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Syntheses and crystal structures of two new cationic 3,5-dimethylpyrazole derivatives containing organoiron mixed-sandwiches as substituent groups

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ABSTRACT

Organometallic hydrazines formulated as $[(\eta^5\text{-Cp})Fe(\eta^6\text{-}p\text{-}MeC_6H_4NHNH_2)]^+PF_6^-$, Cp = C_5H_5 ($[\mathbf{1}]^+PF_6^-$) and $[(\eta^5-Cp^*)Fe(\eta^6\text{-}C_6H_5NHNH_2)]^+PF_6^-$, $Cp^* = C_5Me_5$ ($[\mathbf{2}]^+PF_6^-$), react with 2,4-pentanedione in acetonitrile to afford 3,5-dimethylpyrazole derivatives $[\mathbf{3}]^+PF_6^-$ and $[\mathbf{4}]^+PF_6^-$, respectively, that contain the organoiron mixed-sandwich moieties. The new complexes have been fully characterized by elemental analysis and IR, UV–vis and ^1H and ^{13}C NMR spectroscopies and authenticated by single crystal X-ray diffraction analysis. Complexes $[\mathbf{3}]^+PF_6^-$ ($C_{17}H_{19}F_6FeN_2P$) and $[\mathbf{4}]^+PF_6^-$ ($C_{21}H_{27}F_6FeN_2P$) crystallize in the space group $P2_1/n$.

1. Introduction

The design and synthesis of new pyrazole derivatives have long been the focus of numerous biological and pharmacological studies. In particular, this important class of heterocyclic compounds have attracted considerable attention due to the broad range of biological activities they possess, including anti-microbial, anti-viral, anti-tumor, anti-inflammatory, anti-fungal, anti-hypertensive, anti-depressant, anti-diabetic, anti-cancer, hypoglycemix, and analgesic properties [1]. Nevertheless, in the search for new families of pyrazole derivatives, in the last few years new derivatives containing organometallic moieties such as the ferrocenyl substituent have been reported in the literature [2]. It is believed that the incorporation of this well known electron-donor group in the structures of these heterocyclic compounds could enhance their biological activities or generate new pharmacological properties which are absents or less manifest in their parent molecules [3]. In this context, and considering the high reactivity displayed by organometallic hydrazines formulated as $[CpFe(p\text{-}MeC_6H_4\text{-}NHNH_2)]^+PF_6^-$ [4], $[\mathbf{1}]^+PF_6^-$, and $[(C_5Me_5)Fe(C_6H_5\text{-}NHNH_2)]^+PF_6^-$ [5], $[\mathbf{2}]^+PF_6^-$, toward ketones and aldehydes [6], we have initiated a programme in order to synthesize new substituted heterocyclic compounds, as potential pharmaceuticals, containing the well known electron-acceptor mixed sandwiches $[CpFe(p-MeC_6H_{4^-})]^+$ and $[C_5Me_5Fe(C_6H_{5^-})]^+$. Likewise, the salt form of such structures could be an important factor in terms of biological activity considering its solubility in water. In this work we describe the synthesis of the substituted heterocyclic compounds $[\mathbf{3}]^+PF_6^-$ and $[\mathbf{4}]^+PF_6^-$ obtained by reaction of $[\mathbf{1}]^+PF_6^-$ and $[\mathbf{2}]^+PF_6^-$ with 2,4-pentanedione. These compounds have been fully characterized by IR, UV–vis and ^1H and ^{13}C NMR spectroscopy and authenticated by X-ray diffraction analysis.

2. Experimental

2.1. Materials and general procedures

All manipulations were carried out under a dinitrogen atmosphere using standard Schlenk techniques. Solvents were dried by common procedures and distilled under dinitrogen before use. Reagents were purchased from commercial sources and used as received. The organometallic hydrazines $[(\eta^5\text{-Cp})Fe(\eta^5\text{-}p\text{-}MeC_6H_4\text{-}NHNH_2)]^+PF_6^-$, $[\mathbf{1}]^+PF_6^-$, and $[(\eta^5\text{-Cp}^*)Fe(\eta^5\text{-}C_6H_5\text{-}NHNH_2)]^+PF_6^-$, $[\mathbf{2}]^+PF_6^-$, were synthesized according to procedures we have published elsewhere[4,5]. Elemental analyses were made by standard micromethods. IR spectra were obtained as KBr disks on a Perkin–Elmer Model 1600 FT-IR spectrophotometer, in the range of 4000–450 cm^{-1}. The electronic spectra were recorded in CH_2Cl_2 solutions with a Spectronic, Genesys 2, spectrophotometer. ^1H- and ^{13}C-NMR spectra were acquired at 297 K on a multinuclear Brucker AC 400 spectrometer in CD_3CN at 297 K. The NMR spectra

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are reported in ppm (δ) relative to tetramethylsilane, with the residual solvent proton resonances and carbon resonances used as internal standards. Coupling constants (*J*) are reported in Hertz (Hz), and integrations are reported as number of protons.

2.2. Preparation of complex $[\mathbf{3}]^+PF_6^-$

In a Schlenk tube a mixture of 503 mg (1.30 mmol) of the organometallic hydrazine $[\mathbf{1}]^+PF_6^-$ and 0.13 mL (1.30 mmol) of 2,4-pentanedione in 15 mL of dry MeCN was stirred under dinitrogen at room temperature for 15 h. The filtrated solution was layered with 15 mL of diethyl ether and allowed to stand at −30 °C. After three days a red-orange solid was deposited, filtered off and washed with diethyl ether. The solid was recrystallized from methanol by slow diffusion with diethyl ether. Suitable single crystals for X-ray diffraction studies were obtained during this recrystallization step. Standard work up provided 447 mg (Yield 76%), m.p. 201 °C (dec). $C_{17}H_{19}F_6FeN_2P$ (452.16 g mol^{-1}): Anal. calc. C, 45.16; H, 4.24; N, 6.20; Found C, 45.02; H, 4.16; N, 6.14%. UV–vis, λ_{max} (log ε) (CH_2Cl_2, 1.28 mM): = 257 (3.50), 290sh (2.60); 310sh (2.70); 395 (1.40). IR (KBr): ν(C–H) 3118 (vw), 3094 (vw), 2971 (vw), 2920 (vw), 2870 (vw); ν(C⋯N) and ν(C⋯N) 1567 (w), 1545 (w), 1497 (m); ν(PF_6) 832 (vs); δ(P–F) 557 (s). ^{1}H NMR (CD_3CN, 400.13 MHz): δ = 2.26 (s, 3H, C*H*$_3$-Pz), 2.38 (s, 3H, C*H*$_3$-Pz), 2.43 (s, 3H, C*H*$_3$, coord-Ph), 4.99 (s, 5H, C_5H_5), 6.28 (d, J_{H-H} = 6.8 Hz, 2H, coord-Ph), 6.65 (d, J_{H-H} = 6.8 Hz, 2H, coord-Ph). ^{13}C{^{1}H} NMR (CD_3CN, 100.61 MHz): δ = 12.84 (C-16), 13.66 (C-12), 20.27 (C-17), 79.18 (C-9), 79.20 (Cp), 82.31 (C-7 and C-11), 88.09 (C-8 and C-10), 103.3 (C_{ipso} C_6H_4), 110.4 (C-14), 143.20 (C-15), 152.5 (C-13).

2.3. Preparation of complex $[\mathbf{4}]^+PF_6^-$

Using the same Schlenk technique, a mixture of 110 mg (0.248 mmol) of the organometallic hydrazine $\mathbf{2}]^+PF_6^-$ and 26 μL (0.248 mmol) of 2,4-pentanedione in 5 mL of dry MeCN was refluxed for 2 h. The solution was cooled and layered with 5 mL of diethyl ether and allowed to stand at −30 °C. After 3 days a yellow-orange solid was deposited, which was filtered off and washed with diethyl ether. The solid was recrystallized from methanol by slow diffusion with diethyl ether. Suitable single crystals for X-ray diffraction studies were obtained during this recrystallization step. Standard work up provided 90 mg (Yield 71%), m. p. 238 °C (dec). $C_{21}H_{27}F_6FeN_2P$ (508.26 g mol^{-1}): Anal. calc. C, 49.62; H, 5.35; N, 5.51; Found C, 49.32; H, 5.28; N, 5.46%. UV–vis, λ_{max} (log ε) (CH_2Cl_2, 1.69 mM): = 259 (3.50); 309sh (2.40), 328sh (2.50), 394 (2.00). IR (KBr): ν(C–H) 3101(vw), 2964 (vw), 2920 (w), 2848 (vw); ν(C⋯N) and ν(C⋯N) 1570 (w), 1530 (m), 1480 (w); ν(PF_6) 851(s), 832 (vs); δ(P–F) 557 (s). ^{1}H NMR (CD_3CN, 400.13 MHz): δ = 1.77 (s, 15H, C_5Me_5); 2.28 (s, 3H, C*H*$_3$-Pz), 2.44 (s, 3H, C*H*$_3$-Pz), 5.76 (pseudo t, 1H, C_6H_5), 5.90 (t, J_{H-H} = 6.4 Hz, 2H, coord-Ph), 6.12 (s, 1H, C*H*-Pz), 6.27 (d, J_{H-H} = 6.8 Hz, 2H, coord-Ph). ^{13}C{^{1}H} NMR (CD_3CN, 100.61 MHz): 9.74 (C_5Me_5), 13.58 (C-16), 13.70 (C-12), 81.56 (C-7 and C-11), 89.26 (C-8 and C-10), 89.36 (C_{ipso} C_6H_5), 90.22 (C-9), 93.09 (C_5 Cp*), 111.0 (C-14), 143.2 (C-15), 152.4 (C-13).

2.4. X-ray analyses

Single crystals of complexes $[\mathbf{3}]^+PF_6^-$ and $\mathbf{4}]^+PF_6^-$, obtained as noted above, were mounted on the tip of a glass fiber in a random orientation. Intensity data were collected on a Bruker Smart Apex diffractometer equipped with a bidimensional CCD detector using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). Face indexing absorption correction was applied to complex $[\mathbf{3}]^+PF_6^-$ and semi-empirical corrections, via ψ-scans, were applied for absorption on $[\mathbf{4}]^+PF_6^-$. The diffraction frames were integrated using the SAINT package [7], and corrected for absorption with XPREP in SHELXTL-PC [8] and SADABS [9] The structures were solved using XS in SHELXTL-PC [8] by direct methods and completed (non-H atoms) by difference Fourier techniques. Refinement was performed by the full-matrix least-squares method based on F^2. All non-hydrogen atoms were anisotropically refined. Hydrogen atoms were placed in their calculated positions, assigning them fixed isotropic thermal parameters and allowed to ride on their respective parent atoms. A summary of the data collections and structure refinement parameters is given in Table 1. ORTEP's plots of complexes $[\mathbf{3}]^+PF_6^-$ and $[\mathbf{3}]^+PF_6^-$ with displacement ellipsoids at the 30% probability level (Figs. 1 and 2, respectively) were generated with XP in SHELXTL-PC [8].

Table 1
Crystallographic data for complexes $[\mathbf{3}]^+PF_6^-$ and $[\mathbf{4}]^+PF_6^-$.

	Complex **3**	Complex **4**
Empirical formula	$C_{17}H_{19}F_6FeN_2P$	$C_{21}H_{27}F_6FeN_2P$
Formula mass (g mol^{-1})	452.16	508.27
Collection *T* (K)	150(2) K	298(2) K
Crystal system	Monoclinic	Monoclinic
Space group	*P*2(1)/*n*	*P*2(1)/*n*
a (Å)	10.2368(5)	8.3004(6)
b (Å)	15.2113(8)	13.6098(10)
c (Å)	11.5618(6)	20.1712(15)
ß (°)	95.7560(10)	91.657(2)
V (Å^3)	1791.27(16)	2277.7(3)
Z	4	4
D_{calcd} (g cm^{-3})	1.677	1.482
Crystal size (mm^3)	0.3 × 0.2 × 0.06	0.32 × 0.13 × 0.10
F(000)	920	1048
Absorption coefficient (mm^{-1})	0.995	0.791
θ range (°)	2.22–27.87	1.81–28.43
Range *h*,*k*,*l*	$-13 \le h \le 13$, $-18 \le k \le 19$, $-15 \le l \le 15$	$-11 \le h \le 11$, $-18 \le k \le 18$, $-27 \le l \le 26$
No. independent reflections	18908	19949
No. unique reflections (>2)	4033 [$R_{(int)}$ = 0.0598]	5706 [$R_{(int)}$ = 0.0940]
Data/restraints/parameters	4033/0/247	5706/0/287
Final *R* indices [I > 2sigma(*I*)]	R_1 = 0.0497, wR_2 = 0.1081	R_1 = 0.0675, wR_2 = 0.1611
R indices (all data)	R_1 = 0.0777, wR_2 = 0.1208	R_1 = 0.1586, wR_2 = 0.2010
Goodness of fit/F^2	1.021	0.817
Largest diffraction peak and hole (e A^{-3})	0.566 and −0.261	0.715 and −0.325 e Å^{-3}

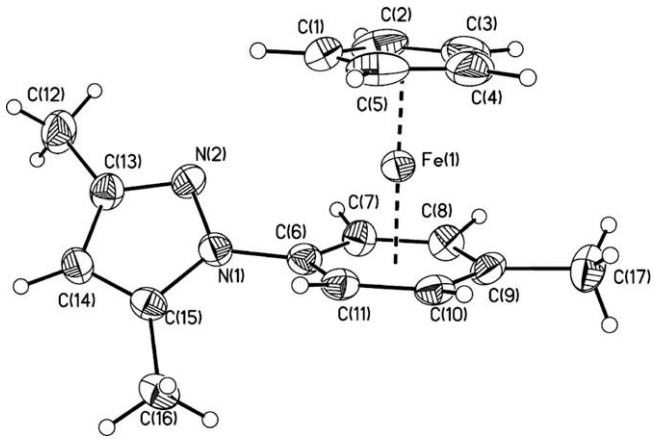

Fig. 1. ORTEP view of complex $[\mathbf{3}]^+$ with an atom-numbering scheme. Displacement-ellipsoids are drawn at the 30% probability.

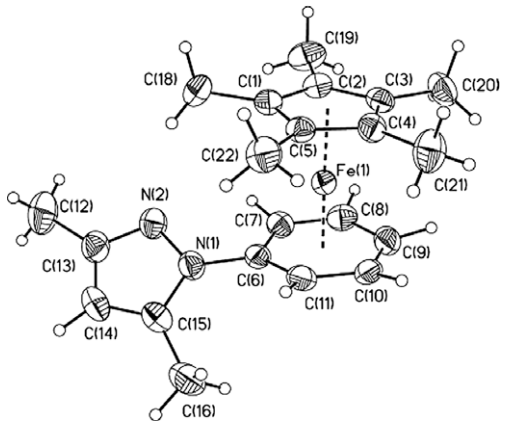

Fig. 2. ORTEP view of complex $[\mathbf{4}]^+$ with an atom-numbering scheme. Displacement-ellipsoids are drawn at the 30% probability.

3. Results and discussion

3.1. Synthesis and spectroscopic characterization

The 3,5-dimethylpyrazole complexes $[\mathbf{3}]^+PF_6^-$ and $[\mathbf{3}]^+PF_6^-$ were synthesized by an one-pot cyclocondensation reaction, similar to that described by Krishnaiah et al. [10] using, in the present case, the organometallic hydrazines $[\mathbf{1}]^+PF_6^-$[4] and $[\mathbf{2}]^+PF_6^-$[5] with 2,4-pentanedione in dry MeCN under dinitrogen. Complexes $[\mathbf{3}]^+PF_6^-$ and $[\mathbf{4}]^+PF_6^-$ were isolated as red-orange and yellow-orange crystalline solids in 76% and 71% yields, respectively. The complexes exhibit a good solubility in polar solvents such as MeCN, MeOH, CH_2Cl_2, Me_2CO, DMSO and water but they are slightly soluble in non-polar solvents such as hexane, pentane and diethyl ether, and were fully characterized by IR, UV–vis and ^1H and ^{13}C NMR spectroscopies. Additionally, the crystal and molecular structures of these complexes were solved by single crystal X-ray diffraction analysis.

The solid IR spectra of complexes $[\mathbf{3}]^+PF_6^-$ and $[\mathbf{4}]^+PF_6^-$ exhibit similar features indicating analogous molecular structures. One of the very weak (C–H) stretching absorption bands observed in complex $[\mathbf{3}]^+PF_6^-$ at 2920 cm^{-1} and attributed to the methyl groups, becomes ostensibly more intense in complex $[\mathbf{4}]^+PF_6^-$ due to the presence of the η^5-$[C_5Me_5]^-$ ligand. On the other hand, the absorption bands observed in the 1570–1480 cm^{-1} range can be attributed to the ν(C···N) and/or ν(C···N) stretching vibrations in the Pz, Ph, Cp and Cp* moieties. Finally, the typical strong bands observed at 832 and 558 cm^{-1}, attributed to the $\nu(PF_6)$ and (P–F) modes, indicate the presence of the counterion PF_6^-. On the other hand, the UV–vis spectra of both organometallic pyrazole derivatives exhibit, in CH_2Cl_2, similar features according with their analogous molecular structures. The spectra of the complexes recorded in CH_2Cl_2 present a prominent band at *ca.* 260 nm and two overlapped absorption bands corresponding to intraligand CT excitations. At longer wavelength both compounds exhibit at ca. 395 nm a very broad low-intensity MLCT band. The broadening of this low-energy band is probably the result of the overlap of broad d-d visible bands of the $[Cp'Fe(\eta^6\text{-arene})]^+$ fragments, Cp′ = Cp, Cp* [11].

3.2. Structural results

Complete details of the crystal, X-ray data collection and structure solution are provided as Supporting Information. Selected bond distances and angles are listed in Table 2. For the sake of comparison, ORTEP drawings of the two cationic organometallic pyrazole derivatives, $[\mathbf{3}]^+$ and $[\mathbf{4}]^+$, with the atom-labeling schemes, are presented in similar perspectives in Figs. 1 and 2. In general, these molecular parameters are rather similar, however, the most striking difference between complexes $[\mathbf{3}]^+$ and $[\mathbf{4}]^+$, in solid state, lies in their molecular conformations. In fact, the pyrazole and the phenyl rings of the iron mixed-sandwiches are individually planar but they are twisted about the N(1)–C(6) bonds being 38.3(4) and 25.3(7)° their respective dihedral angles (see Table 2). These dihedral angles suggest that the pyrazole group is not involved in the conjugation of the phenyl ring and, consequently, is not affected by the electronic effects of the $CpFe^+$ and Cp^*Fe^+ moieties. The bond distances and angles observed in the pyrazole groups of both complexes support this hypothesis (see Table 2). On the other hand, in both complexes the hybridization of N(1) and C(6) atoms is sp^2 but the bond distances N(1)-C(6) = 1.409(4) and 1.405(6) Å, respectively, indicate clearly the presence of a single bond which allows, in solution, the unrestrained rotation. Finally, no hydrogen bonds are observed in the crystalline packing of both structures. However, some C–H···F weak interactions are observed helping to the arrangement between the organometallic and the hexafluorophosphate ions in the crystal packing [12]. These weak interactions are summarized in Tables 3 and 4.

Table 2
Selected bond distances (Å) and angles (°) for complexes $[\mathbf{3}]^+PF_6^-$ and $[\mathbf{4}]^+PF_6^-$.

Bond distances	Complex $[\mathbf{3}]^+PF_6^-$	Complex $[\mathbf{4}]^+PF_6^-$
Fe(1)–C(1–5)	2.038[a]	2.066[a]
Fe(1)–C(6–11)	2.082[a]	2.091[a]
C(6)–N(1)	1.409(4)	1.405(6)
N(1)–N(2)	1.375(3)	1.367(5)
N(2)–C(13)	1.322(4)	1.327(6)
C(13)–C(14)	1.406(4)	1.366(7)
C(14)–C(15)	1.369(4)	1.336(7)
C(15)–N(1)	1.368(4)	1.376(6)
C(13)–C(12)	1.501(4)	1.484(8)
C(15)–C(16)	1.485(4)	1.495(8)
Fe(1)–Cp_{CNT}[b]	1.671	–
Fe(1)–Cp^*_{CNT}	–	1.657
Fe(1)–Ph_{CNT}[b]	1.556	1.536
Bond and torsion angles		
C(7–C(6)–N(1)	120.5(3)	120.1(5)
C(6–N(1)–N(2)	118.8(2)	118.5(4)
C(11)–C(6)–N(1)	120.1(3)	120.4(5)
C(6)–N(1)–C(15)	128.8(3)	129.8(5)
C(7–C(6)–N(1)–N(2)	−38.3(4)[c]	−25.3(7)[c]
C(11)-C(6)-N(1–N(2) Cp_{CNT}–Fe(1)–Ph_{CNT}	135.8(3)[c]	150.9(5)[c]
Cp^*_{CNT}–Fe(1)–Ph_{CNT}	178.4	–

[a] Average.
[b] Abbreviations: Cp = C_5H_5, Cp* = C_5Me_5, Ph = C_6H_4 or C_6H_5. CNT = centroid.
[c] Dihedral angle.

Table 3
C–H···F weak interactions for $[\mathbf{3}]^{+}PF_6^{-}$.

Donor–H···acceptor	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
C(2)–H(2)···F(4)[a]	0.98	2.37	3.2491	149
C(8)–H(8)···F(6)[a]	0.98	2.48	3.2481	135
C(10)–H(10)···F(2)	0.98	2.47	3.4432	174
C(10)–H(10)···F(3)	0.98	2.45	3.1128	124
C(11)–H(11)···F(3)	0.98	2.53	3.1390	120

Symmetry transformations used to generate equivalent atoms.
[a] 1 + *x*, *y*, *z*

Table 4
C–H···F weak interactions for $[\mathbf{4}]^{+}PF_6^{-}$.

Donor–H···acceptor	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
C(9)–H(9)···F(2)[a]	0.98	2.50	3.3720	147
C(21)–H(21B)···F(4)[a]	0.96	2.35	3.2772	162

Symmetry transformations used to generate equivalent atoms.
[a] 1/2 − *x*,−1/2 + *y*, 1/2 − z.

4. Concluding remarks

To sum up, as a result of our studies we have successfully prepared and characterized by spectroscopic methods and by single crystal X-ray diffraction analysis the new functionalized pyrazole derivatives $\mathbf{3}]^{+}PF_6^{-}$ and $[\mathbf{3}]^{+}PF_6^{-}$. These compounds, synthesized by a straightforward 1:1 condensation of 2,4-pentanedione and the corresponding organometallic hydrazines, contain mixed-sandwich moieties, $[(\eta^5\text{-Cp})Fe(\eta^5\text{-}p\text{-}MeC_6H_4)]-$ and $[(\eta^5\text{-Cp}^*)Fe(\eta^5\text{-}C_6H_5)]-$ as substituent groups whose electron-acceptor influences on the pharmacological properties of the pyrazole rings could be compared with that exhibited by the ferrocenyl moiety. In both cases these 3,5-dimethylpyrazole derivatives have been isolated as single products.

5. Supplementary data

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-697105 for compound $[\mathbf{3}]^{+}PF_6^{-}$ and no. CCDC-697106 for compound $[\mathbf{4}]^{+}PF_6^{-}$. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336- 033; e-mail: deposit@ ccdc.cam.ac.uk).

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