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Heteropolymetallic complexes containing 1,1′-diphenylphosphino-ferrocene

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Abstract

The paper explores the capability of [(dppf)Pt(H–*n*bu$_2$–DTO)]Cl (**2**) (dppf = 1,1′-diphenylphosphinoferrocene; H–*n*bu$_2$–DTO = di-*n*butyl-dithioxamidate) to act as a starting module for heterometallic linear chains. Actually, the reaction of **2** with [RuCl$_2$(*p*-cymene)]$_2$ affords the heterotrimetallic complex [Cl(*p*-cymene) Ru(μ-*n*bu$_2$–DTO κ-N,N Ru κ-S,S Pt)Pt(dppf κ-P,P Pt)]$_2$ (**4**). However **2**, allowed to stand, provides a blue compound of formula [(dppf)Pt(H–*n*bu$_2$–DTO)]$_n$Cl$_n$ (**3**), the most reliable value of *n* being 6. The oxidation behavior of the new species **2**–**4** has also been investigated. In particular, the oxidation behavior of cyclic compound **3** is quite unusual, and suggests a large delocalization of the HOMO over the whole multicomponent molecule.

Keywords: Heteropolymetallic complexes; Diphenylphosphinoferrocene (ddpf); Platinum complexes; Ruthenium complexes; Cyclic voltammetry

1. Introduction

A frontier research in coordination and organometallic chemistry is the functional assembling by bottom-up approach [1] of submicrometric aggregates, potentially useful as molecular devices. The electronic, geometric, and structural properties of the molecular components used as building blocks determine interaction and forces featured by the multicomponent final structure. Therefore it is not surprising if the use of complexes as ligands for the step-by-step syntheses of polymetallic compounds is assuming increasing importance in the modern inorganic chemistry [2]. In particular, the sequential synthesis of linear metallic chains plays an important role since such a synthetic procedure allows to insert the individual properties of various components into a multicomponent molecular system. Many efforts have been devoted to find binucleating ligands suitable to link metal ions in successive steps; reliable approaches have exploited heterotopic ligands, which can accomplish a sequential synthesis since the different reactivity of the various chelating systems. In this context, oxamato ligands have been extensively used to generate families of polymetallic compounds according to a sequential strategy [3]; however, the limitation of this generation of oxamato complexes was the isolation of only heterobimetallic compounds. Notwithstanding, oxamato ligands properly designed have overcome this inconvenience and heterotrimetallic and heterotetrametallic complexes have been recently obtained [4,5].

Another binucleating ligand, 1,10-phenanthroline-5,6-dione, has been used as a building block for polymetallic systems: it possesses a bifunctional character and exhibits different reactivity of its functionalities. This binucleating ligand has provided bi and trimetallic derivatives in some cases structurally characterized [6–9]. In the past few years, we have found that platinum fragments linked to a deprotonated secondary dithioxamide through the sulfur-chelating system can function as a ligand complex: the N–H···N

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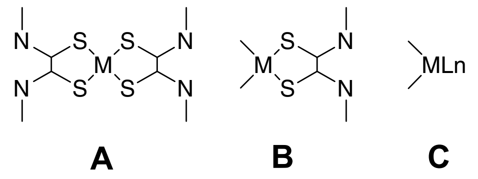


Scheme 1.

frame of the *S*,*S*-coordinated ligand is nucleophilic enough to split chloro-bridged dimers so that bimetallic complexes can be readily obtained [10]. Following our previous results, we started to build up linear polymetallic chains through a modular use of bischelate dithioxamide complexes of type A (Scheme 1), [M(HR$_2$DTO)$_2$] (M = divalent transition metal ions, R = alkyl groups), monochelate [LnM(HR$_2$DTO)] precursors (B), and non-ligating fragments coming from chloro-bridged dimers (C).

In trimetallic complexes of the type C–A–C (C = Pd-(η^3-allyl); Ru(*p*-cymene)Cl; Rh(2-phenyl-pyridine N,C); Rh(cyclo-octadiene); Rh(pentamethyl-cyclopentadienyl)Cl; A = platinum(II)-bis(di-alkyl-dithiooxamidate)) have already been published [11].

The present paper starts from the fact that one of the methods used to prepare heteropolynuclear compounds is based on the use of ferrocenyl substrates containing heteroatoms (mainly nitrogen, sulfur, phosphorus, or oxygen) and/or unsaturated groups with good donor abilities, which allow the coordination of one or more metal ions [12]. Thus we have reacted 1,1′-diphenyl-phosphino ferrocene with a module like B, i.e., the new platinum complex (Me$_2$SO)ClPt(di-*n*butyldithiooxamidate κ-S,S Pt); the bimetallic complex (1,1′-diphenylfosphino-ferrocenyl κ-P,P Pt)Pt(di-*n*butyldithiooxamidate κ-S,S Pt) has been obtained, which could be viewed as a starting module for a monodirectional growth of a polymetallic chain. The use of a ferrocenyl derivative as a fragment in a polymetallic chain offers the opportunity to test the mutual electronic influence among metals connected by binucleating ligands.

2. Experimental

2.1. General procedures

cis-[PtCl$_2$(Me$_2$SO)$_2$] [13] and di-*n*butyl-dithiooxamide [14] were prepared according to published methods. Other reagents and solvents were used as received. NMR spectra were recorded with a Bruker AMX 300 spectrometer. The following Bruker programs were used: zg, zgpg, Jmod, COSY, NOESY.TP. Electrochemical measurements were carried out in argon-purged 1,2-dichloroethane at room temperature with a PAR 273 multipurpose equipment interfaced to a PC. The working electrode was a glassy carbon (8 mm^2, Amel) electrode. The counter electrode was a Pt wire, and the reference electrode was an SCE separated with a fine glass frit. The concentration of the complexes was about 5×10^{-4} M. Tetrabutylammonium hexafluorophosphate was used as the supporting electrolyte and its concentration was 0.05 M. Cyclic voltammograms were obtained at scan rates of 20, 50, 200, and 500 mV/s. For reversible processes, half-wave potentials (versus SCE) were calculated as the average of the cathodic and anodic peaks. The criteria for reversibility were the separation of 60 mV between cathodic and anodic peaks, the close to unity ratio of the intensities of the cathodic and anodic currents, and the constancy of the peak potential on changing scan rate. The number of exchanged electrons was measured with differential pulse voltammetry (DPV) experiments performed with a scan rate of 20 mV/s, a pulse height of 75 mV, and a duration of 40 ms, and by taking advantage of the presence of ferrocene used as the internal reference. Experimental uncertainty on redox potentials is ±10 mV.

2.2. Synthesis of [(Me$_2$SO)ClPt(H–nbu$_2$–DTO)] (H–nbu$_2$–DTO = di-nbutyl-dithioxamidate) (**1**)

cis-[Pt(Me$_2$SO)$_2$Cl$_2$] (422 mg, 1 mmol) was suspended in 100 ml of chloroform together with five grams of sodium bicarbonate. The equimolar amount of dibutyldithioxamide (232 mg, 1 mmol) was added in small portions to the stirred suspension. The solution turned orange-yellow and was leaved under magnetical agitation for 1 h. At the end the orange solution was separated from sodium bicarbonate by filtration. The filtrate was concentrated to a small volume (25 ml); then petroleum ether (75 ml) was added and 370 mg of **1** precipitated as a yellow-orange powder (yields = 68%). ^{1}H NMR (CDCl$_3$, 298 K): $\delta = 0.93$ [t, 6H, N–(CH$_2$)$_3$–C*H*$_3$, $^3J_{\mathrm{H-H}} = 7.0$ Hz], 1.39 ppm (m, 4H, N–CH$_2$–CH$_2$–C*H*$_2$–CH$_3$), 1.70 (m, 4H, N–CH$_2$–C*H*$_2$–CH$_2$–CH$_3$), 3,45 [s, SO(C*H*$_3$)$_2$, $^3J_{\mathrm{Pt-H}} = 37.4$ Hz], 6.58 [t, 2H, N–C*H*$_2$–CH$_2$–CH$_2$–CH$_3$, $^3J_{\mathrm{H-H}} = 7.0$ Hz], 6.63 [t, 2H, N–C*H*$_2$–CH$_2$–CH$_2$–CH$_3$, $^3J_{\mathrm{H-H}} = 7.0$ Hz] ppm. ^{13}C{^{1}H} NMR (CDCl$_3$, 298 K): $\delta = 13.7$ [s, 2C, N–(CH$_2$)$_3$–*C*H$_3$], 20.4 (s, 2C, N–CH$_2$–CH$_2$–*C*H$_2$–CH$_3$), 30.45 (s, 1C, N–CH$_2$–*C*H$_2$–CH$_2$–CH$_3$), 30.80 (s, 1C, N–CH$_2$–*C*H$_2$–CH$_2$–CH$_3$), 44.40 [s, 2C, SO(*C*H$_3$)$_2$, $^2J_{\mathrm{Pt-C}} = 47.2$ Hz], 48.4 0 (s, 1C, N–*C*H$_2$–CH$_2$–CH$_2$–CH$_3$), 48.70 (s, 1C, N–*C*H$_2$–CH$_2$–CH$_2$–CH$_3$), 182.00 (s, *C*S), 184.30 (s, *C*S) ppm. *Anal.* Calc. for C$_{12}$H$_{25}$ClN$_2$OPtS$_2$ (508.00): H, 4.96; C, 28.37; N, 5.51; Cl, 6.90. Found: H, 4.85; C, 28.41; N, 5.60; Cl, 6.88%.

2.3. Synthesis of [(dppf)Pt(H–nbu$_2$–DTO)]Cl (dppf = diphenyl-phosphino-ferrocene) (**2**)

[(Me$_2$SO)ClPt(H–*n*bu$_2$–DTO)] (**1**) (539 mg, 1 mmol) was reacted in chloroform (50 ml) with the stoichiometric amount of dppf (554 mg, 1 mmol). The orange solution turns pale yellow immediately after the addition of dppf. On adding petroleum ether (100 ml), [(dppf)Pt(HbuDTO)]Cl precipitated as a pale yellow powder (600 mg, 59.1% yield). ^{1}H NMR (CDCl$_3$, 298 K): $\delta = 0.77$ [t, 6H, N–(CH$_2$)$_3$–C*H*$_3$, $^3J_{\mathrm{H-H}} = 6.8$ Hz], 1.19 (m, 4H, N–CH$_2$–CH$_2$–C*H*$_2$–CH$_3$), 1.54 (m, 4H, N–CH$_2$–C*H*$_2$–CH$_2$–CH$_3$), 3.30 (t, 4H, N–CH_2–CH_2–CH_2–CH_3, $^3J_{H-H} = 6.8$ Hz), 4.18 (s, 4H, 3,3′ Cp protons); 4.34 (s, 4H, 2,2′ Cp protons); 7.1–7.4 (m, 20H, phenyl protons) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K): $\delta = 14.00$ (s, 2C, N–$(CH_2)_2$–CH_3), 28.80 (s, 2C, N–CH_2–CH_2–CH_2–CH_3), 31.60 (s, 2C, N–CH_2–CH_2–CH_2–CH_3), 53.4 (s, 2C, N–CH_2–CH_2–CH_2–CH_3), 73.3 (m, 4C, 3,3′ Cp carbons), 75.80 (m, 4C, 2,2′ Cp carbons), 127.9 (m, 8C, *meta* phenyl carbons), 130.2 (m, 4C, C *ipso*), 131.1 (s, 4C, *para* phenyl carbons); 134.8 (m, 8C, *ortho* phenyl carbons); 186 (t, 2C, CS, $^3J_{P-C} = 5.8$ Hz) ppm. ^{31}P NMR ($CDCl_3$, 298 K): $\delta = 18.5$ (s, Pt–P, $J_{P-Pt} = 3222$ Hz) ppm. *Anal.* Calc. for $C_{44}H_{47}ClFeN_2P_2PtS_2$ (1016.34): H, 4.66; C, 52.00; N, 2.76; Cl, 3.49. Found: H, 4.55; C, 52.09; N, 2.72; Cl, 3.51%.

2.4. Synthesis of [(dppf)Pt(H–nbu$_2$–DTO)]$_6$Cl$_6$ (3)

A concentrated solution of **2** (254 mg, 0.25 mmol, in 10 ml of $CHCl_3$), allowed to stand at room temperature for two days, slowly turns to green. Then this green solution is put at the head of an alumina column equilibrated with petroleum ether. Elution with chloroform/methanol 98:2 mixture separates **2** from **3**. This latter remains as a deep blue compound at the head of the column. When **2** is completely removed, **3** is eluated with a chloroform/methanol 90:10 mixture. The solvent was removed and the blue residue, dissolved in the minimum amount of $CHCl_3$ (10 ml), was precipitated as a deep blue powder with petroleum light (90 ml). By remaking the procedure (four times) 80 mg of pure **3** were collected (31% yield). ^1H NMR ($CDCl_3$, 298 K): $\delta = 0.33$ (m, 12H, N–CH_2–CH_2–CH_2–CH_3), 0.82 (t, 36H, N–CH_2–CH_2–CH_2–CH_3, $^3J_{H-H} = 6.8$ Hz), 0.86 (m, 24H, N–CH_2–CH_2–CH_2–CH_3); 1.14 (m, 12H, N–CH_2–CH_2–CH_2–CH_3), 2.21 (ABX_2 double triplet, 12H, $^3J_{H-H} = 6.6$ Hz; $J_{gem} = 12.8$ Hz), 3.21 (ABX_2 double triplet, 12H, $^3J_{H-H} = 6.6$ Hz; $J_{gem} = 12.8$ Hz), 4.20, 4.23 (2s, 24H, 3,3′ Cp protons), 4.46, 4.55 (2s, 24H, 2,2′ Cp protons), 7.21–7.78 (m, 120H, phenyl protons) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 4.00$ (s, 12C, N–CH_2–CH_2–CH_2–CH_3), 20.90 (s, 12C, N–CH_2–CH_2–C H_2–CH_3), 28.53 (s, 12C, N–CH_2–CH_2–CH_2–CH_3), 55.84 (s, 12C, N–CH_2–CH_2–CH_2–CH_3), 74.00, 74.40 (2m, 24C, 3,3′ Cp carbons), 76.00, 76.10 (2m, 24C, 2,2′ Cp carbons), 128.13, 128.20 (2m, 48C, *meta* phenyl carbons) 129.80 (m, 24C, *ipso* phenyl carbons), 131.90 (s, 24C, *para* phenyl carbons), 134.58, 134.65 (2m, 48C, *ortho* phenyl carbons); 183.26 (t, CS, $^3J_{P-C} = 5.8$ Hz) ppm. ^{31}P NMR ($CDCl_3$, 298 K): $\delta = 18.9$ (s, Pt–P, $J_{P-Pt} = 3242$ Hz) ppm. *Anal.* Calc. for $(C_{44}H_{47}N_2S_2P_2ClFePt)_6$ (6098.04): H, 4.66; C, 52.00; N, 2.76; Cl, 3.49. Found: H, 4.49; C, 51.67; N, 2.70; S, 6.35; Cl, 3.43%.

2.5. Synthesis of [(dppf)Pt(μ-H–nbu$_2$–DTO κ-S,S′ Pt κ-N,N′ Ru)Ru(p-cymene)Cl]Cl (4)

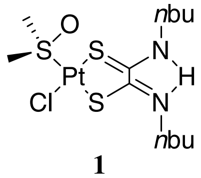
Compound **2** (508 mg, 0.5 mmol) was dissolved in 100 ml of chloroform. To the resulting yellow solution 153 mg (0.25 mmol) of $[RuCl_2(p\text{-cymene})]_2$ was added. The solution turned red and was allowed to stand for 2 h. Then the solvent was removed and the crude product, dissolved in the minimum amount of chloroform, was placed at the head of a neutral alumina column equilibrated with petroleum ether. The red orange eluate was concentrated to a small volume (10 ml); then petroleum ether (40 ml) was added and 368 mg of **4** was collected as a red orange powder (yield = 55%). ^1H NMR ($CDCl_3$, 298 K): $\delta = 0.76$ [t, 6H, N–$(CH_2)_3$–CH_3, $^3J_{H-H} = 6.7$ Hz], 1.10 [m, 4H, N–$(CH_2)_2$–CH_2–CH_3], 1.18 [d, 6H, cymene –CH(CH_3)$_2$, $^3J_{H-H} = 6.7$ Hz], 1.55 (m, 4H, N–CH_2–CH_2–CH_2–CH_3), 2.41 (s, 3H, cymene –CH_3), 2.76 [sl, 1H, cymene –C*H*$(CH_3)_2$, $^3J_{H-H} = 6.7$ Hz], 3.82 (ABX_2 double triplet, 2H, N–CH_2–CH_2–CH_2–CH_3, $^3J_{H-H} = 6.7$ Hz, $J_{gem} = 13.8$ Hz), 3.92 (ABX_2 double triplet, 2H, N–CH_2–CH_2–CH_2–CH_3, $^3J_{H-H} = 6.7$ Hz; $J_{gem} = 13.8$ Hz), 4.25 (br s, 4H, 3,3′ Cp protons), 4.45 (br s, 4H, 2,2′ Cp protons), 5,55 (dd, unresolved AA′XX′ spin system, 4H, cymene ring protons), 7.2–7.7 (m, 20H, phenyl protons) ppm. $^{13}C\{^1H\}$ NMR: $\delta = 13.70$ [s, 2C, N–$(CH_2)_3$–CH_3], 18.50 (s, 1C, cymene –CH_3), 20.50 [s, 2C, N–$(CH_2)_2$–CH_2–CH_3], 22.2 [s, 2C, cymene –CH$(CH_3)_2$], 29.00 (s, 2C, N–CH_2–CH_2–CH_2–CH_3), 31.20 [s, 1C, cymene –CH$(CH_3)_2$], 62.10 (s, 2C, N–CH_2–CH_2–CH_2–CH_3), 71,40 (m, 4C, 3,3′ Cp carbons), 74,10 (m, 4C, 2,2′ Cp carbons), 84.70, 85.10 (2s, 4C, cymene $C^{2,3,5,6}$), 100.00, 105.00 (2s, 2C, cymene $C^{1,4}$) 128.00 (m, 8C, *meta* phenyl carbons); 132.00 (m, 4C, *para* phenyl carbons), 134 (m, 8C, *ortho* phenyl carbons) ppm. ^{31}P NMR: $\delta = 17.60$ (s, $J_{P-Pt}0 = 3101$ Hz) ppm. *Anal.* Calc. for $C_{54}H_{60}Cl_2FeN_2P_2PtRuS_2$ (1286.07): H, 4.70; C, 50.43; N, 2.18; Cl, 5.44. Found: H, 4.65; C, 50.09; N, 2.12; Cl, 5.13%.

3. Results and discussion

[Cl(Me_2SO)Pt(H–*n*bu$_2$–DTO)] (**1**, H–*n*bu$_2$–DTO = di-normalbutyl-dithiooxamidate, Scheme 2) was prepared by reacting equimolar quantities of di-normalbutyl-dithiooxamide and *cis*-$[PtCl_2\ (Me_2SO)_2]$suspended in chloroform in the presence of sodium bicarbonate.

The function of the inorganic salt was to remove HCl from the tight ion pair {$(Me_2SO)ClPt(H\text{–}n\text{bu}_2\text{–DTO})^+$, (Cl^-)} once formed, being the ion pair unstable in solution [15].

Compound **1** was reacted with the equimolar amount of dppf (diphenylphosphinoferrocene) according to Scheme 3.



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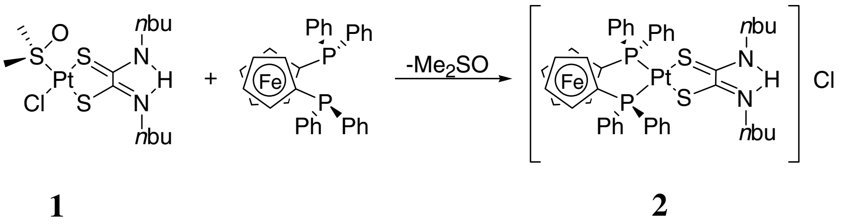
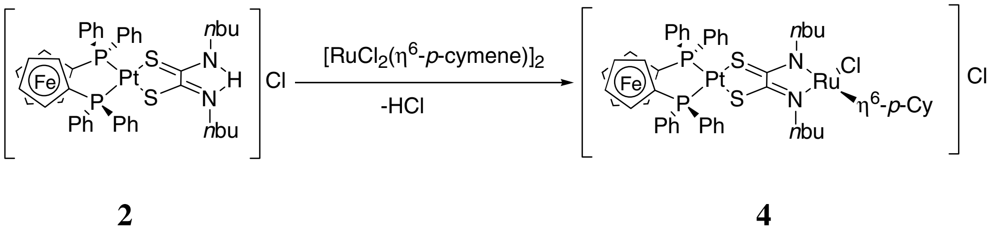
Scheme 2.



Scheme 3.



Scheme 4.

In Scheme 3, the binuclear Fe–Pt complex (**2**) is depicted with the dppf in "synclinal staggered" conformation. Such a diphosphinoferrocene arrangement in complexes showing η^2-chelating dppf seems to be largely preferred [16]. However, an eclipsed nature of the C5 rings in a dppf platinum complex has been shown with a deviation angle of 2.4° [17]. The ^{1}H and ^{13}C NMR of **2** show a single butylic pattern. Because of the rapid conformational flipping of chelated dppf, both proton and carbon spectra of dppf in **2** show chemical equivalence between 2,3 and 2′,3′ CH in each cyclopentadienyl fragment. Phosphorus resonances appear as a singlet flanked by ^{195}Pt satellites.

Concentrated chloroform solutions of **2**, allowed to stand, slowly turn to green. By chromatography of the green mixture on an alumina column, the pale yellow **2** is separated from a deep blue product **3**. Despite the dramatic change in color, both **2** and **3** have the same composition; i.e., in **3** there is a dppf unit per Pt(HbuDTO) fragment. Compound **3** is a cyclic compound of formula $[\mathbf{2}]_n$ where the most probable value n is 6.[1] The cyclic nature of **3** is mainly suggested by the presence of only one P–Pt signal and only one butylic pattern, more easily detectable in ^{13}C NMR spectra . Furthermore, in the ^{13}C NMR spectrum of **3** four multiplets are detectable for **2** and **3** carbons of ferrocene cp rings. This means that **2** and **3** carbons of one ring are unequivalent with respect to the similar carbons of the other ring in the same ferrocenyl reel probably because dppf spacers are blocked in an eclipsed synclinal conformation of Cp rings. Moreover, the phenyl rings of each phosphorus atom in dppf ligand become non-equivalent since the rigidity of the cyclic structure; thus the non-1:2:1 triplets of the phenyl carbons[2] [18], observed in **2**, appear splitted in the ^{13}C NMR spectrum of **3**. Innumerable attempts of crystallization of **3** merely produced amorphous powders; for this reason we find it hazardous to propose any temptative structure for **3** only on the basis of NMR evidences, which allow to say only that **3** is the result of a cyclic self-assembling of platinum dithioxamidate metal fragments, alternated by dppf reels as spacers.

Being the above cyclization a slow process, it is possible to exploit **2** as a ligand complex, and link a further metal fragment according to the known procedures [10,11].

Thus, by the reaction of **2** with an half molar quantity of $[\mathrm{RuCl_2}(\eta^6\text{-}p\text{-cymene})]_2$, the following process took place (Scheme 4).

The tetrahedral arrangement of ligands around ruthenium atom in **4** causes the plane passing through arene centroid and chlorine to be a symmetry plane, while that one containing nitrogen atoms, which also contains the platinum square plane, is not a symmetry plane. Consequently, in the ^{1}H NMR spectrum of **4** there is only one butylic spectral pattern, in which methylene hydrogens, being chemically non-equivalent, exhibit complex ABX_2 resonancies.

We wish to point here that the process in Scheme 4 represents a route for a systematic access to trinuclear heterotrimetallic complexes.

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[1] In principle, tetrameric and octameric conformations cannot be excluded, but an hexamer is by far to be preferred for geometrical reasons. Other evidences (electrochemistry, see later in the main text) strongly support the proposed nuclearity.

[2] Aromatic and Cp carbons appear in the spectrum as quintets, non-1:3:1 triplets, doublet of doublets, because of virtual coupling [18]. We have reported these signals as multiplets.

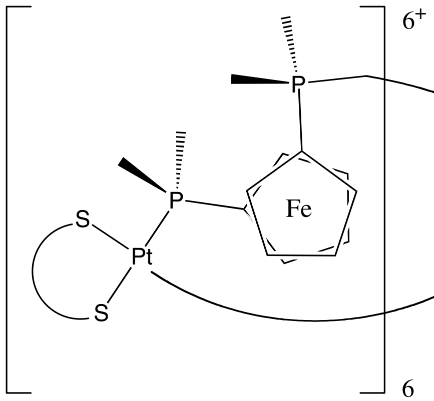

Fig. 1. Proposed formula for cyclic oligomer **3**.

4. Electrochemistry

The cyclic voltammogram (CV) of complex **2** in 1,2-dichloroethane exhibits a reversible one-electron oxidation process at +1.13 V versus SCE. Such a process is assigned to the ferrocene/ferrocinium couple; it is strongly shifted to more positive potentials compared to the oxidation of ferrocene (+0.48 V under these experimental conditions), as expected because of the presence of the diphenylphosphino substituents. However, it is also much more positive than the oxidation process found for dppf under the same experimental conditions (+0.67 V), and close to those reported for (dppf)PtCl$_2$ and (dppf)Pt(*i*-mnt) (*i*-mnt = 2,2-dicyano-1,1-ethylenedithiolate), which undergo reversible dppf-based oxidation at +1.27 V and +1.22 V versus Ag/Ag$^+$ in dichloromethane [19]. The significant positive shift of the oxidation in **2** compared to that of dppf is attributed to the electron withdrawing ability of the dithioxamide ligand, which drains electronic charge from the dppf ligands via the Pt(II) center.

The cyclic multinuclear system **3** undergoes a reversible oxidation process at +0.38 V followed by a quasi-reversible process at +1.17 V (Fig. 2).

By comparison between the intensities of the peaks of **3** with those of **2** and that of ferrocene, used as standard, in CV experiments, we assigned the first process of **3** to a one-electron oxidation and the second one to two closely-spaced one-electron processes dealing with two weakly interacting sites.

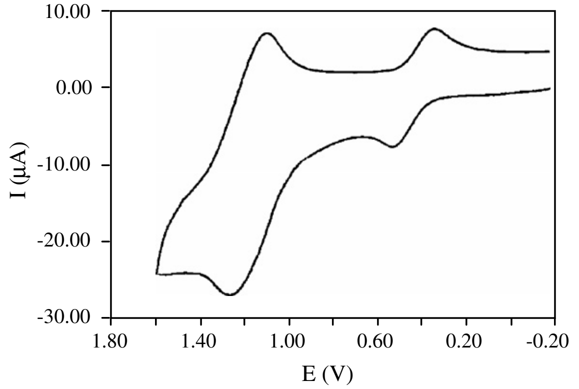

Fig. 2. Cyclic voltammogram (CV) of complex **3** in 1,2-dichloroethane. Scan rate 200 mV/s.

To rationalize this behavior it is useful to consider that bridging Pt(II) centers may allow a good electronic interaction between redox-active groups: this is the case for the 'rod-like' organometallic complex *trans*-[Pt(ethynylferrocene)$_2$(PPh$_3$)$_2$], for which the two ferrocene-centered oxidations are splitted by 260 mV [20]. Although the Pt(II) center in **3** is quite different from that in *trans*-[Pt(ethynylferrocene)$_2$(PPh$_3$)$_2$], and the geometrical arrangements of the species are also different, it is reasonable to assume that two nearby dppf subunits in **3** are significantly coupled via the Pt(II) centers. Since all the dppf subunits in **3** are identical to one another (as evidences by NMR spectra), the coupling can easily be extended to all the dppf subunits which are present in the cyclic multinuclear array. The consequence is that the HOMOs of the six redox centers can give rise to delocalized orbitals which are stabilized compared to the HOMO of the 'isolated' subunit, and to delocalized ones which result to be highly destabilized. It is one of these latter delocalized orbitals which is held responsible for the oxidation process at +0.38 V. A platinum-centered assignment for the oxidation process can be ruled out since the precursor [Pt(dithioxamide)(dmso)Cl] (**1**) complex does not undergo any oxidation process at potential less positive than +1.70 mV and the trinuclear species [Ru(Cp)Cl(μ-dithioxamide)Pt(dppf)]$^+$ (**4**) exhibits the first oxidation process at +1.10 V.

The strong differences in the electronic properties of **2** and **3** indicated by the redox data are also evidenced by the absorption spectra. The lowest-energy absorption feature of **2** in dichloromethane solution is a structured band with maximum at about 420 nm, whereas the lowest-energy absorption feature of **3** is also a structured band, but the maximum is displaced at 680 nm. Energy separation between the maxima within each structured absorption bands (i.e., the vibrational progression) is about 1500 cm^{-1} in both **2** and **3**. The similarities in the shapes of the bands in **2** and **3** suggest a similar origin. So, the red-shift of the low-energy band of **3** with respect to **2** can be directly related to the difference in the first oxidation potentials of the two compounds[3] [21].

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[3] Absorption bands similar (although at slightly higher energy) to that exhibited by **1** have been reported for homoleptic Pt(II) species with dithioxamide ligands, and have been attributed to charge-transfer (CT) bands involving an acceptor orbital mainly centered on the peripheral moiety of the dithioxamide ligands [20]. Visible ferrocenylborane-to-polypyridine CT bands have also been recently reported [20]. So we tentatively attribute the lowest energy absorption band of **1** and **2** to a dppf-to-dithioxamide charge transfer (ligand-to-ligand charge transfer, LLCT) transition, where probably the donor orbital receives partial contribution from the platinum orbitals. The red-shift of the band in **2** is justified by the fact that the donor orbital (in this case, the delocalized orbitals involving the dppf centers) is much easier to be oxidized.

Finally, we wish to point out that a further and definite strong indication concerning the nuclearity of **3** comes from electrochemical data: comparison between cyclic voltammograms of **2**, **3**, and the trinuclear species $[Ru(Cp)Cl(\mu\text{-dithioxamide})Pt(dppf)]^+$ (**4**) allows to obtain integer numbers of exchanged electrons for the redox processes of **3** only when a molecular weight corresponding to the structure in Fig. 1 is used. The details of this methodology have been reported by Olbrich et al. [22].

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