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Carbonyl-Isocyanide Mono-Substitution in $[\text{Fe}_2\text{Cp}_2(\text{CO})_4]$: a Re- Visitation[†]

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[†] This work is dedicated to Prof. Maurizio Peruzzini, on the occasion of his 65th birthday

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Abstract

The reactions of $[\text{Fe}_2\text{Cp}_2(\text{CO})_4]$ with a series of isocyanides, CNR, were conducted in acetonitrile and afforded, after a thermal treatment, the mono-isocyanide derivatives $[\text{Fe}_2\text{Cp}_2(\text{CO})_3(\text{CNR})]$ [R = 1H-indol-5-yl, **1**; $\text{CH}_2\text{P}(\text{O})(\text{OEt})_2$, **2**; Cy = C_6H_{11} , **3**; 4- $\text{C}_6\text{H}_4\text{OMe}$, **4**; Xyl = 2,6- $\text{C}_6\text{H}_3\text{Me}_2$, **5**; Me, **6**; 2-naphthyl, **7**; Bn = CH_2Ph , **8**]. In order to avoid multiple substitution, the diiron reactant was used in a molar excess with respect to the isocyanide (1.6 equivalents; 1.1 for the synthesis of **8**). The products were separated from unreacted $[\text{Fe}_2\text{Cp}_2(\text{CO})_4]$ by chromatography or via reversible protonation, and finally isolated in 50-83 % yields. IR and NMR spectroscopy indicate that the isocyanide ligand is bridging coordinated in **2** and **7**, terminal in **3** and **5**, while in the remaining cases a mixture of terminal- and bridging-CNR isomers is obtained. The molecular structure of **5** was ascertained by X-ray diffraction. In general, the coordination mode of the isocyanide is scarcely influenced by the environment (solvents with different polarities, solid state). Sluggish partial isocyanide migration from terminal to bridging position was recognized for **3** and **5** upon heating in refluxing toluene, a process which was reproduced by DFT calculations.

Keywords: diiron complexes, carbonyl ligand, isocyanide ligands, substitution reaction, DFT calculations

Introduction

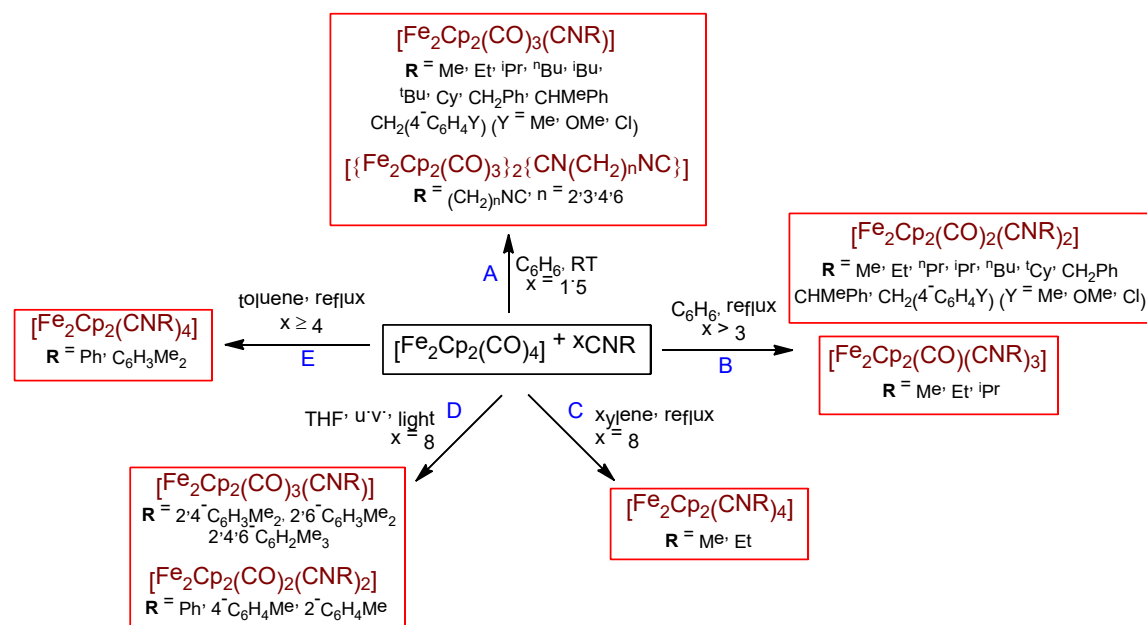
Isocyanides are ubiquitous ligands in coordination chemistry [¹], and their incorporation in organometallic structures is often achieved through the replacement of carbon monoxide ligands [²]. Cyclopentadienyl iron(II) dicarbonyl dimer, $[\text{Fe}_2\text{Cp}_2(\text{CO})_4]$ (Cp = $\eta^5\text{-C}_5\text{H}_5$), is an easily available and robust platform, for which the reactivity with isocyanides aroused the interest of several research groups for more than 20 years in the last century [³]. In principle, the resulting complexes may exist as

mixtures of isomers, originated from cis or trans mutual orientation of the Cp ligands and terminal or bridging coordination of the isocyanide ligand(s); this situation is often complicated by the occurrence of interconversion processes in solution [4, 5]. Various monosubstituted derivatives were afforded in ca. 60% yields from the reaction of $[\text{Fe}_2\text{Cp}_2(\text{CO})_4]$ with a slight molar excess of a variety of alkyl-isocyanides in benzene at room temperature, Scheme 1A [6]. Similarly, the di-isocyanides $\text{CN}(\text{CH}_2)_n\text{NC}$ ($n = 2,3,4,6$) were used to build dinuclear structures, $[\{\text{Fe}_2\text{Cp}_2(\text{CO})_3\}_2\{\mu\text{-CN}(\text{CH}_2)_n\text{NC}\}]$ [7], and it was found that the terminal coordination of the bidentate isocyanide is favored on increasing the length of the alkyl chain. The synthesis of $[\text{Fe}_2\text{Cp}_2(\text{CO})_3(\text{CN}^t\text{Bu})]$ was alternatively carried out in the presence of a catalytic amount of BEt_3 [5c, 8]: in this case, a radical chain mechanism was proposed, essentially based on the transfer of an ethyl group to a CO ligand, favoring its extrusion.

A series of di-alkyl-isocyanide complexes were prepared in approximately 50% yields by reacting $[\text{Fe}_2\text{Cp}_2(\text{CO})_4]$ with a large excess of the organic reactant in benzene at reflux temperature, Scheme 1B [9, 10]. Few tri-isocyanide species were obtained upon prolonged heating of these mixtures and finally isolated in low yield after work-up [10]. In order to realize the full substitution of the four carbonyl ligands in $[\text{Fe}_2\text{Cp}_2(\text{CO})_4]$, the reactions with an eight-fold excess of methyl- and ethyl-isocyanides required to be conducted in refluxing xylene, Scheme 1C [11]; under these experimental conditions, only the bis-substituted product was obtained from benzyl-isocyanide.

In general, aryl-isocyanides are more reactive towards $[\text{Fe}_2\text{Cp}_2(\text{CO})_4]$, and the isolation of mono-derivatives is tricky; interestingly, an IR spectroscopy study on the 1:1 reaction with CNXyl ($\text{Xyl} = 2,6\text{-C}_6\text{H}_3\text{Me}_2$) indicated that $[\text{Fe}_2\text{Cp}_2(\text{CO})_3(\text{CNXyl})]$ adds further CNXyl more rapidly than $[\text{Fe}_2\text{Cp}_2(\text{CO})_4]$ [12]. Manning and co-workers described the photolytic reaction of $[\text{Fe}_2\text{Cp}_2(\text{CO})_4]$ with a three-fold excess of aryl-isocyanides in THF solution in the light, affording either $[\text{Fe}_2\text{Cp}_2(\text{CO})_3(\text{CNR})]$ or $[\text{Fe}_2\text{Cp}_2(\text{CO})_2(\text{CNR})_2]$ in 60-70% yields, depending on the steric hindrance of the aryl group [13, 14], Scheme 1D. For instance, the former type of product is almost exclusively generated from 2,6-dimethylphenyl-isocyanide, while the latter from phenyl-isocyanide (Scheme 1D). The high

temperature reactions of $[\text{Fe}_2\text{Cp}_2(\text{CO})_4]$ with a four-fold excess of CNAr ($\text{Ar} = \text{Ph}, \text{Xyl}$) proceed smoothly to give the tetra-isocyanides in over 60% yields, Scheme 1E [12].



Scheme 1. Former studies on the substitution reactions of $[\text{Fe}_2\text{Cp}_2(\text{CO})_4]$ with isocyanides. References: A [6], B [9,10], C [11], D [13,14], E [12].

The structures of some derivatives were ascertained by single crystal X-ray diffraction. It can be generally observed that the isocyanide moiety, when terminally coordinated to one iron center, typically exhibits a linear C-N-R geometry [5c, 12, 15]; otherwise, bridging isocyanides substantially deviate from linearity and feature an elongated carbon-nitrogen bond, thus suggesting a substantial imine character which is in alignment with IR data [9, 16]. As a representative example, a view of the X-ray structure of *cis*- $[\text{Fe}_2\text{Cp}_2(\text{CO})(\mu\text{-CO})(\text{CN}^i\text{Pr})(\mu\text{-CN}^i\text{Pr})]$, containing one terminal and one bridging isopropyl-isocyanide units, is shown in Figure 1 with relevant bonding parameters listed in the caption [10].

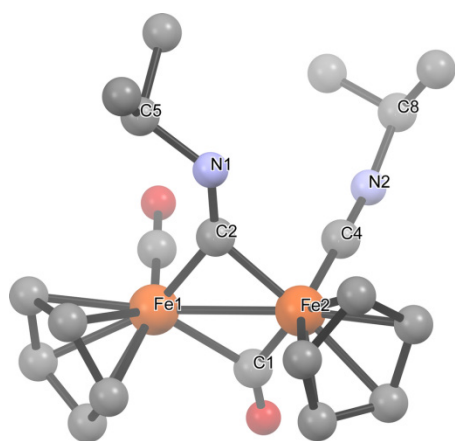
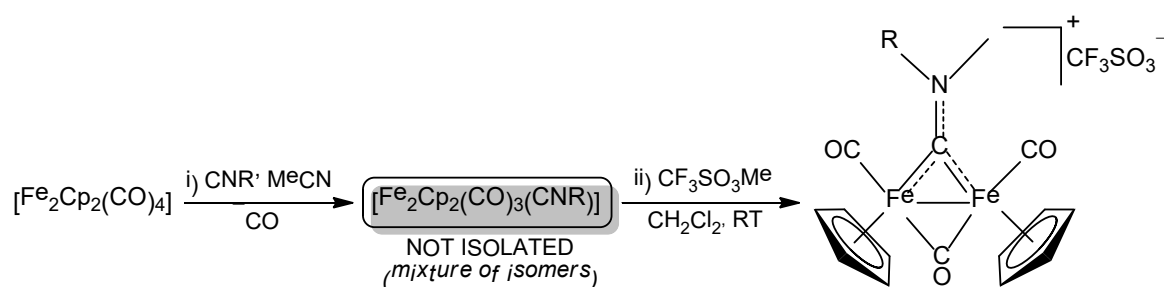


Figure 1. A) View of the X-ray structure of *cis*-[Fe₂Cp₂(CO)(μ-CO)(CNⁱPr)(μ-CNⁱPr)], from reference [10]; Selected bond lengths (Å) and angles (°): Fe1-Fe2 2.521(7), Fe1-C21.89(3), Fe2-C2 1.88(4), Fe1-C1 2.01(3), Fe2-C2 1.86(3), C2-N1 1.26(3), N1-C5 1.45(4), Fe2-C4 1.76(3), C4-N2 1.22(3), N2-C8 1.55(4), C2-N1-C5 128(3), Fe2-C4-N2 179(3), C4-N2-C8 171(3).

Compounds derived from [Fe₂Cp₂(CO)₄] by carbon monoxide/isocyanide single replacement are particularly of interest, since the subsequent alkylation of the nitrogen provides the access to cationic aminocarbyne complexes [17]. This transformation usually converges to a unique isomeric form, with the aminocarbyne ligand in bridging position and the Cp rings adopting the *cis* configuration. Such aminocarbyne compounds exhibit a rich chemistry and represent useful starting materials for the preparation of potential anticancer drugs [18]. Recently, we described a straightforward and general method to synthesize diiron aminocarbyne compounds (Scheme 2) [17], whereby the preliminary CO/CNR substitution (Scheme 2, step i) is selective upon reaction of a variety of alkyl- and aryl-isocyanides with an excess (ca. 1.6 equivalents) of [Fe₂Cp₂(CO)₄] in acetonitrile. The elaborated chromatographic separation of the mono-isocyanide adducts from the unreacted tetracarbonyl species is avoided, and the cationic products are finally isolated in yields up to 95% (Scheme 2, step ii).



Scheme 2. Synthesis of cationic diiron μ -aminocarbyne complexes from $[\text{Fe}_2\text{Cp}_2(\text{CO})_4]$ through the preliminary formation of neutral mono-isocyanide adducts. R, reaction temperature: Me, reflux; CH_2Ph , reflux; 2,6- $\text{C}_6\text{H}_3\text{Me}_2$ (Xyl), RT; 2,6- $\text{C}_6\text{H}_3\text{MeCl}$, RT; 2-naphthyl, RT.

Herein, we present a systematic study focused on the mono-isocyanide adducts $[\text{Fe}_2\text{Cp}_2(\text{CO})_3(\text{CNR})]$: using the optimized synthetic approach (Scheme 2, step i), a series of compounds (including two unprecedented compounds and three isolated for the first time) has been prepared, isolated and characterized by IR and ^1H and ^{13}C NMR spectroscopy. With the assistance of DFT calculations, the relative stability of the isomeric forms is elucidated and rationalized.

There is a debate on the existence of an iron-iron bond in $[\text{Fe}_2\text{Cp}_2(\text{CO})_4]$ [¹⁹], which might be reasonably extended to $[\text{Fe}_2\text{Cp}_2(\text{CO})_3(\text{CNR})]$; however, here we will keep the bond in the pictures, basically because we consider this representation more in alignment with the chemistry of the complexes.

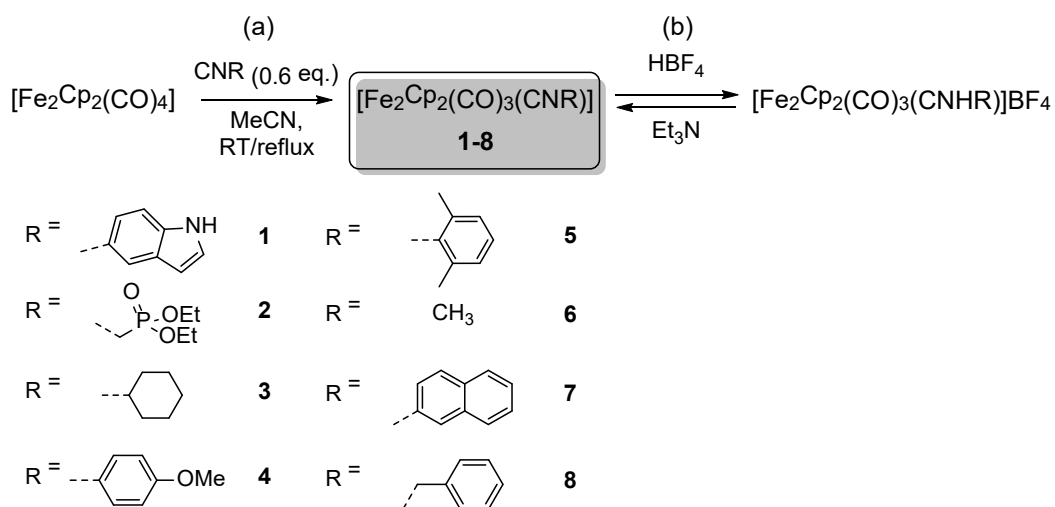
Results and discussion

1) Synthesis and isolation of complexes

The reactions of diethyl isocyanomethylphosphonate and 1H-indol-5-yl isocyanide with ca. 1.6 equivalents of $[\text{Fe}_2\text{Cp}_2(\text{CO})_4]$ in acetonitrile, proceeded with selective carbonyl mono-substitution to give the novel compounds **1-2**. By means of the same procedure, we prepared the previously reported **3-8** (Scheme 3a), of which **4**, **5** and **7** were isolated for the first time. Compound **8** was synthesized using only a slight excess of $[\text{Fe}_2\text{Cp}_2(\text{CO})_4]$ (1.1 eq), following the previous indication that benzyl isocyanide has a low tendency to poly-substitution [10, ²⁰]. All the products underwent a thermal treatment ($T \geq 90$ °C) for at least 3 hours, to ensure complete consumption of the isocyanide, and were obtained in admixture with unreacted $[\text{Fe}_2\text{Cp}_2(\text{CO})_4]$. The separation of **1**, **2** and **4**, containing N/O functions in the isocyanide group, was easily achieved on neutral alumina or Florisil[®] columns (see Experimental for details). On the other hand, chromatographic separation of the remaining, less polar compounds proved

to be more challenging, and only **3** was isolated in low yield. Therefore, we moved towards a different strategy, relying on the reversible protonation of the isocyanide ligand (Scheme 3b)^[21].

Treatment of Et₂O solutions of **3-8** with aqueous tetrafluoroboric acid afforded the insoluble aminocarbyne salts [Fe₂Cp₂(CO)₃(CNHR)]BF₄, which could be separated from [Fe₂Cp₂(CO)₄] by filtration. Next, triethylamine was employed to regenerate the isocyanide function and the neutral compounds were finally purified by alumina chromatography. Compounds **1-8** were finally obtained as dark red-purple solids which appeared to be rather inert to air/moisture; they were kept under N₂ for long-term storage. Conversely, solutions of **1-8** in any common organic solvent underwent appreciable degradation when exposed to ambient air over few hours, with precipitation of a rusty-brown solid / film over glassware.



Scheme 3. (a) Synthesis of diiron bis-cyclopentadienyl isocyanide complexes **1-8** by CO/CNR exchange from [Fe₂Cp₂(CO)₄]; (b) Subsequent protonation/deprotonation steps for the isolation of **3-8**.

2) IR and NMR spectroscopy and X-ray diffraction

In principle, four isomers are predictable for the mono-isocyanide adducts **1-8** (see Introduction), and these are shown in Figure 2. According to the mechanism based on NMR studies and proposed by Adams and Cottons for [Fe₂Cp₂(CO)₄], cis and trans isomers may interconvert in solution through a bridge-opened structure and rotation around the Fe-Fe bond^[22]. It was quantified that approximately 10% of [Fe₂Cp₂(CO)₄] is present in solution in such form displaying all terminal ligands [4]. Adams

and Cotton expanded their concepts to $[\text{Fe}_2\text{Cp}_2(\text{CO})_3(\text{CNR})]$ complexes [5c], for which the bridge-opened structure (structure **bo** in Figure 2) gives rise to several conformers; the activation energy for the bridge opening and closing was determined to be $9.4 \text{ kcal mol}^{-1}$ in the case of **6** in CD_2Cl_2 solution [4].

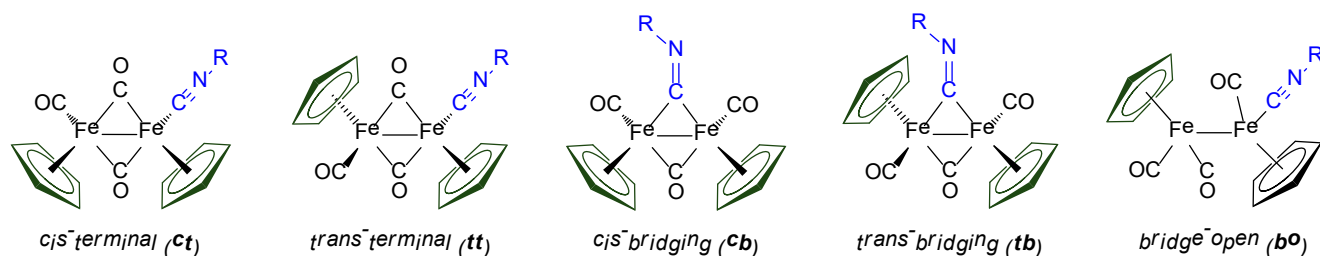


Figure 2. Structures of the four possible isomers of $[\text{Fe}_2\text{Cp}_2(\text{CO})_3(\text{CNR})]$, and the bridge-opened intermediate for isomer interconversion in solution.

It was previously observed that the isomeric composition in this class of complexes is variable in different solvents, the more polar solvents usually favoring the more polar isomers (especially cis vs. trans) [5b]. Thus, we collected the IR spectra of **1-8** in MeCN ($\mu = 3.92 \text{ D}$), CH_2Cl_2 ($\mu = 1.60 \text{ D}$) and toluene ($\mu = 0.36 \text{ D}$) solution as well as in the solid state. For each compound, the coordination mode of the isocyanide can be recognized from the infrared bands associated to the CN stretching vibration. The latter falls in within the intervals 2050-2150 and $1690\text{-}1720 \text{ cm}^{-1}$ for terminal and bridging isocyanides, respectively. Note that values related to terminal isocyanides are $10\text{-}30 \text{ cm}^{-1}$ lower than those available for the corresponding non-coordinated isocyanides (Table 1), indicating the occurrence of an appreciable Fe^I to ligand backdonation in **1-8**. With reference to CH_2Cl_2 solutions (Table 1), the isocyanide in **2** and **7** manifests a strong tendency to occupy a bridging site, whereas in **3** and **5** the terminal coordination is largely favored. The result obtained for **3** and **5** is coherent with former findings [6, 12]. In the other cases (**1**, **4**, **6** and **8**), a mixture of terminal- and bridging-isocyanide isomers in comparable amounts is inferred. The result concerning **6** is in accordance with the former literature findings (vide infra) [4].

Table 1. IR data related to the isocyanide moiety in $[\text{Fe}_2\text{Cp}_2(\text{CO})_3(\text{CNR})]$ complexes (CH_2Cl_2 solution) and non-coordinated CNR molecules.

[Fe ₂ Cp ₂ (CO) ₃ (CNR)]					CNR
R	Cpd.	$\tilde{\nu} / \text{cm}^{-1[\text{a}]}$		Isocyanide coordination mode [b]	$\tilde{\nu}(\text{C}\equiv\text{N})/\text{cm}^{-1[\text{a}]}$
		t-CN	μ -CN		
1H-indol-5-yl	1	2106	1703	<i>bridging > terminal</i>	2117(KBr) ²³
CH ₂ PO ₃ Et ₂	2	-	1690	bridging	2140 ²⁴
C ₆ H ₁₁	3	2128	-	terminal	2144 ²⁵
4-C ₆ H ₄ OMe	4	2102	1698	<i>bridging > terminal</i>	2125 ²⁶
Xyl	5	2090	-	terminal	2120
Me	6	2153	1719	<i>terminal > bridging</i>	2166 (gas) ²⁷
2-naphthyl	7	-	1694	bridging	2124(KBr) ²⁸
CH ₂ Ph	8	2131	1710	<i>bridging > terminal</i>	2152 ²⁹

[a] **1-8**: CH₂Cl₂ solution; non-coordinated CNR: neat liquid/solid state, unless otherwise specified. [b] According to the relative transmittance of t-CN (**ct** + **tt** isomers in Fig. 2) and μ -CN (**cb** + **tb** isomers in Fig. 2) stretching bands.

X-ray quality crystals of **5-ct** were collected from a solution, and a view of the structure of this compound is shown in Figure 3, with relevant bonding parameters given in the caption.

5-ct adds to the very few [Fe₂Cp₂(CNR)(CO)(μ -CO)₂] complexes structurally characterized [ref: R. D. Adams, F. A. Cotton, J. M. Troup, Inorg. Chem. 1974, 13, 257; I. L. C. Campbell, F. S. Stephens, J. Chem. Soc. Dalton Trans. 1975, 982]. Its molecular structure and bonding parameters are comparable to those previously reported. Thus, the Cp ligands adopt a *cis* geometry, and the two μ -CO ligands display a marked asymmetry [Fe(1)-C(2) 1.947(3), Fe(2)-C(2) 1.893(3), Fe(1)-C(3) 1.941(3), Fe(2)-C(3) 1.911(3)] in view of the greater π -acidity of t-CO compared to t-CNR. The C(11)-N(1)-C(12) [169.6(4)°] group is almost linear as expected for a terminal isonitrile.

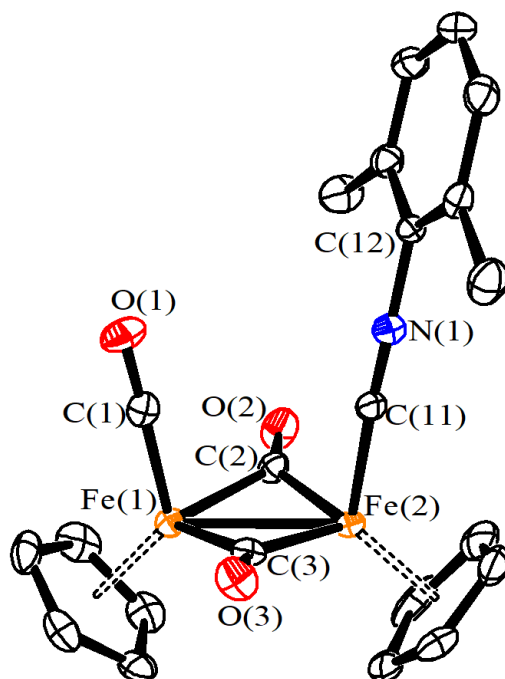


Figure 3. Molecular structure of *cis*-[Fe₂Cp₂(CNXyl)(CO)₂(μ-CO)], **5a-ct**, with labelling. Displacement ellipsoids are at the 30% probability level. H-atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Fe(1)-Fe(2) 2.5267(7), Fe(1)-C(1) 1.752(4), Fe(1)-C(2) 1.947(3), Fe(2)-C(2) 1.893(3), Fe(1)-C(3) 1.941(3), Fe(2)-C(3) 1.911(3), Fe(2)-C(11) 1.816(3), C(1)-O(1) 1.142(4), C(2)-O(2) 1.161(4), C(3)-O(3) 1.164(4), C(11)-N(1) 1.161(4), N(1)-C(12) 1.398(4), Fe(1)-C(1)-O(1) 178.0(3), Fe(2)-C(11)-N(1) 177.1(3), C(11)-N(1)-C(12) 169.6(4), Fe(1)-C(2)-Fe(2) 82.29(13), Fe(1)-C(3)-Fe(2) 81.99(13).

In general, the coordination mode adopted by the isocyanide ligand is negligibly affected by the environment, and the IR spectra in the solid-state (Figures S1-S8 in the SI) and in acetonitrile and toluene solutions (Figures S9-S16) are substantially comparable to those recorded in CH₂Cl₂. Exceptions are discussed in the following.

First, despite the xylyl-isocyanide ligand in **5** is always found terminal, the number and the relative intensity of CO/CN absorptions are variable. Two bands of comparable intensity due to terminal CNXyl (at 2136 and 2082 cm⁻¹) and other two bands due to bridging CO (at 1775 and 1756 cm⁻¹) appear in acetonitrile solution. For sake of comparison, the IR spectrum of **5** in the solid state displays only one CNXyl band (at 2081 cm⁻¹) and one CO band (at 1943 cm⁻¹), and the same qualitative pattern was found in toluene and dichloromethane.

Presumably, both the **tt** and **ct** isomers of **5** are stable in acetonitrile, while the **tt** structure is dominant in less polar solvents and in the solid state (where the **ct** isomer is also present and has been detected by X-ray diffraction, see above).

The second exception to the general trend was observed for **4** and **8**: while these complexes exist as mixtures of terminal- and bridging-isocyanide isomers in solution (with prevalence of the latter), the disappearance of the band around 2100 cm^{-1} in the solid state indicates the absence of **ct** and **tt** isomers (Figures 2 and 4). This feature seems imputable to solid state effects, on considering that no marked differences were observed in the relative intensities of terminal and bridging isocyanide absorptions on changing the solvent polarity.

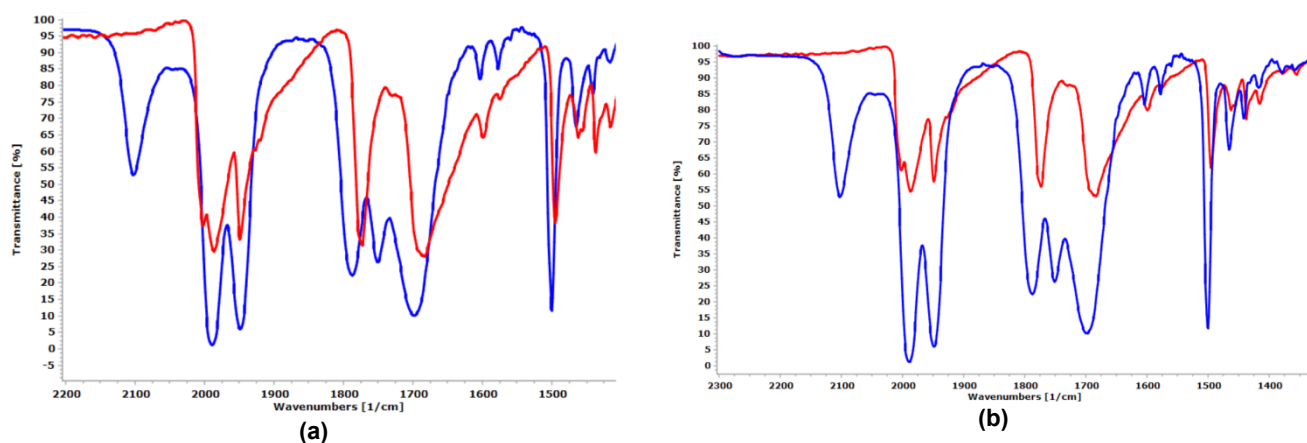


Figure 4. Comparison of IR spectra ($1500\text{-}2300\text{ cm}^{-1}$) in CH_2Cl_2 solution (blue line) and in the solid state (red line) for $[\text{Fe}_2\text{Cp}_2(\text{CO})_3\{\text{CN}(4\text{-C}_6\text{H}_4\text{OMe})\}]$, **4(a)** and $[\text{Fe}_2\text{Cp}_2(\text{CO})_3(\text{CNCH}_2\text{Ph})]$, **8 (b)**.

A previous NMR study assessed the percentage of the isomers of **6** at $-26\text{ }^\circ\text{C}$ in CD_2Cl_2 solution, resulting 77% (**ct**), 2% (**tt**), 16% (**cb**), 5% (**tb**) [4]: a strong prevalence is evidenced of cis isomers (**ct** + **cb**, 93%) and terminal coordination of methylisocyanide (79%). In the low temperature ^{13}C NMR spectrum, the resonances due to terminal and bridging coordination of CNMe are diagnostic, falling at 160 and 250 ppm, respectively. On the other hand, the carbonyl ligands in the same complex resonate at ca. 210 and ca. 280 ppm when occupying terminal and bridging sites.

The NMR spectra of **1-8** were recorded in CDCl_3 at room temperature, and they generally display broadened signals indicative of fluxionality (see Figure 2). Overall, the detected ^{13}C NMR signals for the isocyanide ligands (Table 2) are substantially in alignment with the IR features; in particular, **2** and **7** exhibits one broad signal due to the bridging isocyanide at ca. 260 ppm, while the signal for the isocyanide in **3** and **5** falls at around 170 ppm as expected for terminal coordination. The ^{13}C NMR chemical shifts of the compounds existing as mixtures of terminal- and bridging-isocyanide isomers (**1**, **4**, **6** and **8**) are not averaged, but consistent with

the predominant isocyanide coordination mode as assessed by IR spectroscopy. For instance, the CN resonance falls at *ca.* 250 ppm for **1**, **4**, **8** and *ca.* 160 ppm for **6**. For the latter compound, two methyl resonances are visible (at 47 and 30 ppm), as in the low-temperature spectrum [4].

Table 2. ^{13}C NMR spectral assignments for *ct* and *cb* isomers of $[\text{Fe}_2\text{Cp}_2(\text{CO})_3(\text{CNMe})]$ (**6**) according to the literature^[a] and comparison of selected $^{13}\text{C}\{^1\text{H}\}$ NMR data for complexes **1-8**.^[b]

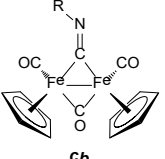
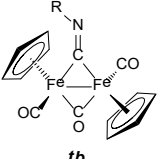
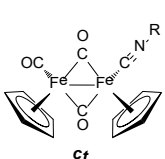
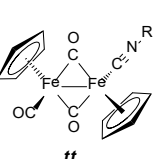
Compound	R	δ / ppm			
		$\mu\text{-CO}$	t-CO	<u>CNR</u>	Cp
1 ^[c]	1H-indol-6-yl	274	214	249	89br
2	$\text{CH}_2\text{PO}_3\text{Et}_2$	272	213, 210	260	90, 88
3	C_6H_{11}	282	217, 213	162	87, 86sh
4	4- $\text{C}_6\text{H}_4\text{OMe}$	273	217br, 211	254	89br, 88
5	Xyl	278br	215-212br	176br	88
6	Me	281	213, 211	163	87
7	2-naphthyl	272	213br, 211	255	90br, 88
8	CH_2Ph	280br, 273	215-212br, 211	251	88

[a] Spectra recorded in CD_2Cl_2 at -26°C [4]; [b] Spectra recorded in CDCl_3 at 298 K unless otherwise specified; [c] CD_3CN solution.

3) DFT calculations

The relative stability of the possible isomers of complexes **1-8** (Figure 2) was evaluated by DFT calculations with reference to dichloromethane medium, and the results are reported in Table 3.

Table 3. Relative energies of the four isomers predictable for complexes **1-8** (C-PCM, CH_2Cl_2).

Complex	R				
		<i>cb</i>	<i>tb</i>	<i>ct</i>	<i>tt</i>
1	1H-indol-6-yl	0.0	0.4	2.5	2.8
2	$\text{CH}_2\text{PO}_3\text{Et}_2$	0.0	1.3	1.8	3.6
3	C_6H_{11}	0.0	1.1	1.0	1.6
4	4- $\text{C}_6\text{H}_4\text{OMe}$	0.0	0.4	2.8	3.2
5	Xyl	0.0	0.4	0.9	1.3
6	Me	0.0	1.1	0.9	1.6

7	2-naphthyl	0.0	0.5	4.1	4.4
8	Bn	0.0	2.4	2.4	3.0

The **cb** isomer is always the most stable one, although in some cases the energy difference with respect to the other isomers is low (note that differences smaller than $0.5 \text{ kcal mol}^{-1}$ exceed the accuracy of the DFT methods). For instance, the **cb** and **tb** isomers of **1**, **4**, **5** and **7** are practically isoenergetic. The geometries of the four isomers of **6** are shown in Figure 5, while those ones of **1-5** and **7-8** are supplied as Supporting Information.

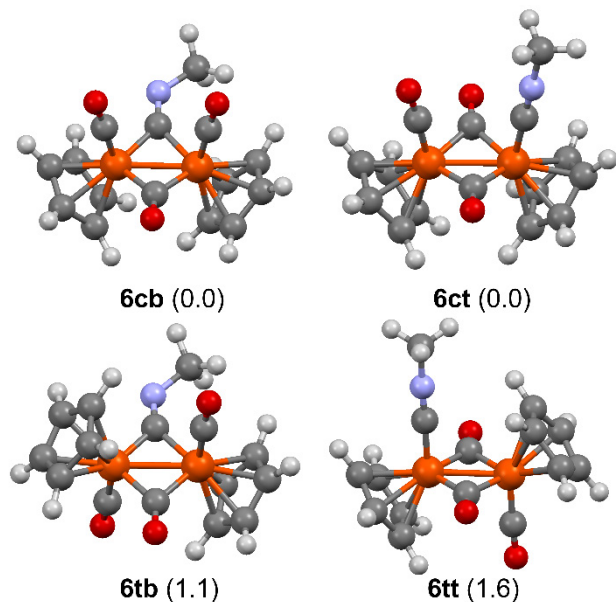


Figure 5. DFT-optimized geometries of the four isomers of **6**. Relative energies are indicated in brackets and expressed in kcal mol^{-1} .

Overall, the calculations highlight the higher stability provided by the bridging coordination of the isocyanide ligand. This contrasts especially with the experimental evidence that **3** and **5** are obtained almost exclusively as terminal-isocyanide structures through a synthetic procedure including high temperature treatment in a high polar solvent (refluxing acetonitrile, $T \geq 90^\circ\text{C}$). It is noteworthy that additional calculations pointed out that the relative energies of the isomers of **5** do not significantly change in acetonitrile medium with respect to dichloromethane (variations are within $0.1 \text{ kcal mol}^{-1}$). When toluene solutions of **3** and **5** were heated at reflux ($T \approx 110^\circ\text{C}$), a sluggish, partial conversion into the predicted stable “bridging” products was ascertained by IR spectroscopy, and the new IR patterns were maintained at ambient temperature (see Experimental and figures S41-S42 for details). It is reasonable that, in general, the kinetic product of the CO/CNR substitution features a

terminal isocyanide (structures **ct** and **tt** in Figure 2), on considering that the binding of the terminal CO ligands in $[\text{Fe}_2\text{Cp}_2(\text{CO})_4]$ is weaker than that of the bridging ones. It seems that the subsequent bridge closing from **bo**, placing the isocyanide group in bridging position to afford either **cb** or **tb**, is inhibited with encumbered R groups such as cyclohexyl and 2,6-dimethylphenyl.

Conclusions

A series of mono-isocyanide complexes obtained by substitution reactions from $[\text{Fe}_2\text{Cp}_2(\text{CO})_4]$ has been synthesized using an optimized procedure, isolated and characterized by spectroscopic techniques and by X-ray diffraction in one case. Consistently with previous literature studies, different isomers are generally observed both in the solid state and in solution, where interconversion can take place following the Adams-Cotton mechanism. Although the polarity of the solvent is expected to significantly affect the cis/trans ratio, on the other hand it scarcely influences the coordination mode of the isocyanide ligand. DFT calculations indicate the bridging coordination as the most stable one, and experiments reveal that the exclusive observation of terminal isocyanide structures in some cases (cyclohexyl-isocyanide, xylyl-isocyanide) is related to kinetic reasons associated to steric issues.

Experimental

1. General experimental details.

[Fe₂Cp₂(CO)₄] (99%) was purchased from Strem Chemicals, other reactants and solvents were obtained from Alfa Aesar, Merck, Apollo Scientific or TCI Chemicals and were of the highest purity available. Methyl isocyanide was prepared according to the literature [30], while other isocyanides were commercial products stored at low temperature and used as received. Contaminated labware was treated with bleach. The syntheses of diiron compounds were carried out under dry N₂ using standard Schlenk techniques and MeCN distilled from CaH₂. Chromatography separations were carried out under N₂ on neutral alumina (≈ 150 mesh, dry / Brockmann Number I, unless otherwise specified) or Florisil[®] (60-100 mesh) columns. Aqueous HBF₄ nominally 48% w/w was titrated with NaOH (acidity 8.4 mol/L). Solutions of diiron compounds were always prepared and manipulated under N₂. Solid samples containing the diiron compounds were manipulated with no special precaution over short times but were eventually stored under N₂. NMR spectra were recorded at 25 °C on a Bruker Avance II DRX400 instrument equipped with a BBFO broadband probe. CDCl₃ and CD₃CN stored in the dark over 3A MS were used for NMR analysis. Chemical shifts (expressed in parts per million) are referenced to the residual solvent peaks [31] (¹H, ¹³C) or to external standards [32] (³¹P to 85% H₃PO₄). ¹H and ¹³C spectra were assigned with the assistance of ¹H{³¹P}, ¹³C DEPT 135 and ¹H-¹³C *gs*-HSQC experiments [33]. IR spectra of solid samples (650-4000 cm⁻¹) were recorded on a Perkin Elmer Spectrum One FT-IR spectrometer, equipped with a UATR sampling accessory. IR spectra of solutions were recorded using a CaF₂ liquid transmission cell (1500-2300 cm⁻¹) on a Perkin Elmer Spectrum 100 FT-IR spectrometer. IR bands and ¹³C NMR resonances attributed to terminal and bridging CO/CNR ligands are indicated as t-CO/t-CN and μ-CO/μ-CN, respectively. IR spectra were processed with Spectragryph software [34].

2. Synthesis and characterization of diiron compounds.

Carbon monoxide/isocyanide exchange (general procedure). In a Schlenk flask under N₂, the selected isocyanide, or its solution in MeCN (5 mL, for solid compounds), was added dropwise to a suspension of [Fe₂Cp₂(CO)₄] (1.6

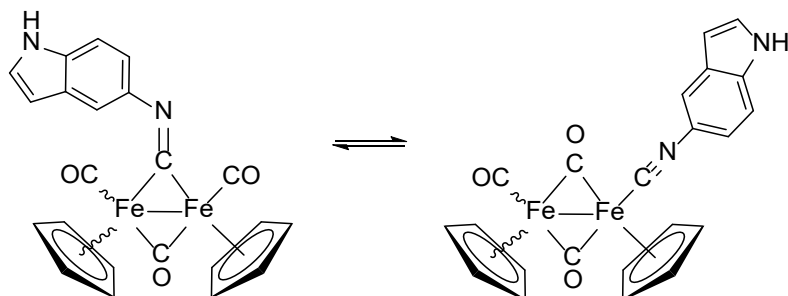
eq for **1-7**; 1.1 eq for **8**) in anhydrous MeCN. Alkyl isocyanides: the mixture was heated at reflux ($T \geq 90\text{ }^{\circ}\text{C}$) for 8 h, then stirred at room temperature for additional 14 h. Aryl isocyanides: the mixture was stirred at room temperature for 14 h then heated at reflux ($T \geq 90\text{ }^{\circ}\text{C}$) for 3 h. After the conversion was checked by IR, the dark red-brown suspension was dried under vacuum ($40\text{ }^{\circ}\text{C}$). The resulting brown solid is predominantly a mixture of $[\text{Fe}_2\text{Cp}_2(\text{CO})_4]$ and $[\text{Fe}_2\text{Cp}_2(\text{CO})_3(\text{CNR})]$, according to the Fe/isocyanide molar ratio used.

Compounds **1-4** were purified from the raw material by column chromatography, as detailed below for each compound. Compounds **3** and **5-8** were purified via the protonation/deprotonation route, as described in the following general procedure.

Purification by protonation/deprotonation (general procedure). In a 100 mL Schlenk flask under N_2 , the brown solid was suspended in Et_2O (30 mL) under vigorous stirring. Dropwise addition of 48% aqueous HBF_4 (1.6 eq.) resulted in the immediate, massive formation of a bright red solid. The mixture was vigorously stirred for 30' then filtered (G4 porous filter). The solid was thoroughly washed with Et_2O to remove $[\text{Fe}_2\text{Cp}_2(\text{CO})_4]$. Next, the solid was moved back into the 100 mL Schlenk tube under N_2 and suspended in Et_2O (20 mL) under vigorous stirring. Dropwise addition of Et_3N (1.7 eq) was subsequently followed by a color change to dark red-violet and (partial) dissolution of the solid. The mixture was stirred for 30' then moved on top of an alumina column (h 5 cm, d 2.8 cm). Impurities were eluted with Et_2O , then a red-violet band containing the title product was eluted with a $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ 1:1 v/v solution. Volatiles were removed under vacuum ($40\text{ }^{\circ}\text{C}$), affording a dark red-purple solid.

$[\text{Fe}_2\text{Cp}_2(\text{CO})_3\{\text{CN}(\text{1H-indol-6-yl})\}]$, **1 (Chart 1).**

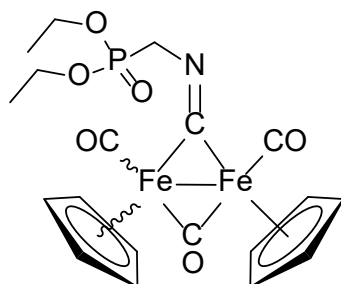
Chart 1. Structures of **1**.



Prepared from $[\text{Fe}_2\text{Cp}_2(\text{CO})_4]$ (2.060 g, 5.82 mmol) and 1H-indol-6-yl isocyanide (530 mg, 3.73 mmol), in MeCN (90 mL). The raw product was dissolved in toluene and moved on top of a Florisil[®] column (h 5.5 cm, d 4.5 cm). A reddish-brown band containing $[\text{Fe}_2\text{Cp}_2(\text{CO})_4]$ was eluted with a toluene/ CH_2Cl_2 10:1.5 v/v mixture then a dark-red band containing the title product was eluted with THF. Volatiles were removed under vacuum (40 °C), the residue was dissolved in CH_2Cl_2 and gently evaporated under vacuum (RT), affording a dark red-purple solid. Yield: 77 % (with respect to isocyanide). Compound **1** is soluble in THF, CH_2Cl_2 , Et_2O , MeCN, poorly soluble in hexane. IR(solid state): $\tilde{\nu}/\text{cm}^{-1}$ = 3387w-br (NH), 3107w, 2953w-sh, 2922m, 2853m; 2099m, 2077m-sh (t-CN); 1973s, 1933s (t-CO); 1788s-sh, 1736s (μ -CO); 1697s-br, 1661s (μ -CN); 1616s-sh, 1573m, 1507w, 1464m, 1416m, 1377w, 1357w, 1342w, 1313m, 1262w, 1243w, 1214w, 1174w, 1118w, 1089w, 1060m, 1035w, 1014m, 1001m, 941w, 928w, 893w, 865m-sh, 821m, 805m, 760m, 726w, 694w. IR (CH_2Cl_2): $\tilde{\nu}/\text{cm}^{-1}$ = 2106m, 2085m-sh (t-CN); 1988s, 1948s (t-CO); 1779s, 1749s (μ -CO); 1703s (μ -CN), 1618w, 1576w, 1466m, 1417w, 1344w, 1321w, 1312w. IR (MeCN): $\tilde{\nu}/\text{cm}^{-1}$ = 2104m, 2081w-sh (t-CN); 1983s, 1944s (t-CO); 1784m-sh, 1753s (μ -CO); 1706m/s (μ -CN), 1576w. IR (toluene): $\tilde{\nu}/\text{cm}^{-1}$ = 2102m, 2079w-sh (t-CN); 1988s, 1945s (t-CO); 1792s, 1763s (μ -CO); 1708s (μ -CN). ¹H NMR (CDCl_3): δ/ppm = 8.30 (s-br, 1H), 7.50–7.31, 7.24, 7.20–7.08, 6.62–6.43 (m-br, 4H) (C_8H_5); 4.72 (s-br, 10H, Cp). ¹³C {¹H} NMR (CDCl_3): δ/ppm = 251 (br, μ -CN); 213-211 (br, t-CO); 144.2-142.2, 134-133, 128, 125.8-125.2, 120-117 (br.), 111.5, 103.1 (C_8H_5); 87.9 (br, Cp). ¹H NMR (CD_3CN): δ/ppm = 9.38 (s-br, 1H, NH); 7.29 (m-br), 6.49 (s-br) (5H, C_8H_5); 4.78 (s-br, 10H, Cp). ¹³C {¹H} NMR (CD_3CN): δ/ppm = 273.6 (μ -CO); 249.2 (μ -CN); 213.5 (t-CO); 143.7, 135.4, 134.2, 129.9, 129.2, 127.9, 126.8, 118.3, 112.7, 111.9, 102.8 (C_8H_6); 88.9 (br, Cp).

$[\text{Fe}_2\text{Cp}_2(\text{CO})_3\{\text{CN}(\text{CH}_2\text{PO}_3\text{Et}_2)\}]$, **2 (Chart 2).**

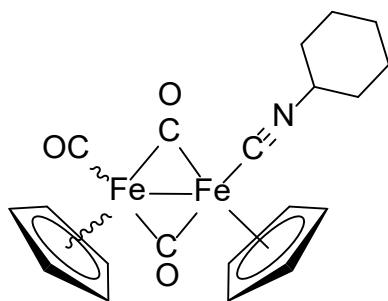
Chart 2. Structure of **2**.



Prepared from $[\text{Fe}_2\text{Cp}_2(\text{CO})_4]$ (1.73 g, 4.87 mmol) and diethyl isocyanomethylphosphonate (0.50 mL, 3.12 mmol) in MeCN (90 mL). The raw product was suspended in Et_2O and moved on top of alumina column (containing 4 % w/w water; h 8 cm, d 3.2 cm). A reddish-brown band containing $[\text{Fe}_2\text{Cp}_2(\text{CO})_4]$ was eluted with Et_2O , then a raspberry red band containing the title product was eluted with a THF/MeCN 95:5 v/v solution. Volatiles were removed under vacuum and the resulting red-violet solid was stored under N_2 . Yield: 910 mg, 58 % (with respect to isocyanide). Compound **2** is soluble in CH_2Cl_2 , MeOH, MeCN, toluene, poorly soluble in Et_2O , hexane and insoluble in water. IR (solid state): $\tilde{\nu}/\text{cm}^{-1} = 3109\text{w}, 3086\text{w}, 2986\text{w}, 2906\text{w}, 2886\text{w}; 1975\text{s}, 1937\text{s}$ (t-CO); 1771s (μ -CO), 1687s-br (μ -CN), 1480w, 1440w, 1418m, 1405m, 1390w, 1367w, 1359w, 1290w, 1263m-sh, 1238s, 1163m, 1096w, 1050s, 1024s, 980m-sh, 957s, 945s, 892m, 849m-sh, 830s, 797m, 774m, 721m, 671s. IR (CH_2Cl_2): $\tilde{\nu}/\text{cm}^{-1} = 1992\text{s}, 1952\text{m}$ (t-CO); 1789m (μ -CO), 1690m-br (μ -CN). IR (MeCN): $\tilde{\nu}/\text{cm}^{-1} = 1987\text{s}, 1946\text{w}$ (t-CO); 1788m (μ -CO), 1692m-br (μ -CN). IR (toluene): $\tilde{\nu}/\text{cm}^{-1} = 1990\text{s}, 1950\text{m}$ (t-CO); 1795m (μ -CO), 1693m-br (μ -CN). ^1H NMR (CDCl_3): $\delta/\text{ppm} = 4.88, 4.78$ (s-br, 10H, Cp); 4.40 (d-br, $^2J_{\text{HP}} = 13.5$ Hz, 2H, NCH_2), 4.29 (m-br, 4H, OCH_2), 1.42 (m-br, 6H, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): $\delta/\text{ppm} = 272.0$ (μ -CO); 212.8, 210.4 (t-CO); 260.6–260.2 (m, μ -CN); 89.5, 87.6 (Cp); 62.7 (d, $^2J_{\text{CP}} = 6$ Hz, OCH_2), 57.5 (d, $^1J_{\text{CP}} = 162$ Hz, NCH_2), 16.7 (d, $^3J_{\text{CP}} = 4$ Hz, CH_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): $\delta/\text{ppm} = 22.7$.

$[\text{Fe}_2\text{Cp}_2(\text{CO})_3\{\text{CN}(\text{C}_6\text{H}_{11})\}]$, **3 (Chart 3)[6, ³⁵].**

Chart 3. Structure of **3**.



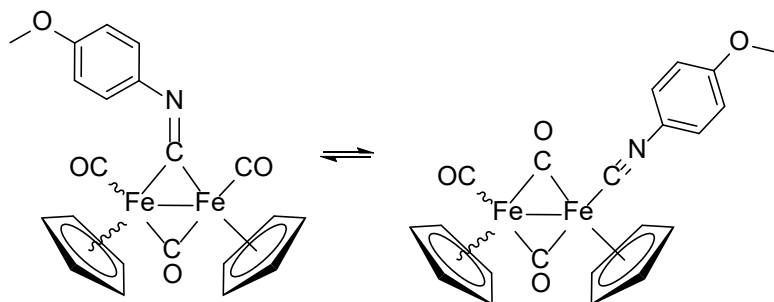
Prepared from $[\text{Fe}_2\text{Cp}_2(\text{CO})_4]$ (1.0 g, 2.83 mmol) and cyclohexyl isocyanide (0.21 mL, 1.69 mmol) in MeCN (30 mL). Purified by the protonation/deprotonation route. Yield: 625 mg, 82 % (with respect to isocyanide).

Alternatively, the raw product was dissolved in toluene and moved on top of a Florisil[®] column (h 5 cm, d 4.5 cm). A reddish-brown band containing $[\text{Fe}_2\text{Cp}_2(\text{CO})_4]$ was eluted with a toluene/ CH_2Cl_2 10:1.5 v/v mixture then

a dark red band containing the title product was eluted with Et₂O. Volatiles were removed under vacuum (40 °C), affording a dark red-purple solid. Yield: 211 mg, 29 % (with respect to isocyanide). Compound **3** is soluble in CH₂Cl₂, acetone, MeCN, toluene, poorly soluble in MeOH, insoluble in water. IR (solid state): $\tilde{\nu}/\text{cm}^{-1}$ = 3108w, 2932m, 2856w, 2117s-br (t-CN); 1954s-sh, 1940s-br (t-CO); 1766w-sh, 1726s-br (μ -CO); 1650-1550m-br, 1448m, 1432m, 1416m, 1353m, 1316m, 1270w, 1238w, 1150w, 1129w, 1114w, 1061w, 1013m, 997m, 927w, 864m-sh, 824m, 809m, 664m. IR (CH₂Cl₂): $\tilde{\nu}/\text{cm}^{-1}$ = 2128s (t-CN), 1985w, 1947s (t-CO), 1780w-sh, 1746s (μ -CO). IR (toluene): $\tilde{\nu}/\text{cm}^{-1}$ = 2122s (t-CN), 1988w, 1946s (t-CO), 1784w, 1760s (μ -CO). IR (MeCN): $\tilde{\nu}/\text{cm}^{-1}$ = 2125s (t-CN); 1980w, 1943s (t-CO); 1782w-sh, 1749s (μ -CO); 1636w-br. ¹H NMR (CDCl₃): δ/ppm = 4.68, 4.61 (s-br, 10H, Cp); 3.36 (s, 1H, NCH); 1.69–1.52, 1.45–1.30 (m, 10H, CH₂). ¹³C{¹H} NMR (CDCl₃): δ/ppm = 281.7 (μ -CO); 217.3, 212.7 (t-CO); 161.9 (t-CN); 87.2, 86.7sh. (Cp); 55.0 (NCH); 33.0, 25.1, 23.0 (CH₂).

[Fe₂Cp₂(CO)₃{CN(4-C₆H₄OMe)}], **4 (Chart 4)^[36].**

Chart 4. Structures of **4**.

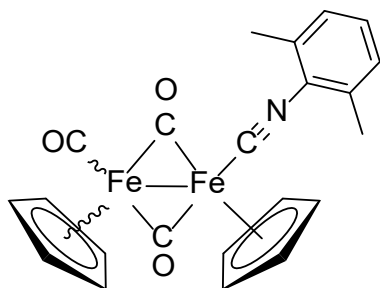


Prepared from [Fe₂Cp₂(CO)₄] (4.205 g, 11.88 mmol) and 4-methoxyphenyl isocyanide (1.0 g, 7.51 mmol) in MeCN (80 mL). The raw product was dissolved in toluene and moved on top of an alumina column (h 5.5 cm, d 4.5 cm). A reddish-brown band containing [Fe₂Cp₂(CO)₄] was eluted with a toluene/CH₂Cl₂ 10:1.5 v/v mixture then a dark red band containing the title product was eluted with Et₂O. Volatiles were removed under vacuum (40 °C), affording a dark red-purple solid. Yield: 80 % (with respect to isocyanide). Compound **4** is soluble in CH₂Cl₂, acetone, MeCN, toluene moderately soluble in Et₂O, poorly soluble in pentane. IR (solid state): $\tilde{\nu}/\text{cm}^{-1}$ = 3109w, 3024w, 2958w, 2924m, 2853w; 2002s-sh, 1966s, 1949s (t-CO); 1774s (μ -CO), 1684s-br (μ -CN); 1599m-sh, 1575w, 1496s, 1463m, 1437m, 1416m, 1378w, 1356w, 1284m, 1260m, 1238s, 1197m, 1178m, 1161m, 1102m,

1059m, 1026s, 1013m, 859w-sh, 830s, 817s, 806s, 727w-sh, 718s, 668s. IR (CH₂Cl₂): $\tilde{\nu}/\text{cm}^{-1} = 2102\text{m}$ (t-CN); 1989s, 1949s (t-CO); 1788s, 1751s (μ -CO); 1698s-br (μ -CN), 1604w, 1575w, 1500s, 1466w, 1442w. IR (MeCN): $\tilde{\nu}/\text{cm}^{-1} = 2100\text{w}$ (t-CN); 1984s, 1945m (t-CO); 1788m, 1754m (μ -CO); 1698s-br (μ -CN). IR (toluene): $\tilde{\nu}/\text{cm}^{-1} = 2097\text{w}$ (t-CN); 1990s, 1947s (t-CO); 1795s, 1764m (μ -CO); 1703s-br (μ -CN). ¹H NMR (CDCl₃): $\delta/\text{ppm} = 7.11$ (m-br, 2H), 6.97 (m-br, 2H) (C₆H₄); 4.72 (s-br, 10H, Cp), 3.85 (s-br, 3H, OCH₃). ¹³C{¹H} NMR (CDCl₃): $\delta/\text{ppm} = 272.6$ (μ -CO); 253.6 (μ -CN); 217br., 211.0 (t-CO); 156.2, 143.5, 121.9, 114.5 (C₆H₄); 89.0br., 87.9 (Cp); 55.7 (OCH₃).

[Fe₂Cp₂(CO)₃{CN(2,6-C₆H₃Me₂)}], 5 (Chart 5)^[37].

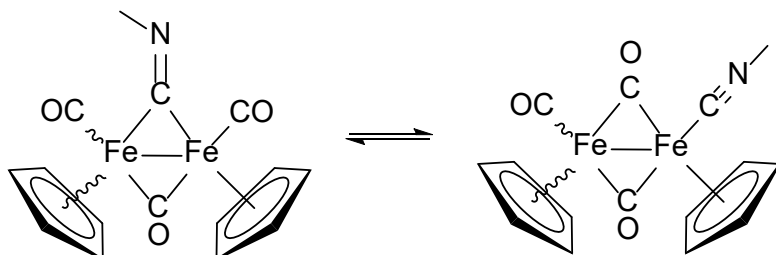
Chart 5. Structure of **5**.



Prepared from [Fe₂Cp₂(CO)₄] (9.66 g, 27.3 mmol) and xylyl isocyanide (2.25 g, 17.17 mmol) in MeCN (100 mL). A fraction of the raw material (542 mg) was purified by the protonation/deprotonation route. Yield: 308 mg, 83 % (with respect to isocyanide; re-scaled from the mass fraction of the raw material). Compound **5** is soluble in CH₂Cl₂, CHCl₃, toluene, moderately soluble in Et₂O, poorly soluble in MeCN. IR (solid state): $\nu/\text{cm}^{-1} = 2081\text{s}$ (t-CN); 2000w; 1943s (t-CO); 1901w-sh; 1733m, 1739s (μ -CO); 1589w, 1470w, 1432w, 1418w, 1382w, 1358w, 1261w, 1186w, 1165w, 1117w, 1092w, 1059w, 1037w, 1012w, 923w, 864w, 819m-sh, 810m, 779m, 739w, 720w, 676w. IR (CH₂Cl₂): $\nu/\text{cm}^{-1} = 2090\text{s-br}$ (t-CN); 1989m, 1950s (t-CO); 1783w-sh, 1752s (μ -CO), 1605w, 1589w. IR (MeCN): $\nu/\text{cm}^{-1} = 2136\text{m}$, 2082m-br (t-CN); 1989s, 1947m (t-CO); 1775m, 1756m (μ -CO), 1711w (μ -CN). IR (toluene): $\nu/\text{cm}^{-1} = 2082\text{s-br}$ (t-CN); 1989m, 1949s (t-CO); 1784w-sh 1764s, 1741w-br (μ -CO). ¹H NMR (CDCl₃): $\delta/\text{ppm} = 6.96$ (s, 3H, C₆H₃), 4.73 (s, 10H, Cp), 2.26 (s, 6H, CH₃). ¹³C{¹H} NMR (CDCl₃): $\delta/\text{ppm} = 278$ (br., μ -CO); 215-212 (br., t-CO); 176 (br., t-CN); 134.3 (br.), 127.8, 126.8 (br.) (C₆H₃Me₂); 87.6 (Cp), 18.9 (CH₃). Crystals suitable for X-ray analysis were collected from a ... solution of **5**....

[Fe₂Cp₂(CO)₃(CNMe)], 6 (Chart 6)[35].

Chart 6. Structures of **6**.



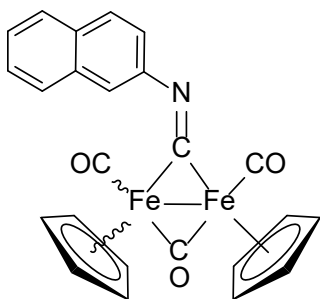
Prepared from [Fe₂Cp₂(CO)₄] (25.7 g, 72.6 mmol) and freshly prepared methyl isocyanide (2.5 mL, 44.4 mmol) in MeCN (150 mL). A fraction of the raw material (510 mg) was purified by the protonation/deprotonation route.

Yield: 190 mg, 60 % (with respect to isocyanide; re-scaled from the mass fraction of the raw material).

Compound **6** is soluble in CH₂Cl₂, toluene, MeCN, less soluble in Et₂O. IR (solid state): $\tilde{\nu}/\text{cm}^{-1}$ = 2144m (t-CN); 1985w, 1944s (t-CO); 1770m-sh, 1730s-br (μ -CO); 1700m-sh (μ -CN); 1454w, 1415w, 1355w, 1260w, 1113w, 1062w, 1013w, 1001w, 930w, 876w, 863w, 840m-sh, 820m, 692w, 656w. IR (CH₂Cl₂): $\tilde{\nu}/\text{cm}^{-1}$ = 2153m (t-CN); 1988m, 1948s (t-CO); 1778w, 1745s (μ -CO), 1719w-sh (μ -CN). IR (MeCN): $\tilde{\nu}/\text{cm}^{-1}$ = 2155m (t-CN); 1982s, 1944s (t-CO); 1788w, 1749s (μ -CO); 1727w-sh (μ -CN). IR (toluene): $\tilde{\nu}/\text{cm}^{-1}$ = 2147m (t-CN); 1989s, 1946s (t-CO); 1791w, 1760s (μ -CO); 1731w (μ -CN). ¹H NMR (CDCl₃): δ/ppm = 4.70 (s-br, 10H, Cp); 3.00 (s-br, 3H, CH₃). ¹³C {¹H} NMR (CDCl₃): δ/ppm = 280.6 (μ -CO); 213.0, 210.5 (t-CO); 162.5 (t-CN); 87.3 (Cp); 46.6, 30.5 (CH₃).

[Fe₂Cp₂(CO)₃{CN(2-C₁₀H₇)}], 7 (Chart 7)[17].

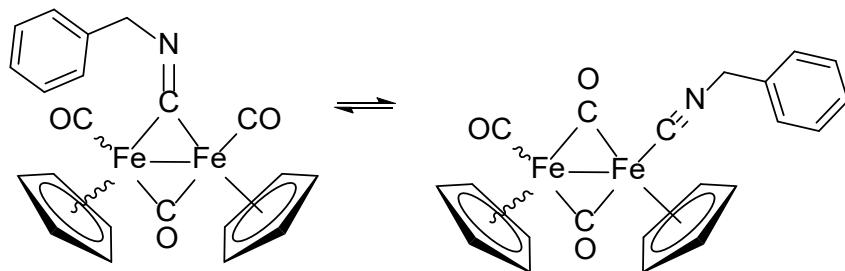
Chart 7. Structure of **7**.



Prepared from $[\text{Fe}_2\text{Cp}_2(\text{CO})_4]$ (455 mg, 1.29 mmol) and 2-naphthyl isocyanide (124 mg, 0.809 mmol) in MeCN (30 mL). Purified by the protonation/deprotonation route. Yield: 194 mg, 50 % (with respect to isocyanide). Compound **7** is soluble in CH_2Cl_2 , toluene, MeCN, Et_2O , hexane. IR (solid state): $\tilde{\nu}/\text{cm}^{-1} = 3107\text{w}$, 3053w, 2963w, 2853w; 1973s, 1934s (t-CO); 1782s-sh, 1752w (μ -CO), 1679s-br (μ -CN); 1616s, 1589s, 1501m, 1461m, 1432m, 1417m, 1379m, 1357m, 1266w, 1245w, 1206w, 1157m, 1116w, 1060w, 1013m, 999m, 956w, 879w-sh, 854m-sh, 839m-sh, 829m-sh, 814s, 749m, 711w, 679w. IR (CH_2Cl_2): $\tilde{\nu}/\text{cm}^{-1} = 1991\text{s}$, 1951m (t-CO); 1790m (μ -CO); 1694m-br (μ -CN), 1623w, 1593w. IR (MeCN): $\tilde{\nu}/\text{cm}^{-1} = 1986\text{s}$, 1947m (t-CO); 1790m (μ -CO); 1694m-br (μ -CN), 1623w. IR (toluene): $\tilde{\nu}/\text{cm}^{-1} = 1991\text{s}$, 1948s (t-CO); 1797s, 1756w (μ -CO); 1740w-sh, 1700s-br (μ -CN); 1623w. ^1H NMR (CDCl_3): $\delta/\text{ppm} = 7.91$ (d, $J = 8.7$ Hz), 7.86 (t, $J = 7.6$ Hz), 7.53–7.47 (m), 7.46–7.40 (m) (7H, C_{10}H_7); 4.75, 4.72 (s-br, 10H, Cp). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): $\delta/\text{ppm} = 271.9$ (μ -CO); 255.2 (μ -CN); 213 (br.), 211.0 (t-CO); 147.0, 134.5, 130.7, 129.3, 128.0, 127.7, 126.6, 124.8, 122.1, 117.0 (C_{10}H_7); 89.5 (br.), 87.9 (Cp).

$[\text{Fe}_2\text{Cp}_2(\text{CO})_3(\text{CNCH}_2\text{Ph})]$, **8 (Chart 8)[35].**

Chart 8. Structures of **8**.



Prepared from $[\text{Fe}_2\text{Cp}_2(\text{CO})_4]$ (337 mg, 0.96 mmol) and benzyl isocyanide (0.10 mL, 0.82 mmol) in MeCN (25 mL). Purified by the protonation/deprotonation route. Yield: 241 mg, 66 % (with respect to isocyanide). Compound **8** is soluble in CH_2Cl_2 , MeCN, toluene, less soluble in Et_2O . IR (solid state): $\tilde{\nu}/\text{cm}^{-1} = 3103\text{w}$, 3066w, 3032w, 2965w, 2912w, 2850w; 1968s, 1922s (t-CO); 1757s (μ -CO); 1712-1699s-br (μ -CN); 1494w, 1453w, 1430w, 1418m, 1357w, 1314m, 1262w, 1198w, 1070w, 1059w, 1027w, 1013w, 1005w, 953w, 881w, 867w-sh, 845m-sh, 826s, 749m, 737w, 699s-sh, 684s-br. IR (CH_2Cl_2): $\tilde{\nu}/\text{cm}^{-1} = 2131\text{m}$ (t-CN); 1989s, 1948s (t-CO); 1784m, 1747s (μ -CO); 1710m (μ -CN). IR (MeCN): $\tilde{\nu}/\text{cm}^{-1} = 2132\text{w}$ (t-CN); 1983s, 1943m (t-CO);

1785m, 1750m (μ -CO); 1713m (μ -CN). IR (toluene): $\tilde{\nu}/\text{cm}^{-1} = 2126\text{w}$ (t-CN); 1989s, 1947s (t-CO); 1793m, 1760m (μ -CO); 1710m (μ -CN). ^1H NMR (CDCl_3): $\delta/\text{ppm} = 7.51$ (s-br), 7.37 (s-br), 7.32–7.27 (m), 7.20 (s-br) (5H, C_6H_5); 5.18 (s-br, 1H, CH_2); 4.82, 4.69 (s-br, 10H, Cp); 4.45 (br, 1H, CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) $\delta/\text{ppm} = 280\text{br}$, 273.3 (μ -CO); 251.1 (μ -CN); 215–212br, 210.8 (t-CO); 139.9, 128.9, 128.1, 127.1, 126.8 (C_6H_5); 87.5 (Cp); 64.9, 49br (CH_2).

3. X-ray crystallography

Crystal data and collection details for **5-ct** are reported in Table 4. Data were recorded on a Bruker APEX II diffractometer equipped with a PHOTON2 detector using Mo– $\text{K}\alpha$ radiation. Data were corrected for Lorentz polarization and absorption effects (empirical absorption correction SADABS).³⁸ Structures were solved by direct methods and refined by full-matrix least-squares based on all data using F^2 .³⁹ Hydrogen atoms were fixed at calculated positions and refined by a riding model. All non-hydrogen atoms were refined with anisotropic displacement parameters.

Table 4. Crystal data and measurement details for **5-ct**.

	5-ct
Formula	$\text{C}_{22}\text{H}_{19}\text{Fe}_2\text{NO}_3$
FW	457.08
T, K	293(2)
λ , Å	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$
a , Å	8.1610(7)
b , Å	10.7531(10)
c , Å	21.4677(19)
β , °	96.282(3)
Cell Volume, Å ³	1869.5(3)
Z	4
D_c , g·cm ⁻³	1.624
μ , mm ⁻¹	1.575
F(000)	936
Crystal size, mm	0.16×0.14×0.11
θ limits, °	1.909–25.100
Reflections collected	18556
Independent reflections	3312 [$R_{int} = 0.0491$]

Data / restraints	3312 / 0 / 255
/parameters	
Goodness on fit on F^2	1.143
R_1 ($I > 2\sigma(I)$)	0.0432
wR_2 (all data)	0.0993
Largest diff. peak and hole, $e \text{ \AA}^{-3}$	0.509 / -0.311

4. Computational studies

All geometries were optimized with ORCA 4.0.1.2, using the B97 functional in conjunction with a triple- ζ quality basis set (def2-TZVP). The dispersion corrections were introduced using the Grimme D3-parametrized correction and the Becke–Johnson damping to the DFT energy. Most of the structures were confirmed to be local energy minima (no imaginary frequencies), but in some case a small, unavoidable negative frequency relative to the Cp rotation around the M-Cp axis was observed. The solvent was considered through the Continuum-like Polarizable Continuum Model (C-PCM, dichloromethane).

5. Thermal isomerization study

Dark red-brown solutions of **3** and **5** (20 mg) in anhydrous toluene (5 mL) were heated at reflux under a N_2 atmosphere for 3 h while periodically sampled for IR analysis. The appearance of new weak absorption peaks, ascribable to isocyanide-bridging isomers, was observed. Next, solutions were cooled to room temperature and IR spectra were recorded again, showing no variations. Following volatiles removal under vacuum, the solid-state spectra of the brown residues were recorded, displaying a different CO/CNR band pattern with respect to those of the starting materials, consistent with the presence of the isocyanide-bridging isomers. IR data are reported in the following, and the spectra are displayed in Figures S41 and S42. *Compound 3*. IR (toluene): new absorptions at 1996w (t-CO), 1782w-sh (μ -CO), 1696w-br (μ -CN) cm^{-1} . IR (solid state): $\nu/\text{cm}^{-1} = 2118\text{m}$ (t-CN); 1991m, 1952s-sh, 1940s-br (t-CO); 1772s-sh, 1752s, 1731s (μ -CO); 1695m-sh (μ -CN). *Compound 5*. IR (toluene): new absorptions at 1995w (t-CO), 1782w-sh (μ -CO), 1720w-br (μ -CN) cm^{-1} . IR (solid state): $\nu/\text{cm}^{-1} = 2081\text{s}$ (t-CN); 1995w, 1958w-sh, 1932s (t-CO); 1767m-sh, 1755m-sh, 1741s (μ -CO); 1706s-sh (μ -CN).

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Supporting Information Available

IR and NMR spectra of products; DFT geometries of **1-5** and **7-8**.CCDC reference number XXXXX (**5-ct**) contains the supplementary crystallographic data for the X-ray study reported in this paper. This data can be obtained free of charge at <https://www.ccdc.cam.ac.uk/structures/>.Cartesian coordinates of the DFT-optimized structures are collected in a separated .xyz file.

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