



Original Article

Theoretical insight of substituent effect in *para* substituted Fe(CO)₄-pyridine complexes

R. Ghiasi^{1,*}, M. Daghighi Asl², S. Azmayesh², P. Makkipour¹

¹ Department of chemistry, Basic science faculty, East Tehran Branch, Islamic Azad University

² Department of chemistry, Basic science faculty, Central Tehran Branch, Islamic Azad University, Tehran, Iran

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Abstract:

Systematic studies on the substituent effect in *para* substituted Fe(CO)₄-pyridine complexes have been studied on the basis of DFT quantum-chemical calculations. The following substituents were taken into consideration: NO₂, CN, CHO, F, H, CH₃, and OH. Additionally, the Fe–N and Fe–C bonds were characterized on the basis of Atoms in Molecules topological analysis of electron density. It has been found that the substituents in position 4 of the pyridine ring influence the Fe–N bond of Fe(CO)₄-pyridine complex in a systematic manner, as a result of with, the pyridine moiety has a diversified ability of participating in the interaction with the Fe atom of Fe(CO)₄ moiety. It has also been found, that the electron withdrawing substituents additionally stabilize the Fe–N bond, whereas the electron donating ones weaken it. The substituent effect mainly affects the component of the Fe–N bond.

Keywords: complexes, Fe–N bond, DFT, Fe(CO)₄-pyridine

(*) Corresponding Author: e-mail: rezaghiasi1353@yahoo.com, rghyasi@qdiau.ac.ir

1. Introduction:

The chemistry of $M(\text{CO})_4\text{-L}$ transition metal complexes is thoroughly explored because of unique properties of the compounds belonging to this organometallic species. These kinds of compounds are used in industry as important homogeneous and heterogeneous catalysts [1]. Spectroscopically well-characterized or isolable complexes containing iron-nitrogen multiple bonds are of interest given their role in enzymatic transformations and potential to mediate atom- and group-transfer processes [2]. Iron amides (Fe-NR_2) [3], imides (Fe=NR), and nitrides ($\text{Fe}\equiv\text{N}$) [4] have special relevance given their potential intermediacy in nitrogen fixation schemes [5].

Substituent effect in *para* substituted $\text{Cr}(\text{CO})_5\text{-pyridine}$ complexes has been studied theoretically [6]. In this work quantum chemical methods were used in order to gain a deeper insight into the phenomenon of the substituent effect in a series of *para* substituted $\text{Fe}(\text{CO})_4\text{-pyridine}$ complexes. Additionally, the metal–ligand bonds were characterized by means of the Atoms in Molecules topological analysis of electron density function.

2. Computational methods:

All calculations were carried out with the Gaussian 2003 suite of program [7] using the standard 6-31G(d,p) basis set calculations of systems contain C, H, and N [8]. For Fe element standard LANL2DZ basis set [9] are used and Fe described by effective core potential (ECP) of Wadt and Hay pseudopotential [10] with a doublet- ξ valance using the LANL2DZ. Geometry optimization was performed utilizing Becke's hybrid three-parameter exchange functional and the nonlocal correlation functional of Lee, Yang, and Parr (B3LYP) [11]. A vibrational analysis was performed at each stationary point found, that confirm its identity as an energy minimum. The AIM2000 program [12] was used for the topological analysis of electron density, and the characteristics of ring critical points (RCPs) were taken into account: density at RCP ($\rho(\text{rc})$), and its Laplacian ($\nabla^2\rho(\text{rc})$).

3. Results and discussion:

3.1 Relative energies.

Table 1 shows the energy (E), relative energy (ΔE) values of the various isomers of the *para* substituted $\text{Fe}(\text{CO})_4\text{-py}$ complexes (Figure 1). These values indicate that the *axial* isomer of *para* substituted $\text{Fe}(\text{CO})_4\text{-py}$ complexes is found to be the most stable in energy in all complexes. Thus, the π -acceptor ligand (CO) prefers the equatorial sites. This structural preference can be rationalized in terms of the relative number of the $d\pi$ orbitals available to ligands at the axial and equatorial sites [13].

Table 1. The energy (E , Hartree), relative energy (ΔE , kcal/mol), substituent constants values of the various isomers of the *para* substituted $\text{Fe}(\text{CO})_4\text{-py}$ complexes.

X	E (equatorial)	E (axial)	ΔE	σ^+	σ^-	F	R^+	R^-
H	-825.0990	-825.1060	4.3426	0.00	0.00	0.00	0.00	0.00
F	-924.3294	-924.3362	4.2405	-0.07	-0.03	0.45	-0.52	-0.48
Me	-864.4215	-864.4285	4.4044	-0.31	-0.17	0.01	-0.32	-0.18
OH	-900.3225	-900.3294	4.3205	-0.92	-0.37	0.33	-1.25	-0.70
CN	-917.3300	-917.3368	4.2757	0.66	1.00	0.51	0.15	0.49
NO_2	-1029.5856	-1029.5924	4.2762	0.79	1.27	0.65	0.14	0.62
CHO	-938.4150	-938.4219	4.3496	0.73	1.03	0.33	0.40	0.70

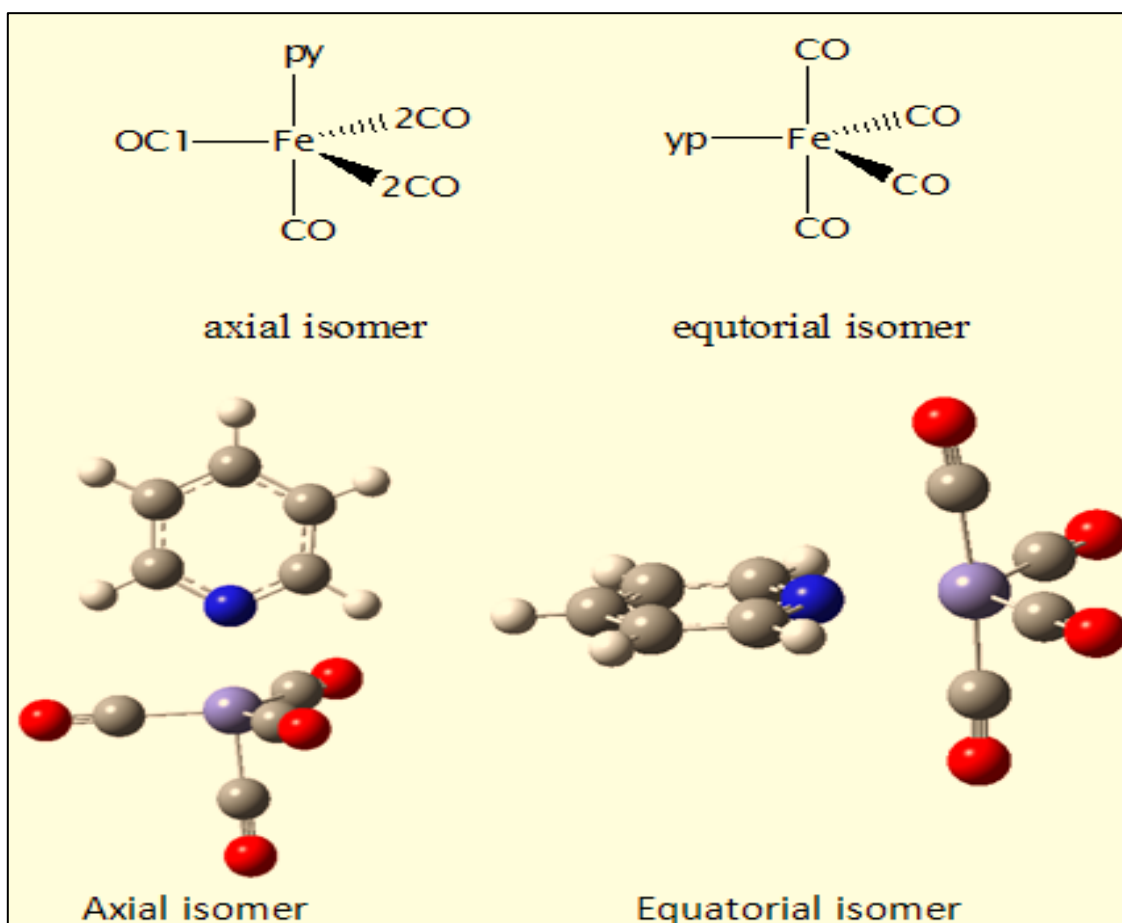


Figure1. The structures of *para* substituted $\text{Fe}(\text{CO})_4\text{-py}$ complexes.

3.2 Bond distances

As it can be seen in Table 3, the Fe–N(pyridine) bond length in substituted Fe(CO)₄–pyridine is changing due to the presence of the substituent in position 4 of the pyridine ring. For the strongest electron withdrawing substituents (these having large positive values of substituent constants, e.g.: NO₂) [14] the Fe–N bond is shorter than in the unsubstituted Fe(CO)₄–pyridine system, whereas for the electron donating substituents (these having large negative values of substituent constants, e.g. OH) this bond is, respectively, longer. Therefore, the electron withdrawing substituents additionally stabilize the Fe–N bond, while the electron donating ones weaken it.

This can be surprising, considering the fact that the surplus of negative charge on the N atom should result in stronger basic properties of the pyridine ligand and therefore, it should additionally stabilize the bond under discussion. It should be pointed out, however, that in the case of pyridine system the substituents do not affect the σ -donating component of the M–N bond, or at least this component is affected very weakly, as it can be concluded on the basis of H-bond investigations⁶. Therefore, it can be supposed that the substituents in *para*-position of pyridine affect the π -component of the Fe–N(pyridine) bond. It is also worth taking a closer look on the possible canonical structures of the substituted pyridine. It has been shown in Fig. 2, that the substituent effect for electron withdrawing substituents results in a partial lack of π -electrons on the N atom. This leads to a decrease of the π -donating, or an increase of the π -accepting properties of pyridine moiety. The latter can result in additional stabilization via back-bonding effect in the M–N bond. When the electron withdrawing substituent is replaced with the electron donating one (Fig. 2), the π -donating properties of the pyridine ligand increase (or π -accepting properties decrease) which in the case of the analyzed systems seems to destabilize the interaction between pyridine ligand and the rest of the complex.

It seems therefore that the communication between the substituents and the Fe(CO)₄ moiety through the pyridine ring has the same character as the interaction between a given substituent and the center which introduces the electrons onto the aromatic ring due to communication with this substituent (see the definition of substituted constants used in this work). This observation additionally corroborates the stabilizing effect of the back-donation. The clearest interdependence observed for R⁻ can additionally prove that the main factor influencing the Fe–N bonding within the investigated set of Fe(CO)₄–pyridine systems is connected with the π -electron effects, particularly as it is difficult to find a clear relationship between the field/inductive substituent constant F and the considered bond lengths.

It is worth mentioning here that the introduction of a given substituent into position 4 of the pyridine ring results in small but systematic changes in the Fe–C(carbonyl) bonding. This results from an obvious connection between the back-donations in the Fe–N(pyridine) and Cr–C(carbonyl) bonds. An increase in Cr–N back-donation goes with a reduction in Fe–CO *trans* back-donation, since the same occupied orbital of the metal is involved in both these π -electronic effects.

Table 3. The bond lengths and selected AIM based parameters for Fe-N, and Fe-C: Electron density (ρ), laplacian of electron density ($\nabla^2\rho$), kinetic electron energy density, $G(\rho)$, the total electron energy density, $H(\rho)$, potential electron energy density, $V(\rho)$ of the various isomers of the para substituted Fe(CO)₄-py complexes.

Fe-N, axial						
X	r	ρ	$\nabla^2\rho$	G	H	V
H	2.101	0.0633	0.3592	0.0936	-0.0038	-0.0973
F	2.104	0.0623	0.3580	0.0929	-0.0033	-0.0962
Me	2.100	0.0635	0.3588	0.0936	-0.0039	-0.0975
OH	2.103	0.0629	0.3555	0.0925	-0.0037	-0.0962
CN	2.094	0.0636	0.3701	0.0963	-0.0038	-0.1001
NO₂	2.093	0.0632	0.3740	0.0971	-0.0036	-0.1006
CHO	2.093	0.0640	0.3687	0.0962	-0.0040	-0.1002

Fe-N, equatorial						
X	r	ρ	$\nabla^2\rho$	G	H	V
H	2.1114	0.0669	0.3687	0.0950	-0.0029	-0.0979
F	2.1172	0.0656	0.3651	0.0935	-0.0023	-0.0958
Me	2.1112	0.0669	0.3674	0.0947	-0.0029	-0.0976
OH	2.1142	0.0662	0.3640	0.0936	-0.0026	-0.0963
CN	2.1084	0.0667	0.3754	0.0967	-0.0028	-0.0994
NO₂	2.1119	0.0662	0.3744	0.0960	-0.0025	-0.0985
CHO	2.1070	0.0662	0.3640	0.0936	-0.0026	-0.0963

Fe-C trans, axial

X	r	ρ	$\nabla^2\rho$	G	H	V
H	1.7787	0.1447	0.5595	0.2143	-0.0744	-0.2887
F	1.7787	0.1446	0.5589	0.2140	-0.0743	-0.2884
Me	1.7782	0.1448	0.5606	0.2147	-0.0745	-0.2892
OH	1.7777	0.1451	0.5605	0.2150	-0.0748	-0.2898
CN	1.7812	0.1436	0.5601	0.2132	-0.0732	-0.2865
NO₂	1.7815	0.1433	0.5620	0.2133	-0.0728	-0.2861
CHO	1.7806	0.1439	0.5597	0.2135	-0.0735	-0.2870

Fe-C cis, equatorial (1)

X	r	ρ	$\nabla^2\rho$	G	H	V
H	1.7996	0.1451	0.4902	0.2008	-0.0783	-0.2791
F	1.7995	0.1451	0.4911	0.2011	-0.0783	-0.2794
Me	1.7991	0.1452	0.4902	0.2010	-0.0785	-0.2795
OH	1.7980	0.1457	0.4904	0.2016	-0.0790	-0.2806
CN	1.8016	0.1443	0.4889	0.1997	-0.0775	-0.2772
NO₂	1.8026	0.1438	0.4879	0.1989	-0.0770	-0.2759
CHO	1.8008	0.1445	0.4905	0.2003	-0.0777	-0.2781

Fe-C cis, equatorial (2)

X	r	ρ	$\nabla^2\rho$	G	H	V
H	1.8063	0.1429	0.4799	0.1959	-0.0759	-0.2718
F	1.8067	0.1427	0.4807	0.1959	-0.0757	-0.2716
Me	1.8061	0.1429	0.4796	0.1959	-0.0760	-0.2719
OH	1.8062	0.1430	0.4796	0.1959	-0.0760	-0.2719
CN	1.8076	0.1424	0.4792	0.1953	-0.0754	-0.2707
NO ₂	1.8078	0.1422	0.4800	0.1953	-0.0753	-0.2705
CHO	1.8073	0.1426	0.4789	0.1953	-0.0756	-0.2709

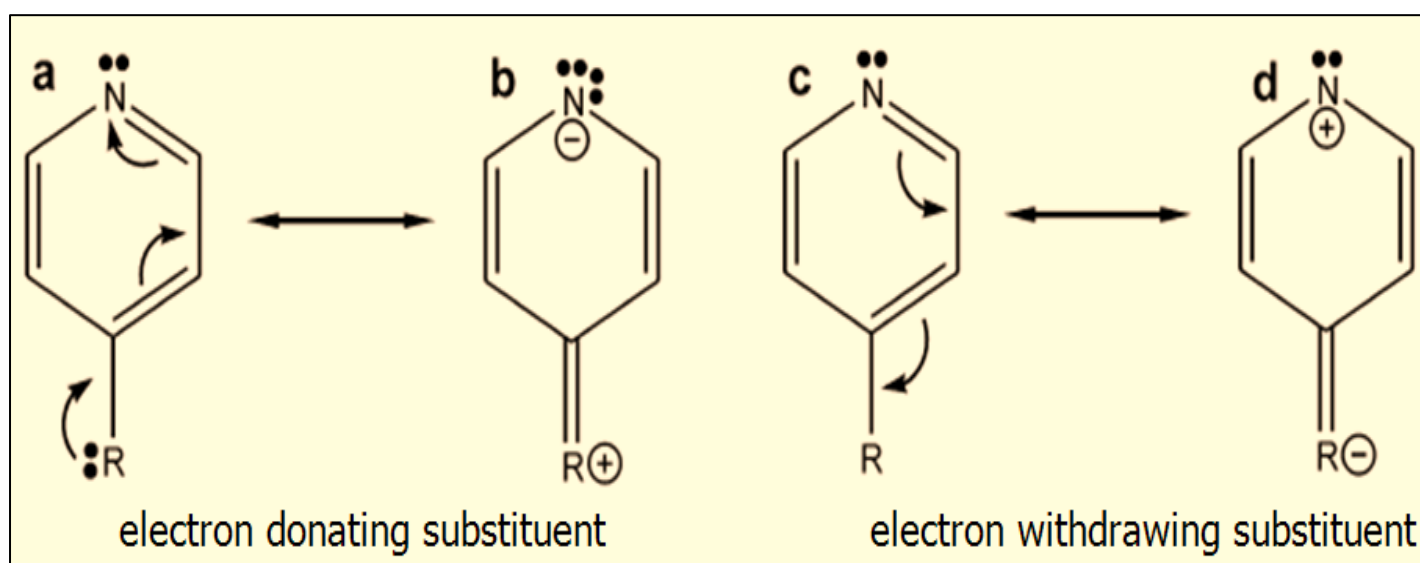


Figure 2. Selected resonance structures of pyridine substituted with electron donating (a) and (b), and electron withdrawing (c) and (d), substituent.

3.3 Frontier orbital energies and chemical hardness.

The frontier orbital energies and the hardness of all complexes computed are given in the Table 2. Furthermore, graphical representations of HOMO and LUMO orbitals of pyridine and Fe(CO)₄ fragments are indicated in Figure 3. As it can be seen, the HOMO orbital of Fe(CO)₄ can be involved in π -bonding interaction with the LUMO orbital of pyridine.

Thus it can be expected that in the case of electron-withdrawing substituents the energy of the LUMO orbital should be lowered, which should favour back-donation. In the case of electron donating substituents an opposite effect should be observed. In fact, the data collected in Table 1 is in excellent agreement with the above statement. For significantly electron-withdrawing substituents the E(LUMO)_{py} is considerably lower when compared with the case of the substituents considered as electron-donating ones.

There is even a direct relation between the E(LUMO)_{py} and Fe–N distance (cc. = 0.859). Therefore, it can be stated that in the Fe(CO)₄–pyridine complexes the back bonding effect is the one which additionally stabilizes the Fe–N(pyridine) bond, similarly as it occurs in the case of M–CO bond.

To evaluate the hardness and chemical potential of these complexes, these values can be calculated from the HOMO and LUMO orbital energies using the following approximate expression:

$$\mu = (\epsilon_{\text{HOMO}} + \epsilon_{\text{LUMO}}) / 2$$

$$\eta = (\epsilon_{\text{HOMO}} - \epsilon_{\text{LUMO}}) / 2$$

Where μ is the chemical potential (the negative of the electronegativity), and η is the hardness¹⁵.

The hardness values of in Table 2 indicate the increasing of these values in donating substituents. On the other hand, these values decrease in electron-withdrawing substituents.

The collected values of chemical potential in Table 2 show that the decreasing of these values in donating substituents. From the other point of view, these values increase in electron-withdrawing substituents.

Table2. The frontier orbitals energies (Hartree), HOMO-LUMO gap energy (ΔE , eV), Hardness, chemical potential, and electrophilicity values of the various isomers of the para substituted Fe(CO)₄-py complexes.

(a) Axial isomer

	E(HOMO) _{py}	E(LUMO) _{py}	E(HOMO)	E(LUMO)	ΔE	η	μ	ω
H	-0.2526	-0.0232	-0.2094	-0.0689	3.8271	1.9136	-0.1392	0.0051
F	-0.2638	-0.0223	-0.2125	-0.0672	3.9581	1.9791	-0.1398	0.0049
Me	-0.2494	-0.0182	-0.2068	-0.0627	3.9257	1.9629	-0.1348	0.0046
OH	-0.2516	-0.0109	-0.2067	-0.0528	4.1938	2.0969	-0.1298	0.0040
CN	-0.2794	-0.0764	-0.2216	-0.1118	2.9919	1.4959	-0.1667	0.0093
NO ₂	-0.2836	-0.1082	-0.2238	-0.1345	3.6642	1.8321	-0.1792	0.0088
CHO	-0.2667	-0.0849	-0.2059	-0.1156	3.1480	1.5740	-0.1607	0.0082

(b) Equatorial isomer

	E(HOMO)	E(LUMO)	ΔE	η	μ	ω
H	-0.1985	-0.0675	3.5680	1.7840	-0.1330	0.0050
F	-0.2016	-0.0655	3.7089	1.8544	-0.1336	0.0048
Me	-0.1960	-0.0613	3.6680	1.8340	-0.1287	0.0045
OH	-0.1960	-0.0512	3.9451	1.9725	-0.1236	0.0039
CN	-0.2104	-0.1107	2.7162	1.3581	-0.1605	0.0095
NO ₂	-0.2114	-0.1343	3.6582	1.8291	-0.1729	0.0082
CHO	-0.2174	-0.1162	2.7554	1.3777	-0.1668	0.0101

3.4 AIM analysis

It has been proved, that the AIM-based analysis of electron density can provide valuable information on many physical and chemical properties of the molecular systems. (It is fair to mention here some criticism of AIM Quantum Theory. It has been found for instance that the value of electron density (ρ) and its laplacian ($\nabla^2\rho$) estimated at bond critical point (BCP) of a given bond correlate very well with the strength of this bond, as well as with its length, since, as it is well known, both the strength and the length of a given bond are mutually dependent. The selected AIM based parameters for Fe-N, and Fe-C are show in Table 3.

A linear relationship can be observed between $\rho(\text{N-Fe})$ and $r(\text{N-Fe})$ (c.c. = 0.895) in axial isomers. Similarly, the laplacian of $\rho(\text{N-Cr})$, ($\nabla^2\rho$), fulfils such a linear relationship (c.c. = 0.989).

Additional valuable information on chemical bond properties is available from the total electron energy density, $H(\rho)$, and its components; kinetic electron energy density, $G(\rho)$, positive by definition, and potential electron energy density, $V(\rho)$, negative by definition. The following relation is known for $H(\rho)$ and its components:

$$H(\rho) = V(\rho) + G(\rho)$$

It is known that in the region of the bond CP of weak closed-shell interatomic interactions the kinetic energy density dominates, with $G(\rho)$ magnitude being slightly greater than the potential energy density $|V(\rho)|$ which implies the total energy density $H(\rho) > 0$ and close to zero, whereas for strong covalent interactions $V(\rho)$ dominates over the kinetic energy density and $H(\rho) < 0$. This is usually accompanied by $\nabla^2\rho > 0$ for the proper case and $\nabla^2\rho < 0$ for the latter one (there is one exception mentioned in the further part of the discussion).

Interestingly, both $G(\rho)$ and $|V(\rho)|$ values increase with electron-withdrawing properties of substituents in the *para*-position of the pyridine ring. However, $H(\rho)$ is invariably negative and very close to zero. Probably, this could be due to the changes in the Fe-N bond length. As already mentioned, the Fe-N(pyridine) distance decreases with an increase of electron-withdrawing properties of the attached substituents. It can thus be expected that the shorter is the bond, the more covalent is its character, which implies an increase of $|V(\rho)|$ magnitude.

However, this is compensated by an increase of $G(\rho)$ which is related with Pauli repulsion between two closed shells. As a result, the $H(\rho)$ varies within a very small range. These changes are relatively small because of a limited possibility of the influence of substituents on the Cr-N(pyridine) bond, and can be more significant in the case of a larger spectrum of variability of a given bond.

4. Conclusion:

The $\nabla^2\rho$ values indicate, in the case of all the *cis*, and *trans*-Fe-C_{carbonyl} bonds at corresponding BCPs are positive, as it was found for closed-shell interactions.

On the other hand, the $H(\rho)$ values are negative, as found for shared interactions. This is in agreement with observations made for the Ti-C bonds in titanium complexes [53], in the case when the metal-ligand bonding has a characteristic that represents a mix of the closed-shell and shared parameters.

Moreover, the $H(\rho)$ values are more negative for Fe-C_{cis} bonds, which is directly connected with relative greater predominance of $|V(\rho)|$ magnitude over the $G(\rho)$ magnitude. This suggests a more covalent character of the Fe-C_{cis} bond as compared with the *trans* ones, and is also in line with general knowledge, according to which low-field ligands (e.g. pyridine) weaken the *cis* placed M-carbonyl bonds. Generally, the

greater value of $|H(\rho)|$ (with negative sign), the more covalent character of the bond. It seems therefore that the covalent character of the Fe–C_{carbonyl} bonds increases with electron donating properties of the substituent attached to the pyridine ring.

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