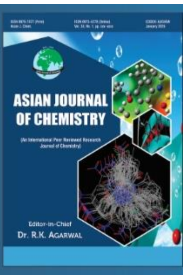
Asian Journal of Chemistry; Vol. 38, No. 1 (2026), 243-248

ASIAN JOURNAL OF CHEMISTRY

https://doi.org/10.14233/ajchem.2026.35243



Cationic Iron Half-Sandwich Complexes of Aminopyridines: Synthesis and Characterisation

KINGSLEY MICHIEKA*, EVANS CHANGAMU and KATANA CHENGO

Department of Chemistry, Kenyatta University, Nairobi, Kenya

*Corresponding author: Tel: +254 759685564; E-mail: 20873.2020@students.ku.ac.ke; chemistry@ku.ac.ke

Received: 12 November 2025 *Accepted*: 19 December 2025 *Published online*: 31 December 2025 AJC-22244

The reaction of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^+$, with the aminopyridine ligands lead to formation of cationic organometallic complexes of the general formula $[(\eta^5\text{-}C_5H_5)Fe(CO)_2L]^+$ (where L = 2-Apy, 3-Apy, 4-Apy and Apy = aminopyridine). These ligands have the ability to coordinate to a metal center in monodentate fashion *via* the pyridine ring or amine nitrogen atoms, can form chelate complexes with one metal center or bridge two metal ions. Spectroscopic data (FTIR, ^1H and ^{13}C NMR and elemental analysis) collected for the five metal complexes is consistent with monodenate coordination mode through the pyridyl nitrogen in complexes **2**, **3** and **4** atoms and amine nitrogen in complexes **1** and **4**.

Keywords: Iron complexes, Half-sandwich, Aminopyridines, Synthesis.

INTRODUCTION

Among the N-containing ligands, aminopyridine (Apy) has drawn attention because of their potentially ambidentate nature and pharmacological properties [1-7]. They have also demonstrated remarkable electronic and steric tunability, characterised by σ-donor and π-acceptor abilities [8,9]. These ligands bind to metal ions and organometallic fragments in a variety of coordinating modes such as monodentate as well as bidentate ligands [10-17].

Metal complexes derived from aminopyridine (Apy) ligands have attracted considerable attention due to their versatile coordination behaviour and broad applicability in catalysis and medicinal chemistry [10-24]. Notably, chiral manganese complexes such as $[Mn(2,6\text{-}Me_2Ap)_2]$ have been reported as efficient oxidation catalysts, capable of activating inert aliphatic C–H bonds. In the presence of hydrogen peroxide, these systems selectively oxidize substrates like cyclohexane and cumene to afford the corresponding alcohols, cyclohexanol and 2-phenyl-2-propanol, as well as ketonic products including cyclohexanone and acetophenone [22]. Similarly, titanium based aminopyridine complexes, *e.g.* $[Ti(2,6\text{-}Me_2Ap)Cl_2]$, have demonstrated promising performance in olefin polymerisation processes. These complexes effectively catalyse the polymerisation of ethylene and styrene, yielding polyethylene and polystyrene, respectively, highlighting their potential in polymer chemistry [23]. In addition to the catalytic applications, Apy-containing metal complexes have shown noteworthy biological activity. The tetranuclear silver complex $[Ag_4(3\text{-aminopyridine})_4(NO_3)_4]$ has exhibited pronounced antibacterial effects against *Escherichia coli* and *Shigella sonnei* [21]. Furthermore, cobalt(II) complexes incorporating 2-aminopyridine ligands, such as *bis*(2-aminopyridine)-μ-*bis*(dicyanamido)cobaltate(II), have demonstrated antimicrobial efficacy against *Candida albicans*, *Salmonella typhi* and *Escherichia coli* [24]. These findings collectively underscore the structural versatility and functional relevance of aminopyridine-based metal complexes across catalytic and biological domains.

Till now, there has been little exploration on Apy as ligands in half-sandwich organometallic compounds, in which it acts as either a monodentate ligand or a bridging ligand. Reports of half-sandwich organometallic complexes incorporating Apy include; $[(\eta^5\text{-}C_5H_5)Ru(L)(CH_3CN)_2]PF_6$ (where L = 2-Apy) [18], $[(p\text{-cymene})RuCl_2L]$: (L = 2-aminopyridine and 4-aminopyridine) [19] and $[Ru(\eta^6\text{-arene})LCl]^+$ (L = 2-Apy) [20], $[Cp^*MCl_2(L)]$ (where M = Rh, Ir and L= 2-Apy) [11]. Given the well-established nature of half-sandwich complexes especially those of cyclopentadienyliron dicarbonyl [25-29], it is rather unexpected that compounds featuring simple Lewis's acid, $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^+$ with Apy ligands remain unknown. In the present contribution, we report synthesis of cationic

---

iron half-sandwich organometallic complexes of the form, $[(\eta^5\text{-}C_5H_5)(CO)_2FeL]^+$, (L= 2-Apy, 3-Apy and 4-Apy).

EXPERIMENTAL

All reactions and handling procedures were performed under a nitrogen atmosphere using Schlenk line methodology. All solvents used were dried using standard methods. Starting materials were procured from Sigma Aldrich and used without further purification. Starting material $[(\eta^5\text{-}C_5H_5)Fe(CO)_2I]$ was prepared following the method described in the literature [30]. Solid state IR spectra were recorded on a Shimadzu IR Tracer-100 spectrophotometer in the range of 4000 and 400 cm^{-1}. Elemental analyses were performed using server 112 series elemental analyser. ^1H and ^{13}C spectra were recorded on Bruker topspin 400 and 600 MHz spectrometers at probe temperature using commercially available deuterated solvents. ^1H and ^{13}C NMR chemical shifts were recorded in parts per million (ppm) downfield from internal standard Me_4Si.

Complex 1: A solution of $[\eta^5\text{-}C_5H_5)Fe(CO)_2I]$, (1.00 g, 3.290 mmol) in CH_2Cl_2 (15 mL) and $AgNO_3$ (0. 6285 g, 3.700 mmol) in a Schlenk tube was refluxed under inert atmosphere for 1.5 h. The resultant mixture was cooled to room temperature and filtered through a canula. 2-Aminopyridine (0.3106 g, 3.300 mmol) was added to the filtrate and the mixture refluxed for 6 h. A brown solution was formed. The solvent was removed at reduced pressure to yield 0.82 g (82%) of a brown solid. IR (solid state): $\nu_{as}(NH_2)$ 3339 cm^{-1} and $\nu_s(NH_2)$ 3183 cm^{-1}, $\nu_{as}(C{\equiv}O)$ 2033 cm^{-1} and $\nu_s(C{\equiv}O)$ 1986 cm^{-1}, $\nu_{as}(NO_3)$ 1380 cm^{-1}, ring breath 989 cm^{-1} and $\nu(C{=}N)$ 1600 cm^{-1}. Elemental analysis calcd. (found) %: C, 43.30 (43.20); H, 3.30 (3.20), N, 12.60 (12.40).

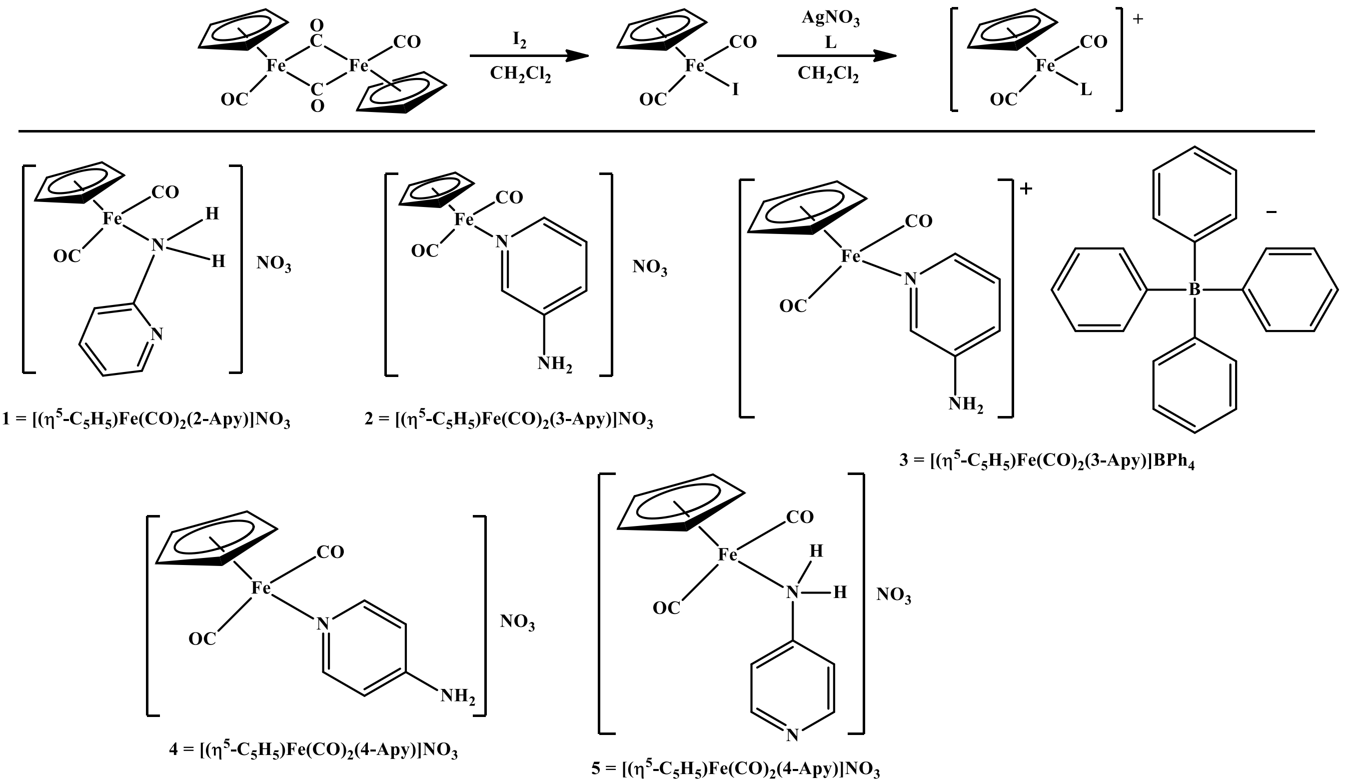
Complexes 2 and 3: Complex **2** was obtained by following the same reaction procedure as described above for 2-aminopyridine with the following quantities of the reagents: $[\eta^5\text{-}C_5H_5)Fe(CO)_2I]$ (1.00 g, 3.290 mmol), $AgNO_3$ (0. 6285 g, 3.700 mmol) and 3-aminopyridine (0.3106 g, 3.300 mmol). A dark brown solid (complex **2**) was obtained, 0.86 g (86%). Solution of complex **2**, (1 g, 3.00 mmol) and 1 g (2.922 mmol) of sodium tetra-phenylborate in in CH_2Cl_2 (15 mL) refluxed for 1 h. The mixture was allowed to cool to room temperature; diethyl ether was added and the mixture allowed to stand for 20 min when a yellow precipitate formed. Mixture filtered *via* canula and precipitate washed with portions of diethyl ether to obtain 0.7 g (70% yield) of yellow solid complex **3**. IR (solid state) of complex **2**: $\nu_{as}(NH_2)$ 3461 cm^{-1} and $\nu_s(NH_2)$ 3369 cm^{-1}, $\nu_{as}(C{\equiv}O)$ 2057 cm^{-1} and $\nu_s(C{\equiv}O)$ 2007 cm^{-1}, $\nu_{as}(NO_3)$ 1320 cm^{-1}, ring breath 1028 cm^{-1} and $\nu(C{=}N)$ 1597 cm^{-1}; ^1H NMR (62.73 MHz, $(CD_3)_2SO$, δ ppm): 4.33 (s, br, $5H_{cp}$), 5.35 (s, br, $2H_e$), 6.99 (d, H_d), 7.49 (d, H_c), 7.84 (d, H_b), 8.20 (d, H_a); ^{13}C NMR (400 MHz, $(CD_3)_2SO$, δ ppm): 210 (CO); 148 (C1); 129 (C2); 128 (C3); 127 (C4); 126 (C5); 88 ($\eta^5\text{-}C_5H_5$). Elemental analysis calcd. (found) %: C, 43.3 (43.0); H, 3.3 (3.4); N, 12.6 (12.1); IR (solid state) of complex **3**: $\nu_{as}(NH_2)$ 3461 cm^{-1} and $\nu_s(NH_2)$ 3421 cm^{-1}, $\nu_{as}(C{\equiv}O)$ 2043 cm^{-1} and $\nu_s(C{\equiv}O)$ 1992 cm^{-1}, i.p.s Ph ν(C-C) 1479, 1426 cm^{-1}, ring breath 1026 cm^{-1} and $\nu(C{=}N)$ 1600 cm^{-1}. Elemental analysis calcd. (found) %: C, 73.2 (73.5); H, 5.2 (5.1); N, 4.7 (4.4).

Complexes 4 and 5: The reaction was carried out through a procedure analogous to that described above for $[(\eta^5\text{-}(C_5H_5)\text{-}Fe(CO)_2(2\text{-}Apy)]NO_3$ (**1**) with the following quantities of reagents: $[(\eta^5\text{-}C_5H_5)Fe(CO)_2I]$ (1.00 g, 3.290 mmol), $AgNO_3$ (0.6285 g, 3.700 mmol) and 4-aminopyridine (0.3106 g, 3.300 mmol). Upon cooling the reaction mixture to room temperature, a brown solid precipitated, which was collected by filtration to afford a brown residue and a yellow filtrate. The residue was washed with several portions of DCM and dried to give 0.53 g of a brown solid-complex **4**. The solvent was removed from filtrate at reduced pressure to obtain 0.28 g of a yellow residue complex **5**. IR (solid state) complex **3**: $\nu_{as}(NH_2)$ 3388 cm^{-1} and $\nu_s(NH_2)$ 3216 cm^{-1}, $\nu_{as}(C{\equiv}O)$ 2047 cm^{-1} and $\nu_s(C{\equiv}O)$ 1989 cm^{-1}, $\nu_{as}(NO_3)$ 1326 cm^{-1}, ring breath 1018 cm^{-1} and $\nu(C{=}N)$ 1620 cm^{-1}. Complex **4**: $\nu_{as}(NH_2)$ 3343 cm^{-1} and $\nu_s(NH_2)$ 3216 cm^{-1}, $\nu_{as}(C{\equiv}O)$ 2058 cm^{-1} and $\nu_s(C{\equiv}O)$ 2007 cm^{-1}, $\nu_{as}(NO_3)$ 1336 cm^{-1}, ring breath 993 cm^{-1} and $\nu(C{=}N)$ 1601 cm^{-1}; ^1H NMR (62.73 MHz, $(CD_3)_2SO$, δ ppm): 5.38 (s, $5H_{cp}$), 6.41 (s, br, $2H_c$), 6.70 (d, $2H_b$), 7.78 (d, $2H_a$); ^{13}C NMR (400 MHz, $(CD_3)_2SO$, δ ppm): 212(CO); 157 (C1); 140 (C2); 109; 88 ($\eta^5\text{-}C_5H_5$); Elemental analysis calcd. (found) %: C, 43.3 (43.2); H, 3.3 (3.1); N, 12.6 (12.2). For complex **5**: ^1H NMR (62.73 MHz $(CD_3)_2SO$, δ ppm): 5.27 (s, br, $5H_{cp}$), 6.73 (s, br, $2H_c$), 6.81 (d, $2H_b$), 7.89 (d, 2Ha); ^{13}C NMR (400 MHz, $(CD_3)_2SO$, δ ppm): 212 (CO); 160 (C1); 156 (C2); 112; 88 ($\eta^5\text{-}C_5H_5$); Elemental analysis calcd. (found) %: C, 43.3 (43.3); H, 3.3 (3.3); N, 12.6 (12.5).

RESULTS AND DISCUSSION

The novel cationic iron half-sandwich complexes of Apy have been synthesised from the reaction of $[\eta^5\text{-}C_5H_5Fe(CO)_2]^+$ with 1:1 molar equivalent of aminopyridine ligands in dichloromethane (**Scheme-I**). These complexes were isolated in good yields. The synthesized complexes were obtained as yellow to brown solids and exhibited stability under ambient atmospheric conditions. Complexes **1**, **2**, **3** and **5** are soluble in DMSO, DCM, acetone, acetonitrile and chloroform. In contrast, complex **4** is readily soluble in DMSO and sparingly soluble in DCM, acetone, acetonitrile and chloroform. All these complexes were characterised by FT-IR, ^1H & ^{13}C NMR spectroscopy and elemental analysis. Our efforts to obtain the crystals by exchanging the nitrate counter ion with bulky tetraphenyl borate counter ion was unsuccessful (yielded yellow powder upon precipitation by diethyl ether).

Spectral studies: In the solid state, the FT-IR spectral data (Table-1) show the expected absorptions corresponding to the Apy ligands, in addition to distinct bands arising from the cyclopentadienyl and carbonyl moieties, which serve as diagnostic features. Bands characteristic of the cyclopentadienyl ligand in all the complexes observed in the range 3112 -3095 cm^{-1}. This observation agrees with a previous published study by Phiri [25], who found cyclopentadienyl C-H stretching frequency within the same range. Two terminal carbonyls on the iron center were evident in all the complexes by the presence of two very strong bands in the range 2058-1976 cm^{-1}. This is consistent with spectral data reported for cationic iron half sandwich complexes [26,27]. The presence



1 = $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(2\text{-}Apy)]NO_3$ **2** = $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(3\text{-}Apy)]NO_3$ **3** = $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(3\text{-}Apy)]BPh_4$ **4** = $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(4\text{-}Apy)]NO_3$ **5** = $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(4\text{-}Apy)]NO_3$

Scheme-I: Synthesis of cationic iron half-sandwich complexes of aminopyridines $[(\eta^5\text{-}C_5H_5)Fe(CO)_2L]^+$

TABLE-1
FT-IR SPECTRA DATA (cm^{-1})

Band assignment	Complexes									
	1	Δ	**2**	Δ	**3**	Δ	**4**	Δ	**5**	Δ
Cp ν(C–H)	3110		3102		3095		3095		3112	
ν_{as}(CO)	2033		2057		2043		2047		2058	
ν_s(CO)	1986		2007		1992		1989		2008	
δ(NH_2)	1668	+45	1633	+6	1620	-7	1651	+5	1652	+7
ν_s(NH_2)	3183	-100	3369	+68	3421	+120	3216	-84	3216	-84
ν_{as}(NH_2)	3339	-104	3461	+88	3461	+88	3388	-96	3343	-90
ν(C=N)	1600	+5	1597	+12	1600	+15	1620	+22	1601	+3
Ring breath	989	+4	1028	+14	1026	+12	1018	+30	993	+5
ν_{as}(NO_3)	1380		1320		–		1326		1336	
i.p.s Ph ν(C-C)	–		–		1479, 1426		–		–	

ν = stretching, δ = scissoring, as = asymemetric and s = symmetric, Cp = cyclopentadienyl, i.p.s Ph = in-plane skeletal C-C stretching modes of the phenyl ring in BPh_4, Δ = differences between the wavenumbers of the coordinated and free aminopyridine. Coordination sensitive wavenumbers are marked as bold. **1** = $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(2\text{-}Apy)]NO_3$, **2** = $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(3\text{-}Apy)]NO_3$, **3** = $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(3\text{-}Apy)]BPh_4$, **4** = $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(4\text{-}Apy)]NO_3$ (A), **5** = $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(4\text{-}Apy)]NO_3$ (B).

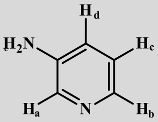
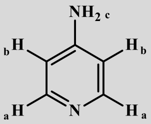
of nitrate counter ion, was confirmed by observation of a bands in range at 1380-1320 cm^{-1} assignable for $\nu_{as}(NO_3)$, which agrees with reports by Sall *et al.* [31] and Mihaylov *et al.* [32]. The BPh_4 counter ion was also confirmed present in complex **3** by observation of bands at 1479 cm^{-1} and 1446 cm^{-1} assignable to the in-plane skeletal C-C stretching modes of the phenyl ring in BPh_4 [33]. The bands at 3339 and 3183 cm^{-1} (**1**), 3461 and 3369 cm^{-1} (**2**), 3461 and 3421 cm^{-1} (**3**), 3337 cm^{-1} and 3214 cm^{-1} (**4**) and 3343 and 3216 cm^{-1} (**5**) are assignable to asymmetric and symmetric N–H stretching modes of the amino group. The data is consistent with those reported by M'thiruaine *et al.* [27]. The absorption band at 1600 cm^{-1} and 989 cm^{-1} (**1**), 1597 cm^{-1} and 1028 cm^{-1} (**2**), 1600 cm^{-1} and 1026 cm^{-1} (**3**), 1620 cm^{-1} and 1018 cm^{-1} (**4**), 1601 cm^{-1} and 993 cm^{-1} (**5**) were assigned to the C=N stretch and the ring breathing mode of the pyridine ring which is in agreement with research by Yenikaya *et al.* [34] and Büyükmurat *et al.* [35].

Relative to the free ligand the N–H stretching frequencies ($\nu_s(NH_2)$, $\nu_{as}(NH_2)$) of the coordinated 2-aminopyridine and 4-aminopyridine are shifted to lower wavenumbers by 104 and 100 cm^{-1} (**1**), -86 and -96 cm^{-1} (**4**) and -84 and -90 cm^{-1} (**5**), respectively, suggesting that the nitrogen of amino group ($-NH_2$) is involved in coordination to the organometallic fragment [26-28] or loss of intramolecular hydrogen bonding Gokhale *et al.* [36]. Upon coordination, the N–H bond is weakened and the N–H stretching frequencies are lowered. The stronger the metal-nitrogen bond, the weaker is the N–H bond and the lower are the nitrogen-hydrogen stretching frequencies [37]. Further, a blue shift of N–H scissoring wavenumbers by ≈ 45 cm^{-1} upon coordination of 2-Apy in complex **1** indicate that amino group maybe involved in coordination to organometallic fragment [28]. On the other hand, C=N stretch and ring breath vibration modes are very sensitive to coordination of the pyridine ring from the endocyclic nitrogen lone pair of electrons. If coordination takes place through the ring nitrogen lone pair of electrons increase in wave number is expected [17,38,39]. Slight blue shift of 5 and 4 cm^{-1} (**1**), of 3 cm^{-1} and 5 cm^{-1} (**5**), respectively indicates that the pyridine ring nitrogen is not directly involved in coordination whereas blue shifts by 12 and 14 cm^{-1} (**2**), 12 cm^{-1} and 15 cm^{-1} (**3**), 22 and 30 cm^{-1} (**4**), respectively the C=N stretch ring breathing vibration frequencies of the coordinated ligand relative to the free ligand indicates that the ring nitrogen was involved in coordination [17,20,39].

The chemical shift at δ 5.35 ppm (**2**), 5.38 ppm (**4**) and 5.27 ppm (**5**) were assigned to five equivalent cyclopentadienyl ring protons, which agrees with literature [27,40]. The chemical shift at δ 4.33 ppm (**2**), 6.41 ppm (**4**) and 6.73 ppm (**5**) were assigned to amino group protons. The chemical shifts for the pyridine protons were observed at δ 6.99-8.20 ppm [38] in complex **2**. The doublets at δ 7.78 and 6.70 ppm in complex **4** and δ 7.89 and 6.81 ppm in complex **5** are assigned to the *ortho*- and *meta*-pyridine ring protons, respectively, in agreement with what has been reported in the literature [41]. In complexes **2** and **4** the *ortho*-protons were generally shielded relative to the *meta*-protons. When nitrogen of the pyridine ring system is involved in coordination, the *ortho*-protons are shielded while *meta*-protons are deshielded [42]. Thus, these results indicate that the nitrogen of the ring system was involved in coordination to the metal centre. Further, the chemical shifts observed for the pyridine ring protons in complexes **2** and **4** are very close to those of the free ligand revealing that the deshielding expected upon σ-coordination of 3-aminopyridine and 4-aminopyridine is compensated for by the shielding due to π-back electronic flow to the coordinated 3-aminopyridine molecule. This agrees with literature reports by Dhaveethu *et al.* [38] and Côrte-Real *et al.* [43]. The observed amino group protons downfield shift by 0.69 ppm (6.04 ppm in free 4-aminopyridine *versus* 6.73 ppm in complex **5**) suggests that coordination of the central metal atom in Fp to the 4-Apy molecule took place at the amino group nitrogen (Table-2), which agrees with a literature report by M'thiruaine *et al.* [27]. Thus, this shift can be attributed to the deshielding of the amino group proton as nitrogen donates its lone pair to the metal. This observation corroborates the FTIR results and the results from the ^{13}C NMR chemical shift data.

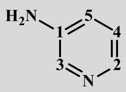
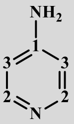
Chemical shifts at δ 212.2 ppm (**4** and **5**) and 210.1 ppm (**2**) is assignable to terminal carbonyl carbon atoms. The chemical shift due to the equilibrated carbon atoms of the cyclopentadienyl ring was observed at δ 88.0 ppm (**4** and **5**) and 88.4 ppm (**2**) (Table-3) and is consistent with established literature report [29]. In complexes **2** and **4** the carbon atom on *ortho*-position greatly shielded due to π-back-bonding from two orthogonal metal orbitals to the π*-orbitals of the 3-apy and 4-Apy moiety increasing electron density at these sites while carbon atoms on the *meta*-position are deshielded. This indicates that pyridine ring nitrogen is involved in coordination. This is consistent with established literature [34,44]. In complex **5**, carbon atom C(1) bearing amine group, is greatly deshielded by 6.0 ppm (152.2 ppm in free ligand relative to 160.2 ppm in complex salt) which can be attributed to nitrogen of the amine group donating its lone pair of electrons to the cationic metal fragment.

TABLE-2
^{1}H NMR DATA OF **2**, **4** AND **5**. THE VALUES IN BRACKETS REPRESENT THE DIFFERENCES OF CHEMICAL SHIFT ON PROTONS BETWEEN THE COORDINATED AND THE FREE AMINOPYRIDINE LIGANDS

Complex	Assignment	^{1}H δ (In $(CD_3)_2SO$)	Ligand structure
2	H_a	8.20 (+0.12)	
	H_b	7.84 (-0.15)	
	H_c	7.49 (+0.46)	
	H_d	6.99 (+0.02)	
	H_e	4.33 (+0.44)	
	H_{Cp}	5.35	
4	H_a	7.78(d, 2H) (-0.20)	
	H_b	6.70 (d, 2H) (+0.23)	
	H_c	6.41 (s, 2H) (+0.37)	
	H_{Cp}	5.38 (s, 5H)	
5	H_a	7.89 (d, 2H) (-0.09)	
	H_b	6.81 (d, 2H) (+0.24)	
	H_c	6.73 (s, 2H) (+0.69)	
	H_{Cp}	5.27 (s, 5H)	

H_{cp} = protons of the cyclopentadienyl ring.

TABLE-3
^{13}C NMR DATA OF **2**, **4** AND **5**. THE VALUES IN BRACKETS REPRESENT THE DIFFERENCES OF CHEMICAL SHIFT ON CARBON ATOMS BETWEEN THE COORDINATED AND THE FREE AMINOPYRIDINE LIGANDS

Complex	Assignment	^{13}C δ (In $(CD_3)_2SO$)	Ligand structure
2	C(1)	148.3 (+5.8)	
	C(2)	129.2 (-10.2)	
	C(3)	128.1 (-9.2)	
	C(4)	127.5 (+3.9)	
	C(5)	126.9 (+5.6)	
	Ccp	88.0	
	CO	210.1	
4	C(1)	157.5 (+4.3)	
	C(2)	140.6 (-8.8)	
	C(3)	109.3 (+0.5)	
	Cp	88.0	
	CO	212.2	
5	C(1)	160.2 (+6.0)	
	C(2)	156.5 (+7.1)	
	C(3)	112.2 (+2.4)	
	Cp	88.0	
	CO	212.2	

Ccp = Carbon atoms of the cyclopentadienyl ring.
CO = Carbonyl carbon atoms of organometallic fragment.

Conclusion

Lewis acid, $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^+$ have been shown to react with aminopyridine ligands to form mononuclear complexes of the form, $[(\eta^5\text{-}C_5H_5)Fe(CO)_2L]^+$ (where L = 2-aminopyridine, 3-aminopyridne and 4-aminopyridine). All the complexes were characterised by the usual spectroscopic techniques (FTIR and NMR). The NMR and FTIR spectral data of the salt complexes show that Apy ligands exhibited unique coordination properties, as they are expected to coordinate to the metal fragment through the pyridine ring nitrogen. However, unexpected donor-site preferences were shown by the Lewis acid $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^+$ across the Apy series. Moreover, 2-Apy coordinates *via* the amino group nitrogen probably due to the steric reasons, 3-Apy binds exclusively through the pyridine ring nitrogen and uniquely 4-Apy affords two isolable isomers featuring each donor site independently, structural feature not previously reported in this class of iron complexes. The formation of both isomers is rationalised mechanically: the cationic $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^+$ fragment can coordinate either donor site. Minimal steric difference between the *para*-positions enable both amino and pyridine ring donors energetically accessible. This diversity is both unique and previously underexplored for the cyclopentadienyliron dicarbonyl metal fragment.

ACKNOWLEDGEMENTS

The authors thank Kenyatta University for providing the necessary laboratory facilities for this synthetic work.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

DECLARATION OF AI-ASSISTED TECHNOLOGIES

The authors declare that no AI tools were used in the preparation or writing of this research/review article.

REFERENCES

1. T. Khalid, A. Malik, N. Rasool, A. Kanwal, H. Nawaz and I. Almas, *RSC Adv*., **15**, 688 (2025); https://doi.org/10.1039/D4RA07438F
2. M. Okamoto, K.-I. Takahashi, T. Doi and Y. Takimoto, *Anal. Chem.*, **69**, 2919 (1997); https://doi.org/10.1021/ac960910s
3. X. Zheng, S.R. Salgia, W.B. Thompson, E.O. Dillingham, S.E. Bond, Z. Feng, K.R. Prasad and R. Gollamudi, *J. Med. Chem.*, **38**, 180 (1995); https://doi.org/10.1021/jm00001a023
4. K. Uemura, S. Kitagawa, M. Kondo, K. Fukui, R. Kitaura, H.-C. Chang and T. Mizutani, *Chemistry*, **8**, 3586 (2002); https://doi.org/10.1002/1521-3765(20020816)8:16<3586::AID-CHEM3586>3.0.CO; 2-K
5. K. Uemura, S. Kitagawa, K. Fukui and K. Saito, *J. Am. Chem. Soc.*, **126**, 3817 (2004); https://doi.org/10.1021/ja039914m
6. D.K. Kumar, A. Das and P. Dastidar, *CrystEngComm*, **9**, 548 (2007); https://doi.org/10.1039/B701782K
7. A.Z. El-Sonbati, A.A. El-Bindary, N.M. Mansour and M.M. El-Zahed, *BMC Chem.*, **19**, 177 (2025); https://doi.org/10.1186/s13065-025-01561-8
8. S. Akyüz, *J. Mol. Struct.*, **482–483**, 171 (1999); https://doi.org/10.1016/S0022-2860(98)00638-3
9. M. Swiatkowski, T. Sieranski, M. Bogdan and R. Kruszynski, *Molecules*, **24**, 3357 (2019); https://doi.org/10.3390/molecules24183357
10. A.P. Sadimenko, *ChemInform*, **42**, chin.201119226 (2011); https://doi.org/10.1002/chin.201119226
11. M. Kalidasan, S. Forbes, Y. Mozharivskyj and M.R. Kollipara, *J. Chem. Sci.*, **127**, 1135 (2015); https://doi.org/10.1007/s12039-015-0846-6
12. A. Noor, *Top. Curr. Chem.*, **379**, 6 (2021); https://doi.org/10.1007/s41061-020-00320-8
13. X. Wang and D.-S. Yang, *Can. J. Chem.*, **87**, 297 (2009); https://doi.org/10.1139/v08-146
14. B. Dojer, A. Pevec, P. Šegedin, Z. Jagličić, Č. Stropnik, M. Kristl and M. Drofenik, *Inorg. Chim. Acta*, **363**, 1343 (2010); https://doi.org/10.1016/j.ica.2009.12.052
15. N. Yu, B. Zhang, S. Liang, M. Shi, F. Han, C. Zhang, Q. Yang and C. Miao, *New J. Chem.*, **49**, 1430 (2025); https://doi.org/10.1039/D4NJ04346D
16. F.A. Mautner, P.V. Jantscher, R.C. Fischer, A. Torvisco, K. Reichmann and S.S. Massoud, *Transition Met. Chem.*, **46**, 191 (2021); https://doi.org/10.1007/s11243-020-00436-2
17. Y. Buyukmurat and S. Akyuz, *J. Mol. Struct.*, **651–653**, 533 (2003); https://doi.org/10.1016/S0022-2860(02)00674-9
18. C.M. Standfest-Hauser, K. Mereiter, R. Schmid and K. Kirchner, *Dalton Trans.*, 2329 (2003); https://doi.org/10.1039/b302416d
19. M.G. Fuster, I. Moulefera, M.G. Montalbán, J. Pérez, G. Víllora and G. García, *Molecules*, **27**, 7264 (2022); https://doi.org/10.3390/molecules27217264
20. F. Marszaukowski, I.D.L. Guimarães, J.P. Da Silva, L.H. Da Silveira Lacerda, S.R. De Lazaro, M.P. De Araujo, P. Castellen, T.T. Tominaga, R.T. Boeré and K. Wohnrath, *J. Organomet. Chem.*, **881**, 66 (2019); https://doi.org/10.1016/j.jorganchem.2018.11.036
21. M.M. Abu-Youssef, V. Langer and L. Öhrström, *Dalton Trans.*, 2542 (2006); https://doi.org/10.1039/B516723J
22. R.V. Ottenbacher, E.P. Talsi and K.P. Bryliakov, *Chem. Rec.*, **18**, 78 (2018); https://doi.org/10.1002/tcr.201700032
23. M. Hafeez and M. Riaz, *Appl. Petrochem. Res.*, **6**, 307 (2016); https://doi.org/10.1007/s13203-016-0170-1
24. A.C.B. Yuoh, M.O. Agwara, D.M. Yufanyi, M.A. Conde, R. Jagan and K.O. Eyong, *Int. J. Inorg. Chem.*, **2015**, 106838 (2015); https://doi.org/10.1155/2015/106838
25. L. Phiri, M.Sc. Thesis, Spectroscopic Studies of η^5-Cyclopentadienyl Iron Dicarbonyl Ketone Complexes, The University of Zambia, Lusaka, Zambia (2011).
26. C.M. M'thiruaine, H.B. Friedrich, E.O. Changamu and M.D. Bala, *Inorg. Chim. Acta*, **390**, 83 (2012); https://doi.org/10.1016/j.ica.2012.04.003
27. C.M. M'thiruaine, H.B. Friedrich, E.O. Changamu and M.D. Bala, *Inorg. Chim. Acta*, **366**, 105 (2011); https://doi.org/10.1016/j.ica.2010.10.018
28. K. Chengo, Ph.D. Thesis, Synthesis, Characterization, Bioassay and Density Functional Theory Studies of Cationic Iron Half Sandwich Complexes of Selected Heterofunctional Active Pharmaceutical Agents, School of Pure and Applied Sciences, Kenyatta University, Nairobi, Kenya (2020).
29. C.M. M'thiruaine, H.B. Friedrich, E.O. Changamu and B. Omondi, *J. Organomet. Chem.*, **717**, 52 (2012); https://doi.org/10.1016/j.jorganchem.2012.06.034
30. R.B. King, F.G.A. Stone, W.L. Jolly, G. Austin, W. Covey, D. Rabinovich, H. Steinberg and R. Tsugawa, *Inorg. Synth.*, **7**, 99 (1963); https://doi.org/10.1002/9780470132388.ch31
31. A.S. Sall, F.B. Tamboura and M. Gaye, *Bull. Chem. Soc. Ethiopia*, **17**, 27 (2003); https://doi.org/10.4314/bcse.v17i1.61726
32. M.Y. Mihaylov, V.R. Zdravkova, E.Z. Ivanova, H.A. Aleksandrov, P.S. Petkov, G.N. Vayssilov and K.I. Hadjiivanov, *J. Catal.*, **394**, 245 (2021); https://doi.org/10.1016/j.jcat.2020.06.015

33. R.R. Schrock and J.A. Osborn, *Inorg. Chem.*, **9**, 2339 (1970); https://doi.org/10.1021/ic50092a027
34. C. Yenikaya, M. Poyraz, M. Sarı, F. Demirci, H. İlkimen and O. Büyükgüngör, *Polyhedron*, **28**, 3526 (2009); https://doi.org/10.1016/j.poly.2009.05.079
35. Y. Büyükmurat, E. Akalin, A.E. Özel and S. Akyüz, *J. Mol. Struct.*, **482-483**, 579 (1999); https://doi.org/10.1016/S0022-2860(99)00022-8
36. N. Gokhale, S. Padhye, D. Rathbone, D. Billington, P. Lowe, C. Schwalbe and C. Newton, *Inorg. Chem. Commun.*, **4**, 26 (2001); https://doi.org/10.1016/S1387-7003(00)00185-4
37. K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Hoboken, NJ, USA: John Wiley & Sons, edn. 6 (2008).
38. K. Dhaveethu, T. Ramachandramoorthy and K. Thirunavukkarasu, *J. Korean Chem. Soc.*, **57**, 712 (2013); https://doi.org/10.5012/jkcs.2013.57.6.712
39. D.M. Yufanyi, H.J. Nono, A.C.B. Yuoh, C.D. Tabong, W. Judith and A.M. Ondoh, *Open J. Inorg. Chem.*, **11**, 63 (2021); https://doi.org/10.4236/ojic.2021.113005
40. A. Pilon, A.R. Brás, L. Côrte-Real, F. Avecilla, P.J. Costa, A. Preto, M.H. Garcia and A. Valente, *Molecules*, **25**, 1592 (2020); https://doi.org/10.3390/molecules25071592
41. K. Dhaveethu, T. Ramachandramoorthy and K. Thirunavukkarasu, *J. Korean Chem. Soc.*, **57**, 341 (2013); https://doi.org/10.5012/jkcs.2013.57.3.341
42. J.L. Templeton, *J. Am. Chem. Soc.*, **101**, 4906 (1979); https://doi.org/10.1021/ja00511a020
43. L. Côrte-Real, M.P. Robalo, F. Marques, G. Nogueira, F. Avecilla, T. J.L. Silva, F. C. Santos, A.I. Tomaz, M.H. Garcia and A. Valente, *J. Inorg. Biochem.*, **150**, 148 (2015); https://doi.org/10.1016/j.jinorgbio.2015.06.015
44. M.D. Fryzuk and S.A. Johnson, *Coord. Chem. Rev.*, **200-202**, 379 (2000); https://doi.org/10.1016/S0010-8545(00)00264-2