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# Stepwise construction of a 4-hydroxyphenyl functionalized O,N,N-tridentate ferrocene-containing enaminone: Spectral, analytical and structural studies

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This article is dedicated to the memory of our friend and colleague Dr. Andrés Goeta.

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# 1. Introduction

### ABSTRACT

Tetrahydropyranylation of methyl-4-hydroxybenzoate proceeds with formation of its corresponding THP aromatic ether THP-O-*p*-C<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>CH<sub>3</sub> (1; THP = tetrahydropyranyl, C<sub>5</sub>H<sub>9</sub>O). Reaction with *in situ* generated carbanion of acetylferrocene gave the protected organometallic complex Fc-C(=O)CH=C(OH) (*p*-C<sub>6</sub>H<sub>4</sub>-O-THP) (**2**, Fc=( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Fe( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>)) featuring keto-enol functionality; subsequent acidic treatment of **2** afforded the 4-hydroxyphenyl substituted counterpart Fc-C(=O)CH=C(OH)(*p*-C<sub>6</sub>H<sub>4</sub>OH) (**3**) that exists as a 73/27 mixture of keto-enol/β-diketone tautomers in DMSO solution. The functionalized tridentate metalloligand Fc-C(=O)CH=C(*C*-G<sub>4</sub>H<sub>4</sub>OH)N(H)CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub> (**4**) incorporating O,N, N-donors is readily obtained upon Schiff base condensation of **3** with 1,2-diaminoethane. Complex **4** exists exclusively as its ferrocenyl-enaminone tautomer in solution and in the solid state. Compounds **1–4** were characterized by NMR (<sup>1</sup>H, <sup>13</sup>C) and IR spectroscopy as well as by elemental analysis and single-crystal X-ray diffraction.

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In the beginning of the 1980's, Costes and co-workers reported on the monocondensation reaction of 2,4-pentanedione with 1,2diaminoethane leading to the formation and the first isolation of the stable and easily handled O,N,N-tridentate unsymmetrical Schiff base 7-amino-4-methyl-5-aza-3-hepten-2-one, CH<sub>3</sub>C(=0)  $CH=C(CH_3)N(H)CH_2CH_2NH_2$  [1]. Its organometallic counterpart containing the ubiquitous ferrocenyl subunit Fc-C(=O)  $H=C(CH_3)N(H)CH_2CH_2NH_2$  (Fc=( $\eta^5-C_5H_5$ )Fe( $\eta^5-C_5H_4$ )) was prepared during the same decade [2], and structurally characterized by us almost twenty years later [3]. At the same time, we also reported on the synthesis and X-ray crystal structure of its relative O,N,N-tridentate metalloligand formed from monocondensation of ferrocenoylacetone and 1,2-phenylenediamine [4]. In the middle of the 2000's, Shi et al. also disclosed related tridentate metalloligand exhibiting O,N,S [5], O,N,O [6], and O,N,N-donor sets [7]; they were obtained by monocondensation of ferrocenoylacetone with S-

benzyldithiocarbazate, 2-aminoethanol or hydroxyanilines, and 2-(aminomethyl)pyridine, respectively. Both organic and organometallic singly condensed compounds are referred as "half units" or "hemi-ligands" [1,8], and in solution they can exist as a tautomeric mixture of keto-amine (enaminone) and keto-imine (iminone) forms [9]. The anionic deprotonated forms of the above mentioned tridentate enaminones can be viewed as potentially pseudo-isoelectronic with the cyclopentadienyl anion bearing a pendant donor arm. They could, therefore, serve as good chelating ligands for transition metals, lanthanides and main group elements with for instance, potential applications in catalysis [10,11]. On the other hand, replacement of the terminal methyl group of the parent enaminone by the electronically related three-dimensional ferrocenyl fragment brought about not only an expansion of the important structural organic moiety into the third dimension [12], but also the very useful redox properties [13], and the extremely rich chemistry of ferrocene [14]. Accordingly, our interest in the development of half unit metalloligands stemmed from their potential as building blocks for the preparation, upon condensation with salicylaldehydes, of a new class of unsymmetrical tetradentate salen-type ligands and their metal-centered complexes substituted with donor and acceptor organometallic moieties [15], exhibiting second-order nonlinear optical (NLO) responses [16].



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Thus, in pursuit of this work, we have focused on the design of a novel metalloligand functionalized with a phenolic group at the three-position of the hex-2-en-4-azo chain thus, leaving the O,N,N-donor set of the enaminone core available for further reactivity. The potential anchoring group might then be covalently bound to an organic or inorganic substrate through a single point of attachment, in order to immobilize catalysts [17] or to obtain oriented non-centrosymmetric materials showing NLO activity [18].

Herein, we report on the stepwise synthetic approach of the 4hydroxyphenyl functionalized organometallic enaminone, Fc- $C(=O)CH=C(p-C_6H_4OH)N(H)CH_2CH_2NH_2$  (4), as well as of its three precursors isolated along its four-step construction, using only commercially available reagents. The first step consists in the protection of hydroxyl group of methyl-4-hydroxybenzoate via a tetrahydropyranylation reaction [19], to produce the corresponding THP aromatic ether derivative **1** (THP = tetrahydropyranyl). Its reaction with the *in situ* generated carbanion of acetvlferrocene gave the protected organometallic  $\beta$ -diketone **2**, of which the THP protecting group is subsequently removed by acidic treatment to afford the 4hydroxyphenyl substituted  $\beta$ -diketone **3**. Finally, the unprecedented functionalized tridentate metalloligand 4 incorporating O,N,N-donors is obtained upon Schiff base condensation of 3 with 1,2-diaminoethane. The formation of 1-4 (see formulae in Schemes 1 and 2) was proven by FT-IR and NMR spectroscopy, and unambiguously established by single-crystal X-ray structural analyses.

### 2. Experimental

#### 2.1. General experimental methods

Reactions were performed under a nitrogen atmosphere using standard Schlenk techniques. Solvents were dried and distilled under dinitrogen by standard methods prior to use. All chemicals were purchased from Aldrich and used without further purification. IR spectra of solid samples of complexes 1-4 were recorded on a Perkin Elmer model 1600 FT-IR spectrophotometer, in the range 4000–450 cm<sup>-1</sup>. NMR spectra were obtained at 298 K on a Bruker Avance III 400 spectrometer (<sup>1</sup>H NMR at 400.13 MHz and <sup>13</sup>C NMR at 100.6 MHz). The chemical shifts are referenced to the residual deuterated solvent peaks. Chemical shifts ( $\delta$ ) and coupling constants (J) are expressed in parts per million (ppm) and hertz (Hz), respectively. Microanalyses were conducted on a Thermo-FINNIGAN Flash EA 1112 CHNS/O analyzer by the Microanalytical Service of the CRMPO at the University of Rennes 1, France. Melting points were measured in evacuated capillaries on a Kofler Bristoline melting point apparatus.

#### 2.2. Syntheses and characterization

# 2.2.1. Synthesis of 1

To a solution of methyl-4-hydroxybenzoate (1.00 g, 6.57 mmol) and of pyridinium-*p*-toluensulfonate (PPTS) (0.35 g, 1.4 mmol) in methylene chloride (50 mL), was added 3,4-dihydro-2H-pyran (DHP) (0.72 mL, 7.89 mmol). The reaction mixture was stirred for 5.0 h at room temperature (rt), and then washed with a saturated



Scheme 1. Synthesis of the protected tetrahydropyranyl aromatic ether 1.



**Scheme 2.** Synthesis of the protected and deprotected organometallic diketones **2** and **3**, and of the O,N,N-tridentate metalloligand **4**.

aqueous solution of NaCl (30 mL) to remove PPTS. The obtained emulsion was treated with diethyl ether (50 mL) giving two phases. The saline aqueous phase containing PPTS was discarded. This procedure was repeated three times. Finally, the organic phase was dried over MgSO<sub>4</sub>, filtered, evaporated and chromatographed through silica gel 70-230 mesh, using a mixture of hexane/ethyl acetate (4:1) as eluent. The solvents were removed under vacuum and evaporated to dryness, and the residue recrystallised from diethyl ether/hexane (1:1) to give the pure colorless crystalline solid of **1**. Yield: 1.01 g, 65%. A suitable crystal of this crop was used for a X-ray crystal structure determination. Mp: 62 °C. Anal. Calc. for C<sub>13</sub>H<sub>16</sub>O<sub>4</sub> (236.27 g mol<sup>-1</sup>): C, 66.09; H, 6.83. Found: C, 66.26; H, 6.79%. IR (KBr pellet, cm<sup>-1</sup>): 3066 (vw), 3017 (w) v(CH arom), 2985 (w), 2969 (w), 2950 (m), 2892 (w), 2846 (w) v(CH aliph), 1713 (vs) v(C=O), 1286 (vs), 1243 (vs), 1172 (vs) v(C-O). <sup>1</sup>H NMR (CDCl<sub>3</sub>): 1.63 (m, 2H, CH<sub>2</sub> THP), 1.82 (m, 2H, CH<sub>2</sub> THP), 1.94 (m, 2H, CH<sub>2</sub> THP), 3.58 (m, 1H, CH<sub>2</sub>-O), 3.79 (m, 1H, CH<sub>2</sub>-O), 3.83 (s, 3H,  $CH_3$ ), 5.55 (t,  ${}^{3}J_{H,H}$  = 3.2 Hz, 1H, O–CH–O), 7.11 (d,  ${}^{3}J_{H,H}$  = 8.8 Hz, 2H, C<sub>6</sub>H<sub>4</sub>), 7.94 (d,  ${}^{3}J_{H,H}$  = 8.8 Hz, 2H, C<sub>6</sub>H<sub>4</sub>).

#### 2.2.2. Synthesis of 2

To a solution of acetylferrocene (0.81 g, 3.56 mmol) in THF (15 mL) was added potassium tert-butoxide (0.48 g, 4.27 mmol) and the reaction mixture was stirred at room temperature (rt) for 45 min. Then, a solid sample of 1 (1.00 g, 4.27 mmol) was added to the reaction medium which was allowed to stir for 5 h before addition of a 0.5 M aqueous hydrochloric acid solution (20 mL). The obtained emulsion was treated with diethyl ether  $(3 \times 50 \text{ mL})$ according to the method described in Section 2.2.1. The resulting concentrated organic phase was absorbed on silica gel (70-230 mesh) and eluted with a mixture of hexane/diethyl ether (1:4). Slow evaporation of this eluate deposited orange-red, rod-shaped crystals of 2 suitable for X-ray single crystal analysis. Yield: 0.93 g, 51%. Mp: 178 °C. Anal. Calc. for  $C_{24}H_{24}FeO_4$  (432.30 g mol<sup>-1</sup>): C, 66.68; H, 5.60. Found: C, 66.69; H, 5.68%. IR (KBr pellet, cm<sup>-1</sup>): 3437 (w) v(OH), 3098 (vw), 3086 (vw) v(CH arom), 2940 (w), 2875 (vw), 2850 (vw) v(CH aliph), 1603 (vs) v(C=O), 1556 (s) v(C=C), 1237 (vs), 1174 (vs) v(C-O). <sup>1</sup>H NMR (CDCl<sub>3</sub>): 1.61(m, 2H, CH<sub>2</sub> THP), 1.70 (m, 2H, CH<sub>2</sub> THP), 1.89 (m, 2H, CH<sub>2</sub> THP), 3.63 (m, 1H, CH<sub>2</sub>-O), 3.87 (m, 1H, CH<sub>2</sub>-O), 4.22 (s, 5 H, C<sub>5</sub>H<sub>5</sub>), 4.54(s, 2H,  $H_{\beta} C_5 H_4$ ), 4.88 (s, 2H,  $H_{\alpha} C_5 H_4$ ), 5.53 (t,  ${}^{3}J_{H,H}$  = 2.5 Hz, 1H, O–CH– O), 6.33 (s, 1H, CH=C), 7.13 (d,  ${}^{3}J_{H,H}$  = 8.8 Hz, 2H, C<sub>6</sub>H<sub>4</sub>), 7.90 (d,  ${}^{3}J_{H,H}$  = 8.8 Hz, 2H, C<sub>6</sub>H<sub>4</sub>), 16.67 (s, 1H, OH).

# 2.2.3. Synthesis of 3

To a solution of **2** (0.90 g, 2.08 mmol) in THF (20 mL) was added a 2.0 M aqueous hydrochloric acid solution (20 mL). The reaction mixture was stirred for 30 min at rt before being treated with diethyl ether  $(3 \times 30 \text{ mL})$  according to the method described in Section 2.2.1. The organic phase was evaporated to dryness and the obtained solid was chromatographed on silica gel and eluted with pentane/diethyl ether (7:3). The eluate was then allowed to stand at -3 °C for 7 d, which results in the separation of red crystals of 3, of which a clear dark red one was selected for a X-ray single crystal analysis. Yield: 0.58 g, 81%. Mp: 125 °C. Anal. Calc. for C<sub>19</sub>H<sub>16</sub>FeO<sub>3</sub> (348.18 g mol<sup>-1</sup>): C, 65.54; H, 4.63. Found: C, 65.67; H, 4.67%. IR (KBr pellet, cm<sup>-1</sup>): 3445 (vw) v(OH), 3121 (m), 3094 (m) v(CH arom), 2952 (w), 2736 (w), 2674 (w), 2601 (w) v(CH aliph), 1607 (vs) v(C=O), 1577 (s) v(C=C). <sup>1</sup>H NMR ((CD<sub>3</sub>)<sub>2</sub>SO): Keto-enol tautomer, 4.21 (s, 5 H,  $C_5H_5$ ), 4.62 (br s, 2H,  $H_\beta$   $C_5H_4$ ), 5.05 (br s, 2H,  $H_{\alpha}$  C<sub>5</sub>H<sub>4</sub>), 6.68 (s, 1H, CH=C), 6.90 (d, <sup>3</sup>J<sub>H,H</sub>=8.3 Hz, 2H, C<sub>6</sub>H<sub>4</sub>), 7.96 (d,  ${}^{3}J_{H,H}$  = 8.3 Hz, 2H, C<sub>6</sub>H<sub>4</sub>), 10.30 (br s, 1H,  $C_6H_4OH$ ;  $\beta$ -diketone tautomer, 4.26 (s, 5 H,  $C_5H_5$ ), 4.41 (s, 2H, CH<sub>2</sub>), 4.62 (br s, 2H, H<sub>B</sub> C<sub>5</sub>H<sub>4</sub>), 4.83 (br s, 2H, H<sub> $\alpha$ </sub> C<sub>5</sub>H<sub>4</sub>), 6.86 (d,  ${}^{3}J_{H,H}$  = 8.5 Hz, 2H, C<sub>6</sub>H<sub>4</sub>), 7.92 (d,  ${}^{3}J_{H,H}$  = 8.5 Hz, 2H, C<sub>6</sub>H<sub>4</sub>), 10.40 (br s, 1H,  $C_6H_4OH$ ). <sup>13</sup>C{<sup>1</sup>H} NMR ((CD<sub>3</sub>)<sub>2</sub>SO): Keto-enol tautomer, 68.55 (C $_{\alpha}$  C $_{5}H_{4}$ ), 69.99 (C $_{5}H_{5}$ ), 71.99 (C $_{\beta}$  C $_{5}H_{4}$ ), 77.94 (C $_{ipso}$  C $_{5}H_{4}$ ), 92.29 (CH=C), 115.42 (C<sub>6</sub>H<sub>4</sub>), 125.25 (C<sub>ipso</sub> C<sub>6</sub>H<sub>4</sub>), 129.09 (C<sub>6</sub>H<sub>4</sub>), 161.40 (C-OH), 180.23 (CH=C), 192.03 (C=O); β-diketone tautomer, 50.17 (CH<sub>2</sub>), 69.53 ( $C_{\alpha}$  C<sub>5</sub>H<sub>4</sub>), 69.70 (C<sub>5</sub>H<sub>5</sub>), 72.50 ( $C_{\beta}$  C<sub>5</sub>H<sub>4</sub>), 79.12 (C<sub>ipso</sub> C<sub>5</sub>H<sub>4</sub>), 115.23 (C<sub>6</sub>H<sub>4</sub>), 128.28 (C<sub>ipso</sub> C<sub>6</sub>H<sub>4</sub>), 131.24 (C<sub>6</sub>H<sub>4</sub>), 162.34 (C-OH), 192.88 (C(=O)-C<sub>6</sub>H<sub>4</sub>), 198.00 (C(=O)- $C_5H_4$ ).

### 2.2.4. Synthesis of 4

To a solution of 3 (0.50 g, 1.44 mmol) in ethanol (10 mL) in a Schlenk flask equipped with a condenser were added a solution of ethylenediamine (0.30 mL, 4.32 mmol) in ethanol (5 mL) and two drops of glacial acetic acid. The reaction mixture was refluxed for 3 h. The red solid formed was filtered off and washed with cold ethanol ( $3 \times 5$  mL) and then with diethyl ether ( $3 \times 5$  mL). Recrystallization from hot methanol gave the orange-red crystalline solid **4**. Yield: 0.25 g, 45%. A clear light orange crystal from this crop was selected for X-ray crystallography. Mp: 186 °C (dec). Anal. Calc. for  $C_{21}H_{22}FeN_2O_2$  (390.27 g mol<sup>-1</sup>): C. 64.63: H. 5.68: N. 7.18. Found: C, 64.09; H, 5.71; N, 6.91%. IR (KBr pellet, cm<sup>-1</sup>): 3437 (w) v(OH), 3366 (m) v sym(NH<sub>2</sub>), 3280 (w) v(NH), 3100 (vw), 3080 (vw) v(CH arom), 2976 (vw), 2962 (vw), 2921 (vw), 2876 (vw) v(CH aliph), 1610 (m) v(C=O), 1582 (vs) v(C=C), 1545 (m)  $\delta$ (NH<sub>2</sub>). <sup>1</sup>H NMR ((CD<sub>3</sub>)<sub>2</sub>SO): 2.63 (t,  ${}^{3}J_{H,H}$  = 6.0 Hz, 2H, CH<sub>2</sub>NH<sub>2</sub>), 3.14 (q,  ${}^{3}I_{H,H}$  = 5.5 and 6.0 Hz, 2H, N(H)CH<sub>2</sub>), 4.13 (s, 5H, C<sub>5</sub>H<sub>5</sub>), 4.38 (t,  ${}^{3}J_{H,H}$  = 1.8 Hz, 2H, H<sub>β</sub> C<sub>5</sub>H<sub>4</sub>), 4.72 (t,  ${}^{3}J_{H,H}$  = 1.8 Hz, 2H, H<sub>α</sub> C<sub>5</sub>H<sub>4</sub>), 5.36 (s, 1H, CH=C), 6.82 (d,  ${}^{3}J_{H,H}$  = 8.4 Hz, 2H, C<sub>6</sub>H<sub>4</sub>), 7.22 (d,  ${}^{3}J_{H,H}$  = 8.4 Hz, 2H, C<sub>6</sub>H<sub>4</sub>), 10.83 (t,  ${}^{3}J_{H,H}$  = 5.5 Hz, 1H, NH).  ${}^{13}C{}^{1}H$ NMR (( $(CD_3)_2SO$ ): 42.10 ( $CH_2NH_2$ ), 47.32 ( $N(H)CH_2$ ), 68.05 ( $C_{\alpha}$ C<sub>5</sub>H<sub>4</sub>), 69.36 (C<sub>5</sub>H<sub>5</sub>), 70.29 (C<sub>β</sub> C<sub>5</sub>H<sub>4</sub>), 82.98 (C<sub>ipso</sub> C<sub>5</sub>H<sub>4</sub>), 93.66 (CH=C), 115.20 (C<sub>6</sub>H<sub>4</sub>), 125.98 (C<sub>ipso</sub> C<sub>6</sub>H<sub>4</sub>), 129.37 (C<sub>6</sub>H<sub>4</sub>), 158.57 (C-OH), 164.16 (CH=C), 190.44 (C=O).

#### 2.3. Crystal structure determinations

Diffraction data were collected at 120 K on a Oxford Diffraction Gemini CCD diffractometer and processed using the Oxford Diffraction CrysAlis<sup>PRO</sup> software for **1**, **3** and **4**, and at 150 K on an APEX II Bruker-AXS diffractometer for **2**, using in both cases graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Using OLEX2 [20], the structures of **1**, **3** and **4** were solved with the sHELXS structure solution program [21], using direct methods, while the structure of **2** was solved by direct methods using SIR97 [22]. They were refined with the sHELXL refinement package [21], using full-matrix least squares techniques based on  $F^2$  with aid of WINGX program [23]. All non-hydrogen atoms were finally included in their cal-

culated positions. Details about the data collection and refinement for the X-ray structures of compounds **1–4** are documented in Table 1, and additional crystallographic details are in the CIF files.

# 3. Results and discussion

In 1957, Hauser and Lindsay first reported the preparation of the parent–diketone derivative 1-ferrocenyl-3-phenylpropane-1,3-dione resulting from condensation of acetylferrocene with methyl benzoate, by using potassium amide as the active base additive in liquid ammonia [24]. Fifty years later, we disclosed that the deprotonation of acetylferrocene can be effected under more practical conditions by using potassium tert-butoxide as the active base initiator in tetrahydrofuran (THF) at room temperature [15a]. In order to introduce a functional 4-hydroxyphenyl group onto the ferrocenyl  $\beta$ -diketone framework under basic conditions the hydroxyl group must first be protected. This was achieved using the tetrahydropyranylation reaction that has been recognized as an useful and representative method for the protection of alcohols under mild conditions [19].

# 3.1. Synthesis, characterization and X-ray diffraction study of the protected tetrahydropyranyl aromatic ether **1**

Treatment of methyl-4-hydroxybenzoate solution in dichloromethane with a slight excess of 3,4-dihydro-2H-pyran in the presence of pyridinium-*p*-toluensulfonate (PPTS) as catalyst [19], at ambient temperature for 5 h, led to the tetrahydropyranylation product with composition ( $C_5H_9O$ )-*p*-OC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>CH<sub>3</sub> (1), in 65% yield (Scheme 1, see Section 2.2.1 for experimental details). Compound **1** is a colorless crystalline solid with good solubility in THF, diethyl ether and acetone.

The formation of the THP ether species **1** was readily noticed in the <sup>1</sup>H NMR spectrum. Beside the sharp singlet at  $\delta$  = 3.83 ppm for the methyl ester group, **1** exhibited a series of five multiplets ranging between  $\delta$  = 1.63 and 3.79 ppm, and a triplet at  $\delta$  = 5.55 ppm for the THP ring protons in CDCl<sub>3</sub>. In the solid state IR spectrum, the ester functionality is identified by an intense v(C=O) stretching band at 1713 cm<sup>-1</sup>. In addition, the structure of compound **1** was unambiguously established by low-temperature single-crystal Xray structure analysis.

The molecular structure of **1** is displayed in Fig. 1, with selected bond distances and angles given in the caption. It showed the effective tetrahydropyranylation of the phenol group, with THP ring adopting a rigid chair conformation (Fig. 1). A structural feature of this THP ring to be noted is the two different oxygen-carbon bond lengths, O(4)-C(9) and O(4)-C(13) of 1.4178(16) and 1.4411(15) Å, respectively. That could be attributed to the moderate electron withdrawing effect of the  $p-O-C_6H_4CO_2CH_3$  group at the C(9) atom. The C–C distances in the phenylene ring fall between 1.3820(18) and 1.3936(19) Å (avg = 1.3898(18) Å) whereas those of the pyranyl group are found between 1.5120(18) and 1.5303(19) Å (avg = 1.5222(18) Å).

# 3.2. Synthesis and characterization of protected and deprotected ferrocenyl $\beta$ -diketones **2** and **3**

The stirring of a THF suspension of  $[Fc-C(=O)CH_2]K$ , *in situ* generated by deprotonation of acetylferrocene with *t*BuOK, with a slight excess of the organic species **1** for 5 h at room temperature yielded the THP-protected organometallic precursor Fc-C(=O)CH=C(OH){*p*-C<sub>6</sub>H<sub>4</sub>(2–O–C<sub>5</sub>H<sub>9</sub>O)} (2), isolated as orange-red crystalline solid in 51% yield (Scheme 2). Subsequent acid hydrolysis (2.0 M aq. HCl) of a THF solution of **2** afforded the deprotected organometallic β-diketone Fc-C(=O)CH=C(OH)(*p*-C<sub>6</sub>H<sub>4</sub>OH) (**3**,

1	0	7
I	0	1

Table 1	
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Crystallographic data, details of data collection and structure refinement parameters for compounds 1-4.

Compound	1	2	3	4
Empirical formula	$C_{13}H_{16}O_4$	C <sub>24</sub> H <sub>24</sub> FeO <sub>4</sub>	$C_{19}H_{16}FeO_3$	C21H22FeN2O2
Formula weight, (g mol <sup>-1</sup> )	236.26	432.28	348.17	390.26
Collection T (K)	120(2)	150(2)	120(0)	120(2)
Crystal system	monoclinic	monoclinic	orthorhombic	monoclinic
Space group	C2/c	$P2_1/a$	Pbca	$P2_1/c$
a (Å)	19.1563(10)	10.1967(7)	9.7943(6)	9.1849(2)
b (Å)	7.5570(4)	11.9793(9)	17.2850(16)	9.72339(18)
<i>c</i> (Å)	17.1881(9)	16.1904(11)	17.4952(5)	20.6783(4)
β(°)	110.869(3)	90.853(3)	90.00	101.185(2)
V (Å <sup>3</sup> )	2325.0(2)	1977.4(2)	2961.8(3)	1811.68(7)
Ζ	8	4	8	4
$D_{\text{calc}}$ (g cm <sup>-3</sup> )	1.350	1.452	1.562	1.431
Crystal size (mm)	$0.25\times0.3\times0.5$	$0.4 \times 0.1 \times 0.06$	$0.27\times0.1\times0.04$	$0.28\times0.1\times0.09$
F(000)	1008	904	1440	816
Absorption coefficient (mm <sup>-1</sup> )	1.031	0.791	0.100	0.850
$\theta$ Range(°)	5.21-58.53	3.40-27.48	2.28-52.04	5.44-58.38
Range h, k, l	-23/23, -9/9, -21/21	-13/10, -15/15, -19/21	-13/12, -23/23, -23/23	-12/12, -13/13, -28/26
Total reflections	11677	29524	37603	63872
Unique reflections	2294	4499	3744	4717
Comp. to $\theta_{max}$ (%)	99.9	99.1	92.1	95.8
Maximum/minimum transmission		0.954/0.735	1.000/0.848	1.000/0.868
Data/restraints/parameters	2294/0/155	4499/0/262	3744/0/210	4717/4/246
Final R indices $[I > 2(I)]$	$R_1 = 0.0396, wR_2 = 0.1066$	$R_1 = 0.0771$ , $wR_2 = 0.2294$	$R_1 = 0.0312, wR_2 = 0.0679$	$R_1 = 0.0389, wR_2 = 0.0758$
R indices (all data)	$R_1 = 0.0501, wR_2 = 0.1129$	$R_1 = 0.0952, wR_2 = 0.2425$	$R_1 = 0.0411$ , $wR_2 = 0.0724$	$R_1 = 0.0645, wR_2 = 0.0856$
Goodness of fit (GOF) on $F^2$	1.045	1.153	1.052	1.035
Largest difference in peak and hole (e $Å^{-3}$ )	0.283/-0.224	1.247/-0.626	0.382/-0.349	0.401/-0.412



**Fig. 1.** Molecular structure of **1** with the atom numbering scheme. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at 50% probability. Selected bond distances (Å) and angles (°): O(1)-C(1) 1.4488(15), O(1)-C(2) 1.3453(16), O(2)-C(2) 1.2074(16), O(3)-C(6) 1.3744(15), O(3)-C(9) 1.4123(15), O(4)-C(9) 1.4178(16), O(4)-C(13) 1.4411(15), C-C(Ph) avg = 1.3898(18), C-C(pyr-anyl) avg = 1.5222(18); C(1)-O(1)-C(2) 114.92(10), O(1)-C(2)-O(2) 123.21(12), C(6)-O(3)-C(9) 118.73(10), O(3)-C(9)-O(4) 106.83(10), C(9)-O(4)-C(13) 110.65(10).

81%) as dark red crystals upon work up (Scheme 2). Both **2** and **3** are soluble in THF, diethyl ether and methylene chloride. The two air and thermally stable complexes were characterized by spectroscopic, elemental and X-ray diffraction analyses (see Section 3.4).

The solid state IR spectra of **2** and **3** showed C=O and C=C intense stretching bands at 1603/1556 and 1607/1577 cm<sup>-1</sup>, respectively, in agreement with keto-enol tautomeric forms. The <sup>1</sup>H NMR<sup>1</sup>H NMR spectra of **2** and **3** showed common similar resonances consistent with the [Fc-C(=O)CH=C(p-C<sub>6</sub>H<sub>4</sub>--)] framework; those are a singlet and two triplets or broad singlets for the ferrocenyl fragment, a singlet for the methine proton and two doublets for the p-phenylene group (see Section 2 for details). Additionally, the spectrum of **2** recorded at 25 °C in CDCl<sub>3</sub> exhibited the same signal pattern for the THP group as that observed for **1**, and only one set of two singlets at 6.33 and 16.67 ppm for the C-H and O-H protons of the enol form, respectively. This solution behavior is similar to that reported for the parent derivative Fc-C(O)CH=C(Ph)OH, for which the percentage of keto-enol tautomeric form was determined under the same conditions to be 95% [25]. This

is presumably due to the high solubility of 2 in chloroform allowing the preparation of saturated NMR solutions. It is known that high concentrations drive the keto-enol equilibrium towards the enol side [25]. By contrast, the <sup>1</sup>H NMR<sup>1</sup>H NMR spectrum of the much less soluble compound **3**, recorded at 25 °C in DMSO- $d_6$ , showed that it does exist as a mixture of keto-enol and β-diketone tautomers in a 73:27 ratio. The vinylic C-H singlet at 6.68 ppm (1H) for the keto-enol form gave rise to a sharp resonance at 4.41 ppm (2H) for the  $\beta$ -diketone isomer. The broad downfield shifted O-H enol proton was not observed but has been located at 17.15 ppm in acetone- $d_6$ , in which solvent a complete enolization is achieved (see Supplementary information). The phenolic proton resonates at 10.30 and 10.40 ppm, respectively and vanish upon addition of  $D_2O$ . The <sup>13</sup>C NMR spectrum of **3** in DMSO- $d_6$  confirms the existence of the keto-enol/β-diketone tautomeric mixture. The methyne carbon (C(12)), see Fig. 2 for the labeling scheme) resonates at 92.29 ppm for the keto-enol form, while it shows up at 50.17 ppm for the  $\beta$ -diketone derivative. At the same time, C(13) experiences a downfield shift from 180.23 to 192.88 ppm.

# 3.3. Synthesis and characterization of the O,N,N-tridentate metalloligand **4**

The phenol substituted ferrocenyl keto-amine complex **4** ("half unit") with composition  $Fc-C(=O)CH=C(p-C_6H_4OH)N(H)CH_2CH_2$ NH<sub>2</sub> was successfully prepared by the monocondensation reaction between ethylenediamine and precursor **3** (3:1) in refluxing ethanol for 3 h (Scheme 2). The tridentate metalloligand **4** incorporating O and N donors was isolated as an orange-red crystalline solid in 45% reasonable yield. This air and thermally stable compound exhibits a good solubility in DMSO and MeOH but is insoluble in non-polar solvents. FT-IR and multinuclear and 2D NMR spectroscopies, single-crystal X-ray diffraction, and elemental analysis served to confirm its structure. In addition, high resolution ESI-MS of **4** gave an exact mass of m/z = 413.0928 for [M+Na]<sup>+</sup> that matched the calculated value of 413.09284 (Relative error: 0 ppm),



**Fig. 2.** Molecular structures of **2** (top), **3** (middle), and **4** (bottom) with the atom numbering schemes. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at 50% probability.

and the expected isotopic distribution for the molecular ion peak (Supplementary information, Fig. B1).

Like for precursors **2** and **3**, the solid state IR spectrum of **4** showed C=O and C=C intense stretching bands at 1610/1582 cm<sup>-1</sup>, in accordance with a keto-enamine tautomeric form. In addition, spectrum of **4** exhibited both symmetric and deformation stretching modes of the terminal NH<sub>2</sub> group at 3366 and 1545 cm<sup>-1</sup>, respectively, and a weak band at 3280 cm<sup>-1</sup> attributed to the stretching vibration of the enamine N–H group. This band is shifted to a lower energy as a consequence of the N–H···O intramolecular hydrogen bond [9].

The metalloligands **4** was obtained as *Z* isomer, as determined by <sup>1</sup>H NMR<sup>1</sup>H NMR spectroscopy carried out in DMSO- $d_6$  at 25 °C, which showed a deshielded triplet of the amino proton at 10.83 ppm due to hydrogen bonding between N–H and the

Table 2	
Selected bond distances (Å) and a	ngles (°) for compounds 2, 3, and 4.

		-	
	2	3	4
Bond distances			
C(6)-C(11)	1.465(7)	1.461(2)	1.480(2)
O(1)-C(11)	1.253(6)	1.2740(18)	1.265(2)
C(11)-C(12)	1.453(7)	1.422(2)	1.423(3)
C(12)-C(13)	1.356(8)	1.375(2)	1.386(2)
C(13)-X <sup>a</sup>	1.346(6)	1.3283(18)	1.348(2)
C(13)-C(14)	1.481(7)	1.464(2)	1.486(3)
C(17)-X <sup>b</sup>	1.370(7)	1.3507(19)	1.357(2)
C-C(Ph) <sup>c</sup> avg	1.390(8)	1.390(2)	1.388(3)
Fe(1)-C(Cp) <sup>c</sup> avg	2.043(5)	2.0463(17)	2.044(2)
Fe-C(Cp') <sup>c</sup> avg	2.040(5)	2.0440(16)	2.0434(18)
Angles (°)			
O(1)-C(11)-C(12)	121.0(5)	120.41(14)	122.76(16)
C(11)-C(12)-C(13)	121.2(5)	121.25(14)	123.81(17)
C(12)-C(13)-X <sup>a</sup>	120.9(5)	120.73(14)	121.74(17)

<sup>A</sup> X = O(2) for **2** and **3**; X = N(1) for **4**.

<sup>b</sup> X = O(3) for **2** and **3**; X = O(2) for **4**.

<sup>c</sup> Abbreviations:  $Cp = C_5H_5$ ,  $Cp' = C_5H_4$ ,  $Ph = C_6H_4$ .

C=O group. The downfield position of this signal that disappeared on deuteration with D<sub>2</sub>O, is in full agreement with the above discussed IR data and also supported by the crystal structure of enaminone **4** (*vide infra*). Such observations are similar to that reported for the monocondensation product obtained by reaction of ferrocenoylacetone with ethylenediamine [2,3], 2-aminoethanol [6], alkylanilines and o-anisidine [7,26]. In addition, the spectrum of 4 contained a upfield shifted sharp vinylic C-H resonance at 5.36 ppm, compared to the 6.33 and 6.68 ppm chemical shifts observed for 2 and 3, respectively. The methylene triplet and quadruplet resonances at 2.63 (2H) and 3.14 (2H) ppm, respectively, reflect the asymmetry of the ligand. The terminal NH<sub>2</sub> and phenolic protons were not observed. The unsymmetrical nature of 4 is confirmed by the 13 lines observed in its decoupled <sup>13</sup>C NMR spectrum. Specifically, the two methylene carbons resonate at 42.10 and 47.32 ppm, and the three carbons of the enaminone core show up at 93.66 ppm for the C(12)-methyne, 164.16 ppm for the C(13)ene and 190.44 ppm for the C(11)-carbonyl carbon nuclei, respectively (see Fig. 2 for the numbering scheme).

# 3.4. Molecular structures

Perspective views of the two organometallic keto-enol tautomers **2** and **3**, and of the O,N,N-tridentate enaminone **4** are shown in Fig. 2, with selected bond distances and angles listed in Table 2. The single-crystal X-ray diffraction studies confirm both the monomeric nature and that each compound exists as the Z–s–Z conformational form.<sup>1</sup> Complexes **2–4** contain a ferrocenyl unit with an iron atom coordinated to the free and substituted cyclopentadienyl rings at a ring centroid-iron distances of 1.652/1.642, 1.652/1.645 and 1.647/1.645 Å, with ring centroid-iron-ring centroid angle of 178.8°, 178.6° and 177.9°, respectively, indicating that there is a Fe(II) oxidation state in each metallocene [27].

In the [O(1)-C(11)-C(12)-C(13)-X] central cores (X=O(2) for **2** and **3**, N(1) for **4**), the angles at C(11), C(12) and C(13) lie between 120.41(14)° and 123.81(17)° (Table 2) and that at N(1) (C(13)-N(1)-C(20)) is of 125.73(16)°. Those values are very close to the idealized value of 120° expected for a sp<sup>2</sup>-hybridized atom. The O(1)-C(11, C(11)-C(12), C(12)-C(13) and C(13)-X bond lengths

<sup>&</sup>lt;sup>1</sup> Such Fc-C(=O)CH=C-(R)XH derivatives may have the following four isomers: Es-E, E-s-Z, Z-s-E, and Z-s-Z in which E and Z refer to two possible geometric conformations for the carbon-carbon double bond and s-E and s-Z to both isomerism about the carbon-carbon single bond between the carbon-carbon and carbonoxygen double bonds; see Ref. [9].

observed in this planar skeleton correspond to alternating double-, single-, double- and single-bonds (Table 2) [28], thus exhibiting partial delocalization of the O=C-C=C-X system. Those metrical parameters are consistent with a keto-enol tautomeric form for 2 and 3 and a keto-enamine form for 4, with an intramolecular  $O(1) \cdots H-X$  which closes a six-membered pseudo-aromatic ring through the resonant ... O=C-C=C-XH... fragment [29]. The  $O \cdots X$  separations are equal to 2.521(5), 2.4937(16) and 2.674(2) Å, respectively, in accordance with previously reported structural data for ferrocene containing keto-enol or enaminone derivatives [2,3,6,7,26,30]. In 2-4, the plane of the [OCCCX] framework makes dihedral angles with the substituted cyclopentadienyl ring of 25.3°, 16.5° and 7.3°, respectively, whereas the phenylene ring is oriented out of this plane with dihedral angles of 19.5°, 23.1° and 53.1°, respectively. Clearly, for 4, the substituted cyclopentadienyl ring may in part conjugate with the enaminonic skeleton whereas the phenylene ring is not involved in the conjugation of this skeleton. In addition, the structure of complex 2 shows that the tetrahydropyranyl protecting group adopts the same chair conformation as already seen in its precursor 1 with two distinct intracyclic C-O distances of 1.397(8) and 1.425(9) Å and C-C bond lengths falling between 1.497(10) and 1.542(10) Å (avg = 1.506(10) Å). In complex 4, the C–N distances in the ethylene diamine arm are identical (1.461(2) and 1.468(2) Å) and longer by  $\sim 0.12$  Å than the C(13)–N(1) (1.348(2) Å) which is part of a delocalized enaminonic system.

#### 4. Conclusion

In conclusion, we have presented a convenient stepwise construction of the air and thermally stable, O,N,N-tridentate ferrocenyl containing enaminone functionalized with a 4-hydroxyphenyl group at the three-position of the hex-2-en-4-azo chain, Fc- $C(=O)CH=C(p-C_6H_4OH)N(H)CH_2CH_2NH_2(4)$  that exists exclusively as its ferrocenyl-enaminone tautomer in solution and in the solid state. The four-step synthesis of structurally characterized metalloligand 4 needs only standard laboratory equipment, inexpensive and readily available starting materials. This certainly opens the door for this tridentate metalloligand incorporating O,N,N-donors to become a versatile building block in organometallic and coordination chemistry. For instance, it could be used as a precursor for the synthesis of unsymmetrical tetradentate Schiff bases upon reaction with salicylic aldehydes and their corresponding unsymmetrical square-planar transition metal complexes [15,16]. Moreover. This tridentate synthon which is characterized by the presence of different functional groups, has the potential to be active in other synthetic scenarios especially in those involving its embedding into a matrix toward formation of supported catalysts, main-chain or side-chain polymers and in supramolecular chemistry. Further studies are currently underway along those lines and to study the applicability of the present system to other reactions.

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#### **Appendix A. Supplementary material**

CCDC-844554 (for 1), 844937 (for 2), 844555 (for 3) and 844556 (for 4); contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2012.04.028.

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