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1,1′-Ferrocene dicarboxylic acid pyridin-4-yl ester: A new bidentate ligand in arene ruthenium chemistry

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Abstract

1,1′-Ferrocene dicarboxylic acid pyridin-4-yl ester (**1**) is prepared from 1,1′-ferrocene dicarbonyl chloride and 4-hydroxypyridine. This new bidentate ferrocenoyl ligand reacts with the monocationic complex $[(\eta^6\text{-}p\text{-cymene})_2Ru_2(\mu\text{-OH})_3]^+$ to give the dicationic complex $[(\eta^6\text{-}p\text{-cymene})_2Ru_2(\mu\text{-OH})_2(1,1'\text{-}(NC_5H_4\text{–}OOC)_2\text{–Fc})]^{2+}$ (**2**) (Fc: C_5H_4–Fe–C_5H_4), isolated as a tetrafluoroborate salt. The single-crystal X-ray structure analysis of $[\mathbf{2}][BF_4]_2$ reveals the ferrocenoyl pyridine ligand **1** to act as μ_2-η^2 chelating ligand in the dinuclear complex, having replaced a μ_2-η^1-hydroxo ligand.

Keywords: Arene-ruthenium complexes; Hydroxo bridges; Bidentate ligands; Ferrocene; UV spectra

Since the discovery of the Josiphos ligand [1] by Togni et al. in 1994, a considerable number of bidentate ligands derived from ferrocene have been developed and used to catalyse various organic reactions [2]. Another interesting aspect of these bidentate ligands is the use of 1,1′-substitued ferrocenes for the construction of macromolecular structures, for the design and synthesis of host/guest complexes [3] or as building blocks for antitumor agents [4]. To our knowledge, ferrocene-based bidentate ligands have never been used with dinuclear hydroxo-bridged arene ruthenium complexes [5], although the chemistry of these complexes is quite well established [6,7].

In this communication we report the synthesis of a new ferrocenoyl pyridine ligand and its coordination to a dinuclear hydroxo-bridged arene ruthenium complex, as well as the molecular structure of the new complex obtained.

1,1′-Ferrocene dicarbonyl chloride [8] reacts with 4-hydroxypyridine in dichloromethane at room temperature to give 1,1′-ferrocene dicarboxylic acid pyridin-4-yl ester 1,1′-$(NC_5H_4\text{–}OOC)_2$–Fc (Fc: C_5H_4–Fe–C_5H_4) (**1**) [9]. This new bidentate ligand based on ferrocene is obtained as an air-stable red crystalline powder. Its ^{1}H NMR spectra is in accordance with the structure expected, the two 1- and 1′-arms being equivalent. The ligand **1** reacts with the triply hydroxo-bridged complex $[(\eta^6\text{-}p\text{-cymene})_2Ru_2(\mu\text{-OH})_3]^+$ [5] to give the dicationic complex $[(\eta^6\text{-}p\text{-cymene})_2Ru_2(\mu\text{-OH})_2(1,1'\text{-}(NC_5H_4\text{–}OOC)_2\text{–Fc})]^{2+}$ (**2**), isolated as the tetrafluoroborate salt [10] (Scheme 1). This salt is obtained as air-stable orange crystals, which are only soluble in acetone [11]. From the reaction of a dinuclear complex with a bidentate ligand, also a tetranuclear complex may be expected, as in the reaction of 4,4'-bipyridine with $[(\eta^6\text{-}p\text{-cymene})_2Ru_2(\mu\text{-OH})_3]^+$ [12] or with $[(\eta^6\text{-}p\text{-cymene})_2Ru_2(\mu\text{-}\eta^4\text{-}C_2O_4)(CH_3OH)_2]$ [13]. However, the complex **2** is the first example of ''dinuclear ruthenacycle'' containing two hydroxo bridges and a μ_2-η^2-ferrocenoyl pyridine bridge (Figs. 2 and 3).

UV–visible spectra of the free ligand **1** and of the salt $[\mathbf{2}][BF_4]_2$ have been measured in dichloromethane (Fig. 1). The free ligand exhibits an absorption maximum at $\lambda_{max} = 253$ nm, for the complex $\lambda_{max} = 240$ nm, this shift being due to the coordination to the arene-ruthenium

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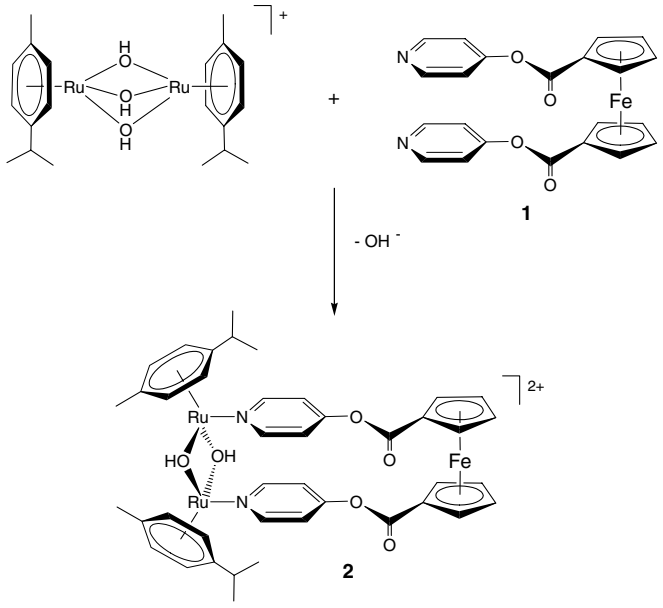

Scheme 1.

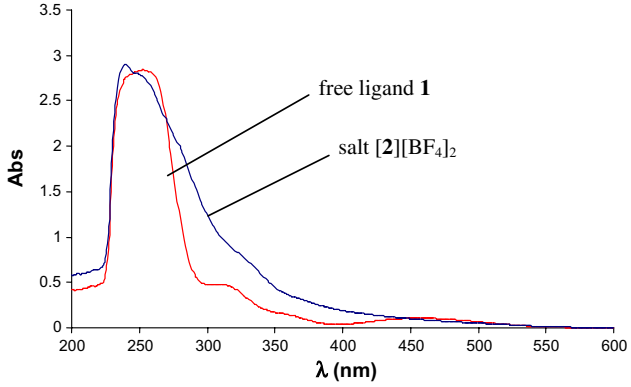

Fig. 1. UV spectra of 1,1′-(NC_5H_4–$OOC)_2$–Fc (**1**) and [(η^6-*p*-cymene)$Ru_2(\mu$-OH$)_2$(1,1′- (NC_5H_4–$OOC)_2$–Fc)][$BF_4]_2$ ([**2**][$BF_4]_2$).

motive. The 320 nm shoulder observed in the spectrum of [**2**][$BF_4]_2$ originates from the weak peak at 309 nm in the spectrum of **1**, which probably can be assigned to the pyridine group.

The compound [**2**][$BF_4]_2$ is crystallised by slow evaporation of an acetone solution. A single-crystal X-ray analysis was performed, confirming the cyclic molecular structure of **2**, see Fig. 2.

The two ruthenium atoms possess a pseudo-octahedral geometry, and the metrical parameters around the metallic core compare well with those of similar three-legged pianostool [(η^6-arene)$RuCl_2(C_5H_4N)$] complexes [14]. The ferrocene moiety is in the eclipsed conformation. The two pyridyl ester substituents are parallel and perfectly coplanar to their cyclopentadienyl unit. Therefore, strong π-interactions between the C_5H_4N rings are observed, the centroid···centroid distance of the aromatic rings being 3.41 Å. Accordingly, due to the formation of the metallacycle upon coordination of the chelating 1,1′-ferrocenoyl ligand, the separation between the oxygen atoms of the carbonyl groups is very short [O(5)···O(6) 3.541(9) Å]. In the trinuclear metallacyclic system, the metal–metal distance is 3.2618(4) Å between the ruthenium atoms, while the distances between the iron and the ruthenium atoms are 9.7681(8) and 9.6255(8) Å, respectively.

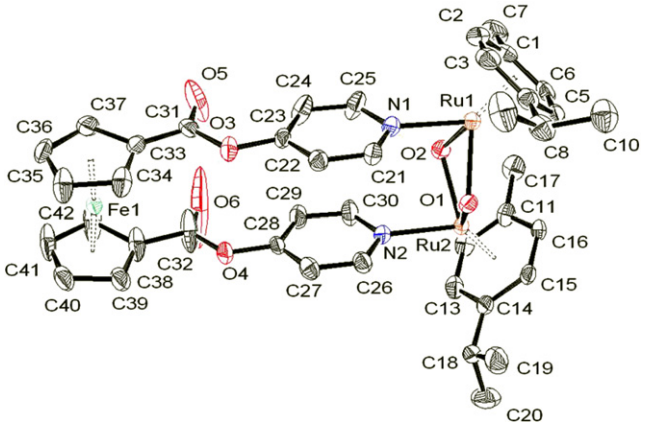

Fig. 2. Molecular structure of **2** at 50% probability level, H atoms, tetrafluoroborate anions and Me_2CO molecules omitted for clarity. Selected bond lengths (Å) and angles (°): Ru(1)–O(1) 2.105(2), Ru(1)–O(2) 2.093(2), Ru(2)–O(1) 2.073(2), Ru(2)–O(2) 2.074(2), Ru(1)–N(1) 2.104(2), Ru(2)–N(2) 2.120(2); Ru(1)–O(1)–Ru(2) 101.96(9), Ru(1)–O(2)–Ru(2) 103.73(10), N(1)–Ru(1)–O(1) 82.54(9), N(1)–Ru(1)–O(2) 80.56(9), N(2)–Ru(2)–O(1) 84.67(9), N(2)–Ru(2)–O(2) 81.31(9), O(1)–Ru(1)–O(2) 74.14(9), O(1)–Ru(2)–O(2) 74.37(9).

In the crystal packing of [**2**][$BF_4]_2 \cdot Me_2CO$, the solvent molecule forms two strong hydrogen bonds with the carbonyl groups of **2**, see Fig. 3. The C–O distances of the C–H···O hydrogen bonds are 3.329(8) and 3.286(11) Å with C–H···O angles of 136.8 and 140.1°, respectively. One tetrafluoroborate anion interacts strongly with **2**, see Fig. 4. The BF_4 anion is encapsulated between the *p*-cymene ligands and forms a hydrogen contact with one of the hydroxo bridges, thus pushing away the two *p*-cymene units. The two C_6H_4 planes of the *p*-cymene ligands are

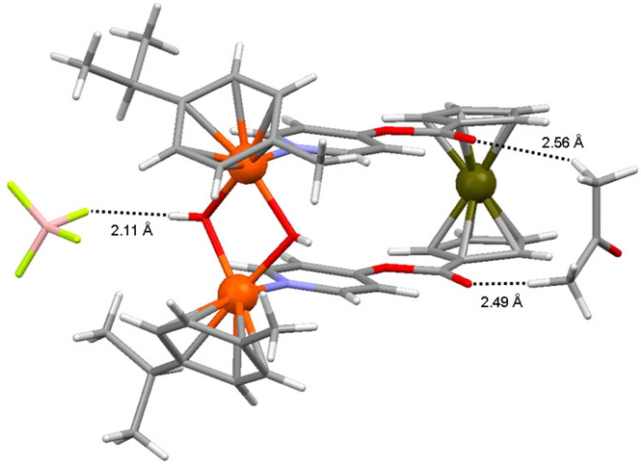

Fig. 3. Hydrogen bonded network in [**2**][$BF_4]_2 \cdot Me_2CO$.

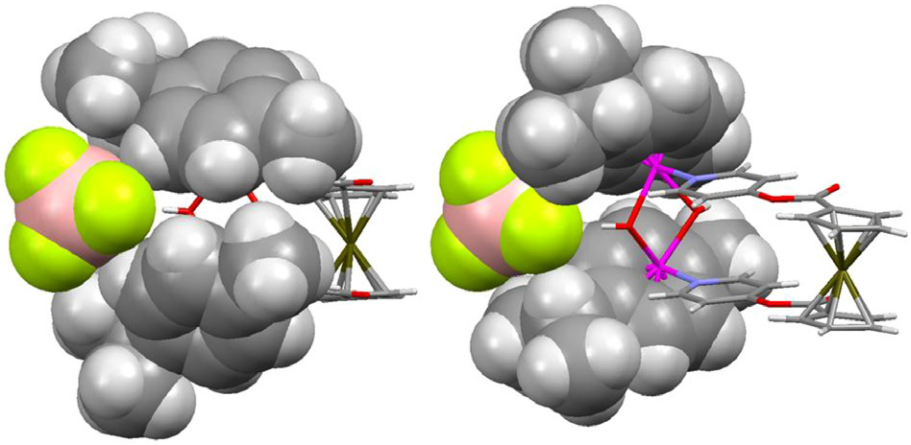

Fig. 4. Space filling representation of the BF_4 anion encapsulated in **2**.

tilted by as much as 81.87(8)°. The O–F distance of this hydrogen contact is 2.901(8) Å with an O–H···F angle of 176.8°. By contrast, the second hydroxo bridge is protected by the methyl groups preventing any possible intermolecular interactions.

Given these observations in the solid state of $[\mathbf{2}][BF_4]_2$, the question arises whether or not the carbonyl functions of the carboxylic groups adopt the same fixed positions also in solution. For this reason we undertook a variable-temperature NMR study of $[\mathbf{2}][BF_4]_2$. At room or low-temperature (from +30 to −30 °C), ^{1}H NMR spectra (Fig. 5) of $[\mathbf{2}][BF_4]_2$ in acetone-d_6 show no signals indicating the presence of diastereotopic atoms, suggesting a fast exchange on the NMR time-scale between the different orientations for the carbonyl functions. However, below −60 °C, the NMR signals start to split, this splitting becomes more distinct at lower temperature. Thus, at −90 °C the two distinct doublets of the pyridyl protons split into eight peaks, probably because the rotation around the O–C(O) bonds becomes restricted, giving rise to different orientations of the carbonyl functions with respect to each other (Fig. 6). It can also be observed that

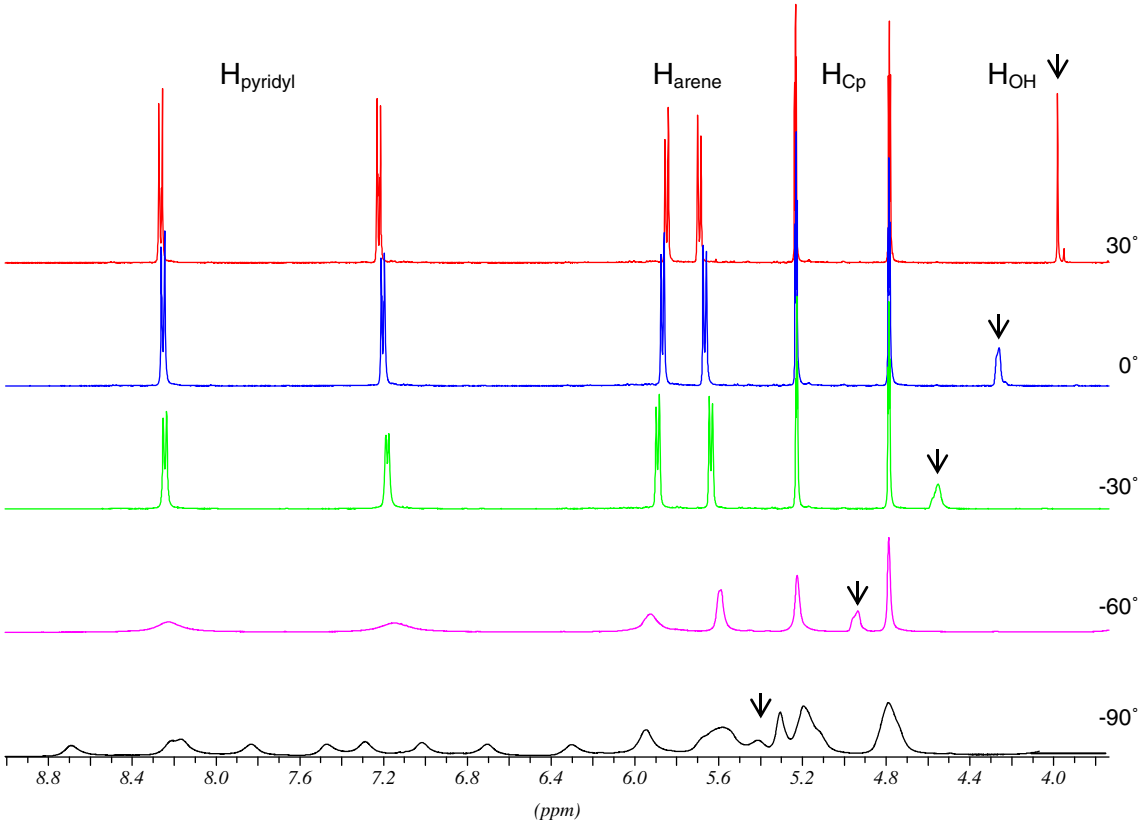

Fig. 5. ^{1}H NMR spectra of $[\mathbf{2}][BF_4]_2$ in acetone-d_6 at selected temperatures ($\downarrow = \delta_{OH}$).

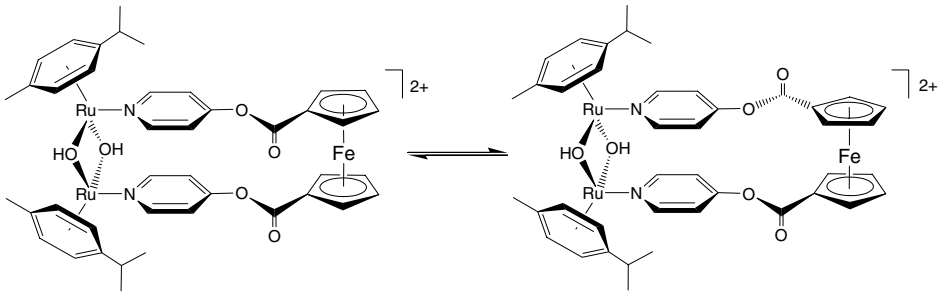

Fig. 6. Two possible "flip-flop" conformations of **2** below −60 °C.

the signal of the equivalent protons of the hydroxo bridges is shifted down-field by lowering of the temperature and moves from $\delta = 4.0$ ppm at +30 °C to $\delta = 5.4$ ppm at −90 °C.

Acknowledgements

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Appendix A. Supplementary material

CCDC 645078 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, fax: (+44) 1223-336-033, or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2007.07.014.

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[9] In a Schlenk tube, to a solution of 1,1′-ferrocene dicarbonyl chloride [8] (1.178 g, 3.43 mmol) in 30 ml of anhydrous and degassed dichloromethane, 4-hydroxypyridine (1.3 g, 13.7 mmol) and triethylamine (2 ml) were added. The mixture was stirred under nitrogen at room temperature during 6 h. The solution was then filtered and 1,1′-ferrocene dicarboxylic acid pyridin-4-yl ester (**1**) was obtained as a red crystalline powder after column chromatography using thf as eluent. Yield: 1.010 g, 62%. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 4.66$ (t, 4H, $J = 2$ Hz, C_5H_4), 5.07 (t, 4H, $J = 2$ Hz, C_5H_4), 7.20 (dd, 4H, $J = 4.8$ Hz, $J = 1.6$ Hz, NC_5H_4), 8.62 ppm (dd, 4H, $J = 4.8$ Hz, $J = 1.6$ Hz, NC_5H_4). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 71.80$, 72.88, 74.04, 117.46, 151.86, 157.84, 168.10. IR (CaF_2, CH_2Cl_2): $\nu_{(OCO)}$ 1741 (m) cm^{-1}. ESI-MS ($CH_3OH/CHCl_3$): $m/z = 429.05$ $[M+H]^+$.

[10] In a Schlenk tube, the salt $[(\eta^6\text{-}p\text{-cymene})_2Ru_2(\mu\text{-}OH)_3][BF_4]$ (250 mg, 0.41 mmol) was dissolved in 20 ml of acetone, then 1,1′-ferrocene dicarboxylic acid pyridin-4-yl ester (**1**) (176 mg, 0.41 mmol) was added to this solution. The mixture was stirred under nitrogen at room temperature for 5 h, after some hours the solution became cloudy. The mixture was filtrated and diethyl ether was added in order to precipitate an orange-red solid. Yield: 100 mg, 27%. ^{1}H NMR (400 MHz, $(CD_3)_2CO$): $\delta = 8.26$ (d, 4H, $J = 6.84$ Hz, H_{pyr}), 7.22 (d, 4H, $J = 6.84$ Hz, H_{pyr}), 5.84 (d, 4H, $J = 6.12$ Hz, C_6H_4), 5.68 (d, 4H, $J = 6.12$ Hz, C_6H_4), 5.23 (t, 4H, $J = 1.96$ Hz, C_5H_4), 4.78 (t, 4H, $J = 1.96$ Hz, C_5H_4), 4.01 (s, 2H, O*H*), 2.62 (sept, 2H, $J = 6.84$ Hz, $CH(CH_3)_2$), 2.53 (s, 6H, CH_3), 1.14 ppm (d, 12H, $J = 6.84$ Hz, $CH(CH_3)_2$). ^{13}C NMR (400 MHz, $(CD_3)_2CO$): $\delta = 205.38$, 166.05, 158.56, 153.77, 118.19, 101.07, 97.27, 80.92, 79.68, 73.75, 72.06, 30.13, 21.66, 17.43 ppm. IR (KBr): $\nu_{(OH)}$ 3486 (br), $\nu_{(OCO)}$1753 (s) cm^{-1}. ESI-MS positive mode (932.81): 467.3 $[M/2+H^+]$, 499.1 $[M/2+CH_3OH]$.

[11] Red crystals of **2** suitable for X-ray diffraction analysis were grown by slow evaporation of a concentrated solution of **2** in Me_2CO. *Crystal data for* $[\mathbf{2}][BF_4]_2 \cdot CH_3COCH_3$: $C_{45}H_{52}B_2F_8FeN_2O_7Ru_2$, monoclinic space group $C2/c$ (No. 15), cell parameters $a = 27.934(2)$, $b = 13.4573(7)$, $c = 27.208(2)$ Å, $\beta = 116.126(8)°$, $V = 9182.7(11)$ Å^3, $T = 173(2)$ K, $Z = 8$, $D_c = 1.685$ g cm^{-3}, $F(000)$ 4704, λ (Mo Kα) = 0.71073 Å, 8945 reflections measured, 6481 unique ($R_{int} = 0.0357$) which were used in all calculations. The structure was solved by direct method (SHELXS-97) and refined (SHELXL-97) by full-matrix least-

squares methods on F^2 with 620 parameters. Despite elongated ellipsoids of the oxygen atoms of the carbonyl groups due to disorder, these two oxygen atoms were refined normally. $R_1 = 0.0310$ ($I > 2\sigma(I)$) and $wR_2 = 0.0698$, GOF = 0.898; max./min. residual density 1.295/−1.211 e $Å^{-3}$.

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