### Inorganica Chimica Acta 374 (2011) 288-301

Contents lists available at ScienceDirect

# Inorganica Chimica Acta



journal homepage: www.elsevier.com/locate/ica

# New thiocyanato and azido adducts of the redox-active $Fe(\eta^5-C_5Me_5)(\eta^2-dppe)$ center: Synthesis and study of the Fe(II) and Fe(III) complexes

Floriane Malvolti<sup>a</sup>, Alexander Trujillo<sup>a</sup>, Olivier Cador<sup>a,\*</sup>, Frédéric Gendron<sup>a</sup>, Karine Costuas<sup>a</sup>, Jean-François Halet<sup>a</sup>, Arnaud Bondon<sup>b</sup>, Loic Toupet<sup>c</sup>, Yann Molard<sup>a</sup>, Stéphane Cordier<sup>a</sup>, Frédéric Paul<sup>a,\*</sup>

<sup>a</sup> Sciences Chimiques de Rennes, UMR CNRS 6226, Université de Rennes 1, 35042 Rennes Cedex, France <sup>b</sup> PRISM. UMR CNRS 6026, Université de Rennes 1, 35043 Rennes Cedex, France

<sup>c</sup> Institut de Physique de Rennes, UMR CNRS 6251, Université de Rennes I, 35042 Rennes Cedex, France

### ARTICLE INFO

Article history: Available online 9 March 2011

Dedicated to Professor W. Kaim.

Keywords: Organometallics Thiocyanato complex Azido complex Spin delocalization Magnetic anisotropy ESR

# ABSTRACT

The new thiocyanato- (**5**) and azido- (**6**) complexes were synthesized and studied under their Fe(II) and Fe(III) redox states. For the first time among the various  $[Fe(\eta^5-C_5Me_5)(\eta^2-dppe)]$ -based cationic radicals studied so far, the magnitude and spatial orientation of the *g*-tensor diagonal values were experimentally determined for **5**[PF<sub>6</sub>]. These data are in good agreement with those issued from a DFT modelization. The changes experienced by the electronic structure of the Fe(II) complexes subsequent to oxidation are reminiscent of these previously observed for the known arylalkynyl analogues, albeit some differences can be pointed out. Thus, the differences observed in the <sup>1</sup>H NMR spectra of **5**[PF<sub>6</sub>] and **6**[PF<sub>6</sub>] are attributed to a slower electronic spin relaxation and to the differently oriented magnetic anisotropy. The sizeable spin density evidenced by DFT on the terminal atom of the ligands of the Fe(III) complexes renders these mew paramagnetic metallo-ligands quite appealing for accessing larger polynuclear molecular assemblies with magnetically interacting centers.

© 2011 Elsevier B.V. All rights reserved.

### 1. Introduction

For some time we have been involved in the study of various families of organic ligands functionalized with redox-active organometallic Fe( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)( $\eta^2$ -dppe) centers such as **2–4**, (Scheme 1) [1–4]. Actually, these "metallo-ligands" are all made in several steps from the chloride precursor complex **1** [5]. They belong to a fairly new and quite attractive class of compounds [6–10], for which the control of the oxidation state of the organoiron substituent provides a simple mean of tuning the electronic properties of the appended coordinating group, and in turn these of any complex to which these ligands are coordinated [2,11–13]. While our previous efforts have mostly focused on the development of metallo-ligands featuring organic coordinating units, we have recently turned our attention to simpler "inorganic" members of this class of compounds, namely the metal–thiocyanate and metal–azido complexes **5** and **6**.

Indeed, considering the impressive number of complexes built so far with the related (iso)cyano- [14-24] or cyanoalkynyl-based [25-29] metallo-ligands ( $7_n$ ), along with the importance of thiocyanato and azido ligands in the field of molecular magnetism [30], and also considering some key organic transformations undergone by these functional groups [31–33], we surmised that compounds such as **5** and **6** would be interesting to synthesize. When used as metallo-ligands, these redox-active organometallic building blocks should open access to polynuclear architectures that might present a large panel of uses in various fields, encompassing molecular based-electronics, optics and even spintronics. Beside this general concern, we were also curious to investigate their electronic properties and especially these of their open-shell cationic Fe(III) derivatives **5**<sup>+</sup> and **6**<sup>+</sup> in order to be able to compare them with known paramagnetic Fe(III) metallo-ligands, such as **2**<sup>+</sup>–**4**<sup>+</sup>.

In this contribution on the thiocyanato and azido complexes, we will report their synthesis and characterization in both the Fe(II) and Fe(III) oxidation states. Their electronic structures will also be investigated experimentally, using usual spectroscopies, cyclic voltammetry and theoretically, using DFT. In these studies, a close attention will be brought to the electronic changes induced by oxidation of the redox-active Fe(II) center. Finally, their structures will be compared to those of well-studied piano-stool analogues such as **8-X**<sup>n+</sup> or **2**<sup>n+</sup> (n = 0, 1).

# 2. Results

## 2.1. Synthesis of the thiocyanato and azido Fe(II) complexes 5 and 6

The desired complexes were obtained from the chloride precursor complex **1** [34,35] following a ligand metathesis reaction



<sup>\*</sup> Corresponding authors. Tel.: +33 02 23 23 57 12; fax: +33 02 23 23 69 39 (O. Cador), Tel.: +33 02 23 23 59 61; fax: +33 02 23 23 69 39 (F. Paul).

E-mail address: frederic.paul@univ-rennes1.fr (F. Paul).

<sup>0020-1693/\$ -</sup> see front matter  $\circledcirc$  2011 Elsevier B.V. All rights reserved. doi:10.1016/j.ica.2011.03.002



**Scheme 1.** Selected organoiron complexes containing the  $Fe(\eta^5-C_5Me_5)(\eta^2-dppe)$  unit.



**Scheme 2.** Synthesis of the Fe(II) and Fe(III) thiocyanato and azido  $Fe(\eta^5-C_5Me_5)(\eta^2-dppe)$  complexes.

in methanol (Scheme 2). Potassium hexafluorophosphate was added to favor chloride dissociation and formation of a hypothetical 16-electron intermediate such as  $[Fe(\eta^5-C_5Me_5)(\eta^2-dppe)]^+$  [34]. The desired complexes were isolated as light purple and deep green solids, respectively, and were fully characterized by usual means. Crystal structures were also obtained for these compounds which confirmed their identity (Fig. 1a and b). Notably, we took a particular care to make sure of the purity of the isolated samples, especially regarding the azido complex **6**, since its color and various other experimental signatures are not very distinct from those of the starting complex **1** [34,35].<sup>1</sup>

In infrared (IR), the presence of the coordinated thiocyanate ligand in **5** was evidenced by a strong absorption near 2099 cm<sup>-1</sup> corresponding to one of the  $v_{NCS}$  stretching modes (Table 1), and a weaker one at 807 cm<sup>-1</sup> corresponding to the other  $v_{NCS}$  mode of this ligand [36]. For the complex **6**, the presence of the azido ligand was evidenced by a strong absorption at 2049 cm<sup>-1</sup> in KBr corresponding to the asymmetric  $v_{NNN}$  mode. Comparison of these data with those reported [36] for the corresponding modes of the "free" anions in potassium thiocyanate (2053 cm<sup>-1</sup>) and potassium azide (2041 cm<sup>-1</sup>) indicate a strengthening of the higher-energy modes upon coordination to the Fe( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)( $\eta^2$ -dppe) fragment, this strengthening being

more pronounced in the case of **5** ( $\geq$ 45 cm<sup>-1</sup>).<sup>2</sup> We shall come back to this statement later on (see the Section 3).

The NCS ligand can bind metal centers from both its sulfur or nitrogen ends. For **5**, the crystallographic structure of the complex shows that the NCS ligand is *N*-bonded to the iron center in the solid state (Fig. 1a). However, considering that several thiocyanato complexes are known to isomerize in solution from one bonding mode to the other [38], we were particularly cautious to ascertain that this bonding mode was preserved in solution. This was suggested by the quite similar IR signature obtained for **5** in dichloromethane solutions (Table 1) in comparison to those obtained for crystalline samples in KBr.<sup>3</sup> Further confirmation of that was obtained from the <sup>13</sup>C NMR shift of the NCS-carbon atom at 144.2 ppm,<sup>4</sup> which is diagnostic of *N*-bonded thiocyanate [40].

UV–Vis reveals that a set of weak absorptions in the visible range (Table 1) are responsible for the strong color of these complexes. Based on previous investigations and considering their intensity, a metal-to-ligand charge transfer (MLCT) origin appears likely for these electronic transitions [41]. Finally, cyclic voltammetry reveals the existence of a chemically reversible metal-centered oxidation at

<sup>&</sup>lt;sup>1</sup> This could be done by checking the complete disappearance of the signal corresponding to the set of *ortho* phenyl dppe hydrogen of **1** in the isolated samples of **6**. Taking the C<sub>5</sub>Me<sub>5</sub> peak as reference at 1.38 ppm, the previous signal comes out at 8.01 ppm for **1** in C<sub>6</sub>D<sub>6</sub> and at 7.78 ppm for **6** in the same solvent.

<sup>&</sup>lt;sup>2</sup> Caution should be used with the azide salts, since their asymmetric stretch is believed to be strongly dependant on the solid structure of the azide salt [37].

<sup>&</sup>lt;sup>3</sup> By themselves, the rather high  $v_{NCS}$  values found are already suggestive of a *N*-bonded NCS ligand, [36] albeit intensity studies should be performed to remove any ambiguity based on  $v_{NCS}$  alone [39].

<sup>&</sup>lt;sup>4</sup> The 135–146 ppm range corresponds to an N-bonded NCS ligand while the 125– 128 ppm range is more characteristic of an S-bonded NCS ligand.



Fig. 1. ORTEP representations of 5 (a) and 6 (b) at 50% probability level. Hydrogen atoms have been omitted for clarity.

Table 1	
Selected spectroscopic data and yields for $[Fe(\eta^5-C_5R_5)(\eta^2-dppe)(X)]^{n+}$ (X = Cl, NCS, N <sub>3</sub> ; R = Me, H; n = 0, 1) completed spectra sp	xes.

Cpnd	X,R	$IR^{a} v_{X} (cm^{-1})$	$\Delta v_{\rm X}$ (Red-Ox) (cm <sup>-1</sup> )	$^{31}$ P NMR <sup>b</sup> $\delta_{dppe}$ (ppm)	CV <sup>c</sup> E <sub>0</sub> (V vs. SCE)	UV–Vis–Near IR <sup>d</sup> $\lambda$ in nm ( $\epsilon \times 10^{-3}$ in M <sup>-1</sup> cm <sup>-1</sup> )
6	Cl, Me	/	1	92.7	-0.23	315[sh, 4.7], 411 [sh, 1.6], 538 [0.5], 638 [0.3] <sup>e</sup>
6[PF <sub>6</sub> ] <sup>e</sup>	Cl, Me	1	1	/		466 [2.4], 550 [sh, ca. 1.0], 1572 [0.01]
5	NCS, Me	2104	63	93.9	0.04	396 [sh, 1.3], 508 [0.58], 542 [sh, 0.52]
5[PF <sub>6</sub> ]	NCS, Me	2041	/	/		480 [sh, 2.4], 552 [5.3], 1700 [0.040]
6	N <sub>3</sub> , Me	2050	12	94.6	-0.24	320 [sh, 4.8], 418 [1.7], 548 [0.58], 618 [sh, 0.48]
6[PF <sub>6</sub> ]	N <sub>3</sub> , Me	2038	1	/		489 [3.5], 568 [sh, 1.4], 1450 [0.025]
<b>7</b> 0 <sup>f</sup>	NCS, H	2084 <sup>g</sup>	44	n.d.	0.32 <sup>h</sup>	510 [0.53]
<b>7</b> <sub>0</sub> [PF <sub>6</sub> ] <sup>i</sup>	NCS, H	2040	1	1		582 [2.3]

<sup>a</sup> In CH<sub>2</sub>Cl<sub>2</sub>/KBr windows unless precised.

<sup>a</sup> In CH<sub>2</sub>Cl<sub>2</sub>/KBF windows timess precised.
 <sup>b</sup> In C<sub>6</sub>D<sub>6</sub> unless precised.
 <sup>c</sup> Conditions: CH<sub>2</sub>Cl<sub>2</sub> solvent, 0.1 M [*n*-Bu<sub>4</sub>N][PF<sub>6</sub>] supporting electrolyte, 20 °C, Pt electrode, sweep rate 0.100 V s<sup>-1</sup>.
 <sup>d</sup> In CH<sub>2</sub>Cl<sub>2</sub> at 20 °C.
 <sup>e</sup> P + C + C = P + C + 421

<sup>e</sup> Data from Ref. [42].

<sup>f</sup> Data from Ref. [14].

<sup>a</sup> In KBr pellets.
 <sup>b</sup> [*n*-Bu<sub>4</sub>N][ClO<sub>4</sub>] used as supporting electrolyte.
 <sup>i</sup> Data from Ref. [43].



Fig. 2. ORTEP representations of  $5[PF_6]$  (a) and  $6[PF_6]$  (b) at 50% probability level. Hydrogen atoms have been omitted for clarity.

#### **Table 2** Experimental ESR g-values<sup>a</sup> vs. computed g-values for $[Fe(\eta^5-C_5Me_5)(\eta^2-dppe)(X)]^*$ (X = NCS, N<sub>3</sub>) complexes **5**[PF<sub>6</sub>] and **6**[PF<sub>6</sub>].

_								
_	Cpnd	R		$g_1$	$g_2$	g <sub>3</sub>	$\langle g  angle$	$\Delta g$
	<b>5</b> <sup>+</sup>	NCS	Exp. <sup>a</sup>	1.979	2.042	2.471	2.164	0.492
			Calc. <sup>b</sup>	1.949	2.067	2.388	2.134	0.439
			Exp. <sup>c</sup>	1.993	2.050	2.442	2.162	0.449
				(±0.004)	(±0.003)	(±0.016)	(±0.007)	(±0.020)
			Calc. <sup>d</sup>	1.962	2.083	2.334	2.126	0.372
	<b>6</b> <sup>+</sup>	N <sub>3</sub>	Exp. <sup>a</sup>	1.996	2.049	2.328	2.124	0.332
			Calc. <sup>b</sup>	1.983	2.055	2.220	2.086	0.237
			Calc. <sup>d</sup>	1.983	2.057	2.239	2.093	0.256

 $^a$  Experimental ESR g-values (±0.005) determined at 65–70 K in CH\_2Cl\_2/1,2-C\_2H\_4Cl\_2 (1:1) glass.

<sup>b</sup> DFT values of optimized structures.

<sup>c</sup> Experimental (mean) ESR g-value determined at 65 K in the solid state for an oriented single crystal of  $\mathbf{5}[\mathsf{PF}_6]$  (see text).

<sup>d</sup> DFT values for solid state geometry.

0.04 V (versus SCE) for **5** and at -0.24 V for **6** (Table 1), which indicates that these compounds can be fairly easily oxidized.

#### 2.2. Synthesis of the thiocyanato and azido Fe(III) complexes

Based on the Fe(III)/Fe(II) redox potentials values measured (Table 1), the chemical oxidation of both 5 and 6 was performed using ferricinium hexafluorophosphate (Scheme 2), resulting in apparent color changes of the reaction media [42,44,45]. Thus, 5 darkens whereas 6 switches from deep green to purple upon oxidation. Cyclic voltammetry confirmed the redox parentage between the isolated products and the starting Fe(II) compounds, while infrared spectroscopy established their different nature. The identities of the compounds were definitively established by X-ray diffraction (Fig. 2a and b). Again, 5[PF<sub>6</sub>] has a N-bonded thiocyanate ligand in the solid state, which remains N-bonded in solution according to IR [36]. For both Fe(III) complexes 5[PF<sub>6</sub>] and 6[PF<sub>6</sub>], a decrease in the frequencies of the stretching modes of the thiocvanato and azido groups is observed relative to their Fe(II) parents (Table 1), indicating that oxidation sizeably weakens the bonding within these inorganic ligands.

The Fe(III) radical cations were then characterized in solution by UV–Vis–Near-IR (Table 1). In line with the color change accompanying the oxidation reaction of  $5[PF_6]$  and  $6[PF_6]$ , their most intense absorption in the visible range is found at lower energies and presents an increased intensity relative to those in **5** and **6** (Table 1). In addition, for the Fe(III) complexes, near IR spectros-copy reveals the presence of a low-intensity electronic transition near 1500–1700 nm, in a spectral range where the Fe(II) complexes are silent. Based on previous investigations with **1**[PF<sub>6</sub>] and **8**-**X**[PF<sub>6</sub>] [42], the absorptions in the visible range certainly correspond to ligand-to-metal charge transfer (LMCT) transitions, and that in the near IR range to a forbidden ligand field (LF) transition.

Magnetization measurements have also been performed on crystalline sample of **5**[PF<sub>6</sub>]. The temperature variation of the molar magnetic susceptibility  $\chi_{\rm M}$  follows the Curie–Weiss law for a radical with  $S = \frac{1}{2}$  (see Supporting Information). The paramagnetic  $(S = \frac{1}{2})$  nature of **5**[PF<sub>6</sub>] and **6**[PF<sub>6</sub>] was also confirmed by ESR and NMR measurements. For both compounds, the ESR spectra in solvent glasses at 77 K reveal the presence of an unpaired electron in a rhombic environment (Table 2), indicative of its metal-centred nature, with a significant anisotropy ( $\Delta g$ ), larger for **5**[PF<sub>6</sub>] than for **6**[PF<sub>6</sub>] [42]. Then, the characteristic <sup>1</sup>H and <sup>13</sup>C NMR isotropic shifts of these compounds recall those previously observed for related Fe(III) radicals [44]. Most of the observed signals can be attributed by comparison with the assignments previously proposed (Scheme 3, Fig. 3 and Supporting Information). Notably, the <sup>1</sup>H NMR spectrum of **6**[PF<sub>6</sub>] is significantly more broadened than that



**Scheme 3.** <sup>1</sup>H nuclei numbering corresponding to the proposed assignment for **5**[PF<sub>6</sub>] and **6**[PF<sub>6</sub>].

of **5**[PF<sub>6</sub>] at 293 K, the signal of the C<sub>5</sub>Me<sub>5</sub> protons being hardly discernible at ambient temperature (see Supporting Information). For **6**[PF<sub>6</sub>], an intense isotropic ESR signal is observed at g = 2.12 in CH<sub>2</sub>Cl<sub>2</sub>/1,2-C<sub>2</sub>H<sub>2</sub>Cl<sub>2</sub> at 295 K, whereas only a barely discernible signal shows up at g = 2.08 for **5**[PF<sub>6</sub>] in solution at ambient temperatures. We therefore surmised that the unusual broadening observed in the <sup>1</sup>H NMR spectrum of the former Fe(III) complex was ascribable to a slower relaxation of the electronic spin which in turn fastens the nuclear spin relaxation of the protons. In line with this hypothesis, heating of a sample of **6**[PF<sub>6</sub>] in nitrobenzene- $d^5$  at 363 K (*ca.* 90 °C) allowed retrieving a comparable resolution than for **5**[PF<sub>6</sub>]. As expected for these low spin (S =  $\frac{1}{2}$ ) Fe(III) complexes [44], heating also produces a Curie-type (1/*T*) shift of the <sup>1</sup>H signals towards the diamagnetic region of the spectrum (see Supporting Information).

### 2.3. Solid state structures of 5, 6, 5[PF<sub>6</sub>] and 6[PF<sub>6</sub>]

The solid state structures reveal that the thiocyanato and azido complexes are isostructural with one another, featuring each time four molecules in the elementary cell (Table 6). The Fe(II) complexes crystallize in the monoclinic  $P2_1/c$  system, while the Fe(III) complexes crystallize in the orthorhombic  $P2_12_12_1$  system (see Section 5). The bond lengths and angles for the dppe and  $C_5Me_5$  ligands within the coordination sphere are classic for such "pianostool" complexes (Table 3) [35,41,42,46].

For the Fe(II) complexes, the Fe1–N1–X angle is not 180°, but 171.6° and 131.2° for the thiocyanato and azido complexes, respectively. For **5** (X = C37), which features the bulkier S-terminal atom on the ligand, this angle remains nearly linear. In contrast, in the case of **6** (X = N1), the angle is closer to the ideal value for a  $sp^2$ hybridized N atom. The Fe1-N1 bond in the NCS complex (1.927 Å) is significantly shorter than those usually found for iron compounds with a single Fe-N bond (2.063 Å) [47], while bonds of within the NCS ligand in **5** are slightly longer than those usually reported for the alkali thiocyanate salts (N–C: 1.15 Å, C–S: 1.63 Å), in line with a possible  $d_{Fe} \rightarrow \pi^*_{NCS}$  contribution to the Fe–N bond [33]. In contrast, the Fe–N bond of 6 is longer than in 5, and stays in the range reported for a single bond (2.009(3) Å) [33]. The bonding within the Fe–N<sub>3</sub> unit is usual, except perhaps for the bending angle of the azido ligand which is less important than 120°. Also, the N-N bonds are slightly shorter and longer, respectively, than those usually reported for the N<sub>3</sub> ligand in organic azides (internal N–N: 1.216 Å, terminal N–N: 1.124 Å) [48]. As discussed below, the distinct bending angles adopted by the cumulenic ligands in 5 and **6** can be explained by considering different hybridizations for the bonded nitrogen (N1) which are induced by different intramolecular electronic and steric effects. Packing forces might also contribute to some extent to influence the bonding within the cumulenic ligand in 5 and 6 in the solid-state, since short contacts are



Fig. 3. <sup>1</sup>H NMR spectra of 8-NO<sub>2</sub>[PF<sub>6</sub>] (a), 5[PF<sub>6</sub>] (b) and 6 [PF<sub>6</sub>] (c) in CD<sub>2</sub>Cl<sub>2</sub> at 25 °C with proposed assignment for selected protons according to Scheme 3.

Table 3	
Selected bond lengths (Å) and angles (°) for <b>5</b> , <b>5</b> [ $PF_6$ ], <b>6</b> and <b>6</b> [ $PF_6$ ].	

Cpnd	5	<b>5</b> [PF <sub>6</sub> ]	6	<b>6</b> [PF <sub>6</sub> ]
Selected bond lengths				
$Fe-(C_5Me_5)_{centroid}$	1.733	1.767	1.728	1.763
Fe-P1	2.2282(9)	2.2794(8)	2.2067(5)	2.2856(7)
Fe-P2	2.2311(9)	2.2896(8)	2.2297(6)	2.2871(7)
Fe-N1	1.927(2)	1.890(2)	2.0267(18)	2.002(2)
N1-C37	1.169(3)	1.168(4)		
C37-S1	1.646(3)	1.608(3)		
N1-N2			1.183(2)	1.034(4)
N2-N3			1.169(3)	1.250(5)
Selected bond angles				
P1-Fe-P2	86.02(3)	83.34(3)	85.52(2)	83.05(3)
P1-Fe-N1	83.11(8)	83.52(8)	85.36(5)	89.94(6)
P2-Fe-N1	90.02(8)	95.10(8)	83.21(5)	83.61(6)
Fe-N1-C37	171.6(2)	160.2(2)		
N1-C37-S1	179.8(3)	179.1(3)		
Fe-N1-N2			131.19(16)	129.1(2)
N1-N2-N3			175.6(2)	173.2(4)

observed in the solid state between the terminal S or N atom and one of the dppe aromatic H atoms (H23 and H27, respectively) of an adjacent molecule (2.983 and 2.718 Å, respectively).

Regarding the Fe(III) complexes **5**[PF<sub>6</sub>] and **6**[PF<sub>6</sub>], the coordination sphere formed by the dppe and  $C_5Me_5$  ligands expands slightly upon oxidation, as usually observed with related piano-stool complexes [41,42,46,49]. In addition, for the thiocyanato complex **5**[PF<sub>6</sub>], a shortening of the Fe1–N1 bond and a slight shortening of the C37–S1 bond, concomitant with a slight decrease in the Fe1–N1–C37 angle takes place upon oxidation. Overall, the NCS ligand remains essentially linear after the oxidation. In comparison, the bending of the N<sub>3</sub> ligand in the azido complex is quite unaffected by oxidation. A shortening of the Fe1–N1 bond, along with a marked shortening of the N1–N2 bond,<sup>5</sup> concomitant with a lengthening of the N2–N3 bond is however observed in **6**[PF<sub>6</sub>].

# 2.4. Solid-state ESR on a monocrystal of the thiocyanato Fe(III) complex

To obtain additional experimental insight on the electronic structure of these isostructural radical cations, we decided to determine the orientation of the diagonal *g*-tensor components of **5**[PF<sub>6</sub>] by performing ESR measurements on a single crystal. Single crystals of **5**[PF<sub>6</sub>] have a "shoe box" shape with the box axis collinear to the crystallographic *c* axis, the largest face coinciding with the [1 1 0] plane. The crystal reference frame (*XYZ*) in which rotations are performed is represented in Scheme 4.

The angular dependences of the ESR spectra have been measured at 65 K in three perpendicular planes (*XY*), (*XZ*) and (*YZ*). In the orthorhombic space group  $P2_12_12_1$  the four molecules are related by 2-fold axes. Thus, four signals are expected for any orientation of the magnetic field because frozen solution measurements clearly demonstrate that the ESR signal is rhombic ( $g_1 = 1.979$ ,  $g_2 = 2.042$  and  $g_3 = 2.471$ ). Two resonance lines are expected when the magnetic field coincides with one of the 2-fold axes. However, only one resonance field with a strong angular dependence is observed for rotation around *Z* and two of the same intensity for rota-

 $<sup>^5</sup>$  The extremely short N1–N2 bond in  $6[PF_6]$  is quite unusual. The latter bond might appear artificially shortened due to librational motions of the  $N_3$  ligand, since no packing effet can be invoked to explain it. A related phenomenon has been stated few year ago with the C–O bond of the  $[Fe(\eta^5-C_5Me_5)(\eta^2-dppe)(CO)][PF_6]$  carbonyl complex [50].



**Scheme 4.** Schematic representation of a crystal of compound **5**[PF<sub>6</sub>] with the reference frame (*XYZ*) in which rotations are performed.

tions about Y and X (see Figs. S7–S9 of the Supporting Information, respectively). These symmetric signals with no hyperfine structure are characteristic of Fe(III) organometallic (S = 1/2) radicals. The angular variations of the resonance positions by means of  $g_{eff}^2$  for the three rotation sets are represented in Fig. 4. Resonance fields have been determined by the maxima of the numerically integrated ESR spectra.

The resonance positions are labeled RZ for rotation about *Z*, RX1 and RX2 for rotations about *X* and RY1 and RY2 for rotation about *Y*. In spite of the four distinct molecules in the unit cell, less than four distinct signals are detected for all orientations. Considering the symmetry of the unit cell and the different signals detected, only two combinations of the resonance lines belonging to the two distinct centers are mathematically possible [(RX1, RY1, RZ), (RX2, RY2, RZ)] and [(RX1, RY2, RZ), (RX2, RY1, RZ)]. These are, respectively, noted A and B in the following. In the following, as a mean to check the consistency of our starting dataset, we have extracted the experimental *g*-tensors for every signal separately.<sup>6</sup> Least-square fitting procedures were performed for each distinct center, in each combination, with the following equation: [51]

$$g_{\text{eff}}^{2} = gg_{XX} \sin^{2} \theta \cos^{2} \phi + 2gg_{XY} \sin^{2} \theta \cos \phi \sin \phi + gg_{YY}$$

$$\times \sin^{2} \theta \sin^{2} \phi + 2gg_{XZ} \cos \theta \sin \theta \cos \phi + 2gg_{YZ}$$

$$\times \cos \theta \sin \theta \sin \phi + gg_{ZZ} \cos^{2} \theta \qquad (1)$$

The best-fitted parameters for each combination are given in Supporting Information. Diagonalization of the resulting matrices provides principal g-values (combination A:  $g_{RX1, RY1, RZ} =$ [1.997, 2.053, 2.427],  $g_{RX2, RY2, RZ} = [1.989, 2.047, 2.456]$ ; combination B:  $g_{RX1, RY2, RZ} = [1.933, 2.135, 2.429]$ ,  $g_{RX2, RY1, RZ} = [1.897, 2.429]$ 2.170, 2.404]). However, only one of these data sets corresponds to the real g-tensor of the complex. Based on symmetry grounds, the diagonal g-values found for one center should be similar to those of the other one<sup>6</sup>. In this respect, the combination A appears more self-consistent. Then, considering that the molecular geometry should be preserved between molecules in the solid and frozen solvent glasses, the principal g-values should not change dramatically from the data found in CH<sub>2</sub>Cl<sub>2</sub>/1,2-C<sub>2</sub>H<sub>2</sub>Cl<sub>2</sub> glasses at 65 K [1.979, 2.042, 2.471] (Table 2). Such an analysis leads to retain combination A as the correct one (mean g-values between the two g-sets of this combination are given in Table 2). The best fitted curves for this combination using Eq. (1) are plotted in Fig. 4. The



**Fig. 4.** Experimental angular variation of the resonance lines (dots or triangles) with the best fitted curves (full line: black for center 1 and red for center 2) for rotations around Z (top), Y (middle) and X (bottom). (For interpretation of the references in color in this figure legend, the reader is referred to the web version of this article.)

agreement is very satisfactory for rotations around *X* and *Y* but less satisfactory for rotations around *Z*. This might be due to the single crystal misalignment in the magnetic field but also to the fact that two signals are contained in one single resonance line. The principal axes orientation are easily computed in unit cell frame by a rotation of 37.072° around *Z* for the resonance lines R1 (RX1, RY1, RZ) and R2 (RX2, RY2, RZ). The principal *g*-values and the cosine directors in the unit cell frame for the two resonance lines are given in Table 4 for this combination.

Then, these diagonal *g*-tensors must be confronted to the crystal structure. It is important to realize that the two tensors are almost collinear to the *b* crystallographic axis. The principal direction corresponding to the smallest *g* value ( $g_x \sim 1.99$ ) coincides with *b*. In Fig. 5, the four molecules in the unit cell are labeled Fe (the asymmetric unit), Fe<sup>i</sup>, Fe<sup>ii</sup> and Fe<sup>iii</sup>. In looking at the crystal structure from *b* axis, one may remark a peculiar feature: C<sub>5</sub>Me<sub>5</sub> rings are almost parallel to *b* which means that the Fe–C<sub>5</sub>Me<sub>5</sub> directions are

<sup>&</sup>lt;sup>6</sup> Since the molecules at the origin of these different signals are symmetry related, an unique set of solutions should be found for the diagonal components of the *g*-tensor in the molecular frame, regardless of the signal initially used.

### 294

#### Table 4

Principal g-values and cosine directors for the two resonance lines R1 and R2 in the unit cell frame for combination A.

R1		R2	
g <sub>x</sub> = 1.997	-0.0245	g <sub>x</sub> = 1.989	-0.15012
	0.99947		-0.96130
	0.02131		-0.23100
$g_y = 2.053$	0.84352	$g_y = 2.047$	-0.81822
	0.03206		0.25195
	-0.5361		-0.51675
$g_z = 2.427$	0.53654	$g_z = 2.456$	-0.55496
	-0.00486		-0.11143
	0.84386		0.82438



**Fig. 5.** View of the unit cell of compound **5**[PF<sub>6</sub>]. Carbon atoms are in grey, sulfur atoms in yellow, nitrogen atoms in green, phosphorous atoms in pink and iron atoms in brown. The arrows represent the orientation of *g*-tensor components  $g_x$ ,  $g_y$  and  $g_z$  for the  $\alpha$  solution. (For interpretation of the references in color in this figure legend, the reader is referred to the web version of this article.)

almost perpendicular to b (86.344(3)°) and are contained in the *ac* plane. Furthermore, the nitrogen atom is out of the ac plane of only 21° which means that the molecule generated by the 2<sub>1</sub> axis along *b* (Fe<sup>iii</sup>) is very similar to the molecule of the asymmetric unit (Fe). As a consequence, these two molecules have similar ESR signatures (*i.e.* they belong to the same resonance lines and have the same gtensor). Similar considerations apply to molecules Fe<sup>i</sup> and Fe<sup>ii</sup>. Therefore, there are two ways of positioning the g-tensors on a given molecule (solution  $\alpha$ : Fe, Fe<sup>*iii*</sup> with R1 and Fe<sup>*i*</sup>, Fe<sup>*ii*</sup> with R2, or solution  $\beta$ : Fe, Fe<sup>iii</sup> with R2 and Fe<sup>i</sup>, Fe<sup>ii</sup> with R1). The first solution ( $\alpha$ ) is given in Fig. 5 while the second solution ( $\beta$ ) is given in Supporting information (Fig. S10). The most important features of the two distributions of g-tensors are the characteristic angles between  $g_{z}$  and the C<sub>5</sub>Me<sub>5</sub> rings. While in the second distribution the angle between  $g_z$  and Fe–C<sub>5</sub>Me<sub>5</sub> directions are comprised between  $68.3^{\circ}$  and  $73.4^{\circ}$ , they are comprised between  $5.6^{\circ}$  and 10.3° in the first distribution. From a strictly experimental point of view, one cannot discriminate between the two solutions, but the DFT modelization of these Fe(III) compounds, as shown hereafter, allowed us to retain the  $\alpha$  set as the correct one (Fig. 5).

# 2.5. DFT computations on **5**, $5^+$ , **6** and $6^+$

These compounds were then studied by DFT both using the solid state geometries (Figs. 1a and b and 2a and b) and optimized geometries, which can be considered as being closer to the molecular arrangement in solution. After optimization, the resulting structures show comparable bond lengths and angles (Supporting Information) than the experimental X-ray structures (Figs. 1 and 2), except for the N<sub>3</sub> fragment in **6**[PF<sub>6</sub>] for which the N1–N2 is much shorter than computed. In regard to the good match found experimentally for the other angles and distances and also for the compounds, this peculiar result suggests that the very short N1–N2 bond has not an intramolecular origin.<sup>5</sup>

Regarding the Fe(II) compounds, the HOMOs of the compounds result from the anti-bonding interaction of the " $t_{2g}$ " set of metallic orbitals of the Fe( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)( $\eta^2$ -dppe) fragment with the  $\pi$ -orbitals of the NCS or N<sub>3</sub> ligands, while the LUMO and LUMO+2 correspond to empty metal-based MO with a strong d<sub>xy</sub> and d<sub>z2</sub> character and belonging to the " $e_g^*$ " set of frontier orbital in an octahedral ML<sub>6</sub> d<sup>6</sup> metal complex (Fig. 6).

Energies of the frontier molecular spin–orbitals (SOs) for **5**<sup>+</sup> and **6**<sup>+</sup> complexes are shown in Fig. 7. The lowest unoccupied spin orbital or LUSO( $\beta$ ) has, in each case, a strong metallic d<sub>xz</sub> metallic character which also presents a non-negligible  $\pi$  character on the remote atom of the cumulenic ligand (S for **5**<sup>+</sup> and N for **6**<sup>+</sup>). The LUSO( $\alpha$ ), LUSO+1( $\alpha$ ) and the corresponding LUSO+1( $\beta$ ) and LU-SO+2( $\beta$ ) are also strongly metallic in character.

Upon oxidation, an electron is formally removed from the HOMO of the Fe(II) parents followed by an electronic and geometrical relaxation. The resulting ionization potentials are calculated to be 5.63 and 4.99 eV for 5 and 6, respectively. These values qualitatively follow the ordering of the redox potentials experimentally found for 5 and 6 (Table 1) and confirm that 6 is easier to oxidize than 5. The computed atomic spin densities are given in Table 5. Very close spin distributions are found for the two Fe(III) complexes (Fig. 8). The ESR g-tensors were also calculated (Fig. 8) and the diagonal g-values computed for solid state structures and for the optimized geometries are given in Table 2, together with the measured values obtained in the solvent glass. The influence of the nature of the R ligand ( $R = NCS, N_3$ ) on the g-tensors values is very well reproduced. The  $g_{iso}$  values are in each case slightly smaller than the experimental measurements and the anisotropy is also slightly underestimated, but overall, the match can be considered as good. These small theoretical deviations are attributed to the lack of the solvent and of the counter-ions contribution in the calculations. Also, the spatial orientation of the three diagonal values of the g-tensor predicted by DFT for **5**<sup>+</sup> seem to match much better with one of the two potential solutions experimentally found for the diagonal g-values of **5**[PF<sub>6</sub>] (solution  $\alpha$ ). Indeed, deviations of 30° and 70° were, respectively, found for the orientation of the computed principal g-component (g<sub>3</sub>) compared to the experimental orientations found for it  $(g_z)$  in solutions  $\alpha$  and  $\beta$ .

### 3. Discussion

The new Fe(II)/Fe(III) complexes **5** and **6** were fully characterized by usual spectroscopic means. Overall, they exhibit classic spectral signatures for Fe(II) piano-stool complexes and DFT calculations reveal electronic properties recalling these of their halide precursor **1** [35]. In order to gain additional insight into their electronic structures, we will first discuss the valence bond (VB) representation of these compounds. In that connection, the various VB mesomers of the free thiocyanato and azido ligand are given in Schemes 5 and 6, respectively. It is important to realize that on purely electronic grounds, the cumulenic VB forms I and I' of these ligands will have a strong tendency to coordinate Lewis-acidic metal centers in a "bent" form due to the sp<sup>2</sup> hybridization of the terminal atoms, while all other VB forms will coordinate in an end-on fashion, due to the sp hybridization of the terminal atoms.



**Fig. 6.** Energy diagram of the molecular frontier orbitals of the optimized systems **5** and **6** in their optimized geometry. The MO percentage of metallic, thiocyanato and azido character is indicated in parentheses. The two highest occupied MOs are plotted (iso-contour ± 0.045 [e/bohr<sup>3</sup>]<sup>16</sup>).



**Fig. 7.** Energy diagram of the frontier spin–orbitals of the optimized systems  $\mathbf{5}^*$  and  $\mathbf{6}^*$  in their optimized geometry. The spin–orbital (SO) percentage of metallic, thiocyanato and azido character are indicated in parentheses. The highest occupied SOs are plotted (iso-contour values:  $\pm 0.045$  [e/bohr<sup>3</sup>]<sup>1/2</sup>).

# 3.1. Valence bond description of the thiocyanato Fe(II) and Fe(III) complexes

As for the cyclopentadienyl analog of that complex (Table 1; **7**<sub>0</sub>[PF<sub>6</sub>]) reported by Treichel et al. in 1979 [14], the thiocyanato Fe(II) complex corresponds to the *N*-bonded isomer both in solution and in the solid state [52,53]. The quite energetic  $v_{NCS}$  mode of the complex **5** might be attributed to the dominant weight

of a VB mesomer such as A. The latter also corresponds to a strong sp-character of the bound nitrogen, in line with the (quasi-linear) end-on binding of this ligand. This VB structure is certainly somewhat stabilized by the strong  $\pi$ -donating character of the Fe( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)( $\eta^2$ -dppe) metal fragment, illustrated by the VB structure B, which possibly contributes to shorten the Fe–N bond of this complex. The weight of such a structure in the VB description nicely explains the more positive oxidation potential found for **5** rel-

# 296

### Table 5

Computed spin densities (e) on selected fragments or atoms for the  $[Fe(\eta^5-C_5Me_5)(\eta^2-dppe)(X)]^*$  (X = NCS, NNN and C=C[4-C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>]) complexes (See Scheme 3 for atom labeling).

Cpnd	Fe	C atoms of C <sub>5</sub> Me <sub>5</sub>	P atoms of dppe <sup>a</sup>	X = ABC			Refs.
				A	В	С	
<b>5</b> <sup>+</sup>	0.867	-0.011	-0.021	0.035	-0.004	0.191	This work
5 <sup>+b</sup>	0.869	-0.022	-0.020	0.028	-0.008	0.189	This work
<b>6</b> <sup>+</sup>	0.899	-0.012	-0.021	0.060	-0.014	0.148	This work
<b>6</b> <sup>+ b</sup>	0.854	-0.010	-0.019	0.032	-0.027	0.214	This work
<b>7</b> -NO <sub>2</sub> <sup>+c</sup>	0.890	-0.030	-0.010	$-0.089^{d}$	0.238 <sup>e</sup>	0.034 <sup>f</sup>	[44]

<sup>a</sup> Values below -0.002 e were found on the carbon atoms of the CH<sub>2</sub> groups of dppe.

<sup>b</sup> Data for non-optimized solid state structure.

<sup>c</sup> Mean values between those computed for conformations with parallel and the perpendicular orientations of the nitrophenyl ring [44].

 $^{d}\,$  Spin density on  $C_{\alpha}.$ 

<sup>e</sup> Spin density on  $C_{\beta}$ .

<sup>f</sup> Sum for the whole 4-nitrophenyl fragment.



**Fig. 8.** Plots of the total spin densities and of the spatial orientation of the three computed diagonal values of the *g*-tensor for  $[Fe(\eta^5-C_5Me_5)(\eta^2-dppe)(X)]^+$  (X = NCS, N<sub>3</sub>) complexes **5**<sup>+</sup> (a) and **6**<sup>+</sup> (b) (isocontour value: ± 0.005 [e/bohr<sup>3</sup>]).



**Scheme 5.** VB representation of the free thiocyanato ligand (inset) and of its complexes  $5^{n+}$  in their two stable redox states (n = 0, 1).

ative to **6** or in comparison to alkynyl complexes such as **8-H** (0.15 V versus SCE) [49], featuring more  $\pi$ -donating ligands than NCS. The participation of a bent VB mesomer such as C is also required considering the non-strictly linear coordination geometry adopted by the thiocyanate ligand in **5** (Fig. 1a). Based on the structural data, it is clear that the conformation presently adopted by the NCS ligand minimizes any intramolecular interaction with the cyclopentadienyl methyl groups and the dppe phenyl groups.

The decreased  $v_{NCS}$  upon oxidation might be attributed to a decreasing weight of the VB mesomer D and to the increasing weight of a VB mesomer such as E or F (and perhaps also G); the latter VB forms contributing to diminish the N–C bond while reinforcing the Fe–N bond strength. The existence of the VB mesomer E is also supported by the sizeable spin density (0.191 *e*) found on the terminal sulfur atom in **5**[PF<sub>6</sub>] in the DFT computations (Table 5). As observed on X-ray data and in the DFT calculations,



**Scheme 6.** VB representation of the free azido ligand (inset) and of its complexes  $6^{n+}$  in their two stable redox states (n = 0, 1).

oxidation leads to a shortening of the Fe–N bond, to a concomitant lengthening of the N–C bond and perhaps to a slight bending of the ligand (due to VB forms F and G). The slight modification of the bending angle (reflecting the terminal nitrogen hybridization) might be further understood considering the existence of destabilizing intramolecular steric effects between the sulfur atom and the other ligands, resulting in a small weight for structures F and G in the VB description.

### 3.2. Valence bond description of the azido Fe(II) and Fe(III) complexes

In the Fe(II) derivative (**6**), likewise to **5**, a slight strengthening of the high energy stretching mode of the azido ligand is stated upon coordination<sup>2</sup>, suggesting an increase of its sp-character upon complexation. However, based on the Fe1–N1–N2 angle close to the ideal value of 120° for a sp<sup>2</sup> hybridization and on the Fe–N bond length typical of a single bond, the bonding in the Fe(II) complex **6** must essentially be described by one VB mesomer such as A' (Scheme 6). Also suggestive of the dominance of a VB form such as A' is the shift towards more negative values of the metal-centered Fe(III)/Fe(II) oxidation potential observed for **6** relative to **5**, which results from the larger  $\pi$ -donating character of the azido ligand relative to the thiocyanato ligand.

As for **5**, chemical oxidation of **6** produces an isolable low spin  $(S = \frac{1}{2})$  Fe(III) radical cation [14,46,54]. No noticeable change in the sp-hybridization is indicated by X-rays for **6**<sup>+</sup>, suggesting that the weight of a mesomer such as D' remains low in the VB description. Again, the decrease stated for the N<sub>3</sub> asymmetric stretch upon oxidation can be attributed to the presence of VB mesomers such as E' or F' which contribute to diminish the N–N bonding, while reinforcing the Fe–N bond. Support for the existence of a VB mesomer such as F' can be found in DFT computations by the sizeable spin density evidenced on the terminal nitrogen atom (0.148 *e*) in **6**<sup>+</sup> (Table 5, Fig. 7).

# 3.3. Comparison of the ligand bonding in the thiocyanato and azido complexes

In line with established trends for these *N*-coordinated pseudohalides [33,52], the main difference between the thiocyanato and the azido ligands is the tendency of the former to coordinate in a linear (end-on) fashion, whereas the second prefers a bent coordination geometry. These different behaviors can be traced

back to the different atoms constituting these ligands, resulting in different hybridizations of the metal-bound nitrogen atom, as rationalized by the VB structures given in Schemes 5 and 6. In this respect, the thiocyanato complex is structurally closer to alkynyl complexes such as  $\mathbf{8}$ - $\mathbf{X}^{n+}$  (n = 0, 1). In spite of their different geometry, DFT calculations reveal no marked differences between **5** and **6** regarding the metal versus ligand composition of the frontier molecular orbitals (FMOs), nor in the energy ordering of these FMOs, and that, even after oxidation. Actually, these features recall these of classic arylalkynyl complexes, such as  $\mathbf{8}$ - $\mathbf{X}^{n+}$  (n = 0, 1). However, a clear difference between  $\mathbf{5}^{n+}$ ,  $\mathbf{6}^{n+}$  and the latter compounds resides in the nodal properties of the ligand-based FMOs which translates into different spin distributions on the ligand for  $\mathbf{5}$ [PF6] or **6**[PF6] relative to  $\mathbf{8}$ - $\mathbf{X}$ [PF6], as we will briefly see below.

### 3.4. Spin distribution and magnetic anisotropy of Fe(III) complexes

The Fe(III) complexes  $5[PF_6]$  and  $6[PF_6]$  possess fairly similar spin distributions (Table 4). Most of the spin density is located on the metal center, but a sizeable spin density is also present on their terminal S  $(5^+)$  or N  $(6^+)$  atom, in line with the unsaturated nature of the ligand. This is an important piece of data since, when used as metallo-ligands, they might be able to magnetically couple with any paramagnetic metal ion coordinated to their end. More precisely, in terms of spin delocalization, DFT computations suggest that the total spin density on the cumulenic ligand compares with that present on functional 4-arylalkynyl Fe(III) complexes possessing strongly electron-withdrawing substituents, such as **8-NO<sub>2</sub>**[PF<sub>6</sub>] (Table 5) [44] or **2**[PF<sub>6</sub>] [1]. However, the spin is now preferentially delocalized on the  $\gamma$ -atom of the ligand relative to the metal center in  $5[PF_6]$  and  $6[PF_6]$ , whereas the  $\beta$ -atom was favored in the case of arylalkynyl Fe(III) complexes. This difference can be ascribed to the different nature of the highest occupied FMOs of the thiocyanato and azido ligands. The latter are essentially non-bonding and present a node on the central atom. This induces a partial delocalization of (positive) spin density on the terminal rather than on the central atom in the SOMO of 5<sup>+</sup> and **6**<sup>+</sup>. Also, DFT calculations indicate that the larger anisotropy ( $\Delta g$ ) experimentally stated by ESR in solvent glasses for 5<sup>+</sup> relative to  $6^+$  (Table 2) does not correlate with a larger spin density on the metal center in computed structures, [42] calling for caution when  $\Delta g$ is used to estimate the spin density present on metal centers [1,55].

Finally, for the first time among all the  $[Fe(\eta^5-C_5Me_5)(\eta^2$ dppe)(X)]<sup>+</sup> radical cations studied so far, the diagonal g-tensor components were experimentally determined by ESR using a single crystal of 5[PF<sub>6</sub>]. This study, consistently with DFT modeling, reveals that the orientation of the main diagonal component of the anisotropy tensor is along the cyclopentadienyl direction, not along the cumulenic ligand direction, in contrast to what was previously proposed for 8-X<sup>+</sup> cations, based on a perturbative approach coupled with a classic ligand-field approach. This change in anisotropy is likely at the origin of the slightly different shifts presently observed for several cyclopentadienyl and methylene protons of 5[PF<sub>6</sub>] and 6[PF<sub>6</sub>] (Fig. 3), since it should significantly modify the pseudo-contact contribution to these shifts  $[44]^7$ . In line with such an hypothesis, DFT data reveal that only slight changes take place in the spin-distribution centered on these fragments, suggesting that the contact contribution to the <sup>1</sup>H NMR shifts should not be significantly modified when proceeding from  $8-X^+$  to 5<sup>+</sup> to 6<sup>+</sup>. This shows that <sup>1</sup>H NMR can also be used in a straightforward way to evidence a change in the orientation of the magnetic anisotropy for such Fe(III) complexes. Another marked difference with related arylalkynyl cations showing a comparable spin density present on the metal center such as  $8-NO_2[PF_6]$  or  $2[PF_6]$  [1], is that both **5**[PF<sub>6</sub>] and **6**[PF<sub>6</sub>] exhibit significantly broadened <sup>1</sup>H NMR signals (Fig. 3). This broadening, particularly striking in the case of **6**[PF<sub>6</sub>], is ascribable to a faster relaxation of the spin of these protons which might originate (i) from a larger spin density present on the metal center, rendering the contact relaxation more efficient for nuclei close to the metal center, or (ii), from a slower relaxation of the unpaired electron, resulting in an increase in the dipolar correlation time [44]. Based on our DFT calculations and ESR studies at 293 K, the second hypothesis is retained as the major cause of the observed broadening compared to the **8-X**<sup>+</sup> cations.

### 4. Conclusion

The new thiocyanato- (5) and azido- (6) complexes were isolated and studied under their Fe(II) and Fe(III) oxidation states. Their electronic structures were also modelized in both redox states by DFT. Moreover, for the first time among the various  $[Fe(\eta^5-C_5Me_5)(\eta^2-dppe)]$ -based cationic radicals studied so far, the g-tensor diagonal values of 5[PF<sub>6</sub>] were experimentally determined. The changes undergone by the Fe(II) complexes subsequent to oxidation are reminiscent of these previously observed for other piano-stool derivatives, such as 1 or 8-X, albeit some notable differences in the electronic properties of the resulting Fe(III) radical cations can be pointed out for 5[PF<sub>6</sub>] and 6[PF<sub>6</sub>]. For instance, a slower electronic spin relaxation and a differently oriented magnetic anisotropy was evidenced in comparison to their carbon-rich analogues such as **2**[PF<sub>6</sub>], which results in diagnostic changes in the <sup>1</sup>H NMR spectra of these Fe(III) compounds. The ESR-anisotropy of  $5[PF_6]$  and  $6[PF_6]$  is thus not simply related to changes in the spin density present on the metal center, in contrast to observations previously made with  $8-X[PF_6]$  derivatives. The precise origin of the factors affecting the electronic relaxation and determining the anisotropy of these Fe(III) piano-stool complexes remain unclear and will make the object of future investigations. Remarkably, in spite of the larger electronegativity and decreased  $\pi$ -donating ability of the NCS and N<sub>3</sub> ligands relative to functional 4-phenylalkynyl ligands, DFT computations reveal that a significant amount of spin density is delocalized on the terminal atom of the cumulenic ligand in these Fe(III) complexes. This property makes **5**[PF<sub>6</sub>] and **6**[PF<sub>6</sub>] much more appealing than longer derivatives such as **2–4**[PF<sub>6</sub>] for using them as paramagnetic metallo-ligands, since they might sustain a sizeable magnetic interaction between their terminal low-spin Fe(III) center and any appended paramagnetic ion coordinated to them. Thus, from the perspective of spintronics, **5**[PF<sub>6</sub>] and **6**[PF<sub>6</sub>] certainly constitute attractive organometallic building blocks for obtaining larger paramagnetic assemblies, based on coordination reactions.

### 5. Experimental

### 5.1. General data

All manipulations were carried out under inert atmospheres. Solvents or reagents were used as follows: Et<sub>2</sub>O and *n*-pentane, distilled from Na/benzophenone; CH<sub>2</sub>Cl<sub>2</sub>, distilled from CaH<sub>2</sub> and purged with argon; HN(*i*Pr)<sub>2</sub>, distilled from KOH and purged with argon. The  $[Fe(\eta^5-C_5H_5)_2][PF_6]$  ferricinium salt was prepared by previously published procedures [57]. Transmittance-FTIR spectra were recorded using a Bruker IFS28 spectrometer (400-4000 cm<sup>-1</sup>). Raman spectra of the solid samples were obtained by diffuse scattering on the same apparatus and recorded in the  $100-3300 \text{ cm}^{-1}$  range (Stokes emission) with a laser excitation source at 1064 nm (25 mW) and a quartz separator with a FRA 106 detector. Near-infrared (NIR) spectra in solution were recorded a Cary 5000 spectrometer or a JASCO V-570 spectrometer (4000-12500 cm<sup>-1</sup>). UV-Vis spectra were recorded on a Cary 5000 or an UVIKON 942 spectrometer (250-1000 nm). SQUID measurements were performed on a MPMS-XL Quantum Design apparatus with crushed crystalline samples of the compounds [58]. NMR experiments were made on a Bruker AVANCE 500 operating at 500.15 MHz for <sup>1</sup>H, 125.769 MHz for <sup>13</sup>C and 201.877 MHz for <sup>31</sup>P, with a 5 mm broadband observe probe equipped with a z-gradient coil at the PRISM platform. ESR spectra were recorded on a Bruker EMX-8/2.7 (X-band) spectrometer equipped with an OX-FORD cryostat and a goniometer. Cyclic voltammograms were recorded using a EG&G potentiostat (M.263) on platinum electrodes referenced toward an SCE electrode and were calibrated with the Fc/Fc<sup>+</sup> couple taken at 0.46 V in  $CH_2Cl_2$  [57]. MS analyses were performed at the "Centre Regional de Mesures Physiques de l'Ouest" (CRMPO, University of Rennes) on a high resolution MS/ MS ZABSpec TOF Micromass Spectrometer. Elemental analyses were performed at the CRMPO or at the Centre for Microanalyses of the CNRS at Lyon-Solaise, France. The chloro complex 1 was obtained as previously reported [34].

### 5.2. Synthesis

### 5.2.1. $Fe(\eta^5 - C_5 Me_5)(\eta^2 - dppe)(NCS)$ (**5**)

Fe( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)( $\eta^2$ -dppe)Cl (1, 0.503 g, 0.80 mmol), KPF<sub>6</sub> (0.163 g, 0.88 mmol) and KSCN (0.085 g, 0.88 mmol) were suspended in 40 mL of methanol and the mixture was stirred for 12 h at 25 °C to give a violet suspension. After concentration to 10 mL and decantation, the solid that formed was filtrated, washed with methanol (5 mL) and extracted with 3 × 10 mL of hot toluene. After filtration and evaporation of the extract and washing by several (2 × 2 mL) *n*-pentane fractions, the desired Fe( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)( $\eta^2$ -dppe)(NCS) complex (**5**) was isolated as a light violet solid (0.410 g, 0.63 mmol, 79%). X-ray quality crystals of **5** were grown by vapor diffusion of *n*-pentane in a dichloromethane solution of the complex.

*Anal.* Calc. for  $C_{37}H_{39}NP_2SFe: C, 68.63; H, 6.07; N, 2.16. Found: C, 68.68; H, 6.14; N, 2.08%. MS (positive ESI, CH<sub>2</sub>Cl<sub>2</sub>):$ *m/z*647.1622 [M]<sup>+</sup>,*m/z* $calc for <math>[C_{37}H_{39}NP_2SFe]^+$  = 647.1628. FT-IR (*v*, KBr, cm<sup>-1</sup>): 2099 (vs, SCN), 808 (s, SCN). Raman (neat, *v*, cm<sup>-1</sup>): 2101

<sup>&</sup>lt;sup>7</sup> An exact computation of these changes for nuclei lying close to a metal center exhibiting rhombic anisotropy is very involved and lies outside of the scope of this paper [56].

(s, SCN), 811 (m, SCN). <sup>31</sup>P NMR ( $\delta$ , C<sub>6</sub>D<sub>6</sub>, 81 MHz): 93.9 (s, dppe). <sup>1</sup>H NMR ( $\delta$ , C<sub>6</sub>D<sub>6</sub>, 200 MHz): 7.78 (m, 4H, H<sub>Ar</sub>); 7.36 (m, 4H, H<sub>Ar</sub>); 7.20–6.90 (m, 12H, H<sub>Ar</sub>); 1.99 (m, 2H, CH<sub>2/dppe</sub>): 1.62 (m, 2H, CH<sub>2/</sub> dppe): 1.28 (s, 15H, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR ( $\delta$ , CH<sub>2</sub>Cl<sub>2</sub>, 50 MHz): 144.2 (s, FeSCN); 136.6–134.0 (m, C<sub>*i*,*i*/Ar/dppe</sub>); 134.2; 133.8, 130.1, 129.8, 128.3, 128.0 (s, CH<sub>Ar/dppe</sub>); 86.0 (s, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>); 29.2 (m, CH<sub>2</sub>/ dppe): 9.6 (s, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>). C.V. (CH<sub>2</sub>Cl<sub>2</sub>, 0.1 M [*n*-Bu<sub>4</sub>N][PF<sub>6</sub>], 20 °C, 0.1 V s<sup>-1</sup>)  $E^{\circ}$  in V versus SCE ( $\Delta$ Ep in V, *i*<sub>pa</sub>/*i*<sub>pc</sub>) 0.04 (0.08, 1.0).

# 5.2.2. $[Fe(\eta^5 - C_5 Me_5)(\eta^2 - dppe)(NCS)][PF_6]$ (**5** $[PF_6]$ )

0.95 equiv. of  $[Fe(\eta^5-C_5H_5)_2][PF_6]$  (0.097 g; 0.293 mmol) was added to a solution of **5** (0.200 g; 0.309 mmol) in 25 mL of dichloromethane resulting in an instantaneous darkening of the purple solution. Stirring was maintained 1 h at 25 °C and the solution was concentrated *in vacuo* to approximately 5 mL. Addition of 50 mL of *n*-pentane allowed precipitation of a purple solid. Decantation and subsequent washings with toluene (2 × 2 mL) followed by diethylether (2 × 2 mL) and drying under vacuum yielded the desired [Fe( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)( $\eta^2$ -dppe)(NCS)][PF<sub>6</sub>] (**5**[PF<sub>6</sub>]) complex as violet solid (0.200 g; 0.252 mmol; 86%). Crystals of **5**[PF<sub>6</sub>] were obtained by vapor diffusion of *n*-pentane into a solution of the complex in dichloromethane.

Anal. Calc. for  $C_{37}H_{39}N_1F_6P_3S_1Fe: C, 56.07; H, 4.96; N, 1.77.$ Found: C, 55.58; H, 4.88; N, 1.70%. FT-IR ( $\nu$ , KBr, cm<sup>-1</sup>): 2036 (vs, SCN), 840 (vs, PF<sub>6</sub>). <sup>1</sup>H NMR ( $\delta$ , CD<sub>2</sub>Cl<sub>2</sub>, 500 MHz): 8.4 (very broad s,  $CH_{2/dppe}$ ); 7.9, 4.0, 2.5 (s,  $H_{Ar}$ ); 7.3, 5.7, 4.3 (s,  $H_{Ar}$ ); -3.2 (broad s,  $CH_{2/dppe}$ ); -21.5 (very broad s,  $C_5(CH_3)_5$ ); one set of  $CH_{2/dppe}$  and one set of  $H_{Ar}$  not detected. <sup>13</sup>C{<sup>1</sup>H} NMR ( $\delta$ , CD<sub>2</sub>Cl<sub>2</sub>, 500 MHz): 257.5 ( $C_5(CH_3)_5$ ); 152.3, 137.5, 136.1, 124.4, 121.9, 100.3 ( $C_{Ar/dppe}$ ); 22.5 ( $C_5(CH_3)_5$ ); -120 ( $C_{Ar/dppe}$  or FeNCS); -197.5 ( $CH_{2/dppe}$ ); 2 signals not detected.

# 5.2.3. $Fe(\eta^5-C_5Me_5)(\eta^2-dppe)(N_3)$ (**6**)

Fe( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)( $\eta^2$ -dppe)(Cl) (**1**, 0.630 g, 1.01 mmol), KPF<sub>6</sub> (0.200 g, 1.08 mmol) and NaN<sub>3</sub> (0.070 g, 1.08 mmol) were suspended in 50 mL of methanol and the mixture was stirred for 12 h at 25 °C to give a dark suspension. After evaporation of the methanol, the solid that deposited was extracted with 3 × 10 mL of toluene to give a greenish solution. After filtration and evaporation of the extract and washing by several *n*-pentane (3 × 5 mL) and diethylether (2 × 5 mL) fractions, the desired Fe( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)( $\eta^2$ -dppe)(N<sub>3</sub>) complex (**6**) was isolated as a dark green solid (0.480 g, 0.760 mmol, 75%). X-ray quality crystals of **6** were grown by vapor diffusion of *n*-pentane in a dichloromethane solution of the complex.

Anal. Calc. for C<sub>36</sub>H<sub>39</sub>N<sub>3</sub>P<sub>2</sub>Fe: C, 68.47; H, 6.22; N, 6.65. Found: C, 68.39; H, 6.07; N, 6.41%. MS (positive ESI, CH<sub>2</sub>Cl<sub>2</sub>): m/z 631.1969 [M]<sup>+</sup>, m/z calc for [C<sub>36</sub>H<sub>39</sub>N<sub>3</sub>P<sub>2</sub>Fe]<sup>+</sup> = 631.1969. FT-IR (v, KBr, cm<sup>-1</sup>); 2049 (vs, N<sub>3</sub>). Raman (neat, v, cm<sup>-1</sup>):  $v_{N3}$  not observed (fluorescence). <sup>31</sup>P NMR ( $\delta$ , C<sub>6</sub>D<sub>6</sub>, 81 MHz): 94.6 (s, dppe). <sup>1</sup>H NMR ( $\delta$ , C<sub>6</sub>D<sub>6</sub>, 200 MHz): 7.85 (m, 4H, H<sub>Ar</sub>); 7.35–7.00 (m, 16H, H<sub>Ar</sub>); 2.05 (m, 2H, CH<sub>2/dppe</sub>); 1.70 (m, 2H, CH<sub>2/dppe</sub>); 1.38 (s, 15 H, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR ( $\delta$ , CH<sub>2</sub>Cl<sub>2</sub>, 50 MHz): 137.6–134.0 (m, C<sub>*i*,*i*/</sub>/A<sub>r/dppe</sub>); 134.2, 133.8, 129.8, 129.6, 128.3, 128.0 (s, CH<sub>Ar/dppe</sub>); 84.2 (s, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>); 29.0 (m, CH<sub>2/dppe</sub>); 9.7 (s, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>). C.V. (CH<sub>2</sub>Cl<sub>2</sub>, 0.1 M [*n*-Bu<sub>4</sub>N][PF<sub>6</sub>], 20 °C, 0.1 V.s<sup>-1</sup>) *E*° in *V* versus SCE (ΔEp in V, *i*<sub>pa</sub>/*i*<sub>pc</sub>): –0.24 (0.08, 1.0).

# 5.2.4. $[Fe(\eta^5 - C_5 Me_5)(\eta^2 - dppe)(N_3)][PF_6]$ (**6** $[PF_6]$ )

 $[Fe(\eta^5-C_5H_5)_2][PF_6]$  (56 mg, 0.168 mmol) was added to a solution of  $Fe(\eta^5-C_5Me_5)(\eta^2-dppe)(N_3)$  (110 mg, 0.175 mmol) in 30 mL dichloromethane. Stirring was maintained for 2 h at 25° C, and the solution was concentrated in vacuo to *ca*. 1 mL. Addition of *n*-pentane afforded the precipitation of **6**[PF<sub>6</sub>], which could be isolated as a brown solid (105 mg, 0.135 mmol, 77%), after subsequent washings with toluene (2 × 2 mL) followed by *n*-pentane

 $(3 \times 5 \text{ mL})$ . Crystals of **6**[PF<sub>6</sub>] were obtained by slow diffusion of *n*-pentane into a solution of the complex in dichloromethane.

FT-IR (ν, KBr, cm<sup>-1</sup>): 2031 (vs, N<sub>3</sub>), 1310 (m, N<sub>3</sub>), 840 (vs, PF<sub>6</sub>). <sup>1</sup>H NMR ( $\delta$ , CD<sub>2</sub>Cl<sub>2</sub>, 500 MHz): 8.0, 7.7, 4.6, 7.4, 6.5 (s, H<sub>Ar</sub>); 1.5 (very broad s, H<sub>Ar</sub>); -8.0 (very broad s, CH<sub>2/dppe</sub>); -20.7 (very broad s, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>); one set of CH<sub>2/dppe</sub> and one set of H<sub>Ar</sub> not detected. <sup>13</sup>C{<sup>1</sup>H} NMR ( $\delta$ , CD<sub>2</sub>Cl<sub>2</sub>, 500 MHz): 145.2, 139.2, 132.1, 123.8, 105.6 (C<sub>Ar/dppe</sub>); 22.1 (C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>); 5 signals not detected.

### 5.3. Solution/solvent-glass ESR measurements

The Fe(III) complexes (1–2 mg) were introduced in a ESR tube under an argon-filled atmosphere and a 1:1 mixture of degassed dichloromethane/1,2-dichloroethane was transferred to dissolve the solid. For solvent glass measurements at 77 K, the solvent mixture was frozen in liquid nitrogen and the tubes were sealed and transferred in the ESR cavity. The spectra were immediately recorded at that temperature and the sample was allowed to come back to room temperature and solution measurements were performed.

### 5.4. Solid-state ESR measurements

A single crystal of **5**[PF<sub>6</sub>] was mounted at room temperature on a Nonius four circle diffractometer equipped with a CCD camera and a graphite monochromated Mo K $\alpha$  radiation source ( $\lambda = 0.71073$  Å), from the Centre de Diffractométrie (CDIFX, Université de Rennes 1, France). The unit cell and the orientation of the crystallographic axes with respect to the crystal shape were then determined. The single crystal was subsequently transferred on the goniometer head for ESR measurements.

### 5.5. Crystallography

Crystals of **5**, **6**, **5**[PF<sub>6</sub>] and **6**[PF<sub>6</sub>] were studied on a Oxford Diffraction Xcalibur Saphir 3 with graphite monochromatized Mo Kα radiation at low temperature (Table 6). The cell parameters were obtained with Denzo and Scalepack with 10 frames (psi rotation: 1° per frames) [59]. Details about the data collection [60] (Ω rotation and HKL range) are given in Table 6. The structures were solved with siR-97 which revealed the non-hydrogen atoms [61]. After anisotropic refinement, the remaining atoms were found by Fourier difference maps. The complete structures were then refined with shelxL97 [62] by the full-matrix least-square technique. Atomic scattering factors were taken from the literature [63]. OR-TEP views of **5**, **6**, **5**[PF<sub>6</sub>] and **6**[PF<sub>6</sub>] were realized with PLATON98 [64].

### 5.6. Computational details

Density functional theory (DFT) calculations were performed with the Amsterdam Density functional (ADF) program [65–67]. All geometries were optimized without any symmetry constraint and were successfully validated by vibrational frequency calculations. Electron correlation was treated within the local density approximation (LDA) in the Vosko-Wilk-Nusair parametrization [68]. The non-local correction of Adamo-Barone [69] and of Perdew-Burke-Ernzerhof [70] were added to the correlation and exchange energies, respectively. The numerical integration procedure applied for the calculations was that developed by te Velde et al. [71]. The basis set used for the metal atom was a triple- $\zeta$  slater-type orbital (STO) basis for Fe 3p, 3d and 4s, with a single- $\zeta$  4p polarization function. A triple-ζ STO basis set was used for 1s of H, 2s and 2p of C and N, 3s and 3p of S and P augmented with a 3d single- $\zeta$  polarization function for C, N, P and S atoms and with a 2p single-ζ polarization function for H atoms. A frozen-core

#### Table 6

Crystal data, data collection, and refinement parameters for **5**, **5**[PF<sub>6</sub>], **6** and **6**[PF<sub>6</sub>].

Cpnd	5	<b>5</b> [PF <sub>6</sub> ]	6	<b>6</b> [PF <sub>6</sub> ]
Formula	C37H39N1P2 S1Fe	C37H39N1P2S1Fe, PF6	$C_{36}H_{39}N_3P_2Fe_1$	C <sub>36</sub> H <sub>39</sub> N <sub>3</sub> P <sub>2</sub> Fe <sub>1</sub> , PF <sub>6</sub>
fw	647.54	792.51	631.49	776.46
<i>T</i> (K)	100(2)	100(2)	150(2)	150(2)
Crystal system	monoclinic	orthorhombic	monoclinic	orthorhombic
Space group	P2 <sub>1</sub> /c	P212121	P2 <sub>1</sub> /c	$P2_{1}2_{1}2_{1}$
a (Å)	11.3320(10)	12.5034(2)	11.1183(2)	12.6251(2)
b (Å)	13.180(2)	16.5322(2)	12.9922(2)	16.6827(2)
<i>c</i> (Å)	21.939(4)	17.4444(3)	21.6846(3)	16.8415(2)
α (°)	90.0	90.0	90.0	90.0
β (°)	95.4950(10)	90.0	93.9570(10)	90.0
γ (°)	90.0	90.0	90.0	90.0
V (Å <sup>3</sup> )	3261.7(8)	3605.91(10)	3124.90(9)	3547.17(8)
Ζ	4	4	4	4
$D_{\text{calc}} (\text{g cm}^{-3})$	1.319	1.460	1.342	1.454
Crystal size (mm)	$0.32 \times 0.16 \times 0.16$	$0.25\times0.20\times0.20$	$0.15\times0.12\times0.10$	$0.20\times0.20\times0.20$
F(0 0 0)	1360	1636	1328	1604
Absorption coefficient (mm <sup>-1</sup> )	0.651	0.669	0.615	0.623
Range HKL	-14/14	-15/15	-14/14	-16/16
	-16/16	-21/21	-16/13	-21/21
	-28/28	-21/22	-16/27	-21/21
Number of total reflections	30 737	36 397	14 778	48 822
Number of unique reflections	7104	7852	6803	7736
Restraints/parameters	0/379	0/442	0/379	0/442
Final R	0.0449	0.0360	0.0344	0.0341
R <sub>w</sub>	0.1075	0.0813	0.0999	0.0743
R indices (all data)	0.0922	0.0506	0.0459	0.0451
R <sub>w</sub> (all data)	0.1156	0.0862	0.1025	0.0762
Sw	0.885	0.748	1.033	0.941
Largest difference in peak and hole (e $Å^{-3}$ )	0.625	0.392	0.539	0.427
	-0.580	-0.376	-0.609	-0.399

approximation was used to treat the core shells up to 1s for C and N, 2p for P and S, and 2p for Fe. Full geometry optimizations were carried out using the analytical gradient method implemented by Versluis and Ziegler [72]. Spin-unrestricted calculations were performed for all the open-shell systems. The *g*-tensor calculations were performed following the procedure describe by van Lenthe et al. [73]. Representation of the molecular orbitals was done using MOLEKEL4.2 [74].

### Acknowledgements

F.P. and Y.M. acknowledge the UMR 6226 for a joint research program. This work was performed using HPC resources from GENCI-CINES and GENCI-IDRIS (Grant 2010-80649). The C.N.R.S. is also acknowledged for financial support.

#### Appendix A. Supplementary material

CCDC 723062, 725071, 745047 and 756190 contain the supplementary crystallographic data for **5** (150 K), **5**[PF<sub>6</sub>] (100 K), **6** (150 K) and **6**[PF<sub>6</sub>] (150 K), respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data\_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.03.002.

### References

- F. Paul, F. Malvolti, G. Da Costa, S.L. Stang, F. Justaud, G. Argouarch, A. Bondon, S. Sinbandhit, K. Costuas, L. Toupet, C. Lapinte, Organometallics 29 (2010) 2491.
- [2] S. Le Stang, F. Paul, C. Lapinte, Inorg. Chim. Acta 291 (1999) 403.
- [3] S. Ibn Ghazala, N. Gauthier, F. Paul, L. Toupet, C. Lapinte, Organometallics 26 (2007) 2308.
- [4] F. Paul, S. Goeb, F. Justaud, G. Argouarch, L. Toupet, R.F. Ziessel, C. Lapinte, Inorg. Chem. 46 (2007) 9036.

- [5] F. Justaud, G. Argouarch, S.I. Gazalah, L. Toupet, F. Paul, C. Lapinte, Organometallics 27 (2008) 4260.
- [6] Y.-C. Lin, W.-T. Chen, J. Tai, D. Su, S.-Y. Huang, I. Lin, J.-L. Lin, M.M. Lee, M.F. Chiou, Y.-H. Liu, K.-S. Kwan, Y.-J. Chen, H.-Y. Chen, Inorg. Chem. 48 (2009) 1857.
- [7] R. Packheiser, P. Ecorchard, B. Walfort, H. Lang, J. Organomet. Chem. 693 (2008) 933.
- [8] Q. Ge, T.C. Corkery, M.G. Humphrey, M. Samoc, T.S.A. Hor, Dalton Trans. (2008) 2929.
- [9] F.E. Kühn, J.-L. Zuo, F.F. de Biani, A.M. Santos, Y. Zhang, J. Zhao, A. Sandulache, E. Herdtweck, New J. Chem. 28 (2004) 43.
- [10] C. Engratkul, W.J. Schoemaker, J.J. Grzybowski, I. Guzei, A. Rheingold, Inorg. Chem. 39 (2000) 5161.
- [11] F. Malvolti, P. Le Maux, L. Toupet, M.E. Smith, W.Y. Man, P.J. Low, E. Galardon, G. Simonneaux, F. Paul, Inorg. Chem. 49 (2010) 9101.
- [12] Q. Ge, G.T. Dalton, M.G. Humphrey, M. Samoc, T.S.A. Hor, Asian Chem. J. 4 (2009) 998.
- [13] Q. Ge, T.C. Corkery, M.G. Humphrey, M. Samoc, T.S.A. Hor, Dalton Trans. (2009) 6192.
- [14] P.M. Treichel, D.C. Molzahn, K.P. Wagner, J. Organomet. Chem. 174 (1979) 191.
- [15] G.J. Baird, S.G. Davies, J. Organomet. Chem. 262 (1984) 215.
- [16] A. Geiss, M. Keller, H. Vahrenkamp, J. Organomet. Chem. 541 (1997) 441.
- [17] A. Geiss, M.J. Kolm, C. Janiak, H. Vahrenkamp, Inorg. Chem. 39 (2000) 4037.
- [18] G.N. Richardson, U. Brand, H. Vahrenkamp, Inorg. Chem. 38 (1999) 3070.
- [19] G.N. Richardson, H. Vahrenkamp, J. Organomet. Chem. 593-594 (2000) 44.
- [20] G.N. Richardson, H. Vahrenkamp, J. Organomet. Chem. 597 (2000) 38.
- [21] T. Sheng, H. Vahrenkamp, Eur. J. Inorg. Chem. (2004) 1198.
- [22] H. Vahrenkamp, A. Giess, G.N. Richardson, J. Chem. Soc., Dalton Trans. (1997) 3643.
- [23] N. Zhu, H. Vahrenkamp, Chem. Ber. 130 (1997) 1241.
- [24] N. Zhu, H. Vahrenkamp, J. Organomet. Chem. 573 (1999) 67.
- [25] M.E. Smith, E.L. Flynn, M.A. Fox, A. Trottier, E. Werde, D.S. Yufit, J.A.K. Howard, K.L. Ronayne, M. Towrie, A.W. Parker, F. Hartl, P.J. Low, Chem. Commun. (2008) 5845.
- [26] R.L. Cordiner, M.E. Smith, A.S. Batsanov, D. Albesa-Jové, F. Hartl, J.A.K. Howard, P.J. Low, Inorg. Chim. Acta 359 (2006) 946.
- [27] M.E. Smith, R.L. Cordiner, D. Albesa-Jové, D.S. Yufit, F. Hartl, J.A.K. Howard, P.J. Low, Can. J. Chem. 84 (2006) 154.
- [28] M.I. Bruce, K. Costuas, B.J. Ellis, J.-F. Halet, P.J. Low, B. Moubaraki, K.S. Murray, N. Ouddaï, G.J. Perkins, B.W. Skelton, A.H. White, Organometallics 26 (2007) 3735.
- [29] R. Kergoat, M.M. Kubicki, L.C. Gomes de Lima, H. Scordia, J.E. Guerchais, P. L'Haridon, J. Organomet. Chem. 367 (1989) 143.
- [30] O. Kahn, Molecular Magnetism, VCH Publisher Inc., New-York Weinheim Cambridge, 1993.

- [31] E.G. Tennyson, R.C. Smith, Inorg. Chem. 48 (2009) 11483.
- [32] U. Siemeling, D. Rother, J. Organomet. Chem. 694 (2009) 1055.
- [33] L. Busetto, F. Marchetti, S. Zacchini, V. Zanotti, Inorg. Chim. Acta 358 (2005) 1204.
- [34] C. Roger, P. Hamon, L. Toupet, H. Rabaâ, J.-Y. Saillard, J.-R. Hamon, C. Lapinte, Organometallics 10 (1991) 1045.
- [35] M. Tilset, I. Fjeldahl, J.-R. Hamon, P. Hamon, L. Toupet, J.-Y. Saillard, K. Costuas, A. Haynes, J. Am. Chem. Soc. 123 (2001) 9984.
- [36] K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, second ed., Wiley-Interscience, N.-Y., 1970.
- [37] H.A. Papazian, J. Chem. Phys. 34 (1960) 1614.
- [38] F. Basolo, W.H. Baddley, K.J. Weidenbaum, J. Am. Chem. Soc. 88 (1966) 1576.
   [39] C. Pecile, Inorg. Chem. 5 (1966) 210.
- [40] J.A. Kargol, R.W. Crecely, J.L. Burmeister, Inorg. Chem. 18 (1979) 2532.
- [41] See for instance: K. Costuas, F. Paul, L. Toupet, J.-F. Halet, C. Lapinte, Organometallics 23 (2004) 2053.
- [42] F. Paul, L. Toupet, J.-Y. Thépot, K. Costuas, J.-F. Halet, C. Lapinte, Organometallics 24 (2005) 5464.
- [43] P.M. Treichel, D.C. Molzahn, Synth. React. Inorg. Met. Org. Chem. 9 (1979) 21.
- [44] F. Paul, G. da Costa, A. Bondon, N. Gauthier, S. Sinbandhit, L. Toupet, K. Costuas, J.-F. Halet, C. Lapinte, Organometallics 26 (2007) 874.
- [45] N.G. Connelly, M.P. Gamasa, J. Gimeno, C. Lapinte, E. Lastra, J.P. Maher, N. Le Narvor, A.L. Rieger, P.H. Rieger, J. Chem. Soc., Dalton Trans. (1993) 2575.
- [46] F. Paul, C. Lapinte, Coord. Chem. Rev. 178/180 (1998) 431.
- [47] A.G. Orpen, L. Brammer, F.H. Allen, O. Kennard, D.G. Watson, R. Taylor, J. Chem. Soc., Dalton Trans. (1989) S1.
- [48] F.H. Allen, O. Kennard, D.G. Watson, L. Brammer, A.G. Orpen, R. Taylor, J. Chem. Soc., Perkin Trans. 2 (1987) S1.
- [49] R. Denis, L. Toupet, F. Paul, C. Lapinte, Organometallics 19 (2000) 4240.
- [50] F. Paul, L. Toupet, T. Roisnel, P. Hamon, C. Lapinte, C. R. Chim. 8 (2005) 1174.
- [51] J.A. Weil, J.R. Bolton, Electron Paramagnetic Resonance. Elementary Theory and Practical Applications, second ed., Wiley Interscience, 2007.
   [52] J.L. Burmeister, Coord. Chem. Rev. 105 (1990) 77.
- [53] F. Basolo, W.H. Baddley, J.L. Burmeister, Inorg. Chem. 3 (1964) 1202.
- [54] F. Paul, C. Lapinte, Magnetic communication in binuclear organometallic complexes mediated by carbon-rich bridges, in: M. Gielen, R. Willem, B.

Wrackmeyer (Eds.), Unusual Structures and Physical Properties in Organometallic Chemistry, Wiley, San-Francisco, 2002, pp. 219–295.

- [55] N. Gauthier, N. Tchouar, F. Justaud, G. Argouarch, M.P. Cifuentes, L. Toupet, D. Touchard, J.-F. Halet, S. Rigaut, M.G. Humphrey, K. Costuas, F. Paul, Organometallics 28 (2009) 2253.
- [56] R.M. Golding, R.O. Pascual, J. Vrbancich, Mol. Phys. 31 (1976) 731.
- [57] N.G. Connelly, W.E. Geiger, Chem. Rev. 96 (1996) 877.
- [58] F. Paul, A. Bondon, G. da Costa, F. Malvolti, S. Sinbandhit, O. Cador, K. Costuas, L. Toupet, M.-L. Boillot, Inorg. Chem. 48 (2009) 10608.
- [59] Z. Otwinowski, W. Minor, Processing of X-ray diffraction data collected in oscillation mode, in: C.W. Carter, R.M. Sweet (Eds.), Methods in Enzymology, Academic press, London, 1997, pp. 307–326.
- [60] B.V. Nonius, Kappa CCD Software, Delft, The Netherlands, 1999.
- [61] A. Altomare, J. Foadi, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, M.C. Burla,
- G. Polidori, J. Appl. Crystallogr. 31 (1998) 74.
  [62] G.M. Sheldrick, SHELX97-2. Program for the Refinement Of Crystal Structures, Univ. of Göttingen, Germany, 1997.
- [63] D. Reidel, International Tables for X-ray Crystallography, Kynoch Press, Birmingham, 1974 (present distrib. D. Reidel, Dordrecht).
- [64] A.L. Spek, PLATON. A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, 1998.
- [65] G. te Velde, F.M. Bickelhaupt, C. Fonseca Guerra, S.J.A. van Gisbergen, E.J. Baerends, J. Snijders, T. Ziegler, Theo. Chem. Acc. 22 (2001) 931.
- [66] C. Fonseca Guerra, J. Snijders, G. te Velde, E.J. Baerends, Theo. Chem. Acc. 99 (1998) 391.
- [67] ADF2009, Vrije Universiteit, Amsterdam, Available at: http://www.scm.com, The Netherlands, 2009.
- [68] S.D. Vosko, L. Wilk, M. Nusair, Can. J. Chem. 58 (1990) 1200.
- [69] C. Adamo, V. Barone, J. Chem. Phys. C 116 (1996) 5933.
- [70] J.P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 77 (1996) 3865.
- [71] G. te Velde, E.J. Baerends, J. Comput. Phys. 99 (1992) 84.
- [72] L. Versluis, T. Ziegler, J. Chem. Phys. 88 (1988) 322.
- [73] E. van Lenthe, A. van der Avoird, P.E.S. Wormer, J. Chem. Phys. 107 (1997) 2488.
- [74] P. Flükiger, H.P. Lüthi, S. Portmann, J. Weber, Swiss Center for Scientific Computing (CSCS), Switzerland, 2000–2002.