of the solid-state IR spectra of these four complexes is the presence of a set of medium to strong intensity bands in the 1638–1507 cm^{-1} region which can be attributed to the ν(C$\stackrel{..}{-}$C), ν(C$\stackrel{..}{-}$N) and/or ν(C$\stackrel{..}{-}$O) stretching modes of the organic Schiff base skeleton. Interestingly, these stretching vibrations are barely shifted towards higher wavenumbers despite the cationic nature of the compounds for the two trinuclear derivatives. The absence of characteristic ν(O–H) and ν(N–H) stretching bands at >3100 cm^{-1} indicates that the ligand is bonded to nickel and copper ions in the dianionic form. In addition, the characteristic band observed at 761 and 758 cm^{-1}, for **1** and **2**, respectively, is attributed to the aromatic δ(C–H) mode associated to the *ortho* substitution, whereas the IR spectra of $[\mathbf{3}]^+PF_6^-$ and $[\mathbf{4}]^+PF_6^-$ show a very strong band at 844 and a medium intensity band at 557 cm^{-1}, attributed to the ν(P–F) and $\delta(PF_6)$ modes of the PF_6^- anion, testifying the presence of the arenophile unit $(\eta^5\text{-Cp*})Ru^+$.

The ^{1}H NMR spectrum of complex **1** exhibits the expected resonance pattern consistent with the proposed structure. The asymmetry of the ligand is, indeed, clearly reflected in the ethylenediamine region, which exhibits two distinct triplet resonances at 3.06 and 3.37 ppm. Moreover, the substituted cyclopentadienyl rings display two broad singlets at 4.24 and 4.65 ppm (Fig. 1(a)), whereas a sharp singlet at 4.16 ppm is due to protons of the unsubstituted cyclopentadienyl rings. In contrast, the methyl protons show a singlet at 1.97 ppm. The singlet at 5.33 ppm may be assigned to the *pseudo*-aromatic methine proton. The phenyl protons appear in the range 6.49–7.17 ppm (Fig. 2(a)), whereas the downfield singlet signal attributed to the azomethine proton showed up at 7.42 ppm.

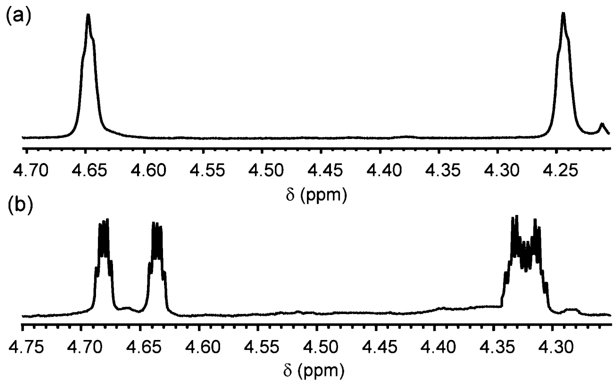


Fig. 1 Resonance patterns of H$_\alpha$ and H$_\beta$ substituted C$_5$-ring proton of the ferrocenyl unit in: (a) complex **1**, (b) complex $[\mathbf{3}]^+PF_6^-$.

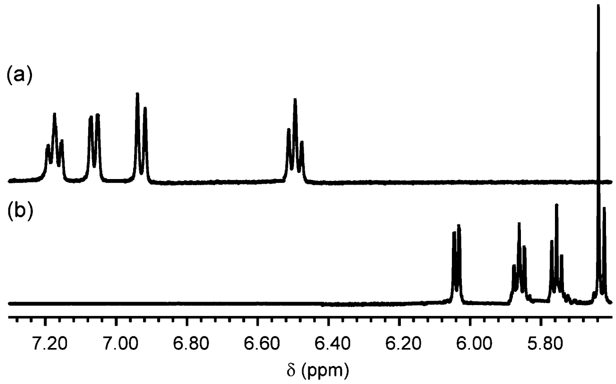


Fig. 2 Proton resonances associated to the *o*-phenylene ring in: (a) complex **1**, (b) complex $[\mathbf{3}]^+PF_6^-$.

In the ^{1}H NMR spectrum of complex $[\mathbf{3}]^+PF_6^-$, the two sharp singlets integrating for 15 H and 5 H at δ 2.15 and 4.17 ppm were unambiguously attributed to the Cp* and Cp protons, respectively. Interestingly, the four multiplets, integrating each for 1 H at 4.31, 4.33, 4.64 and 4.69 ppm, were assigned to the four magnetically inequivalent H_α, $H_{\alpha'}$, H_β and $H_{\beta'}$ protons of the substituted cyclopentadienyl ring (Fig. 1(b)). The free rotation of the ferrocenyl moiety about the C_{ipso}–C bond is probably restricted by the coordination of the bulky $(\eta^5\text{-Cp*})Ru^+$ fragment onto the *o*-disubstituted aromatic ring. A comparison of the ^{1}H NMR spectra of **1** and $[\mathbf{3}]^+PF_6^-$, in the aromatic proton area, clearly indicates the effect of this coordination of $(\eta^5\text{-Cp*})Ru^+$ arenophile to the C_6-ring (Fig. 2(b)). Whereas in the ^{1}H NMR spectrum of **1** the resonance signals appear at $6.49 < \delta < 7.17$ ppm, in the ^{1}H NMR spectrum of the trinuclear derivative their corresponding signals are found at $5.63 < \delta < 6.12$ ppm. Such upfield proton resonance shifts have been reported for many other η^6-arene metal complexes and are explained by charge transfer between the arene and metal that results in a net reduction in C–C bond order.[26] Another interesting feature of the presence of an electron withdrawing group in the molecule is the downfield shift of both the benzylic C–H proton signal (δ 8.06 *vs.* 7.42 for **1**), and of the pseudo-aromatic methyne proton (δ 5.58 *vs.* 5.33 for **1**), clearly showing the electronic influence of the cationic mixed sandwich terminus through the conjugated Ni(ONNO) bridge.

In the case of the two paramagnetic copper(II) compounds, the solution magnetic moments were determined by Evans' NMR method[27] at 297 K to be 1.96 μ_B and 1.88 μ_B for **2** (CD_2Cl_2) and $[\mathbf{4}]^+PF_6^-$ (CD_3COCD_3), respectively. These values, in close agreement with, albeit very slightly greater than, the spin-only value for a d^9 Cu(II) ion ($S = 1/2$, 1.73 μ_B), are in the observed range 1.80–2.00 μ_B and consistent with the expected monomeric structure of the complexes.[6b,28] On the other hand, information regarding the immediate environment about the metal centre in the copper complexes **2** and $[\mathbf{4}]^+PF_6^-$ was obtained from EPR spectroscopy. Indeed, the X-band EPR spectra of both complexes at $T = 295$ K exhibit an asymmetric quadruplet (Fig. 3) with identical $g_\parallel = 2.017$ and $g_\perp = 2.112$ values for **2** and $[\mathbf{4}]^+PF_6^-$, respectively, with an average $A_\parallel$ value of 90 G. Those data are in agreement with a monomeric copper(II) species with the Cu^{2+} ion in a square planar coordination sphere.[2b,6b,9a,k,29] Moreover, the epr spectrum of the trinuclear derivative $[\mathbf{4}]^+PF_6^-$ (Fig. 3) shows a clearly resolved superhyperfine structure ($a_N = 13.3$ G) superimposed on the hyperfine structure, indicating that the environment of the copper centre comprises two nitrogen atoms (^{14}N, $I = 1$). Lastly, no half-field transition ($\Delta M_S = 2$) was observed in the glass spectra (77 K) of **2** and $[\mathbf{4}]^+PF_6^-$, suggesting that formation of dimers do not occur upon freezing.[29] Such a behaviour could have arisen as their corresponding nickel counterparts pack as stacked pairs (see below).

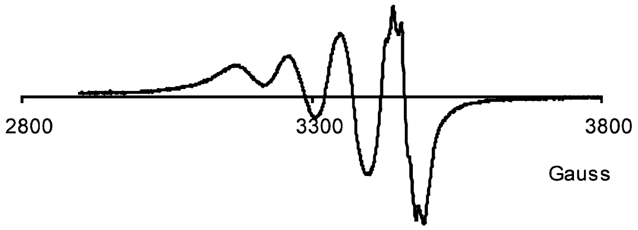


Fig. 3 X-Band EPR spectrum of $[\mathbf{4}]^+PF_6^-$ recorded at 295 K.

Optical spectra

The UV-Vis spectra of the four complexes under investigation, **1**, **2**, $[\mathbf{3}]^+PF_6^-$ and $[\mathbf{4}]^+PF_6^-$, recorded in CH_2Cl_2 ($\varepsilon = 8.90$), consist of two principal features assigned to two different types of transitions.[30] There is a relatively intense band in the region between 270 and 350 nm involving principally intraligand π–π^* transitions and a broader band in the 380–460 nm region, involving both the ligand and the metal–ligand charge transfer (CT) transitions of the central Werner-type bridges of Ni(II) and Cu(II), the ferrocenyl donor fragment and, in the case of $[\mathbf{3}]^+PF_6^-$ and $[\mathbf{4}]^+PF_6^-$, of the acceptor mixed sandwich. Moreover, the lower energy band (>400 nm) exhibits, for the trinuclear derivatives, a significant hypsochromic shift, characteristic of a large dipole moment change between the ground and the excited state, and indicative of CT character. In particular, a negative solvatochromism with increasing solvent polarity (DMSO, $\varepsilon = 47.6$), is observed (Table 1 and Fig. 4), indicating a reduction in the dipole moment upon electronic excitation. It is worth nothing that this blue shift is greater for the d^9 open-shell configuration copper containing complexes: −2 *vs.* −10 nm for **1** and **2**, respectively, and −22 *vs.* −39 nm for $[\mathbf{3}]^+PF_6^-$ and $[\mathbf{4}]^+PF_6^-$, respectively. Such hypsochromic shifts have already been reported for traditional NLO active push–pull Schiff base complexes,[31] and cationic dipolar organometallic chromophores.[13,32]

Electrochemical studies

In order to get a deeper insight into the mutual donor–acceptor electronic influence, we have undertaken cyclic voltammetry (CV) studies of the bimetallic complexes **1** and **2** containing only the ferrocenyl donor group, and of the trimetallic complexes $[\mathbf{3}]^+PF_6^-$ and $[\mathbf{4}]^+PF_6^-$ containing both the same donor fragment and the cationic acceptor sandwich $[(\eta^5\text{-Cp*})Ru(\eta^6\text{-salicylidene})]^+$ linked by the unsymmetrical Ni(II) and Cu(II) classical Werner-type subunit. Cyclovoltammograms were recorded for the four complexes at 20 °C in acetonitrile (see Experimental section for full details). Values

Table 1 UV-Vis data for compounds **1**, **2**, $[\mathbf{3}]^+PF_6^-$ and $[\mathbf{4}]^+PF_6^-$

Compound	λ/nm ($\log\varepsilon$/M^{-1} cm^{-1}) (CH_2Cl_2)	λ/nm ($\log\varepsilon$/M^{-1} cm^{-1}) (DMSO)	$\Delta\lambda$/nm
1	245 (4.54)	—	—
	300 (3.87)	305 (3.88)	+5
	330 (3.87)	346 (3.28)	+16
	387 (3.58)	386 (3.43)	−1
	425 (3.50)	423 (3.34)	−2
2	235 (4.24)	—	—
	277 (3.88)	270 (3.92)	−7
	352 (3.92)	351 (3.92)	−1
	391 (3.04)	387 (3.15)	−4
	447 (2.84)	437 (2.80)	−10
$[\mathbf{3}]^+PF_6^-$	235 (4.56)	—	—
	296 (4.07)	290 (4.13)	−6
	347 (3.85)	359 (3.74)	+12
	382 (3.85)	386 (3.52)	+4
	442 (3.47)	420 (3.44)	−22
$[\mathbf{4}]^+PF_6^-$	228 (4.50)	—	—
	274 (4.24)	267 (4.29)	−7
	350 (3.92)	352 (3.92)	+2
	451 (3.23)	412 (3.32)	−39

Table 2 Electrochemical data[a] for compounds **1**, **2**, $[\mathbf{3}]^+PF_6^-$ and $[\mathbf{4}]^+PF_6^-$

Compound	$E_{pc}{}^b$/V	$E_{1/2}$/V (ΔE^c/mV)	$E_{pa}{}^d$/V
1	—	0.071 (74)	0.700
2	−1.850	0.046 (74)	0.688
$[\mathbf{3}]^+PF_6^-$	−1.250	0.094 (64)	0.725
$[\mathbf{4}]^+PF_6^-$	—	0.074 (64)	—

[a] Recorded in acetonitrile at 293 K with a vitreous carbon working electrode, with 0.1 M n-$Bu_4N^+PF_6^-$ as supporting electrolyte; all potentials are *vs.* $Cp_2Fe^{0/+}$; scan rate = 0.1 V s^{-1}. [b] Peak potential of the irreversible wave corresponding to Ni(II)/Ni(I) and Cu(II)/Cu(I) couples. [c] Peak-to-peak separation between the resolved reduction and oxidation wave maxima. [d] Peak potential of the irreversible wave corresponding to Ni(II)/Ni(III) and Cu(II)/Cu(III) couples.

of the reduction and oxidation potentials and information concerning the reversibilities are gathered in Table 2.

In all the cyclovoltammograms, the reversible one-electron oxidation process arises from the oxidation of the monosubstituted ferrocene unit and corresponds to the generation of the mono- and dicationic Fe(III) species.[33] In the four cases, the E^0 values are positively shifted with respect to that of ferrocene (Table 2), thus featuring the electron withdrawing properties of the neutral (**1** and **2**) and cationic ($[\mathbf{3}]^+PF_6^-$ and $[\mathbf{4}]^+PF_6^-$) Schiff base moieties. A more positive oxidation potential indicates that the ferrocenyl unit is more difficult to oxidise, *i.e.*, less electron rich.

Interestingly, the peak potentials of **1** and $[\mathbf{3}]^+PF_6^-$ are 25 and 20 mV more anodic than that of **2** and $[\mathbf{4}]^+PF_6^-$, respectively, which indicates that the electron-releasing effect of the open shell d^9 copper containing Schiff base complex on the sandwich iron centre is somewhat greater than that of the closed shell d^8 nickel containing subunit. Moreover, complexation of the salicylidene ring by the cationic arenophile (η^5-Cp*)Ru^+ in $[\mathbf{3}]^+PF_6^-$ and $[\mathbf{4}]^+PF_6^-$ significantly affects the oxidation potential of the iron sandwich centre. The Fe(II)/Fe(III) couple is, indeed, anodically shifted by 23 and 28 mV on going from **1** to $[\mathbf{3}]^+PF_6^-$ and from **2** to $[\mathbf{4}]^+PF_6^-$, respectively. This suggests that a strong electronic interaction took place between the two organometallic termini through the entire Schiff base metal framework. This is also in line with the ^1H NMR findings for **1** and $[\mathbf{3}]^+PF_6^-$ (see above).

On the other hand, the cyclovoltammograms of **1** and $[\mathbf{3}]^+PF_6^-$ display an irreversible oxidation wave assigned to the Ni(II)/Ni(III) system.[34] In the case of $[\mathbf{3}]^+PF_6^-$, an irreversible reduction wave attributable to the Ni(II)/Ni(I) couple is also observed. Similarly, the cyclovoltammogram of **2** shows an irreversible wave at 0.688 V presumably due to the oxidation of the Cu(II) metal centre to Cu(III) species. The irreversible reduction wave of the Cu(II) Schiff base complex is observed at low potential (E_{pc} = −1.850 V).[35] Surprisingly, despite the coordination of (η^5-Cp*)Ru^+ that lowers the redox potential of $[\mathbf{4}]^+PF_6^-$, such a reduction wave is not present in the cyclovoltammogram. Whether the ligand or the metal centres are oxidized/reduced and what the nature of the follow-up reactions are questions that cannot be answered at present. Two possibilities that might explain the follow-up reactions are disproportionation of Ni(I) or precipitation of the oxidized M(III) forms of the complexes. Finally, the irreversible reduction wave of the $[(\eta^5\text{-Cp*})Ru(\eta^6\text{-salicylidene})]^+$ entity, expected at a very negative potential ($E_{pc} <$ −2 V)[36] was not observed, being probably shifted beyond the lower limit of the potential interval considered in the experimental measurements.

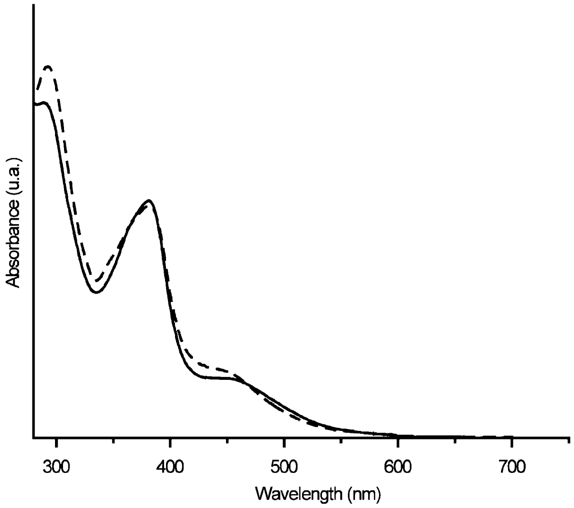


Fig. 4 UV-Vis spectrum of complex $[\mathbf{4}]^+PF_6^-$, recorded in CH_2Cl_2 (solid line) and in DMSO (dotted line).

Crystallography

Crystals suitable for X-ray diffraction studies were obtained by slow diffusion of diethyl ether into a dichloromethane solution (**1**) or toluene into CH_2Cl_2 solutions ($[\mathbf{3}]^+PF_6^-$). In this later case, crystals were of rather poor quality. In the structure refinement for complex $[\mathbf{3}]^+PF_6^-$, the SQUEEZE program[37] was used to deal with severely disordered toluene molecule within the unit cell. Details of the structure

Table 3 Crystal data, data collection, and structure refinement parameters for **1** and [**3**]$^+$PF$_6^-$

	1	[**3**]$^+$PF$_6^-$
Empirical formula	$C_{23}H_{22}FeN_2NiO_2$	$C_{36.5}H_{41}F_6FeN_2NiO_2PRu$
M/g mol^{-1}	472.99	900.31
T/K	298(2)	298(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
a/Å	11.0723(10)	17.118(4)
b/Å	9.9509(9)	11.668(3)
c/Å	18.5611(17)	18.793(5)
β/°	106.6370(10)	99.925(6)
V/Å^3	1959.4(3)	3697.5(17)
Z	4	4
D_c/g cm^{-3}	1.603	1.617
F(000)	976	1828
μ/mm^{-1}	1.723	1.403
θ range/°	1.93 to 28.11	1.77 to 27.76
Range h, k, l	−14/14, −12/12, −24/23	−22/21, −15/15, −24/24
No. independent refl.	4434	8104
Data/restraints/parameters	4434/0/263	8104/0/430
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0438$	$R_1 = 0.0844$
	$wR_2 = 0.1090$	$wR_2 = 0.1926$
R indices (all data)	$R_1 = 0.0573$	$R_1 = 0.2755$
	$wR_2 = 0.1170$	$wR_2 = 0.2538$
Goodness of fit, F^2	1.043	0.801
$\Delta\rho_{\max,\ \min}$/e Å^{-3}	1.014, −0.239	0.821, −0.552

determinations are given in the Experimental section. Table 3 gives experimental and crystallographic data for the two compounds. Selected bond distances and angles for compounds **1** and [**3**]$^+$ are reported in Tables 4 and 5, respectively. Fig. 5 and 6 present ORTEP drawings of the structures of **1** and [**3**]$^+$, respectively, along with the atom numbering scheme. Molecule **1** crystallizes in the monoclinic space group $P2_1/n$, with two binuclear entities present in the asymmetric unit. Compound [**3**]$^+$PF$_6^-$ crystallizes in the monoclinic space group $P2_1/n$ with two molecular entities and one toluene solvent molecule present in the asymmetric unit. Both **1** and [**3**]$^+$ are hybrid compounds that can be described as classical Werner-type complexes that consist in a nickel(II) center coordinated by an unsymmetrical Schiff base ligand derived from the stepwise 1 : 1 : 1 condensation of 1-ferrocenyl-1,3-butanedione, 1,2-ethylenediamine and salicylaldehyde. The quadridentate Schiff base ligand is doubly deprotonated at the enamine nitrogen and phenol oxygen atoms, and formally binds nickel(II) ion through two nitrogen atoms (amido and imine) and two oxygen (carbonyl and phenolato) atom. This multidentate binding leads to the formation of a six-, five-, six-membered chelate ring arrangement (6–5–6) around the central metal atom.

Structure of complex 1

The Ni(II) center displays a square-planar geometry with the nitrogen and oxygen atoms occupying *trans* positions. It is notable that the bond lengths associated with the metal center are nearly identical: Ni(1)–O(1) 1.847(2), Ni(1)–O(2) 1.849(2), Ni(1)–N(1) 1.852(2) and Ni(1)–N(2) 1.844(2) Å; this makes complex **1** a rare example of almost equal Ni–O and Ni–N bond distances.[38] The Ni(II) atom lies in a virtually perfect square-planar environment and is located 0.001 Å from the ONNO mean plane. The maximum deviation from the least-squares (l.s.) basal plane is of 0.052 Å for atom N(2), and the

Table 4 Selected bond distances (Å) and angles (°) for **1**

Ni(1)–N(1)	1.8522(19)	Ni(1)–O(1)	1.8470(17)
Ni(1)–N(2)	1.844(2)	Ni(1)–O(2)	1.8486(16)
O(1)–C(11)	1.290(3)	O(2)–C(23)	1.311(3)
N(1)–C(13)	1.308(3)	N(1)–C(15)	1.466(3)
N(2)–C(17)	1.288(3)	N(2)–C(16)	1.462(3)
C(11)–C(12)	1.371(4)	C(12)–C(13)	1.408(4)
C(15)–C(16)	1.506(4)	C(17)–C(18)	1.422(3)
C(18)–C(23)	1.410(3)	C(11)–C(6)	1.471(3)
Fe(1)–C1–5)$_{av}$	2.025(3)	Fe(1)–C(6–10)$_{av}$	2.032(3)
N(1)–Ni(1)–O(1)	94.89(8)	N(1)–Ni(1)–N(2)	86.69(9)
O(1)–Ni(1)–O(2	84.55(7)	O(2)–Ni(1)–N(2)	94.00(8)
O(1)–Ni(1)–N(2)	176.85(8)	O(2)–Ni(1)–N(1)	177.30(8)
Ni(1)–O(1)–C(11)	126.30(16)	O(1)–C(11)–C(12)	124.6(2)
C(11)–C(12)–C(13)	124.7(2)	C(12)–C(13)–N(1)	122.2(2)
Ni(1)–N(1)–C(13)	126.94(18)	Ni(1)–N(2)–C(17)	127.47(18)
N(2)–C(17)–C(18)	125.2(2)	C(17)–C(18)–C(23)	121.2(2)
C(18)–C(23)–O(2)	123.9(2)	C(23)–O(2)–Ni(1)	127.87(16)

Table 5 Selected bond distances (Å) and angles (°) for [**3**]$^+$PF$_6^-$

Ni(1)–N(1)	1.834(10)	Ni(1)–O(1)	1.825(8)
Ni(1)–N(2)	1.881(10)	Ni(1)–O(2)	1.852(8)
O(1)–C(11)	1.244(14)	O(2)–C(23)	1.309(14)
N(1)–C(13)	1.328(16)	N(1)–C(15)	1.532(16)
N(2)–C(17)	1.249(17)	N(2)–C(16)	1.466(15)
C(11)–C(12)	1.374(17)	C(12)–C(13)	1.416(18)
C(15)–C(16)	1.411(17)	C(17)–C(18)	1.50(2)
C(18)–C(23)	1.438(18)	C(11)–C(6)	1.564(17)
Fe(1)–C(1–5)$_{av}$	2.022(19)	Fe(1)–C(6–10)$_{av}$	2.023(17)
Ru(1)–C(18–23)$_{av}$	2.142(16)	Ru(1)–C(24–28)$_{av}$	2.226(17)
N(1)–Ni(1)–O(1)	94.7(4)	N(1)–Ni(1)–N(2)	86.9(5)
O(1)–Ni(1)–O(2	85.1(4)	O(2)–Ni(1)–N(2)	93.3(5)
O(1)–Ni(1)–N(2)	177.5(5)	O(2)–Ni(1)–N(1)	179.6(4)
Ni(1)–O(1)–C(11)	126.6(8)	O(1)–C(11)–C(12)	126.8(12)
C(11)–C(12)–C(13)	123.3(13)	C(12)–C(13)–N(1)	120.6(13)
Ni(1)–N(1)–C(13)	127.6(9)	Ni(1)–N(2)–C(17)	130.0(11)
N(2)–C(17)–C(18)	123.4(14)	C(17)–C(18)–C(23)	120.1(13)
C(18)–C(23)–O(2)	123.9(14)	C(23)–O(2)–Ni(1)	129.2(9)

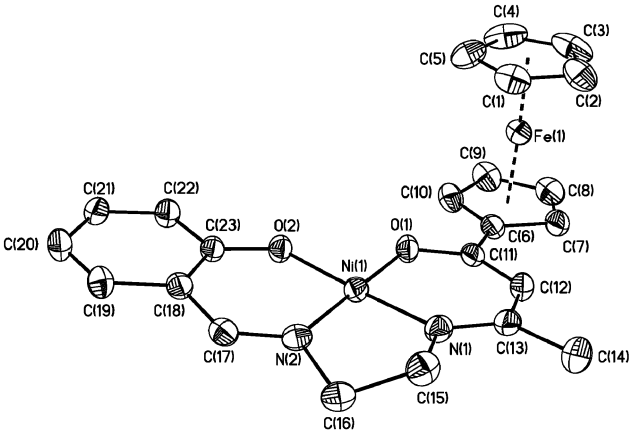


Fig. 5 Molecular structure of compound **1**. Hydrogen atoms have been omitted for clarity. Displacement ellipsoids are at the 30% probability level.

sum of the four angles at nickel is 360°. As expected, the two *pseudo*-aromatic six-membered chelate rings are planar. The plane of the metallocycle involving the 1,3-dione moiety, O(1) to N(1), is co-planar with the substituted cyclopentadienyl ring of the ferrocenyl unit (dihedral angle 0.9°), whereas the Ni(1)–N(2)–C(17)–C(18)–C(23)–O(2) plane makes a dihedral angle of 2.4° with the plane of the salicylidene C_6-ring. The five-membered ring defined by the nickel atom and diaminoethane moiety are definitely nonplanar, the ethylene bridges have a gauche conformation as usually observed with a torsion angle of 35.1°. The bond length pattern within the six-membered ring system O(1) to N(1) suggests partial delocalization of bonding electron density. For instance, the O(1)–C(11), C(11)–C(12), C(12)–C(13) and C(13)–N(1) bond distances of 1.290(3), 1.371(4), 1.408(4) and 1.308(3) Å, respectively, fall between the measured values for related normal single and double bonds,[39] showing that the organometallic enaminoketonate ion is partially delocalized. Both metal centers could therefore electronically communicate through a delocalized π-system. A partial delocalization is also observed for the other six-membered ring O(2) to N(2) (see Table 4).

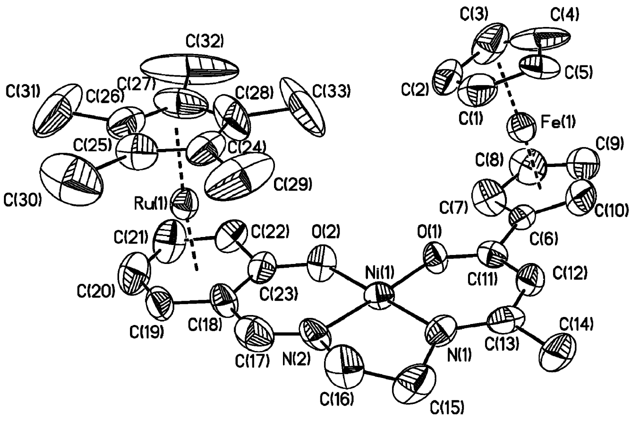


Fig. 6 Molecular structure of compound $[\mathbf{3}]^+PF_6^-$. Hydrogen atoms, PF_6^- counteranions and the crystallization solvent molecule have been omitted for clarity. Displacement ellipsoids are at the 30% probability level.

In the crystal, molecules of compound **1** are packed to form centrosymmetric pairs. The separation between N_2O_2 l.s. planes (3.291 Å) and the magnitude of the Ni···Ni distance (3.457 Å) rather exclude any significant interaction between the metal ions. Such a difference of 0.166 Å between these two values is accounted for by the component molecules only very slightly displaced parallel to their long axis, as observed in the packing of the parent Ni(salen) complex.[40] Lastly, the molecular structure of **1** reveals almost eclipsed cyclopentadienyl rings for the ferrocenyl group. The iron atom is coordinated to the cyclopentadienyl rings at a ring centroid–iron distances of 1.638 and 1.636 Å for the substituted and unsubstituted ring, respectively. The two C_5-ligands are essentially parallel, with the ring centroid–iron-ring centroid angle of 177.8°, which represents a typical η^5-Fe-η^5 coordination.[41]

Structure of complex $[\mathbf{3}]^+PF_6^- \cdot 0.5C_7H_8$

As expected, the major difference between molecular structures of **1** and that of $[\mathbf{3}]^+PF_6^-$ is the hexahapto coordination of the bulky arenophile group, (η^5-Cp*)Ru$^+$, to the aromatic ring of the binuclear precursor Schiff base complex **1** (Fig. 6). Moreover, cation $[\mathbf{3}]^+$ adopts a *syn*-conformation with the two organometallic Cp′M ends located on the same faces of the dinucleating inorganic ligand. As a result, the degree of steric encumbrance is noticeable from the structural data. For example, the angle formed between the metal ligand centroids and the focal metal atom [175.2° (Ru) and 176.2° (Fe)] slightly deviates from linearity probably due to steric hindrance required to accommodate the two metallocenic termini in the *syn*-conformation. These steric constraints are also illustrated in Fig. 6 with the rotation of the substituted cyclopentadienyl ring of the ferrocenyl fragment that makes a dihedral angle of 8.7° with the plane of the six-membered chelate ring [O(1) to N(1)], whereas the C(6)–C(11) bond lengthens by 0.091 Å. In the mixed sandwich fragment, the ruthenium atom is coordinated to the pentamethylcyclopentadienyl ligand at a ring centroid-ruthenium distance of 1.793 Å, and to the salicylidene ring of the Schiff base framework at a ring centroid–ruthenium distance of 1.732 Å. In the ferrocenyl subunit, the iron atom is coordinated to the cyclopentadienyl rings at ring centroid–iron distances of 1.630 and 1.639 Å, for the substituted and the unsubstituted ring, respectively.

The nickel Schiff base framework remains essentially unchanged upon complexation. The two six-membered metallocycles [O(1) to N(1)] and [O(2) to N(2)], are strictly planar and practically coplanar to the coordination basal plane with dihedral angles of 6.0 and 1.0°, respectively. Interestingly, such a quasi-planar overall geometry suggests the possibility of long-range electron delocalization between the donating ferrocenyl substituent and the electron withdrawing mixed ruthenium sandwich. Hence, a charge transfer upon electronic transition could be expected between the two organometallic termini, enabling a potential NLO response.

As observed in **1**, the nickel atom resides in a square-planar environment and is located 0.012 Å from the mean N_2O_2 plane. However, in contrast to **1**, where the four metal–ligand bond distances are almost equal within the error of the measurement (Table 4), in the present case the nickel atom is

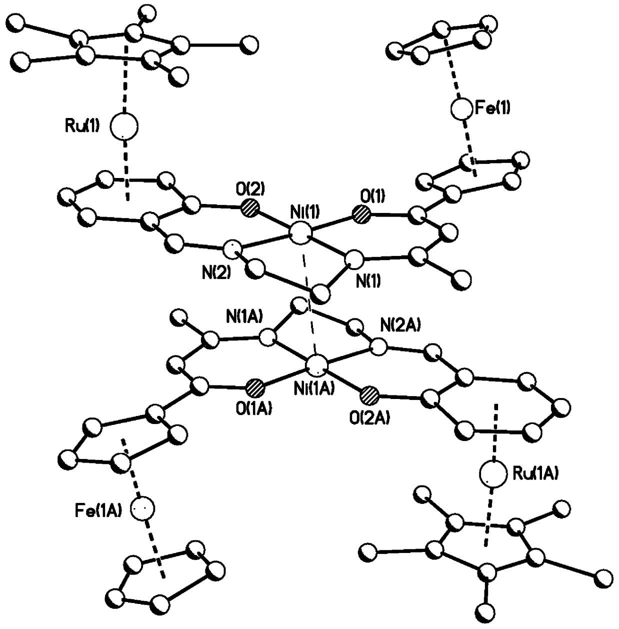


Fig. 7 Ball-and-stick view of a pair of centrosymmetric molecules of compound $[\mathbf{3}]^{+}PF_6^{-}$. Hydrogen atoms, PF_6^{-} counteranions and the crystallization solvent molecule have been omitted for clarity. Symmetry transformations used to generate equivalent atoms, A: $-x$, $1 - y$, $-z$. The Ni···Ni separation is 3.249(3) Å.

slightly displaced toward the ferrocenyl–enaminoketonate chelate ring, the Ni(1)–O(1) and Ni(1)–N(1) bond lengths being significantly shorter than those measured for Ni(1)–O(2) and Ni(1)–N(2) distances (see Table 5). It is also noteworthy that the major structural distorsion observed concerns the bridging ethylene unit with: (i) an increase of 0.07 Å of the N(1)–C(15) distance, (ii) a contraction of 0.09 Å of the C(15)–C(16) bond, (iii) an increase of 7.4° of the C(15)–C(16)–N(2) angle, and (iv) a flattening of the gauche conformation with a reduced torsion angle of 30.3° (compare to 35.1° for **1**). As expected, the six-membered chelate ring [O(2) to N(2)] fused with the arene ring is barely perturbed upon complexation. The C(17)–N(2) distance decreases by 0.04 Å, whereas the C(17)–C(18) and C(18)–C(23) distances lengthen by 0.08 and 0.03 Å, respectively. Similarly, the bond angles at C(17) and C(18) close up by 1.8 and 1.1°, respectively, whereas those at O(2) and N(2) open up by 1.2 and 2.5°, respectively. On the other hand, cation $[\mathbf{3}]^{+}$ crystallizes in stacked couples in a head-to-tail fashion, *i.e.*, with the electron-withdrawing side above the electron-releasing one (Fig. 7). While the nickel atoms may be superimposed on top of each other, the nitrogens in the chelate core from one molecule are aligned with the oxygens in the second molecule and *vice versa*. In such a dimeric structure, the molecules are oriented with the two Cp′M moieties pointing outward. The distances between the N_2O_2 l.s. planes is 3.232 Å within the dimer. The interplanar separation shorten by 0.06 Å on going from the neutral precursor **1** to the ionic derivative $[\mathbf{3}]^{+}PF_6^{-}$. This could arise from the ionic nature of the latter. The Ni···Ni vector is normal to the N_2O_2 planes with a Ni···Ni intermolecular separation of 3.249(3) Å.

Concluding remarks

In summary, four new nickel(II) and copper(II) complexes of unsymmetrical quadridentate organometallic Schiff bases have been prepared and fully characterized by spectroscopic techniques. The binuclear complexes **1** and **2** have been utilized as precursors for the synthesis of two organometallic π-conjugated push–pull chromophores, $[\mathbf{3}]^{+}PF_6^{-}$ and $[\mathbf{4}]^{+}PF_6^{-}$, containing a neutral organometallic electron-releasing group, $[(\eta^5\text{-Cp})Fe(\eta^5\text{-}C_5H_4)]$, and a cationic electron-withdrawing mixed sandwich, $[(\eta^5\text{-Cp*})Ru(\eta^6\text{-}o\text{-phenylene})]^{+}$, linked through a non-conventional spacer, an unsymmetrical, dianionic, tetradentate Schiff base type complex {M(ONNO)}, M = Ni(II), Cu(II). The molecular structure of complexes **1** and $[\mathbf{3}]^{+}PF_6^{-}$ have been authenticated by X-ray diffraction analysis. UV-Vis, ^{1}H NMR and electrochemical data clearly indicate a mutual donor–acceptor electronic influence. Accordingly, complexes $[\mathbf{3}]^{+}PF_6^{-}$ and $[\mathbf{4}]^{+}PF_6^{-}$, can be defined as Type I non-rod-shaped dipolar chromophores.[42] Work is currently underway to determine the potential NLO properties of the reported compounds, and to develop new trinuclear systems possessing a single functional group for immobilisation processes.

Experimental

General remarks

All operations were performed under inert atmosphere using standard vacuum/dinitrogen line (Schlenk) techniques. Solvents were dried and distilled under dinitrogen by standard methods prior to use. Reagents were purchased from commercial suppliers and used without further purification. Tris(acetonitrile)(pentamethylcyclopentadienyl)ruthenium(II) hexafluorophosphate was synthesized according to published procedures.[20] Microanalytical data were obtained on a Perkin Elmer model 2400 elemental analyzer. IR spectra were obtained as KBr disks on a Perkin Elmer model 1600 FT-IR spectrophotometer, in the range 4000–450 cm^{-1}. Electronic spectra were recorded in CH_2Cl_2 and DMSO solutions with a Spectronic, Genesys 2 spectrophotometer. ^{1}H NMR spectra were acquired at 297 K on a multinuclear Bruker AC 400 spectrometer. All ^{1}H NMR chemical shifts were referenced using the chemical shifts of residual solvent resonances. Coupling constants (*J*) are reported in Hertz (Hz), and integrations are reported as number of protons. The following abbreviations are used to describe peak patterns: br = broad, s = singlet, d = doublet, t = triplet, m = multiplet. Solution magnetic susceptibility measurements were done with Evans' method.[27] EPR spectra were recorded on a Bruker EMX-8/2.7 (X-band) spectrometer. Electrochemical measurements were performed using a Radiometer Analytical model PGZ 100 all-in one potentiostat, using a standard three-electrode setup with a platinum electrode, platinum wire auxiliary electrode and Ag/AgCl as the reference electrode. MeCN solutions was 1.0 mM in the compound under study and 0.1 M in the supporting electrolyte $n\text{-}Bu_4N^{+}PF_6^{-}$ with the voltage scan rate = 100 mV s^{-1}. Under these experimental conditions the ferrocene/ferricinium couple, used as an internal reference for the potential measurements, was located at $E_{\frac{1}{2}}$ = 0.460 V

(ΔE_p = 70 mV). $E_{\frac{1}{2}}$ is defined as equal to ($E_{pa} + E_{pc}$)/2, where E_{pa} and E_{pc} are the anodic and cathodic peak potentials, respectively. Mass spectrometric measurements were performed at the Centre Régional de Mesures Physiques de l'Ouest (CRMPO) Rennes, on a high-resolution ZabSpec TOF VG Analytical spectrometer operating in the ESI$^+$ mode; polyethyleneglycol (PEG) was used as internal reference.

Preparation of 1-ferrocenyl-1,3-butanedione

A Schlenk tube was charged with a magnetic stir bar, 5.0 g (22 mmol) of acetylferrocene, 50 cm^3 of THF and 2.7 g (24.2 mmol) of potassium *tert*-butoxide. After 15 min of stirring, a light brown precipitate formed. The reaction mixture was vigorously stirred for an additional half hour. Ethyl acetate (10 cm^3) was added and the vigorous stirring continued for 15 h. Then, distilled water (20 cm^3) and aq. HCl 1M (30 cm^3) were successively added. The product was extracted with 3 × 50 cm^3 of diethyl ether. The organic phases were combined, dried over $MgSO_4$ and the volatiles removed under vacuum. The solid material was purified by column chromatography on silica gel (grade 60) beforehand washed with hexane. Elution with a hexane–diethyl ether mixture (9 : 1) produced the release of a red band, which was collected. The solvents were removed under reduced pressure and recrystallization from CH_2Cl_2–Et_2O, yielded the product as red microcrystalline powder (2.80 g, 48%). The title compound was authenticated by comparison of its IR and ^1H NMR ($CDCl_3$, 297 K) data (keto/enol ratio: 21.6/79.4) with those reported in the literature.[14]

Preparation of $[\{(\eta^5\text{-Cp})Fe(\eta^5\text{-}C_5H_4)C(O)CHC(CH_3){=}NCH_2CH_2N{=}CH\text{-}o\text{-}C_6H_4O\}Ni]$ (1)

A Schlenk tube was charged with a magnetic stir bar, CH_2Cl_2 (10 cm^3), 1-ferrocenyl-1,3-butanedione (135 mg, 0.5 mmol) and ethylenediamine (133 mm^3, ~2 mmol). The reaction mixture was refluxed for 1.5 h, and then the solvent and excess diamine were evaporated under vacuum. The residue, containing the hemi-ligand Fc-$COCH_2C(CH_3){=}NCH_2CH_2NH_2$, was dissolved in 10 cm^3 of a CH_2Cl_2–EtOH mixture (3 : 1) and then salicylaldehyde (53 mm^3, 0.5 mmol) was added and the reaction mixture stirred for 10 min. Then, solid $Ni(CH_3COO)_2 \cdot 4H_2O$ (108 mg, 0.5 mmol) was added and the solution was refluxed for 4 h affording an orange solid which was filtered off and washed with cold MeOH and diethyl ether. Complex **1** was recrystallized from CH_2Cl_2 by slow diffusion of diethyl ether at room temperature (yield: 103 mg, 43%). Found: C, 58.29; H, 4.60; N, 5.82. Calc. for $C_{23}H_{22}FeNiN_2O_2$: C, 58.41; H, 4.69; N, 5.92%. IR (KBr, ν_{max}/cm^{-1}): 3087w (C–H arom.), 2923w (C–H aliph.), 1621s, 1601m, 1578m, 1507vs ($C\doteq C$), ($C\doteq N$), and/or ($C\doteq O$) and 760w (C–H arom). ^1H NMR (400.13 MHz; $CDCl_3$): δ_H 1.97 (3 H, s, CH_3), 3.06 (2 H, t, *J* 6.5, N–CH_2), 3.37 (2 H, t, *J* 6.5, N–CH_2), 4.16 (5 H, s, Cp), 4.24 (2 H, br s, C_5H_4), 4.65 (2 H, br s, C_5H_4), 5.33 (1 H, s, >C–H), 6.49 (2 H, t, ^3J 7.3, C_6H_4), 6.92 (1 H, d, ^3J 8.8, C_6H_4), 7.06 (1 H, d, ^3J 7.8, C_6H_4), 7.17 (2 H, t, ^3J 7.8, C_6H_4), 7.42 (1 H, s, N=CH).

Preparation of $[\{(\eta^5\text{-Cp})Fe(\eta^5\text{-}C_5H_4)C(O)CHC(CH_3){=}NCH_2CH_2N{=}CH\text{-}o\text{-}C_6H_4O\}Cu]$ (2)

The synthesis of this orange complex was carried out following a procedure similar to that described for complex **1**, using in this case $Cu(CH_3COO)_2 \cdot H_2O$ (100 mg, 0.5 mmol). The complex was recrystallized from CH_2Cl_2 by slow diffusion of diethyl ether at room temperature (yield: 91 mg, 38%). Found: C, 57.62; H, 4.56, N, 5.80. Calc. for $C_{23}H_{22}CuFeN_2O_2$: C, 57.81; H, 4.64; N, 5.86%. IR (KBr, ν_{max}/cm^{-1}): 3077w, 2919w (C–H), 1637s, 1601m, 1582m, 1507vs ($C\doteq C$), ($C\doteq N$), and/or ($C\doteq O$) and 758w (C–H arom). μ_{eff} (CD_2Cl_2, 297 K): 1.96 μ_B. ESI$^+$ MS (CH_2Cl_2–methanol (9 : 1), *m*/*z*) calc. for $C_{23}H_{22}N_2O_2{}^{56}Fe^{63}Cu$: 477.03267, found: 477.0319.

Preparation of $[\{(\eta^5\text{-Cp})Fe(\eta^5\text{-}C_5H_4)C(O)CHC(CH_3){=}NCH_2CH_2N{=}CH\text{-}o\text{-}(\eta^6\text{-}C_6H_4O)Ru(\eta^5\text{-}Cp^*)\}Ni]^+PF_6^-$ ($[3]^+PF_6^-$)

A Schlenk tube was charged with a magnetic stir bar, dry CH_2Cl_2 (10 cm^3), complex **1** (100 mg, 0.22 mmol) and $[(\eta^5\text{-}Cp^*)Ru(CH_3CN)_3]^+PF_6^-$ (111 mg, 0.22 mmol). The reaction mixture was refluxed for 15 h resulting in a suspension which was filtered under N_2. The filtrate was reduced to *ca.* 5 cm^3 under vacuum and then diethyl ether was added (*ca.* 10 cm^3) to complete the precipitation of the product. The solid was filtered off, washed with diethyl ether (3 × 10 cm^3) and recrystallized from CH_2Cl_2–Et_2O as a dark red crystalline solid (Yield: 143 mg, 76%). Found: C, 46.30; H, 4.31; N, 3.20. Calc. for $C_{33}H_{37}FeF_6NiN_2O_2PRu$: C, 46.40; H, 4.37; N, 3.28%. IR (KBr, ν_{max}/cm^{-1}): 3086w (C–H arom.), 2916w (C–H aliph.), 1632m, 1577m, 1510s ($C\doteq C$), ($C\doteq N$), and/or ($C\doteq O$), 841vs (P–F) and 558m (PF_6). ^1H NMR (400.13 MHz; CD_3COCD_3): δ_H 2.09 (3 H, s, CH_3), 2.15 (15 H, s, Cp*), 3.24–3.27 (2 H, m, N–CH_2), 3.58–3.71 (2 H, m, N–CH_2), 4.17 (5 H, s, Cp), 4.31 (1 H, m, C_5H_4), 4.33 (1 H, m, C_5H_4), 4.64 (1 H, m, C_5H_4), 4.69 (1 H, m, C_5H_4), 5.56 (1 H, s, >C–H), 5.63 (1 H, d, ^3J 5.6, C_6H_4), 5.75 (1 H, t, ^3J 5.9, C_6H_4), 6.01 (1 H, t, ^3J 6.5, C_6H_4), 6.12 (1 H, d, ^3J 5.5, C_6H_4), 8.06 (1 H, s, N=CH).

Preparation of $[\{(\eta^5\text{-Cp})Fe(\eta^5\text{-}C_5H_4)C(O)CHC(CH_3){=}NCH_2CH_2N{=}CH\text{-}o\text{-}(\eta^6\text{-}C_6H_4O)Ru(\eta^5\text{-}Cp^*)\}Cu]^+PF_6^-$, ($[4]^+PF_6^-$)

The synthesis of this dark red complex was carried out following a procedure similar to that described for complex $[3]^+PF_6^-$, using in this case the precursor **2** (100 mg, 0.21 mmol). The complex was recrystallized from CH_2Cl_2 by slow diffusion of diethyl ether at room temperature (Yield: 120 mg, 67%). Found: C, 45.92; H, 4.26; N, 3.18. Calc. for $C_{33}H_{37}CuFeF_6N_2O_2PRu$: C, 46.14; H, 4.34; N, 3.26%. IR (KBr, ν_{max}/cm^{-1}): 3087w, 2922w (C–H), 1636m, 1568m, 1508s ($C\doteq C$), ($C\doteq N$), and/or ($C\doteq O$), 841vs (P–F) and 558m (PF_6). μ_{eff} (CD_3COCD_3, 297 K): 1.88 μ_B. ESI$^+$ MS ($CHCl_3$–CH_3CN (9 : 1), C$^+$, *m*/*z*) calc. for $C_{33}H_{37}N_2O_2{}^{56}Fe^{63}Cu^{102}Ru$: 714.05439, found: 714.0543.

X-Ray crystal structure determination of 1 and $[3]^+PF_6^-$

Single crystals of compounds **1** and $[3]^+PF_6^-$, obtained as noted above, were mounted with epoxy cement on the tip of a glass fiber in a random orientation. Intensity data were collected on a Bruker Smart Apex diffractometer equipped with a bidimensional CCD detector using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). Crystal data collection parameters for the two complexes are summarized in Table 3. Semi-empirical corrections, *via* ψ-scans, were applied for absorption. The diffraction frames were integrated using the SAINT package,[43] and corrected for absorption with SADABS.[44] The structures were solved using XS in SHELXTL-PC[45] by direct methods and completed (non-H atoms) by difference Fourier techniques. Refinement was performed by the full-matrix least-squares method based on F^2. All non-hydrogen atoms were anisotropically refined. Hydrogen atoms were placed in their calculated positions, assigned fixed isotropic thermal parameters and allowed to ride on their respective parent atoms. The program SQUEEZE was applied to structure $[\mathbf{3}]^+PF_6^-$ to remove the intensity contributions from the disordered toluene solvent molecules.[37] The final refinement of the structure of $[\mathbf{3}]^+PF_6^-$ was carried out using the SQUEEZE modified intensities. The intensity data factor here was high (R_{int} = 0.2755) and goodness-of-fit on F^2 was still somehow low due to the poor quality of the crystals. ORTEP and ball-and-stick views were generated with XP in SHELXTL-PC.[45]

CCDC reference numbers 640626 for **1** and 640625 for $[\mathbf{3}]^+PF_6^-$.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b707934f

Acknowledgements

We thank P. Hamon and F. Justaud (Rennes) for invaluable assistance with the measurements of the magnetic moments and EPR spectra, respectively, of **2** and $[\mathbf{4}]^+PF_6^-$. Thanks are also addressed to Dr P. Jéhan (CRMPO, Rennes) for mass spectrometric measurements. Financial support from the Fondo Nacional de Desarrollo Científico y Tecnológico [FONDECYT (Chile); grant no. 1040851 (C. M. and D. C.)], the ECOS-SUD (France)–CONICYT (Chile) agreement no. C05E03 (C. M., D. C. and J.-R. H.), and the Pontificia Universidad Católica de Valparaíso, Chile (C. M. and D. C.), is gratefully acknowledged. M. F. thanks the CONICYT (Chile), for support of a graduate fellowship.

References

1 R. Hernandez-Molina and A. Mederos, in *Comprehensive Coordination Chemistry II*, ed. J. A. McCleverty and T. J. Meyer, Elsevier Pergamon, New York, 1st edn, 2004, vol. 1, p. 411.

2 See, for example: (*a*) E. Kwiatkowski and M. Kwiatkowski, *J. Chem. Soc., Dalton Trans.*, 1985, 803; (*b*) E. Kwiatkowski and M. Kwiatkowski, *Inorg. Chim. Acta*, 1986, **117**, 145; (*c*) J.-P. Costes, *Inorg. Chim. Acta*, 1987, **130**, 17; (*d*) M. Kwiatkowski, E. Kwiatkowski, A. Olechnowicz, D. M. Ho and E. Deutsch, *J. Chem. Soc., Dalton Trans.*, 1990, 2497; (*e*) M. Kwiatkowski and G. Bandoli, *J. Chem. Soc., Dalton Trans.*, 1992, 379; (*f*) D. M. Boghaei and S. Mohebi, *J. Chem. Res.*, 2002, 72; (*g*) D. Pawlica, M. Marszalek, G. Mynarczuk, L. Sieron and J. Eilmes, *New J. Chem.*, 2004, **28**, 1615; (*h*) E. M. Opozda, W. Lasocha and B. Wlodarczyk-Gajdab, *Z. Anorg. Allg. Chem.*, 2004, **630**, 597; (*i*) S. Chattopadhyay, M. S. Ray, S. Chaudhuri, G. Mukhopadhyay, G. Bocelli, A. Cantoni and A. Ghosh, *Inorg. Chim. Acta*, 2006, **359**, 1367.

3 (*a*) M. Calligaris and L. Randaccio, in *Comprehensive Coordination Chemistry*, ed. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon Press, Oxford, 1987, p. 715; (*b*) Y.-G. Li, D.-H. Shi, H.-L. Zhu, H. Yan and S. W. Ng, *Inorg. Chim. Acta*, 2007, **360**, 2881; (*c*) I. Rousso, N. Friedman, M. Sheves and M. Ottolenghi, *Biochemistry*, 1995, **34**, 12059; (*d*) T. Baasov and M. Sheves, *Biochemistry*, 1986, **25**, 5249; (*e*) R. D. Jones, D. A. Summerville and F. Basolo, *Chem. Rev.*, 1979, **79**, 139.

4 (*a*) I. Ojima, *Catalytic Asymetric Syntheses*, VCH Publishers, New York, 1993; (*b*) D. M. Boghaei and S. Mohebi, *Tetrahedron*, 2002, **58**, 5357; (*c*) C. R. K. Rao, H. Aneetha, B. Srinivas, P. S. Zacharias and A. Ramachandraiah, *Polyhedron*, 1994, **13**, 2659.

5 (*a*) N. T. S. Phan, D. H. Brown, H. Adams, S. E. Spey and P. Styring, *Dalton Trans.*, 2004, 1348; (*b*) P. Styring, C. Grindon and C. M. Fisher, *Catal. Lett.*, 2001, **77**, 219.

6 (*a*) L. Rigamonti, F. Demartin, A. Forni, S. Righetto and A. Pasini, *Inorg. Chem.*, 2006, **45**, 10976; (*b*) J. Gradinaru, A. Forni, V. Druta, F. Tessore, S. Zecchin, S. Quici and N. Garbalau, *Inorg. Chem.*, 2007, **46**, 884.

7 (*a*) G. Cros and J.-P. Costes, *C. R. Acad. Sci. Ser. IIc*, 1982, **294**, 173; (*b*) J.-P. Costes, G. Cros, M. H. Darbieu and J.-P. Laurent, *Inorg. Chim. Acta*, 1982, **60**, 111; (*c*) J.-P. Costes, *Bull. Soc. Chim. Fr.*, 1986, 78; (*d*) J.-P. Costes, *Polyhedron*, 1987, **6**, 2169, and references therein.

8 E. Kwiatkowski, A. Olechnowicz, D. M. Ho and E. Deutsch, *Inorg. Chim. Acta*, 1988, **150**, 65.

9 (*a*) E. Kwiatkowski and M. Kwiatkowski, *Inorg. Chim. Acta*, 1984, **82**, 101; (*b*) N. Matsumoto, T. Akui, H. Murakami, J. Kanesaka, A. Ohyoshi and H. Kawa, *J. Chem. Soc., Dalton Trans.*, 1988, 1021; (*c*) N. Matsumoto, S. Yamashita, A. Ohyoshi, S. Kohata and H. Kawa, *J. Chem. Soc., Dalton Trans.*, 1988, 1943; (*d*) E. Kwiatkowski and A. Olechnowicz, *Inorg. Chim. Acta*, 1984, **90**, 145; (*e*) M. Kwiatkowski, E. Kwiatkowski, A. Olechnowicz, D. M. Ho and E. Deutsch, *J. Chem. Soc., Dalton Trans.*, 1990, 3063; (*f*) J.-P. Costes, F. Dahan and J.-P. Laurent, *Inorg. Chem.*, 1991, **30**, 1887; (*g*) J.-P. Costes, F. Dahan, J. M. Dominguez-Vera, J.-P. Laurent, J. Ruiz and J. Sotiropouloss, *Inorg. Chem.*, 1994, **33**, 3908; (*h*) J.-P. Costes and M. I. Fernandez-Garcia, *Inorg. Chim. Acta*, 1995, **237**, 57; (*i*) X. R. Bu, C. R. Jackson, D. Van Derveer, X. Z. You, Q. J. Meng and R. X. Wang, *Polyhedron*, 1997, **16**, 2991; (*j*) J.-P. Costes, F. Dahan, M. B. Fernandez Fernandez, M. I. Fernandez Garcia, A. M. Garcia Deibe and J. Sanmartin, *Inorg. Chim. Acta*, 1998, **274**, 73; (*k*) J.-P. Costes, F. Dahan, A. Dupuis and J.-P. Laurent, *J. Chem. Soc., Dalton Trans.*, 1998, 1307; (*l*) E. Kwiatkowski, M. Klein and G. Romanowski, *Inorg. Chim. Acta*, 1999, **293**, 115; (*m*) M. S. Ray, R. Bhattacharya, S. Chaudhuri, L. Righi, G. Bocelli, G. Mukhopadhyay and A. Ghosh, *Polyhedron*, 2003, **22**, 617.

10 For reviews, see for example: (*a*) S. Yamada, *Coord. Chem. Rev.*, 1966, **1**, 415; (*b*) J. Costamagna, J. Vargas, R. Latorre, A. Alvarado and G. Mena, *Coord. Chem. Rev.*, 1992, **119**, 67; (*c*) A. D. Garnovskii, A. L. Nivorozhkin and V. I. Minkin, *Coord. Chem. Rev.*, 1993, **126**, 1; (*d*) D. A. Atwood and M. J. Harvey, *Chem. Rev.*, 2001, **101**, 37.

11 Y.-C. Shi, W.-B. Shen, H.-M. Yang, H.-B. Song and X.-Y. Hu, *Polyhedron*, 2004, **23**, 749.

12 R. H. Crabtree, *The Organometallic Chemistry of the Transition Metals*, Wiley-VCH, New York, 3rd edn, 2001.

13 (*a*) L. Millán, M. Fuentealba, C. Manzur, D. Carrillo, N. Faux, B. Caro, F. Robin-Le Guen, S. Sinbandhit, I. Ledoux-Rak and J.-R. Hamon, *Eur. J. Inorg. Chem.*, 2006, 1131; (*b*) M. Fuentealba, L. Toupet, C. Manzur, D. Carrillo, I. Ledoux-Rak and J.-R. Hamon, *J. Organomet. Chem.*, 2007, **692**, 1099.

14 (*a*) V. Weinmayr, *Naturwissenschaften*, 1958, **45**, 311; (*b*) C. E. Cain, T. A. Mashburn and C. R. Hauser, *J. Org. Chem.*, 1961, **26**, 1030; (*c*) P. Zanello, F. Fabrizi de Biani, C. Glidewell, J. Koenig and S. J. Marsh, *Polyhedron*, 1998, **17**, 1795; (*d*) W. R. Cullen, S. J. Rettig and E. B. Wickenheiser, *J. Mol. Catal.*, 1991, **66**, 251; (*e*) W. R. Cullen and E. B. Wickenheiser, *J. Organomet. Chem.*, 1989, **370**, 141; (*f*) W. C. Du Plessis, T. G. Vosloo and J. C. Swarts, *J. Chem. Soc., Dalton Trans.*, 1998, 2507; (*g*) W. Bell, J. A. Crayston, C. Glidewell, M. A. Mazid and M. B. Hursthouse, *J. Organomet. Chem.*, 1992, **434**, 115.

15 L. Kürti and B. Czako, *Strategic Applications of Named Reactions in Organic Synthesis*, Elsevier Academic Press, Amsterdam, 2005, pp. 86–87.

16 Y.-C. Shi, H.-M. Yang, W.-B. Shen, C.-G. Yan and X.-Y. Hu, *Polyhedron*, 2004, **23**, 15.

17 P. Hu, L. Zhang, X. Zhu, X. Liu, L. Ji and Y. Chen, *Polyhedron*, 1989, **8**, 2459.

18 (*a*) B. S. Garg and Deo Nandan Kumar, *Spectrochim. Acta, Part A*, 2003, **59**, 229; (*b*) R. H. Holm, *J. Am. Chem. Soc.*, 1960, **82**, 5632; (*c*) S. Zolezzi, A. Decinti and E. Spodine, *Polyhedron*, 1999, **18**, 897; (*d*) L. C. Nathan, J. E. Koehne, J. M. Gilmore, K. A. Hannibal, W. E. Dewhirst and T. D. Mai, *Polyhedron*, 2003, **22**, 887, and references therein.

19 H. Imai and T. Ota, *Bull. Chem. Soc. Jpn.*, 1974, **47**, 2497.

20 (*a*) P. J. Fagan, M. D. Ward and J. C. Calabrese, *J. Am. Chem. Soc.*, 1989, **111**, 1698; (*b*) B. Steinmetz and W. A. Schenk, *Organometallics*, 1999, **18**, 943; (*c*) M. D. Mbaye, B. Demerseman, J.-L. Renaud, L. Toupet and C. Bruneau, *Adv. Synth. Catal.*, 2004, **346**, 835.

21 $[(\eta^5\text{-Cp})Fe(NCCH_3)_3]^+$ must be photochemically generated and used at temperature below −40 °C. See: T. P. Gill and K. R. Mann, *Inorg. Chem.*, 1983, **22**, 1986.

22 $[(\eta^5\text{-Cp*})Fe(NCCH_3)_3]^+$ is reluctant to ligand exchange with aromatics. See: D. Catheline and D. Astruc, *Organometallics*, 1984, **3**, 1094.

23 (*a*) C. Manzur, M. Fuentealba, L. Millán, F. Gajardo, D. Carrillo, J. A. Mata, S. Sinbandhit, P. Hamon, J.-R. Hamon, S. Kahlal and J.-Y. Saillard, *New J. Chem.*, 2002, **26**, 213; (*b*) C. Manzur, C. Zúñiga, L. Millán, M. Fuentealba, J. A. Mata, J.-R. Hamon and D. Carrillo, *New J. Chem.*, 2004, **28**, 134; (*c*) C. Manzur, L. Millán, M. Fuentealba, J. A. Mata, D. Carrillo and J.-R. Hamon, *J. Organomet. Chem.*, 2005, **690**, 1265.

24 A. N. Nesmeyanov, N. A. Vol’kenau and I. N. Bolesova, *Tetrahedron Lett.*, 1963, **25**, 1725.

25 (*a*) A. N. Nesmeyanov, N. A. Vol’kenau and L. S. Isaeva, *Dokl. Akad. Nauk SSSR*, 1967, **167**, 106; (*b*) D. Astruc, *Tetrahedron*, 1983, **39**, 4027.

26 S. M. Hubig, S. V. Lindeman and J. K. Kochi, *Coord. Chem. Rev.*, 2000, **200–202**, 831.

27 (*a*) D. F. Evans, *J. Chem. Soc.*, 1959, 2003; (*b*) T. H. Crawford and J. Swanson, *J. Chem. Educ.*, 1971, **48**, 382; (*c*) E. M. Schubert, *J. Chem. Educ.*, 1992, **69**, 62.

28 (*a*) F. A. Cotton, G. Wilkinson, C. A. Murillo and M. Bochmann, *Advanced Inorganic Chemistry*, Wiley-Interscience, New York, 1999, p. 867; (*b*) R. Atkins, G. Brewer, E. Kokot, G. M. Mockler and E. Sinn, *Inorg. Chem.*, 1985, **24**, 127.

29 (*a*) J.-P. Costes, G. Cros and J.-P. Laurent, *Inorg. Chim. Acta*, 1985, **97**, 211; (*b*) H. Adams, N. A. Bailey, I. S. Baird, D. E. Fenton, J.-P. Costes, G. Cros and J.-P. Laurent, *Inorg. Chim. Acta*, 1985, **101**, 7.

30 B. Bosnich, *J. Am. Chem. Soc.*, 1968, **90**, 627.

31 S. Di Bella, I. Fragala, I. Ledoux, M. A. Diaz-Garcia and T. J. Marks, *J. Am. Chem. Soc.*, 1997, **119**, 9550.

32 J. Heck, S. Dabek, T. Meyer-Friedrichsen and H. Wong, *Coord. Chem. Rev.*, 1999, **190–192**, 1217.

33 P. Zanello, in *Ferrocenes*, ed. A. Togni and T. Hayashi, VCH, New York, 1995, ch. 7, p. 317.

34 (*a*) R. C. Elder, E. A. Blubaugh, W. R. Heineman, P. J. Burke and D. R. McMillin, *Inorg. Chem.*, 1983, **22**, 2777; (*b*) C. Freire and B. de Castro, *J. Chem. Soc., Dalton Trans.*, 1998, 1491.

35 S. Zolezzi, E. Spodine and A. Decinti, *Polyhedron*, 2002, **21**, 55.

36 (*a*) O. V. Gusev, M. A. Levlev, M. G. Peterleitner, S. M. Peregudova, L. I. Denisovich, P. V. Petrovskii and N. A. Ustynyuk, *Russ. Chem. Bull.*, 1996, **45**, 1601; (*b*) O. V. Gusev, M. A. Ievlev, M. G. Peterleitner, S. M. Peregudova, L. I. Denisovich, P. V. Petrovskii and N. A. Ustynyuk, *J. Organomet. Chem.*, 1997, **534**, 57.

37 (*a*) A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7; (*b*) P. van der Sluis and A. L. Spek, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 1990, **46**, 194.

38 From a search on the Cambridge Crystallographic Data BaseF. H. Allen, *Acta Crystallogr., Sect. B: Struct. Sci.*, 2002, **58**, 380.

39 F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1987, S1.

40 (*a*) A. Gaetani Manfredotti and C. Guastini, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1983, **39**, 863; (*b*) L. M. Shkol’nikova, E. M. Yumal’, E. A. Shugam and V. A. Voblikova, *Zh. Strukt. Khim.*, 1970, **5**, 886.

41 For a reference gathering a large number of interatomic and metal–ligand distances obtained from the Cambridge Crystallographic Data Base Centre, see: A. G. Orpen, L. Brammer, F. H. Allen, D. Kennard, D. G. Watson and R. Taylor, *J. Chem. Soc., Dalton Trans.*, 1989, S1.

42 (*a*) C. Serbutoviez, C. Bosshard, G. Knöpfle, P. Weiss, P. Prêtre, P. Günter, K. Schenk, E. Solari and G. Chapuis, *Chem. Mater.*, 1995, **7**, 1198; (*b*) M. S. Wong, U. Meier, F. Pan, V. Gramlich, C. Bosshard and P. Günter, *Adv. Mater.*, 1996, **8**, 416.

43 *SAINT-PLUS* (Version 6.02), Bruker Analytical X-Ray Systems Inc., Madison, WI, USA, 1999.

44 G. M. Sheldrick, *SADABS (Version 2.05)*, Bruker Analytical X-Ray Systems Inc., Madison, WI, USA, 1999.

45 *SHELXTL Reference Manual* (Version 6.14). Bruker Analytical X-Ray Systems Inc., Madison, WI, USA, 1998.