

# Catalyzed M-C coupling reactions in synthesis of $\sigma$ -(pyridylethynyl)dicarbonylcyclopentadienyliron complexes

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**ABSTRACT:** The reactions between terminal ethynylpyridines, (trimethylsilyl)ethynylpyridines and cyclopentadienyliron dicarbonyl iodide were studied under Pd/Cu-catalyzed conditions. It was found that, depending on the catalyst and reagents used, the reactions could proceed differently to give desired alkynyl complexes or different byproducts. The conditions, catalysts, and reagents that provide the highest yields of desired product were determined. Synthetic approaches to  $\sigma$ -acetylide iron complexes of the type  $\text{Cp}(\text{CO})_2\text{Fe-C}\equiv\text{C-R}$  (R - *ortho*-, *meta*-, *para*-pyridyl) based on the Pd/Cu-catalyzed cross-coupling reactions were elaborated.

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## Introduction

Metal  $\sigma$ -alkynyl complexes displaying such peculiar characteristic as linear geometry, high stability, and  $\pi$ -unsaturated character have been demonstrated to constitute promising building blocks for construction of materials, which can possess such properties as optical nonlinearity<sup>1-5</sup> [H-10, H-11, H-14, H-15, H-13], light-emitting<sup>6-12</sup> [Y-1, Y-2, W-14, L-12, L-11, Z-9, Z-6, Z-7], and electrical conductivity<sup>13-18</sup> [L-13, L-14, L-15, B-45, M-17, Z-8]. Moreover, they are an important class of coordination compounds because of their relevance in synthetic chemistry<sup>19-24</sup> [H-16, N-5, C-26, A-49, G-8, L-9] and in proton reduction catalysis<sup>25-27</sup> [E-5, K-39, V-9]. This versatility of usage of metal  $\sigma$ -alkynyls is driven by the well-developed routes to the alkynyl ligand precursors and the numerous advantages in the design of molecules of the complexes. Nowadays, the growing interest in application of such compounds for construction of materials necessitates the development of the synthetic approaches to complexes containing functionalized alkynyl ligands.

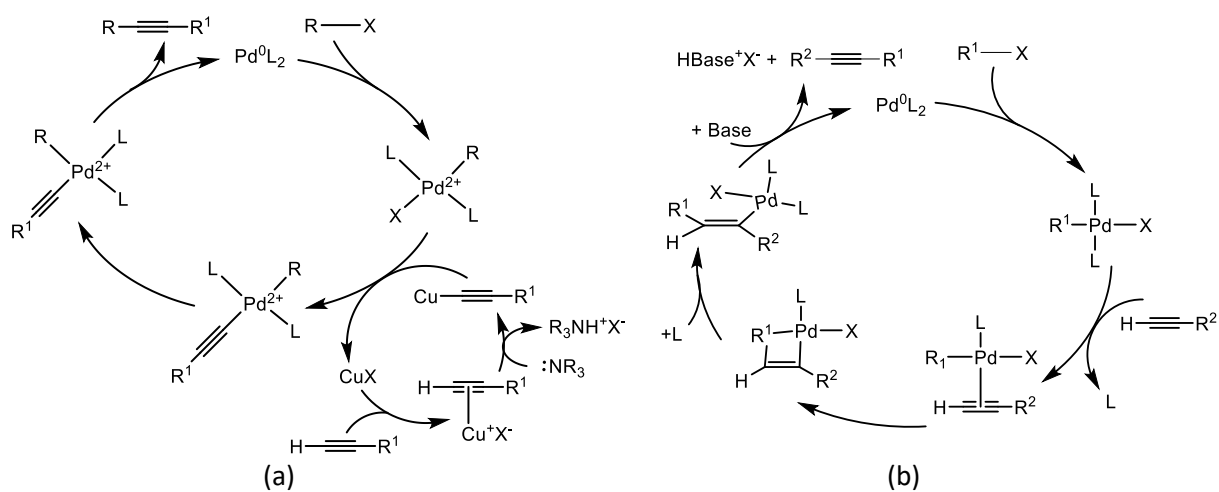
A variety of methods for the synthesis of transition metal acetylides have been developed<sup>24</sup> [L-9]. The most general synthetic route to them is transmetallation reaction, where a generated  $[\text{M-C}\equiv\text{C-R}]$  [M = Cu(I), Ag(I), Au(I), alkali-metal (Li, Na), or an alkaline-earth-metal (MgX, etc.) species acts as an alkynyl transfer reagent to a transition-metal complex  $\text{L}_n\text{MX}$  (X = I, Br, Cl)<sup>28-34</sup> [K-33, F-8, M-19, F-9, C-31, T-10, G-10]. However, in some cases, such reactions may give low yields of desired products and a range of by-products, for example, the complexes in which the copper or the silver fragments is  $\pi$ -coordinated by the transferred alkynyl ligand<sup>35-38</sup> [B-48, B-49, M-18, E-4].

Other general strategy to the preparation of transition metal acetylides takes advantage of the facility of some transition metal complexes catalyze M-C coupling reactions. So, the most general route to  $\sigma$ -alkynyl derivatives of group 10 metals is based on copper(I)-catalyzed dehydrohalogenation reactions between appropriate metal complex and terminal acetylene in an amine solvent<sup>39-42</sup> [S-32, S-33, O-9, O-7]. This method is applicable to the synthesis of alkynyl, polyynyls, and polyynidiyls of tungsten, molybdenum, iron, ruthenium, rhodium, and iridium<sup>5,43-47</sup> [B-50, B-47, B-39, B-46, H-13, H-17]. In some cases the CuI-catalyzed reactions may be performed with stannyl acetylenes and without the amines<sup>48-51</sup> [J-14, Y-3, A-51, K-35].

Palladium catalysts, which are now established as an indispensable tool in organic synthesis, can also be used toward M-C≡C- bond-forming reactions. The group of Claudio Lo Sterzo demonstrated that, in analogy to the behavior of organic electrophiles, transition-metal iodides, in the presence of palladium, undergo a coupling with trialkyltin acetylides resulting in the formation of alkynyl complexes of ruthenium, iron, tungsten, and molybdenum<sup>52-55</sup> [L-16, R-11, C-25, V-11], and besides the role of palladium catalysts in promoting these transformations was also investigated<sup>52,56-59</sup> [A-52, C-30, L-16, T-9, R-14].

Although, the Sterzo's approach was shown to be a valuable route to alkynyl complexes, the preparation of the tin reagents and removal of the tin impurities limit the appeal of this method. To overcome these disadvantages, an organometallic analogue of a Sonogashira protocol may be used, where transition metal halides and terminal alkynes can be reacted to form the metal alkynyl complexes with the Pd/Cu- or Pd-catalyzed dehydrohalogenation route, thus easing purification of reaction mixtures and providing milder reaction conditions. Notwithstanding the availability and perspective of this approach in synthesis of metal acetylides, it has been applied in sole work of Koishira Oshima's group on the synthesis of  $\sigma$ -alkynyliron complexes  $\text{Cp}(\text{CO})_2\text{Fe-C}\equiv\text{C-R}$ , where R is an electron deficient substituent<sup>60</sup> [N-4].

It is worth noting that while the Sonogashira protocol became the most popular route for carrying out the alkynylation of aryl and alkenyl halides<sup>61-64</sup> [C-23, K-37, B-51, R-15], its application in formation of heteroatom-C<sub>sp</sub> bonds are still rare<sup>65,66</sup> [K-36, B-52]. Moreover, despite the extensive investigation on the homogeneous Sonogashira cross-couplings, their exact mechanisms are not well understood, even in the case of Pd-catalyzed and Cu co-catalyzed reactions<sup>62,67</sup> [K-37, S-30]. There are two main variants of Sonogashira protocol, Pd(0)/Cu(I)-catalyzed and Cu-free. The mechanism of the Sonogashira reaction in the presence of copper(I) co-catalyst is fairly well-established (**Fig. 1a**)<sup>62</sup>. In the case of the Cu-free Sonogashira reaction two most common mechanisms "carbopalladation" and "deprotonation" are believed to exist<sup>68-70</sup> [M-21, M-20, M-14]. However, theoretical studies demonstrated that the carbopalladation mechanism has a very high energy barrier<sup>68,70</sup> [M-14, M-21] and therefore should not occur under the reaction conditions (**Fig. 1b**). The "deprotonation" mechanism has two alternative pathways "deprotonation" and "ionic", which share the initial oxidative addition and the final reductive elimination steps, but differ in their steps for the formation of *cis*-Pd(II)L<sub>2</sub>R<sup>1</sup>(-C≡CR) (**Fig. 1c**). The DFT and theoretical studies revealed that the Pd-catalyzed Cu-free Sonogashira reactions should preferably go through deprotonation mechanism<sup>69,70</sup> [M-14, M-20].





coupling reactions of terminal ethynylpyridines and (trimetylsilyl)ethynylpyridines with cyclopentadienyliron dicarbonyl iodide under the different Pd/Cu-catalyzed conditions to obtain the targeted pyridylethynyl iron complexes (**1-3**).

## Results and discussion

### Development of Pd/Cu-catalyzed pyridylethynylation of cyclopentadienyliron dicarbonyl iodide

Following on from the hypothesized reasons of the inability to obtain the ethynylpyridyl iron complexes (**1-3**), we realized that facilitation of transmetallation step (the formation and the transfer of acetylide species) in Pd/Cu-catalyzed reaction between  $\text{Cp}(\text{CO})_2\text{FeI}$  and ethynylpyridines should give us the desired products **1-3**. Therefore, two approaches were proposed to solve this problem: (i) use (trimetylsilyl)ethynylpyridines that in the presence of fluoride ion generate anionic pentacoordinate silicate species, in which the alkynyl group is more nucleophilic and should be smoothly transferred to palladium catalyst (Hiyama coupling)<sup>72</sup> [H-9]; (ii) application of stronger base than secondary and tertiary amines such as 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) to facilitate the acetylide species formation in Pd/Cu-catalyzed reactions. Our preliminary experiments suggested that both proposed approaches can be used for the synthesis of **1-3**. The obtained results on choice of catalysts and reactions' conditions for both approaches are summarized in Table 2 and 3.

The nature of the palladium catalyst appreciably affects the yields of the coupling reaction. For instance, in our firsts experiments the usage of  $\text{PdCl}_2(\text{PPh}_3)_2$  as catalyst led to an unexpected substitution of CO ligands by  $\text{PPh}_3$  to give such side-products as  $\text{Cp}(\text{CO})(\text{PPh}_3)\text{FeI}$  and  $\text{Cp}(\text{CO})(\text{PPh}_3)\text{Fe-C}\equiv\text{C-(2-C}_5\text{H}_4\text{N)}$ , thereby making the separation of reaction mixture more difficult. Obviously, performing the reactions of synthesis of  $\text{Cp}(\text{CO})\text{Fe-C}\equiv\text{C-(n-C}_5\text{H}_4\text{N)}$  ( $n = \textit{meta, para}$ ) with  $\text{PdCl}_2(\text{PPh}_3)_2$  as catalysts also would result in mixtures of the target complexes and the products of CO ligands substitution by  $\text{PPh}_3$  in  $[\text{Cp}(\text{CO})_2\text{Fe}]$  fragment. Therefore, instead of bis(triphenylphosphine)palladium(II) dichloride we decided to use such palladium catalysts that do not contain ligands capable to substitute carbonyl groups in the initial and the target compounds, namely tris(dibenzylideneacetone)dipalladium(0)  $\text{Pd}_2(\text{dba})_3$  and bis(acetonitrile)palladium dichloride  $\text{PdCl}_2(\text{NCMe})_2$ .

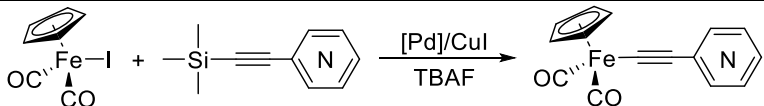
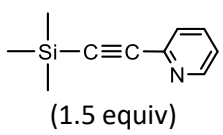
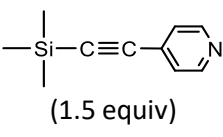
The application of the "(trimetylsilyl)ethynylpyridine" approach resulted in only moderate yields (up to 60%) of desired iron acetylide complexes **1-3**, which may be due to side reactions of the resulting acetylide complexes with fluoride anions and the formation of the cyclopentadienyliron dicarbonyl dimer in about 30% yields. It should be noted that in these conditions the presence of CuI as cocatalyst insignificantly influence the yields of products. Thus, in this approach the anionic pentacoordinated silicone moiety should participate in the transmetallation step (transfer the pyridylacetylide to a FePd complex) instead of Cu-acetylide. A source of tetrabutylammonium fluoride is also important, the reactions performed with tetrabutylammonium fluoride trihydrate gave only half of the complex's yield obtained in the reactions with 1M solution of TBAF in THF.

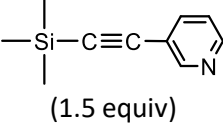
The second "ethynylpyridine" approach was found to be much more effective, the complexes **1-3** were obtained with the yields from 67 to 96%. The best catalytic system here is  $\text{PdCl}(\text{NCMe})_2/\text{CuI}$ , with which iron-ethynylpyridine coupling proceeds efficiently at room temperature in 20 minutes (2 mol% of Pd catalysts and 20 mol% of CuI) or at 60°C in 30 minutes with reduced catalysts loadings (1 and 5 mol%, respectively). However, the presence of CuI in these conditions is important for high-yield synthesis of iron pyridylacetylides, especially for  $\text{Cp}(\text{CO})_2\text{Fe-C}\equiv\text{C-(2-C}_5\text{H}_4\text{N)}$  (**1**). The yields of **2** and **3** in the Cu-free coupling reaction of  $\text{Cp}(\text{CO})_2\text{FeI}$  with the ethynylpyridines (entries 13 and 18) were decreased by about 20%, while the yield of **1** fell to 15% and, moreover, a trace amount of the binuclear complex **4** was isolated (entry 7). The conversion of these reactions were also decreased.

When Pd<sub>2</sub>(dba)<sub>3</sub> was used as a source of a catalytically active species the yields of the target complexes were lowered, moreover, the facile formation of dimerization products such as [Cp(CO)<sub>2</sub>Fe]<sub>2</sub> and 1,4-di(n-pyridine)buta-1,3-diyne<sup>73</sup> [R-10] were observed. However, the absence of the copper co-catalysts did not influence on yields and conversion here, although, in the case of coupling between Cp(CO)<sub>2</sub>FeI and H-C≡C-(2-C<sub>5</sub>H<sub>4</sub>N) traces of **4** also appeared.

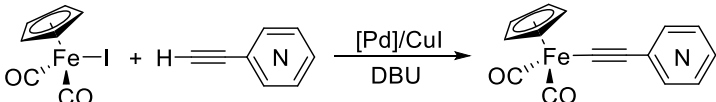
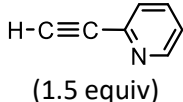
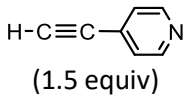
To emphasize the applicability of the developed conditions of the Pd/Cu-catalyzed pyridylethynylation to the synthesis of other compounds, we decided to obtain a dicarbonylcyclopentadienyliron complex containing σ-4-ethynyl-2,1,3-benzothiadiazole ligand, Cp(CO)<sub>2</sub>Fe-C≡C-(4-C<sub>6</sub>H<sub>3</sub>N<sub>2</sub>S) (**5**). Following the developed strategy, we investigated a coupling reactions of Cp(CO)<sub>2</sub>FeI with 4-(trimethylsilyl)ethynyl-2,1,3-benzothiadiazole and 4-ethynyl-2,1,3-benzothiadiazole. All performed experiments demonstrated that the complex **5** can be obtained using both approaches. However, its highest yield in 89% was achieved only in coupling between Cp(CO)<sub>2</sub>FeI and H-C≡C-(4-C<sub>6</sub>H<sub>3</sub>N<sub>2</sub>S) at 60°C using 1 mol% of PdCl<sub>2</sub>(NCMe)<sub>2</sub> and 5 mol% of CuI (Table 3, entry 3).

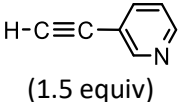
**Table 1. The conditions of the pyridylethynylation of cyclopentadienyliron dicarbonyl iodide by [(trimethylsilyl)ethynyl]pyridines in THF with 1.5 equivalent of TBAF (1M in THF)**

				
ethynyl	entry	Catalysts and conditions	Conversion	Isolated products, %
 (1.5 equiv)	1	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> (10 mol%); CuI (20 mol%); 40°C; 120 min	70%	[Cp(CO) <sub>2</sub> Fe] <sub>2</sub> (3%); Cp(CO)(PPh <sub>3</sub> )FeI (3%); [-C≡C-(2-C <sub>5</sub> H <sub>4</sub> N)] <sub>2</sub> (5%); Cp(CO)(PPh <sub>3</sub> )Fe-C≡C-(2-C <sub>5</sub> H <sub>4</sub> N) (3%); Cp(CO) <sub>2</sub> Fe-C≡C-(2-C <sub>5</sub> H <sub>4</sub> N) (58%)
	2	Pd <sub>2</sub> (bda) <sub>3</sub> (5 mol%); CuI (20 mol%); 36°C; 90 min	98%	[Cp(CO) <sub>2</sub> Fe] <sub>2</sub> (32%); [-C≡C-(2-C <sub>5</sub> H <sub>4</sub> N)] <sub>2</sub> (2%); Cp(CO) <sub>2</sub> Fe-C≡C-(2-C <sub>5</sub> H <sub>4</sub> N) (58%)
	3	Pd <sub>2</sub> (bda) <sub>3</sub> (5 mol%); -; 36°C; 90 min	98%	[Cp(CO) <sub>2</sub> Fe] <sub>2</sub> (28%); [-C≡C-(2-C <sub>5</sub> H <sub>4</sub> N)] <sub>2</sub> (5%); Cp(CO) <sub>2</sub> Fe-C≡C-(2-C <sub>5</sub> H <sub>4</sub> N) (60%)
	4	Pd <sub>2</sub> (bda) <sub>3</sub> (1 mol%); -; 60°C; 90 min	97%	[Cp(CO) <sub>2</sub> Fe] <sub>2</sub> (37%); Cp(CO) <sub>2</sub> Fe-C≡C-(2-C <sub>5</sub> H <sub>4</sub> N) (44%)
	5	PdCl <sub>2</sub> (NCMe) <sub>2</sub> (10 mol%); CuI (20 mol%); 36°C; 90 min	95%	[Cp(CO) <sub>2</sub> Fe] <sub>2</sub> (27%); [-C≡C-(2-C <sub>5</sub> H <sub>4</sub> N)] <sub>2</sub> (3%); Cp(CO) <sub>2</sub> Fe-C≡C-(2-C <sub>5</sub> H <sub>4</sub> N) (58%)
	6	PdCl <sub>2</sub> (NCMe) <sub>2</sub> (5 mol%); -; 50°C; 90 min	93%	[Cp(CO) <sub>2</sub> Fe] <sub>2</sub> (23%); Cp(CO) <sub>2</sub> Fe-C≡C-(2-C <sub>5</sub> H <sub>4</sub> N) (61%)
 (1.5 equiv)	7	Pd <sub>2</sub> (bda) <sub>3</sub> (5 mol%); CuI (20 mol%); 36°C; 90 min	96%	[Cp(CO) <sub>2</sub> Fe] <sub>2</sub> (32%); [-C≡C-(4-C <sub>5</sub> H <sub>4</sub> N)] <sub>2</sub> (6%); Cp(CO) <sub>2</sub> Fe-C≡C-(4-C <sub>5</sub> H <sub>4</sub> N) (49%)

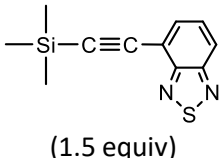
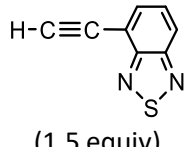
	8	Pd <sub>2</sub> (bda) <sub>3</sub> (5 mol%); -; 36°C; 90 min	98%	[Cp(CO) <sub>2</sub> Fe] <sub>2</sub> (34%); [-C≡C-(4-C <sub>5</sub> H <sub>4</sub> N)] <sub>2</sub> (5%); Cp(CO) <sub>2</sub> Fe-C≡C-(4-C <sub>5</sub> H <sub>4</sub> N) (54%)
	9	PdCl <sub>2</sub> (NCMe) <sub>2</sub> (10 mol%); CuI (20 mol%); 36°C; 90 min	97%	[Cp(CO) <sub>2</sub> Fe] <sub>2</sub> (30%); [-C≡C-(4-C <sub>5</sub> H <sub>4</sub> N)] <sub>2</sub> (2 mg, 3%); Cp(CO) <sub>2</sub> Fe-C≡C-(4-C <sub>5</sub> H <sub>4</sub> N) (44%)
	10	PdCl <sub>2</sub> (NCMe) <sub>2</sub> (5 mol%); -; 50°C; 90 min	92%	[Cp(CO) <sub>2</sub> Fe] <sub>2</sub> (37%); Cp(CO) <sub>2</sub> Fe-C≡C-(4-C <sub>5</sub> H <sub>4</sub> N) (40%)
 (1.5 equiv)	11	Pd <sub>2</sub> (bda) <sub>3</sub> (5 mol%); -; 36°C; 90 min	93%	Cp(CO) <sub>2</sub> Fe] <sub>2</sub> (27%); [-C≡C-(3-C <sub>5</sub> H <sub>4</sub> N)] <sub>2</sub> (1%); Cp(CO) <sub>2</sub> Fe-C≡C-(3-C <sub>5</sub> H <sub>4</sub> N) (56%)
	12	PdCl <sub>2</sub> (NCMe) <sub>2</sub> (5 mol%); -; 50°C; 90 min	95%	[Cp(CO) <sub>2</sub> Fe] <sub>2</sub> (36%); Cp(CO) <sub>2</sub> Fe-C≡C-(3-C <sub>5</sub> H <sub>4</sub> N) (48%)

**Table 2. The conditions of the pyridylethynylation of cyclopentadienyliron dicarbonyl iodide by ethynylpyridines in THF in THF with 1.5 equivalent of DBU**

				
ethynyl	entry	Catalysts and conditions	conversion	Isolated products, %
 (1.5 equiv)	1	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> (10 mol%); CuI (20 mol%); 40°C; 30 min	86%	Cp(CO)(PPh <sub>3</sub> )FeI (3%) Cp(CO)(PPh <sub>3</sub> )Fe-C≡C-(2-C <sub>5</sub> H <sub>4</sub> N) (8%) Cp(CO) <sub>2</sub> Fe-C≡C-(2-C <sub>5</sub> H <sub>4</sub> N) (66%)
	2	Pd <sub>2</sub> (bda) <sub>3</sub> (5 mol%); CuI (20 mol%); 36°C; 90 min	96%	[Cp(CO) <sub>2</sub> Fe] <sub>2</sub> (8%) [-C≡C-(2-C <sub>5</sub> H <sub>4</sub> N)] <sub>2</sub> (3%) Cp(CO) <sub>2</sub> Fe-C≡C-(2-C <sub>5</sub> H <sub>4</sub> N) (84%)
	3	Pd <sub>2</sub> (bda) <sub>3</sub> (5 mol%); -; 36°C; 90 min	95%	[Cp(CO) <sub>2</sub> Fe] <sub>2</sub> (17%) <b>4</b> (7% [36%]) Cp(CO) <sub>2</sub> Fe-C≡C-(2-C <sub>5</sub> H <sub>4</sub> N) (64%)
	4	PdCl <sub>2</sub> (NCMe) <sub>2</sub> (10 mol%); CuI (20 mol%); RT; 20 min	98%	[Cp(CO) <sub>2</sub> Fe] <sub>2</sub> (5%) Cp(CO) <sub>2</sub> Fe-C≡C-(2-C <sub>5</sub> H <sub>4</sub> N) (91%)
	5	PdCl <sub>2</sub> (NCMe) <sub>2</sub> (2 mol%); CuI (20 mol%); RT; 20 min	97%	[Cp(CO) <sub>2</sub> Fe] <sub>2</sub> (2%) Cp(CO) <sub>2</sub> Fe-C≡C-(2-C <sub>5</sub> H <sub>4</sub> N) (94%)
	6	PdCl <sub>2</sub> (NCMe) <sub>2</sub> (1 mol%); CuI (5 mol%); 60°C; 30 min	98%	[Cp(CO) <sub>2</sub> Fe] <sub>2</sub> (4%) Cp(CO) <sub>2</sub> Fe-C≡C-(2-C <sub>5</sub> H <sub>4</sub> N) (92%)
	7	PdCl <sub>2</sub> (NCMe) <sub>2</sub> (5 mol%); -; 60°C; 90 min	29%	[Cp(CO) <sub>2</sub> Fe] <sub>2</sub> (9%) <b>4</b> (3% [55%]) Cp(CO) <sub>2</sub> Fe-C≡C-(2-C <sub>5</sub> H <sub>4</sub> N) (15%)
 (1.5 equiv)	8	Pd <sub>2</sub> (bda) <sub>3</sub> (5 mol%); CuI (20 mol%); 36°C; 90 min	95%	[Cp(CO) <sub>2</sub> Fe] <sub>2</sub> (6%); [-C≡C-(4-C <sub>5</sub> H <sub>4</sub> N)] <sub>2</sub> (2%); Cp(CO) <sub>2</sub> Fe-C≡C-(4-C <sub>5</sub> H <sub>4</sub> N) (86%)
	9	Pd <sub>2</sub> (bda) <sub>3</sub> (5 mol%);	96%	[Cp(CO) <sub>2</sub> Fe] <sub>2</sub> (20%);

		-; 36°C; 90 min		$[-C\equiv C-(4-C_5H_4N)]_2$ (4%); $Cp(CO)_2Fe-C\equiv C-(4-C_5H_4N)$ (67%)
	10	$PdCl_2(NCMe)_2$ (10 mol%); CuI (20 mol%); RT; 20 min	97%	$Cp(CO)_2Fe-C\equiv C-(4-C_5H_4N)$ (91%)
	11	$PdCl_2(NCMe)_2$ (2 mol%); CuI (20 mol%); RT; 20 min	96%	$Cp(CO)_2Fe-C\equiv C-(4-C_5H_4N)$ (92%)
	12	$PdCl_2(NCMe)_2$ (1 mol%); CuI (5 mol%); 60°C; 30 min	99%	$Cp(CO)_2Fe-C\equiv C-(4-C_5H_4N)$ (96%)
	13	$PdCl_2(NCMe)_2$ (5 mol%); -; 60°C; 90 min	75%	$[Cp(CO)_2Fe]_2$ (7%); $Cp(CO)_2Fe-C\equiv C-(4-C_5H_4N)$ (67%)
 (1.5 equiv)	14	$Pd_2(bda)_3$ (5 mol%); CuI (20 mol%); 36°C; 90 min	96%	$[Cp(CO)_2Fe]_2$ (7%) $[-C\equiv C-(3-C_5H_4N)]_2$ (3%); $Cp(CO)_2Fe-C\equiv C-(3-C_5H_4N)$ (87%)
	15	$PdCl_2(NCMe)_2$ (10 mol%); CuI (20 mol%); RT; 20 min	99%	$[Cp(CO)_2Fe]_2$ (13%) $Cp(CO)_2Fe-C\equiv C-(3-C_5H_4N)$ (83%)
	16	$PdCl_2(NCMe)_2$ (2 mol%); CuI (20 mol%); RT; 20 min	98%	$Cp(CO)_2Fe-C\equiv C-(3-C_5H_4N)$ (93%)
	17	$PdCl_2(NCMe)_2$ (1 mol%); CuI (5 mol%); 60°C; 30 min	99%	$Cp(CO)_2Fe-C\equiv C-(3-C_5H_4N)$ (95%)
	18	$PdCl_2(NCMe)_2$ (5 mol%); -; 60°C; 90 min	74%	$[Cp(CO)_2Fe]_2$ (6%) $Cp(CO)_2Fe-C\equiv C-(3-C_5H_4N)$ (66%)

**Table 3. The conditions of the Pd/Cu-catalyzed synthesis of  $Cp(CO)_2Fe-C\equiv C-(4-C_6H_3N_2S)$**

ethynyl	entry	Catalysts and conditions	Conversion	Isolated products, %
 (1.5 equiv)	1	$PdCl_2(NCMe)_2$ (5 mol%); 1.5 equiv of TBAF; 50°C; 90 min; THF	93%	$[Cp(CO)_2Fe]_2$ (23%); $Cp(CO)_2Fe-C\equiv C-(2-C_5H_4N)$ (61%)
 (1.5 equiv)	2	$PdCl_2(NCMe)_2$ (2 mol%); CuI (20 mol%); 1.5 equiv of DBU; RT; 20 min; THF	97%	$[Cp(CO)_2Fe]_2$ (2%) $Cp(CO)_2Fe-C\equiv C-(2-C_5H_4N)$ (94%)
	3	$PdCl_2(NCMe)_2$ (1 mol%); CuI (5 mol%); 1.5 equiv of DBU; 60°C; 30 min; THF	98%	$[Cp(CO)_2Fe]_2$ (4%) $Cp(CO)_2Fe-C\equiv C-(2-C_5H_4N)$ (92%)

### Proposed catalytic cycle

Previously, the Lo Sterzo group clearly demonstrated a close analogy between the Pd-catalyzed carbon-carbon and metal-carbon bond formation mechanisms through reactions between  $[\eta^5\text{-}(1\text{-diphenylphosphino-2,4-diphenyl)cyclopentadienyl}](\text{CO})_3\text{MI}$  ( $\text{M} = \text{Mo}, \text{W}$ ) and  $\text{PdCl}_2(\text{NCMe})_2$  with following treatment of the resulting binuclear MPd oxidative addition complexes with 4-nitro-1-[2-(tributylstannyl)ethynyl]benzene<sup>57,59</sup> [C-30, R-14]. The mechanism of the Pd/Cu- and Pd-catalyzed pyridylethynylation of cyclopentadienyliron dicarbonyl iodide is apparently analogous to that of the Sonogashira carbon-carbon coupling reactions. The binuclear FePd complex **4** could serve as the evidence of this hypothesis because: (i) first of all, its formation was observed only in Pd-catalyzed reactions of 2-ethynylpyridine with  $\text{Cp}(\text{CO})_2\text{FeI}$  (entry 3 and 7); (ii) secondary, it contains iron and palladium moieties that are bridged by the  $\mu$ -pyridylvinylidene ligand, the Fe-Pd distance is short and evidence of bonding interaction between two metals [FePd acta]. So, the first step of the formation of **4** should be an oxidative addition of  $\text{Cp}(\text{CO})_2\text{FeI}$  to  $\text{Pd}^0$  species that resulted in a binuclear FePd intermediate **A**. Then in the absence of an efficient transmetallating agent such as the copper acetylide or anionic pentacoordinate silicate acetylide species a ligand L substitution in the intermediate **A** and  $\pi$ -coordination of the alkyne took place resulting in complex **A'**. In the following step an acetylene-to-vinylidene rearrangement (AVR) of this  $\pi$ -coordinated 2-ethynylpyridine on iron-palladium center takes place to give **4**. Such examples of the acetylene-to-vinylidene tautomerism involving two adjacent metal centers are known and described in several works<sup>74-78</sup> [B-15, C-32, C-33, C-34, K-40], however, they were much less studied in contrast to the well-understood AVR mediated by a single metal center<sup>79,80</sup> [W-15, W-4]. It is also worth to note that the *ortho*-position of the nitrogen atom in 2-ethynylpyridine plays an important role in the process of the binuclear FePd  $\mu$ -pyridylvinylidene complex formation, the Pd-catalyzed reactions of  $\text{Cp}(\text{CO})_2\text{FeI}$  with 3- and 4-ethynylpyridines simply resulted in decrease of yields of **2** and **3** and didn't give any binuclear products (entries 9, 13, and 18).

To prove our hypothesis on mechanistic aspects of the complex **4** formation we try to direct the Pd-catalyzed reaction between  $\text{Cp}(\text{CO})_2\text{FeI}$  and 2-ethynylpyridine to exclusive formation of it. Indeed, with the use of 1 equivalent of  $\text{Pd}_2(\text{dba})_3$  as a source of palladium atoms and  $\text{NEt}_3$  as a solvent, the reaction proceeds along this path to give **4** with 78% yield (Figure 2). However, even in these conditions the catalytic 2-pyridylethynylation of cyclopentadienyliron dicarbonyl iodide is also observed, but in much lesser degree, the yield of 2-ethynylpyridine complex **1** is only 3% here.

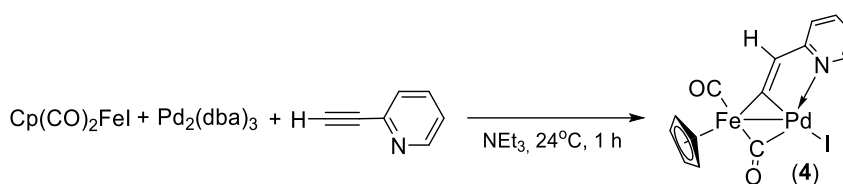


Figure 2

Hence, the formation of the binuclear complex **4** clearly shows that: (i) the oxidative addition of the  $\text{Cp}(\text{CO})_2\text{FeI}$  to the catalytically active  $\text{Pd}^0\text{L}_2$  species occurs; (ii) the coordination of the terminal alkyne to the Pd atom of the binuclear species **A** should also take place to give adduct of the **A'** type. Based on the obtained results and the known mechanistic aspects of the Sonogashira coupling the mechanisms of the pyridylethynylation of cyclopentadienyliron dicarbonyl iodide were proposed (Figure 3). For the Pd/Cu-catalyzed reactions (pathway **A**), a first step of the catalytic cycle would be an oxidative addition of the  $\text{Cp}(\text{CO})_2\text{FeI}$  to the catalytically active  $\text{Pd}^0\text{L}_2$  species to give a binuclear FePd intermediate **A**. Subsequent transmetalation, where transfer of the pyridylacetylide moiety from the Cu-acetylide formed in the copper-cycle to the FePd complex **A** led to a complex **B**, which undergoing *trans* to *cis* isomerization to give a complex **B'**, a following reductive elimination of last results in the Fe-C cross-coupling products  $\text{Cp}(\text{CO})_2\text{Fe-C}\equiv\text{C}(\text{n-C}_5\text{H}_4\text{N})$  ( $\text{n} = \textit{ortho}$  (**1**), *meta* (**2**), *para* (**3**)). In case of the "(trimethylsilyl)ethynylpyridine"



approach the catalytic cycle should be analogous. Only transfer of the pyridylacetylide moiety to the FePd complex **A** should go through anionic pentacoordinate silicate species<sup>72</sup> [H-9]. The initial oxidative addition and the final reductive elimination steps of a mechanism for the Cu-free reaction (pathway **B**) are the same as in the Pd/Cu-catalyzed. However, a ligand L substitution in *the* intermediate **A** by the alkyne took place resulting in complex **A'** with  $\pi$ -coordinated alkyne ligand. The subsequent deprotonation of that then occurs to give the complex **B'**. The formation of the complex **4** in this context can be considered as a side pathway **C** of the Pd-catalyzed reaction between  $\text{Cp}(\text{CO})_2\text{FeI}$  and 2-rhynylpyridine that is facilitated by absence of transmetalating agents and *ortho*-position of the nitrogen atom in the pyridine ring of the alkyne.

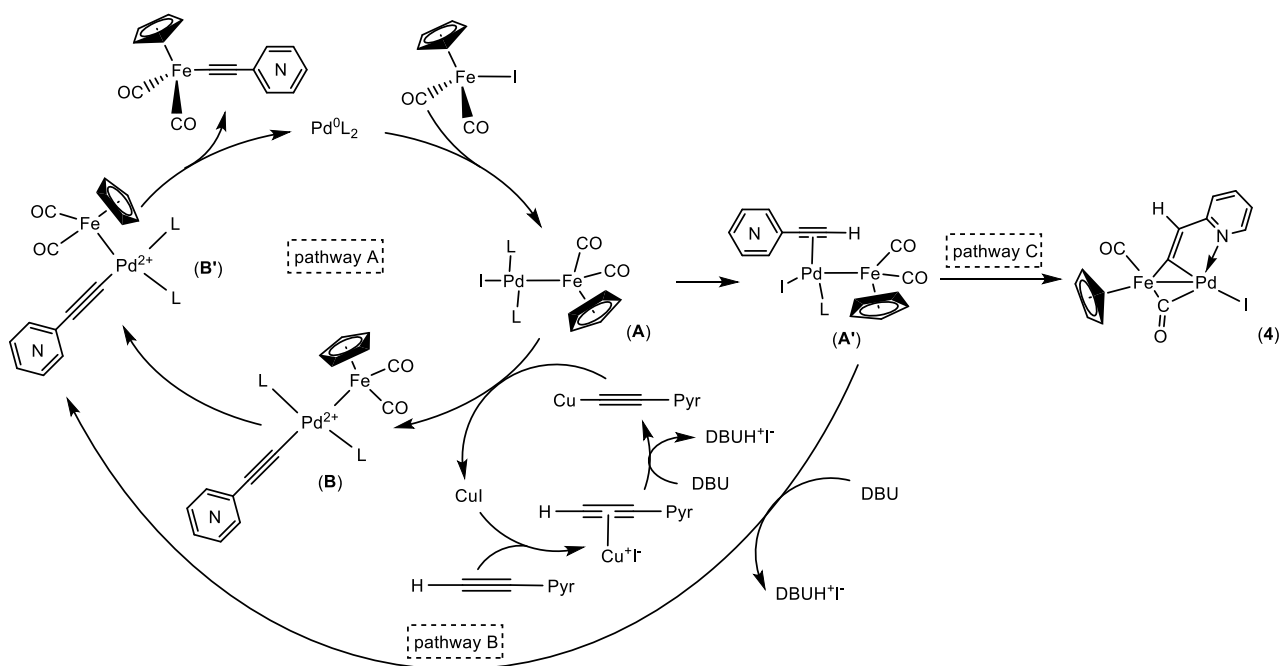


Figure 3

### Characterization of complexes

The IR and the  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR data for the complexes **1-3** and **5** were obtained. The NMR signals were assigned on the basis of  $^1\text{H}$ - $^{13}\text{C}$  correlations measured through HSQC and HMBC experiments, respectively (Table 3). The structure of the complexes can be deduced from the combined NMR and IR data, which are similar to those of previously described  $\sigma$ -alkynyl iron complexes<sup>34,54,60</sup> [N-4, C-25, G-10].

**Table 3.** IR and NMR ( $\delta$ , ppm [ $J$ , Hz]) spectroscopic data for the  $\text{Cp}(\text{CO})_2\text{Fe}-\text{C}\equiv\text{C}-(n-\text{C}_5\text{H}_4\text{N})$  [ $n = \textit{ortho}$  (**1**), *meta* (**2**), *para* (**3**)] and  $\text{Cp}(\text{CO})_2\text{Fe}-\text{C}\equiv\text{C}-(4-\text{C}_6\text{H}_3\text{N}_2\text{S})$  (**5**).

complex	NMR ( $\delta$ , ppm [ $J$ , Hz], $\text{CD}_2\text{Cl}_2$ )					IR, $\text{cm}^{-1}$ ( $\text{CH}_2\text{Cl}_2$ )
	$^1\text{H}$	$^{13}\text{C}$				
	$\text{C}_5\text{H}_5$	$\sigma\text{-C}_\alpha\equiv\text{C}_\beta\text{-(}n\text{-C}_5\text{H}_4\text{N)}$		$\text{C}_5\text{H}_5$	CO	
		$\text{C}_\alpha$	$\text{C}_\beta$			
<b>1</b> ( <i>ortho</i> )	5.14 s	116.7	95.4	85.4	212.2	2112s ( $\nu_{\text{C}\equiv\text{C}}$ ) 2043vs, 1997vs ( $\nu_{\text{CO}}$ ) 1582m, 1556w ( $\nu_{\text{C}=\text{C}}$ and $\nu_{\text{C}=\text{N}}$ )
<b>2</b> ( <i>meta</i> )	5.13 s	112.3	95.7	85.3	212.4	2111s ( $\nu_{\text{C}\equiv\text{C}}$ ) 2044vs, 1996vs ( $\nu_{\text{CO}}$ ) 1580w, 1561w ( $\nu_{\text{C}=\text{C}}$ and $\nu_{\text{C}=\text{N}}$ )

<b>3</b> ( <i>para</i> )	5.13 s	114.3	102.0	85.6	212.3	2110s ( $\nu_{C\equiv C}$ ) 2044vs, 1998vs ( $\nu_{CO}$ ) 1591s ( $\nu_{C=C}$ and $\nu_{C=N}$ )
<b>5</b>	5.20 s	112.3	102.9	85.6	212.3	

The IR spectra of **1-3** in  $\text{CH}_2\text{Cl}_2$  solution shows two very strong absorptions at about 2043 and 1996  $\text{cm}^{-1}$  that corresponds to the  $\nu(\text{C}\equiv\text{O})$  stretching modes of carbonyl groups at the iron atom. An additional absorption with strong intensity at about 2111  $\text{cm}^{-1}$  are attributed to the  $\nu(\text{C}\equiv\text{C})$  stretching frequencies of the alkynyl ligand. The  $\nu(\text{CO})$  and the  $\nu(\text{C}\equiv\text{C})$  frequencies of the complex **5** with  $\sigma$ -4-ethynyl-2,1,3-benzothiadiazole ligand is insignificantly shifted to low-frequency in comparison with **1-3**. The  $^{13}\text{C}$  chemical shifts of  $\alpha$ - and  $\beta$ -alkynyl carbons of **1-3** and **5** resonate as singlets in the regions  $\delta$  112-117 and 95-103 ppm, respectively. Noteworthy that these signals slightly vary with the nature of the substituents in  $\sigma$ -alkynyl ligands, while the chemical shifts of the cyclopentadienyl and carbonyl groups coordinated to the iron atom are almost independent of their nature (Table 3). The presence of the pyridyl substituents in **1-3** is indicated by signals between 7.02 and 8.50 ppm in  $^1\text{H}$  NMR spectra, and between 119 and 152 ppm in  $^{13}\text{C}$  NMR spectra of the complexes. The  $^{13}\text{C}$  and  $^1\text{H}$  chemical shifts of the atoms of the 2,1,3-benzothiadiazole group in **5** resonate in the regions  $\delta$  118-156 and  $\delta$  7.48-7.76 ppm, respectively. So, overall the IR and NMR spectra parameters of **1-3** and **5** are similar to those found for analogous cyclopentadienyliron dicarbonyl complexes with different  $\sigma$ -alkynyl ligands<sup>34,54,60</sup> [N-4, C-25, G-10].

The molecular structures of the complexes  $\text{Cp}(\text{CO})_2\text{Fe}-\text{C}\equiv\text{C}-(2-\text{C}_5\text{H}_4\text{N})$  (**1**),  $\text{Cp}(\text{CO})_2\text{Fe}-\text{C}\equiv\text{C}-(3-\text{C}_5\text{H}_4\text{N})$  (**2**),  $\text{Cp}(\text{CO})_2\text{Fe}-\text{C}\equiv\text{C}-(4-\text{C}_5\text{H}_4\text{N})$  (**3**), and  $\text{Cp}(\text{CO})_2\text{Fe}-\text{C}\equiv\text{C}-(4-\text{C}_6\text{H}_3\text{N}_2\text{S})$  (**5**) were solved on the base of X-ray diffractometry. Suitable crystals of **1-3** and **5** were grown from dichloromethane:hexane mixtures. The views of the structures are shown in Figure 4, selected bond lengths and angles are given in Table. Crystal data and refinement parameters are included in the supporting information.

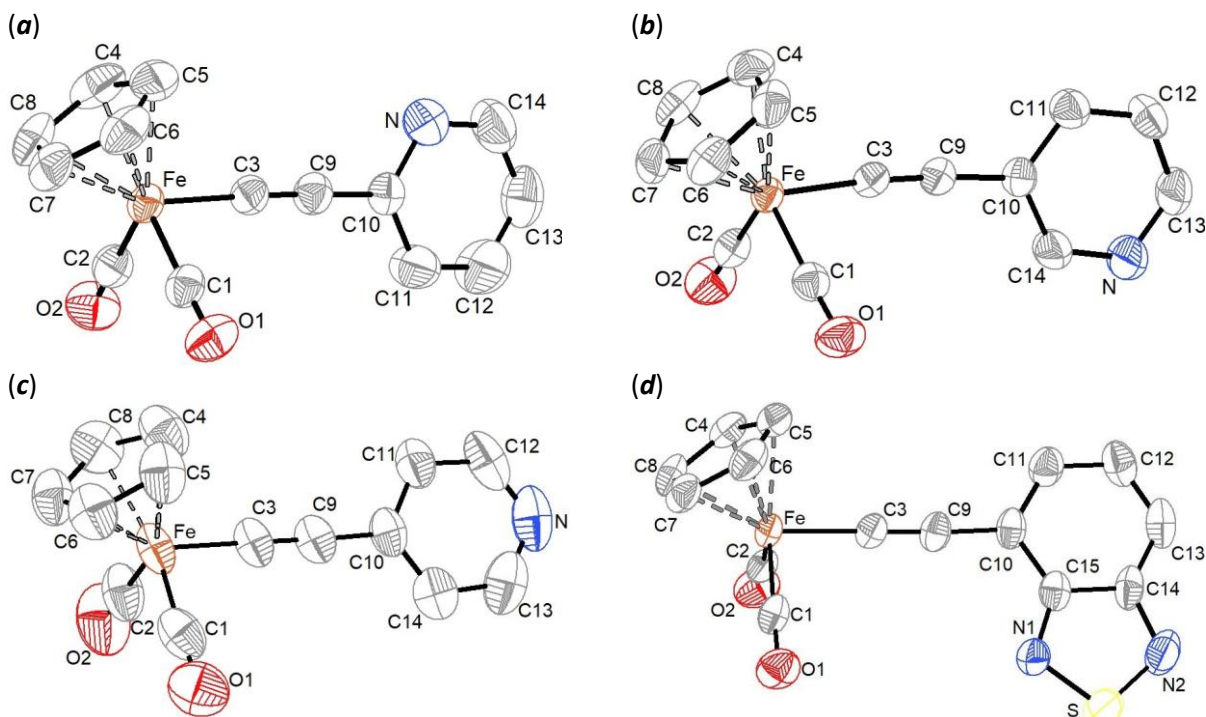


Figure 4. Molecular structures of **1** (a), **2** (b), **3** (c), and **5** (d) with the thermal ellipsoids set at the 50% probability level.

The proximity of crystals **1** and **2** cell parameters (Table 3S) and small differences in the sequence of atoms in their molecules suggest small differences in a packing of molecules. Indeed, structures **1** and **2** are mirror-like each other, and the mirror plane is perpendicular to the cell axis *b*. The iron atom in the obtained complexes **1-3** and **5** is coordinated by a cyclopentadienyl ring in  $\eta^5$ -fashion, two terminal CO ligands, and  $\sigma$ -alkynyl ligand to adopt a typical pseudo-tetrahedral geometry. The bond lengths and angles in **1-3** and **5** are close to each other and are not unusual in comparison with those that were found in the known complexes of the type  $\text{Cp}(\text{CO})_2\text{Fe-C}\equiv\text{C-R}$  []. However, one can be detected some minor differences between the obtained complexes. The ethynyl ligands are in a  $\sigma$ -coordination mode and tend to form an almost linear  $\text{Fe-C}_\alpha\equiv\text{C}_\beta$ - angle, but only in **3** and **5** this one is about  $179^\circ$ , whereas in **1** and **2** it is about  $175^\circ$ . In complex **3** the  $\text{Fe-C}_\alpha$  bond length is shorter by approximately  $0.01\text{\AA}$  than the same bonds in complexes **1**, **2** and **5**. The other differences in geometry of the complexes' molecules are associated with the position of  $\text{C}\equiv\text{C-R}$  moiety relative to the iron fragment. The ethynylpyridyl ligands in **1** and **2** and the 4-ethynyl-2,1,3-benzothiadiazole ligand in **5** lean slightly toward one of the carbonyl group of the iron atom in such a way that the planes between ring of the substituent and  $[\text{Fe}(\text{CO})_2]$  fragment exhibit angles about  $81^\circ$ . At the same time, in the complex **3** the *para*-pyridylethynyl ligand is almost perpendicular to plane formed by two carbonyl ligands and the iron atom. Moreover, an angles between planes of the substituent's ring in the  $\sigma$ -alkynyl and the cyclopentadienyl ligand are about  $70^\circ$  in **3** and **5**, whereas the analogous angles in **1** and **2** are ca.  $85^\circ$ . There are also interesting that the pyridyl substituents in **1** and **2** differ in their orientations, when the nitrogen atom in **1** is oriented to Cp ring, in the complex **2** the nitrogen is placed opposite (oriented to carbonyl groups).

**Table 4.** Selected bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) for the complexes **1-3** and **5**

	<b>1</b>	<b>2</b>	<b>3</b>	<b>5</b>
<i>Distances, <math>\text{\AA}</math></i>				
Fe-C3	1.9159(17)	1.919(2)	1.906(3)	1.9168(1)
C3-C9	1.204(2)	1.200(3)	1.203(5)	1.2060(1)
C9-C10	1.4362(0)	1.4372(1)	1.4247(1)	1.4360(1)
Fe-Cp	1.7223(8)	1.7200(11)	1.7186(19)	1.7230()
<i>Bond angles, <math>^\circ</math></i>				
Fe-C3-C9	175.94(16)	174.3(2)	179.4(4)	178.646(5)
C3-C9-C10	176.54(19)	176.8(3)	177.7(5)	174.532(6)
C3-Fe-C1	89.26(8)	86.8(1)	89.68(17)	88.827(7)
C3-Fe-C2	87.11(8)	89.4(1)	89.07(16)	89.584(3)
<i>Torsion angles, <math>^\circ</math></i>				
	C1-Fe-C13-C12 = 45.06(2)	C1-Fe-C13-N = 49.70(2)	C1-Fe-N-C13 = 21.124(4)	C1-Fe-C13-C14 = 12.787(4)
<i>Angles between planes, <math>^\circ</math></i>				
$\eta^5$ -Cp:Pyr	84.51(7)	84.58(8)	68.64(14)	70.676() <sup>a</sup>
(O1-C1-Fe-C2-O2):Pyr	81.38(6)	80.97(7)	88.27(8)	81.417() <sup>b</sup>
Pyr: (Fe-C3-C9-C10-C11)	5.9(2)	6.4(3)	0.6(3)	8.254() <sup>c</sup>

## Conclusion

In this paper, two approaches have been utilized to perform pyridylethynylation of cyclopentadienyliron dicarbonyl iodide, that based on Pd/Cu- and Pd-catalyzed Fe-C coupling of

(trimethylsilyl)ethynylpyridines and ethynylpyridines with  $\text{Cp}(\text{CO})_2\text{FeI}$ . Although, these two approaches differ only in nature of species participating in transmetallation step (transfer of the pyridylacetylde moiety to the catalytically active species), the second “ethynylpyridine” approach was found to be much more effective, than first one. So, the  $\sigma$ -pyridylethynyl iron complexes  $\text{Cp}(\text{CO})_2\text{Fe}-\text{C}\equiv\text{C}-(n-\text{C}_5\text{H}_4\text{N})$  ( $n = \textit{ortho}$  (**1**), *meta* (**2**), *para* (**3**)) was obtained in heist yields (about 95%) by reactions between ethynylpyridines and  $\text{Cp}(\text{CO})_2\text{FeI}$  in THF with use of 1,8-Diazabicyclo[5.4.0]undec-7-ene as a base, 1 mol% of  $\text{PdCl}_2(\text{NCMe})_2$  and 5 mol% of  $\text{CuI}$  at 60°C in 30 minutes. In case of the Cu-free coupling between  $\text{Cp}(\text{CO})_2\text{FeI}$  and 2-ethynylpyridine the additional side-reaction are observed, resulting in formation of trace amount of the binuclear  $[\text{Cp}(\text{CO})\text{Fe}\{\mu_2-\eta^1(\text{C}_\alpha):\eta^1(\text{C}_\alpha)-\kappa^1(\text{N})-\text{C}_\alpha=\text{C}_\beta(\text{H})(2-\text{C}_5\text{H}_4\text{N})\}\{\mu-\text{CO}\}\text{PdI}]$  complex **4**. This complex was considered by us as a “trapped” oxidation-addition intermediate generated by acetylene-to-vinylidene rearrangement (AVR) of  $\pi$ -coordinated alkyne on iron-palladium center. Therefore, the isolation of this binuclear complex and development of its synthesis allowed to propose mechanisms of the Pd/Cu- and Pd-catalyzed transformations of ethynylpyridines and cyclopentadienyliron dicarbonyl iodide into the  $\sigma$ -pyridylethynyl iron complexes. The developed methodology can be extended to the synthesis of other  $\sigma$ -alkynyl complexes of iron. So, the coupling of cyclopentadienyliron dicarbonyl iodide and 4-ethynyl-2,1,3-benzothiadiazole under the same condition as above was found to proceed efficiently resulting in the complex  $\text{Cp}(\text{CO})_2\text{Fe}-\text{C}\equiv\text{C}-(4-\text{C}_6\text{H}_3\text{N}_2\text{S})$  (**5**). The spectroscopic and structural features of **1-3**, **5** were described.

## Experimental section

All operations and manipulations were carried out under an argon atmosphere. Solvents (dichloromethane, petroleum ether, ethyl acetate, hexane, triethylamine) were purified by distillation from appropriate drying agents and stored under argon. THF was dried by refluxing over sodium/benzophenone and freshly distilled prior to use. The course of reactions was monitored by TLC on Silica gel (Alu foils, Sigma-Aldrich) and IR spectroscopy. Neutral silica gel (Silica 60, 0.2-0.5 mm, Macherey-Nagel) was used for column chromatography. Physical-chemical characteristics were obtained in the Krasnoyarsk Regional Centre of Research Equipment, Siberian Branch of the Russian Academy of Sciences. The IR spectra were recorded on the Shimadzu IR Tracer-100 spectrometer (Japan).  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$ ,  $^{31}\text{P}\{^1\text{H}\}$ , HSQC, and HMBC NMR spectra were obtained using NMR spectrometer AVANCE III 600 (Bruker, Germany). Chemical shifts are reported in ppm units referenced to residual solvent resonances for  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$ , HSQC, and HMBC spectra or to an external 85%  $\text{H}_3\text{PO}_4(\text{aq})$  standard for  $^{31}\text{P}\{^1\text{H}\}$  spectra. The X-ray data for **1-3** were obtained with the Smart Photon II diffractometer (Bruker AXS, Germany).  $\text{Pd}(\text{Cl})_2(\text{PPh}_3)_2$ <sup>81</sup> [H-20],  $\text{Pd}(\text{Cl})_2(\text{NCMe})_2$ <sup>82</sup> [A-53],  $\text{Pd}_2(\text{dba})_3\cdot\text{CHCl}_3$ <sup>83</sup> [Z-2], and  $\text{Cp}(\text{CO})_2\text{FeI}$ <sup>84</sup> [K-38] were prepared according to literature procedures. *Ortho*-, *meta*-, *para*-[(trimethylsilyl)ethynyl]pyridines<sup>85</sup> [S-34] and 4-(trimethylsilyl)ethynyl-2,1,3-benzothiadiazole<sup>86</sup> [P-14] were prepared from ethynyltrimethylsilane. *Ortho*- and *para*-ethynylpyridines were synthesised from 2-methyl-4-(*n*-pyridyl)but-3-yn-2-ol intermediates by elimination of acetone, according to published procedures<sup>73</sup> [R-10]. *Meta*-ethynylpyridine and 4-ethynyl-2,1,3-benzothiadiazole were obtained by desilylation of *meta*-[(trimethylsilyl)ethynyl]pyridine<sup>87</sup> [B-54] and 4-(trimethylsilyl)ethynyl-2,1,3-benzothiadiazole<sup>86</sup> [P-14]. Tetrabutylammonium fluoride solution (1M solution in THF, Aldrich), 1,8-Diazabicyclo[5.4.0]undec-7-ene (Aldrich), 1M and catalyst  $\text{CuI}$  (“Vekton-M” Ltd.) were purchased and used directly. In the experimental part the synthetic procedures to the complexes **1-3** and **5** providing the highest yields are described (Table 2, entries 6, 12, and 17; Table 2, entry 4), the detailed isolation procedures, synthetic procedure to the complexes, and characterization of the products can be found in the Supporting Information.

### Synthesis of $\text{Cp}(\text{CO})_2\text{Fe}-\text{C}\equiv\text{C}-(2-\text{C}_5\text{H}_4\text{N})$ (**1**).

Cyclopentadienyliron dicarbonyl iodide (315 mg, 1.036 mmol) and 2-ethynylpyridine (0.155 mL, 158 mg, 1.534 mmol) were dissolved in freshly distilled THF (10 mL), then DBU (0.23 mL, 234 mg, 1.539 mmol), PdCl<sub>2</sub>(NCMe)<sub>2</sub> (3 mg, 0.012 mmol), and CuI (10 mg, 0.052 mmol) were added. The resulting mixture is stirred at 60°C for 30 minutes, then the reaction mixture was evaporated to dryness; the residue was dissolved in dichloromethane and passed through a pad (0.5 cm) of silica gel by using ethyl acetate as an eluent. The filtrate was concentrated in vacuo and chromatographed on silica gel (9×2cm). A dark-yellow fraction containing the  $\sigma$ -alkynylpyridine iron complex was eluted with petroleum ether-ethyl acetate (3:7) mixture and subsequently with ethyl acetate. The complex Cp(CO)<sub>2</sub>Fe-C≡C-(2-C<sub>5</sub>H<sub>4</sub>N) (**1**) was isolated as brown-yellow solids after evaporation of the solvent (266 mg, 0.953 mmol, 92%). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 25°C)  $\delta$ , ppm [*J*, Hz]: 5.14 (s, 5H, C<sub>5</sub>H<sub>5</sub>); 7.02 (ddd, 1H, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, <sup>3</sup>J<sub>HH</sub> = 5.3 Hz, <sup>4</sup>J<sub>HH</sub> = 0.8 Hz, **H**<sub>para</sub> of (2-Pyr) (H<sup>4</sup>)); 7.22 (d, 1H, <sup>3</sup>J<sub>HH</sub> = 8.0 Hz, **H**<sub>ortho</sub> of (2-Pyr) (H<sup>6</sup>)); 7.53 (td, 1H, <sup>3</sup>J<sub>HH</sub> = 7.7 Hz, <sup>4</sup>J<sub>HH</sub> = 1.6 Hz, **H**<sub>meta</sub> of (2-Pyr) (H<sup>5</sup>)); 8.40 (d, 1H, <sup>3</sup>J<sub>HH</sub> = 5.3 Hz, N-C-**H**<sub>meta</sub> of  $\equiv$ C<sup>2</sup>(2-Pyr) (H<sup>3</sup>)). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 25°C)  $\delta$ , ppm [*J*, Hz]: 85.4 (s, C<sub>5</sub>H<sub>5</sub>); 95.4 (s,  $\equiv$ C<sup>2-</sup>); 116.7 (s, -C<sup>1</sup> $\equiv$ ); 119.9 (s, C<sub>meta</sub> of (2-Pyr) (C<sup>5</sup>)); 125.9 (s, N-C<sub>meta</sub> of (2-Pyr) (C<sup>6</sup>)); 135.3 (s, C<sub>para</sub> of (2-Pyr) (C<sup>4</sup>)); 145.8 (s, C<sub>ipso</sub> of (2-Pyr)); 149.0 (s, C<sub>ortho</sub> of (2-Pyr) (C<sup>3</sup>)); 212.2 (s, 2Fe-CO). IR (CH<sub>2</sub>Cl<sub>2</sub> v/ cm<sup>-1</sup>): 2112s ( $\nu_{C\equiv C}$ ), 2043vs, 1997vs ( $\nu_{CO}$ ), 1582m, 1556w, 1460m ( $\nu_{C=C}$  and  $\nu_{C=N}$ ). IR (KBr v/ cm<sup>-1</sup>): 2108s ( $\nu_{C\equiv C}$ ), 2034vs, 1982vs ( $\nu_{CO}$ ), 1582m, 1556w, 1457m ( $\nu_{C=C}$  and  $\nu_{C=N}$ ). Anal. Found: C, 32.75; H, 1.96%; N, 2.73%. Calc. For C<sub>14</sub>H<sub>9</sub>FeNO<sub>2</sub> (279): C, 60.25%; H, 3.25%; N, 5.02%.

#### Synthesis of Cp(CO)<sub>2</sub>Fe-C≡C-(3-C<sub>5</sub>H<sub>4</sub>N) (**2**).

Following the procedure described for preparation of **1**, complex Cp(CO)<sub>2</sub>Fe-C≡C-(3-C<sub>5</sub>H<sub>4</sub>N) (**2**) was obtained with 95% yield (218 mg, 0.781 mmol) from cyclopentadienyliron dicarbonyl iodide (250 mg, 0.822 mmol) and 3-ethynylpyridine (127 mg, 1.223 mmol) with the use of THF (8 mL), DBU (0.18 mL, 183 mg, 1.204 mmol), PdCl<sub>2</sub>(NCMe)<sub>2</sub> (2 mg, 0.008 mmol), and CuI (8 mg, 0.042 mmol). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 25°C)  $\delta$ , ppm [*J*, Hz]: 5.13 (s, 5H, C<sub>5</sub>H<sub>5</sub>); 7.14 (dd, 1H, <sup>3</sup>J<sub>HH</sub> = 7.3 Hz, <sup>3</sup>J<sub>HH</sub> = 5.0 Hz, **H**<sub>meta</sub> of (3-Pyr) (H<sup>5</sup>)); 7.54 (d, 1H, <sup>3</sup>J<sub>HH</sub> = 8.0 Hz, **H**<sub>para</sub> of (3-Pyr) (H<sup>6</sup>)); 8.30 (d, 1H, <sup>3</sup>J<sub>HH</sub> = 3.2 Hz, **H**<sub>ortho</sub> of (3-Pyr) (H<sup>4</sup>)); 8.49 (s, 1H, N-C-**H**<sub>ortho</sub> of (3-Pyr) (H<sup>2</sup>)). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 25°C)  $\delta$ , ppm [*J*, Hz]: 85.3 (s, C<sub>5</sub>H<sub>5</sub>); 95.7 (s,  $\equiv$ C<sup>2-</sup>); 112.3 (s, -C<sup>1</sup> $\equiv$ ); 122.4 (s, C<sub>meta</sub> of (3-Pyr) (C<sup>5</sup>)); 124.6 (s, C<sub>ipso</sub> of (3-Pyr)) 137.3 (s, C<sub>para</sub> of (3-Pyr) (C<sup>6</sup>)); 145.3 (s, C<sub>ortho</sub> of (3-Pyr) (C<sup>4</sup>)); 152.1 (s, N-C<sub>ortho</sub> of (3-Pyr) (C<sup>2</sup>)) 212.4 (s, 2Fe-CO). IR (CH<sub>2</sub>Cl<sub>2</sub> v/ cm<sup>-1</sup>): 2111s ( $\nu_{C\equiv C}$ ), 2044vs, 1996vs ( $\nu_{CO}$ ), 1580w, 1561w, 1474w ( $\nu_{C=C}$  and  $\nu_{C=N}$ ). IR (KBr v/ cm<sup>-1</sup>): 2103s ( $\nu_{C\equiv C}$ ), 2038vs, 1994vs ( $\nu_{CO}$ ), 1572w, 1555w, 1473w ( $\nu_{C=C}$  and  $\nu_{C=N}$ ). Anal. Found: C, 32.75; H, 1.96%; N, 2.73%. Calc. For C<sub>14</sub>H<sub>9</sub>FeNO<sub>2</sub> (279): C, 60.25%; H, 3.25%; N, 5.02%.

#### Synthesis of Cp(CO)<sub>2</sub>Fe-C≡C-(4-C<sub>5</sub>H<sub>4</sub>N) (**3**).

Similarly, from cyclopentadienyliron dicarbonyl iodide (339 mg, 1.115 mmol) and 4-ethynylpyridine (173 mg, 1.680 mmol) with the use of THF (10 mL), DBU (0.25 mL, 255 mg, 1.678 mmol), PdCl<sub>2</sub>(NCMe)<sub>2</sub> (3 mg, 0.012 mmol), and CuI (11 mg, 0.052 mmol) was obtained Cp(CO)<sub>2</sub>Fe-C≡C-(4-C<sub>5</sub>H<sub>4</sub>N) (**3**) (299 mg, 1.072 mmol, 96%). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 25°C)  $\delta$ , ppm [*J*, Hz]: 5.13 (s, 5H, C<sub>5</sub>H<sub>5</sub>); 7.11 (dd, 2H, <sup>3</sup>J<sub>HH</sub> = 5.4 Hz, **H**<sub>meta</sub> of (4-Pyr)); 8.39 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 4.7 Hz, **H**<sub>ortho</sub> of (4-Pyr)). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 25°C)  $\delta$ , ppm [*J*, Hz]: 85.6 (s, C<sub>5</sub>H<sub>5</sub>); 102.1 (s,  $\equiv$ C<sup>2-</sup>); 114.2 (s, -C<sup>1</sup> $\equiv$ ); 125.5 (s, C<sub>ortho</sub> of (4-Pyr)); 135.3 (s, C<sub>ipso</sub> of (4-Pyr)); 149.3 (s, C<sub>meta</sub> of (3-Pyr)); 212.3 (s, 2Fe-CO). IR (CH<sub>2</sub>Cl<sub>2</sub> v/ cm<sup>-1</sup>): 2110s ( $\nu_{C\equiv C}$ ), 2044vs, 1998vs ( $\nu_{CO}$ ), 1591s ( $\nu_{C=C}$  and  $\nu_{C=N}$ ). IR (KBr v/ cm<sup>-1</sup>): 2109s ( $\nu_{C\equiv C}$ ), 2037vs, 1992vs ( $\nu_{CO}$ ), 1589s, 1526w, 1487w ( $\nu_{C=C}$  and  $\nu_{C=N}$ ). Anal. Found: C, 32.75; H, 1.96%; N, 2.73%. Calc. For C<sub>14</sub>H<sub>9</sub>FeNO<sub>2</sub> (279): C, 60.25%; H, 3.25%; N, 5.02%.

#### [Cp(CO)Fe{ $\mu$ -2- $\eta$ 1(C $\alpha$ ): $\eta$ 1(C $\alpha$ )- $\kappa$ 1(N)-C $\alpha$ =C $\beta$ (H)(2-C<sub>5</sub>H<sub>4</sub>N)}{ $\mu$ -CO}PdI] (**4**).

Cyclopentadienyliron dicarbonyl iodide (162 mg, 0.533 mmol) and Pd<sub>2</sub>(dba)<sub>3</sub>·CHCl<sub>3</sub> (277 mg, 0.268 mmol) were dissolved in triethylamine (8 mL). 2-ethynylpyridine (0.055 mL, 0.545 mmol) was added to the vigorously stirred mixture, which was then stirred for 1 hour at room temperature. Following removal of NEt<sub>3</sub> by evaporation, dichloromethane was added and the solution was filtered through a pad (0.5 cm) of silica gel by using ethyl acetate as an eluent. The filtrate was concentrated to about 1 mL volume and chromatographed on a silica gel column (8 × 1 cm). Four fractions were successively eluted with petroleum ether-ethyl acetate (9:1), (4:1), (3:2) mixtures and finally with ethyl acetate. The first yellow-brown fraction gave 3 mg of an initial Cp(CO)<sub>2</sub>FeI. 167 mg (89%) of dibenzylideneacetone was obtained from the second bright yellow fraction. The binuclear FePd complex **4** was isolated in 78% yield (213 mg, 0.415 mmol) as a brown solid after evaporation of the solvent from the third orange fraction. A fourth dark-yellow fraction contained 4 mg (0.014 mmol, 3% yield) of Cp(CO)<sub>2</sub>Fe-C≡C-(2-C<sub>5</sub>H<sub>4</sub>N) (**1**). A recrystallization of Cp(CO)<sub>2</sub>Fe(μ-C=CH(2-C<sub>5</sub>H<sub>4</sub>N))PdI from CH<sub>2</sub>Cl<sub>2</sub>-hexane (1:2) mixture gave 176 mg of red-brown microcrystals. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 25°C) δ, ppm [*J*, Hz]: 5.25 (s, C<sub>5</sub>H<sub>5</sub>); 6.91 (d, *J*<sub>HH</sub> = 8.2, *H*<sub>ortho</sub> of (2-Pyr)); 7.07 (t, *J*<sub>HH</sub> = 5.9, *H*<sub>meta</sub> of (2-Pyr)); 7.54 s (=C<sup>2</sup>H); 7.69 (t, *J*<sub>HH</sub> = 7.3, *H*<sub>para</sub> of (2-Pyr)); 9.41 (d, *J*<sub>HH</sub> = 3.4, N-C-*H*<sub>meta</sub> of (2-Pyr)). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 25°C) δ, ppm [*J*, Hz]: 88.3 (s, C<sub>5</sub>H<sub>5</sub>); 115.2 (s, C<sub>ortho</sub> of (2-Pyr)); 121.0 (s, C<sub>meta</sub> of (2-Pyr)); 139.1 (s, C<sub>para</sub> of (2-Pyr)); 140.2 (s, =C<sup>2</sup>H); 153.2 (s, N-C<sub>meta</sub> of (2-Pyr)); 171.0 (s, C<sub>ipso</sub> of (2-Pyr)); 206.25 (s, Fe-CO); 230.77 (s, Fe-CO<sub>bridging</sub>); 312.8 (s, μ-C<sup>1</sup>=). IR (CH<sub>2</sub>Cl<sub>2</sub> v/ cm<sup>-1</sup>): 2026s, 1876s (ν<sub>CO</sub>), 1600m, 1582m, 1550m, 1466 m (ν<sub>C=C</sub> and ν<sub>C=N</sub>). IR (KBr v/ cm<sup>-1</sup>): 2005s, 1848s (ν<sub>CO</sub>), 1599m, 1583m, 1546m, 1464 m (ν<sub>C=C</sub> and ν<sub>C=N</sub>). Anal. Found: C, 32.75; H, 1.96%; N, 2.73%. Calc. For C<sub>14</sub>H<sub>10</sub>FeINO<sub>2</sub>Pd (513): C, 32.75; H, 1.96%; N, 2.73%.

#### Synthesis of Cp(CO)<sub>2</sub>Fe-C≡C-(4-C<sub>6</sub>H<sub>3</sub>N<sub>2</sub>S) (**5**).

Following the procedure described for preparation of **1-3**, complex Cp(CO)<sub>2</sub>Fe-C≡C-(4-C<sub>6</sub>H<sub>3</sub>N<sub>2</sub>S) (**5**) was obtained from cyclopentadienyliron dicarbonyl iodide (250 mg, 0.822 mmol) and 4-ethynyl-2,1,3-benzothiadiazole (127 mg, 1.223 mmol) with the use of THF (8 mL), DBU (0.18 mL, 183 mg, 1.204 mmol), PdCl<sub>2</sub>(NCMe)<sub>2</sub> (2 mg, 0.008 mmol), and CuI (8 mg, 0.042 mmol). The product was isolated from the reaction mixture by column chromatography on silica gel (9×2cm). A dark-yellow fraction containing the σ-4-ethynyl-2,1,3-benzothiadiazole iron complex was eluted with petroleum ether-ethyl acetate (4:1) mixture. The complex Cp(CO)<sub>2</sub>Fe-C≡C-(4-C<sub>6</sub>H<sub>3</sub>N<sub>2</sub>S) (**5**) was obtained as brown-yellow solids after evaporation of the solvent (266 mg, 0.953 mmol, 92%).

<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 25°C) δ, ppm [*J*, Hz]: 5.13 (s, 5H, C<sub>5</sub>H<sub>5</sub>); 7.14 (dd, 1H, <sup>3</sup>*J*<sub>HH</sub> = 7.3 Hz, <sup>3</sup>*J*<sub>HH</sub> = 5.0 Hz, *H*<sub>meta</sub> of (3-Pyr) (H<sup>5</sup>)); 7.54 (d, 1H, <sup>3</sup>*J*<sub>HH</sub> = 8.0 Hz, *H*<sub>para</sub> of (3-Pyr) (H<sup>6</sup>)); 8.30 (d, 1H, <sup>3</sup>*J*<sub>HH</sub> = 3.2 Hz, *H*<sub>ortho</sub> of (3-Pyr) (H<sup>4</sup>)); 8.49 (s, 1H, N-C-*H*<sub>ortho</sub> of (3-Pyr) (H<sup>2</sup>)). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 25°C) δ, ppm [*J*, Hz]: 85.6 (s, C<sub>5</sub>H<sub>5</sub>); 102.9 (s, ≡C<sup>2</sup>-); 112.3 (s, -C<sup>1</sup>≡); 118.1 (s, C<sub>para</sub> of (4-C<sub>6</sub>H<sub>3</sub>N<sub>2</sub>S)); 121.1 (s, C<sub>ipso</sub> of (4-C<sub>6</sub>H<sub>3</sub>N<sub>2</sub>S)); 129.4 (s, C<sub>ortho</sub> of (4-C<sub>6</sub>H<sub>3</sub>N<sub>2</sub>S)) and 130.1 (s, C<sub>meta</sub> of (4-C<sub>6</sub>H<sub>3</sub>N<sub>2</sub>S)); 154.8 (s, N-C<sub>meta</sub> of (4-C<sub>6</sub>H<sub>3</sub>N<sub>2</sub>S)); 155.7 (s, N-C<sub>ortho</sub> of (4-C<sub>6</sub>H<sub>3</sub>N<sub>2</sub>S)); 212.3 (s, 2Fe-CO). IR (CH<sub>2</sub>Cl<sub>2</sub> v/ cm<sup>-1</sup>): 2111s (ν<sub>C≡C</sub>), 2044vs, 1996vs (ν<sub>CO</sub>), 1580w, 1561w, 1474w (ν<sub>C=C</sub> and ν<sub>C=N</sub>). IR (KBr v/ cm<sup>-1</sup>): 2095s (ν<sub>C≡C</sub>), 2031vs, 1976vs (ν<sub>CO</sub>), 1636 br.w; 1576w, 1527m (ν<sub>C=C</sub> and ν<sub>C=N</sub>).

Anal. Found: C, 32.75; H, 1.96%; N, 2.73%. Calc. For C<sub>15</sub>H<sub>8</sub>FeN<sub>2</sub>O<sub>2</sub>S (336): C, 53.60%; H, 2.40%; N, 8.33%.

#### X-ray diffraction studies

Crystal data and X-ray experimental details for the complexes **1-3** and **5** are given in Table 4S (the Supporting Information). Brown-yellow crystals of the complexes suitable for X-ray diffraction analysis were obtained by evaporation of a solution of the complexes in a dichloromethane : hexane mixture = 1:2 under argon atmosphere at +5°C. The experimental data were collected on a Smart Photon II diffractometer (Bruker AXS) with CCD area detector and graphite monochromator using MoK $\alpha$  radiation ( $\lambda = 0.71073\text{\AA}$ ,  $2\theta \leq 60^\circ$ ) at room temperature. Absorption corrections ( $\mu_{\text{Mo}} = 1.256 \text{ mm}^{-1}$ ) have been

applied using multiscan procedure<sup>88</sup>. The structures were solved by direct methods and refined by full-matrix least squares on  $F^2$ , using SHELX programs<sup>89,90</sup>. Hydrogen atoms have been placed in calculated positions and taken into account in the final stages of refinement in the “riding model” approximation.

## Associated content

### Supporting information

The Supporting Information is available free of charge on

Experimental details, characterization data, and NMR spectra

### Accession Codes

CCDC 1973678, 1973917, 1973260 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), or by emailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk), or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033

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