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# **Formation and Structural Characterization of a Diiron Aminoalkylidene Complex with *N*-Cyano Substituent<sup>†</sup>**

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<sup>†</sup> To our colleague, friend and mentor Guido Pampaloni, on occasion of his retirement from a brilliant career enjoying coordination chemistry.

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## Abstract

The reaction of the isocyanide complex  $[\text{Fe}_2\text{Cp}_2(\text{CO})_3(\text{CNMe})]$ , **1**<sup>Me</sup>, with BrCN (1.2 eq.), in acetonitrile at 60 °C, led to the low-yield isolation, after work-up, of the unprecedented N-methylcyanamido-(cyano)alkylidene complex  $[\text{Fe}_2\text{Cp}_2(\text{CO})_3\{\mu\text{-C}(\text{CN})\text{N}(\text{CN})\text{Me}\}]$ , **3**. The synthesis of **3** represents an uncommon example of C-C bond forming cyanylation reaction taking place at a metal complex despite competitive oxidative addition pathways; it proceeded with the presumable, intermediate formation of a N-methylcyanamido-alkylidyne precursor readily undergoing CN<sup>-</sup> addition, and was accompanied by the production of minor amounts of  $[\text{Fe}_2\text{Cp}_2(\text{CO})_4]$  and monoiron(II) piano-stool compounds. Compound **3** was fully characterized by single crystal X-ray diffraction, elemental analysis, IR and NMR spectroscopy. The reaction of  $[\text{Fe}_2\text{Cp}_2(\text{CO})_4]$  with cyanogen bromide, under conditions resembling those employed for **1**<sup>Me</sup>/BrCN, afforded a mixture of  $[\text{FeCpBr}(\text{CO})_2]$  and  $[\text{FeCp}(\text{CN})(\text{CO})_2]$ .

**Keywords:** Aminocarbyne; Bridging alkylidene; Diiron complexes; Cyanylation; Cyanamido; Oxidative addition.

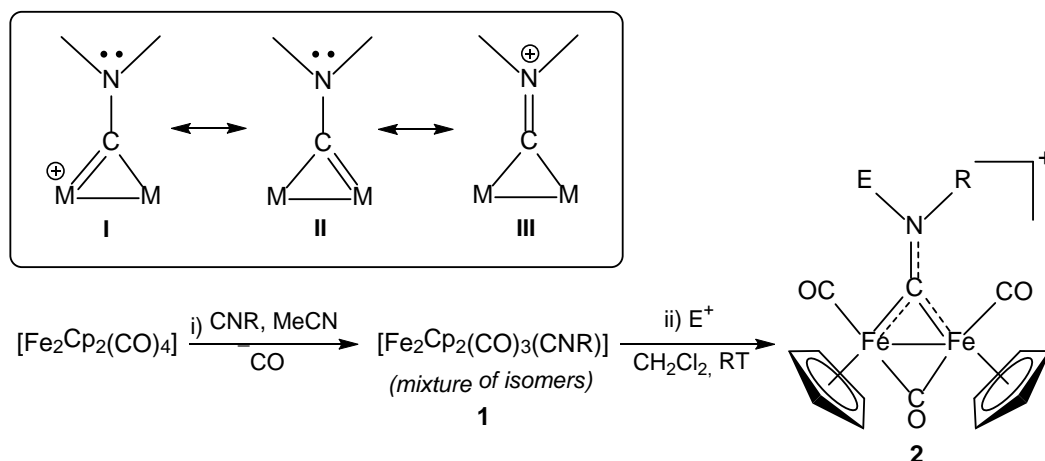
## Introduction

Aminoalkylidyne ligands [<sup>1</sup>] are ubiquitous in organometallic chemistry. Due to their substantial electron withdrawing character, aminoalkylidyne ligands usually adopt bridging coordination in di- and polynuclear complexes, so to enhance the back-donation from the metal centers [<sup>2</sup>, 3]; the bonding to two transition metal atoms may be described in terms of three main canonical forms, accounting for the amino-carbyne and the iminium nature, respectively (Scheme 1). Basically, aminoalkylidyne complexes are available through two main synthetic strategies consisting in the modification of pre-existing ligands, i.e. the addition of suitable electrophiles to the nitrogen atom of isocyanides [4] and the

alkoxide removal from alkoxido-aminoalkylidene precursors [2, <sup>5</sup>]. Regarding the former approach, alkylating agents have been widely employed as electrophiles to afford stable derivatives, while protonation reactions may hold a reversible character [2, 6]. Many diiron  $\mu$ -aminoalkylidyne complexes have been prepared from the commercial  $[\text{Fe}_2\text{Cp}_2(\text{CO})_4]$  by means of a straightforward synthesis working up to a multigram scale [<sup>7</sup>]: first, thermal carbonyl/isocyanide mono-substitution leads to a mixture of isomers interconverting in solution at room temperature [<sup>8</sup>], then electrophilic N-addition yields the alkylidyne product usually occurring in one single isomeric form (Scheme 1). Notably, the isocyanide in the intermediate adducts **1** may be susceptible to attack even by relatively weak electrophiles such as acetyl and benzoyl chlorides [<sup>9</sup>]. However, robust complexes **2** comprise alkyl/aryl amino groups (E and R in Scheme 1), and have aroused a significant attention due to their versatile chemistry, whereby the aminoalkylidynemoiety is converted into a diversity of highly functionalized aminoalkylidene species [10, <sup>11</sup>]; moreover, promising potential applications of complexes **2** in medicine [<sup>12</sup>] and catalysis [<sup>13</sup>] have emerged in the recent years.

We became interested in the possibility of obtaining unconventional aminoalkylidyneligands coordinated to the diiron scaffold  $\{\text{Fe}_2\text{Cp}_2(\text{CO})_3\}$ . In particular, we reckoned that the introduction of the cyano moiety as one of the two nitrogen substituents (E = CN in Scheme 1) could be useful for deriving novel organometallic motifs. In principle, the electron-withdrawing character of  $-\text{C}\equiv\text{N}$  is expected to enhance the electrophilic behavior of the carbyne carbon, furthermore the presence of the heteroatom and the unsaturation could constitute additional centers of reactivity. Notwithstanding, it must be noted that (cyano)aminoalkylidyne species,  $\{\text{M}\equiv\text{CN}(\text{C}\equiv\text{N})(\text{R})\}$ , that might be alternatively described as cyanamido-alkylidynes, are yet unknown in organometallic chemistry, to the best of our knowledge; the same is true for cyanamido-alkylidene complexes of general formula  $[\text{M}=\text{C}(\text{X})\text{N}(\text{CN})(\text{R})]$ , potentially originating from the related alkylidyne compounds by nucleophilic (X) addition.

According to Scheme 1, the design of a (cyano)aminoalkylidyne complex of type **2** should consider two possibilities, i.e. the alkylation of a challenging cyano-isocyanide ligand ( $R = \text{CN}$ ;  $E = \text{alkyl}$ ) [14] or the transfer of a  $\{\text{CN}^+\}$  unit to a more stable isocyanide ( $R = \text{alkyl, aryl}$ ;  $E = \text{CN}$ ). The second option appeared potentially viable and was investigated in this work, thus cyanogen bromide ( $\text{BrCN}$ ) was selected as a cyanylating agent. However, it should be mentioned that, despite  $\text{BrCN}$  is widely employed as  $\{\text{CN}^+\}$  transferor in organic synthesis [15], this outcome is often hampered when metal complexes are involved, since bromination [16] or oxidative addition [17, 18] may become competitive pathways depending on the cases.

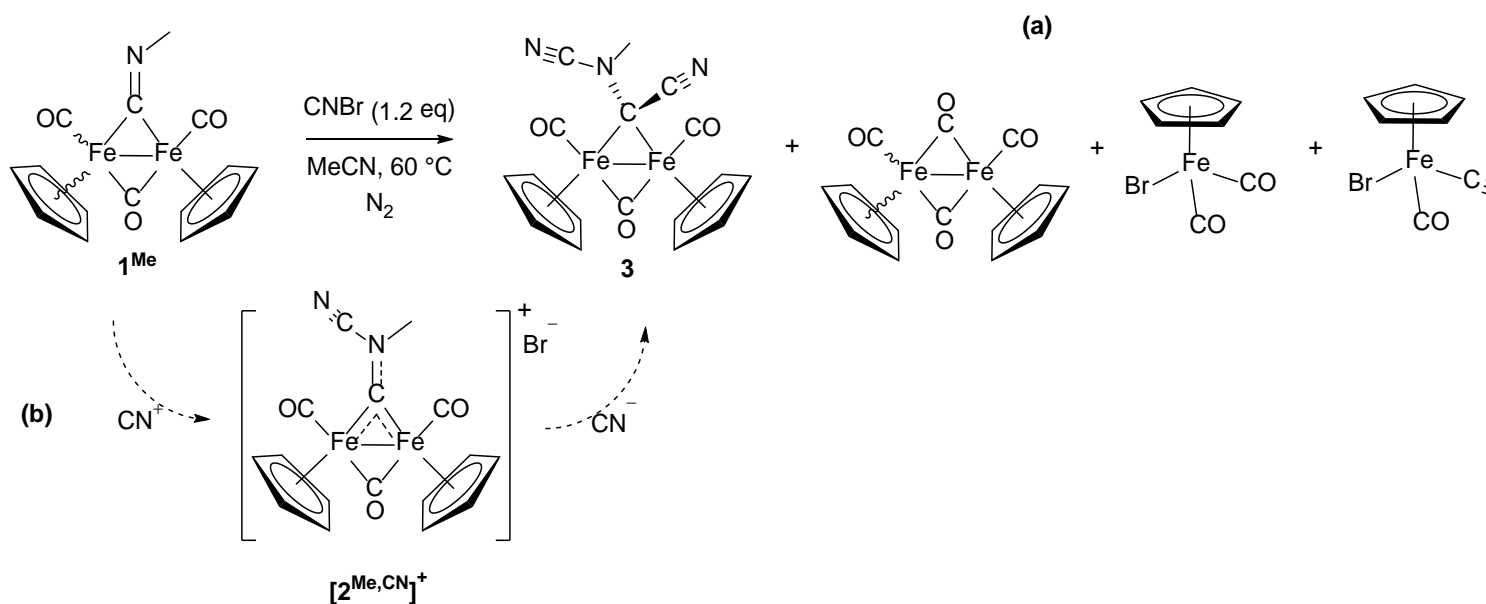


**Scheme 1.** Synthetic pathway to cationic diiron  $\mu$ -aminoalkylidyne complexes from  $[\text{Fe}_2\text{Cp}_2(\text{CO})_4]$  via intermediate formation of mono-isocyanide adducts.  $E = \text{Me, Et, C(O)Me, C(O)CH}_2\text{Ph}$ .  $R$ , reaction temperature: alkyl, reflux; aryl, room temperature. Inset: canonical structures for the bridging aminoalkylidyne ligand in dimetallic complexes. **I** and **II**: amino-carbyne ( $\text{M}_2 \rightarrow \text{C}$ ); **III**: iminium ( $\text{N} \rightarrow \text{C}$  donation).

## Results and discussion

The isocyanide complex  $[\text{Fe}_2\text{Cp}_2(\text{CO})_3(\text{CNMe})]$ , **1**<sup>Me</sup>, was synthesized from  $[\text{Fe}_2\text{Cp}_2(\text{CO})_4]$  and freshly prepared methyl isocyanide in refluxing acetonitrile, following the published procedure [7]. Compound **1**<sup>Me</sup> exists in solution as a mixture of cis-trans and bridging-terminal isomers, with reference to the mutual orientation of the Cp rings and the coordination site occupied by the isocyanide ligand, respectively [8, 19]. Due to efficient back-donation to the bridging isocyanide and the presence of a

small, electron donating group on the nitrogen atom,  $1^{\text{Me}}$  readily undergoes electrophilic additions to afford cationic aminoalkylidyne products (Scheme 1)<sup>[20]</sup>. The reaction of  $1^{\text{Me}}$  with cyanogen bromide was investigated under protected atmosphere and several experimental conditions upon varying the solvent, the temperature and the reagents molar ratio (see Experimental for details). The reaction was generally nonselective in the conditions in which it worked, and the alternative utilization of the milder cyanylating agent [DMAP-CN]Br<sup>[21]</sup>, in the place of BrCN, was not effective. The best result was achieved by using an almost equimolar  $1^{\text{Me}}$ /BrCN ratio and acetonitrile as solvent, at a temperature of ca. 60 °C. Monitoring the reaction via liquid IR spectroscopy permitted to check the complete consumption of the starting metal species after 2.5 hours. Subsequent alumina chromatography led to isolate the unprecedented N-methylcyanamido-(cyano)alkylidene complex  $[\text{Fe}_2\text{Cp}_2(\text{CO})_3\{\mu\text{-C}(\text{CN})\text{N}(\text{CN})\text{Me}\}]$ , **3**, as an air-sensitive red solid in 9% yield. The diiron complex  $[\text{Fe}_2\text{Cp}_2(\text{CO})_4]$  and the monoiron ones  $[\text{FeCpBr}(\text{CO})_2]$  and  $[\text{FeCpBr}(\text{CO})(\text{CNMe})]$  were also separated and identified (see Scheme 2a and Figure S1)<sup>[22, 23]</sup>.

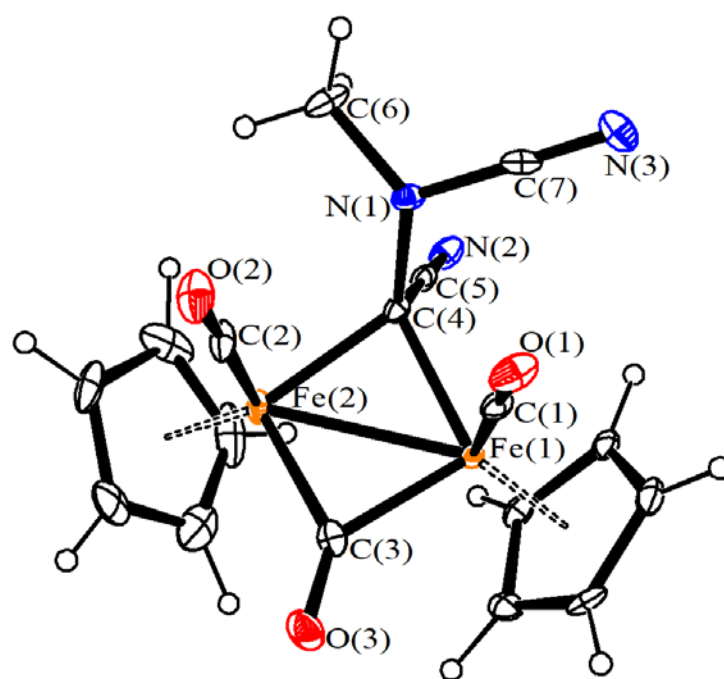
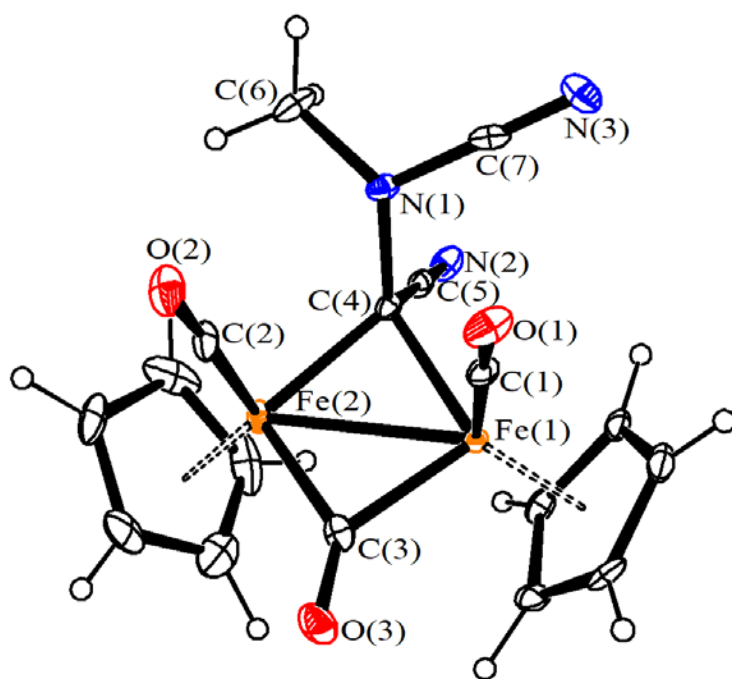


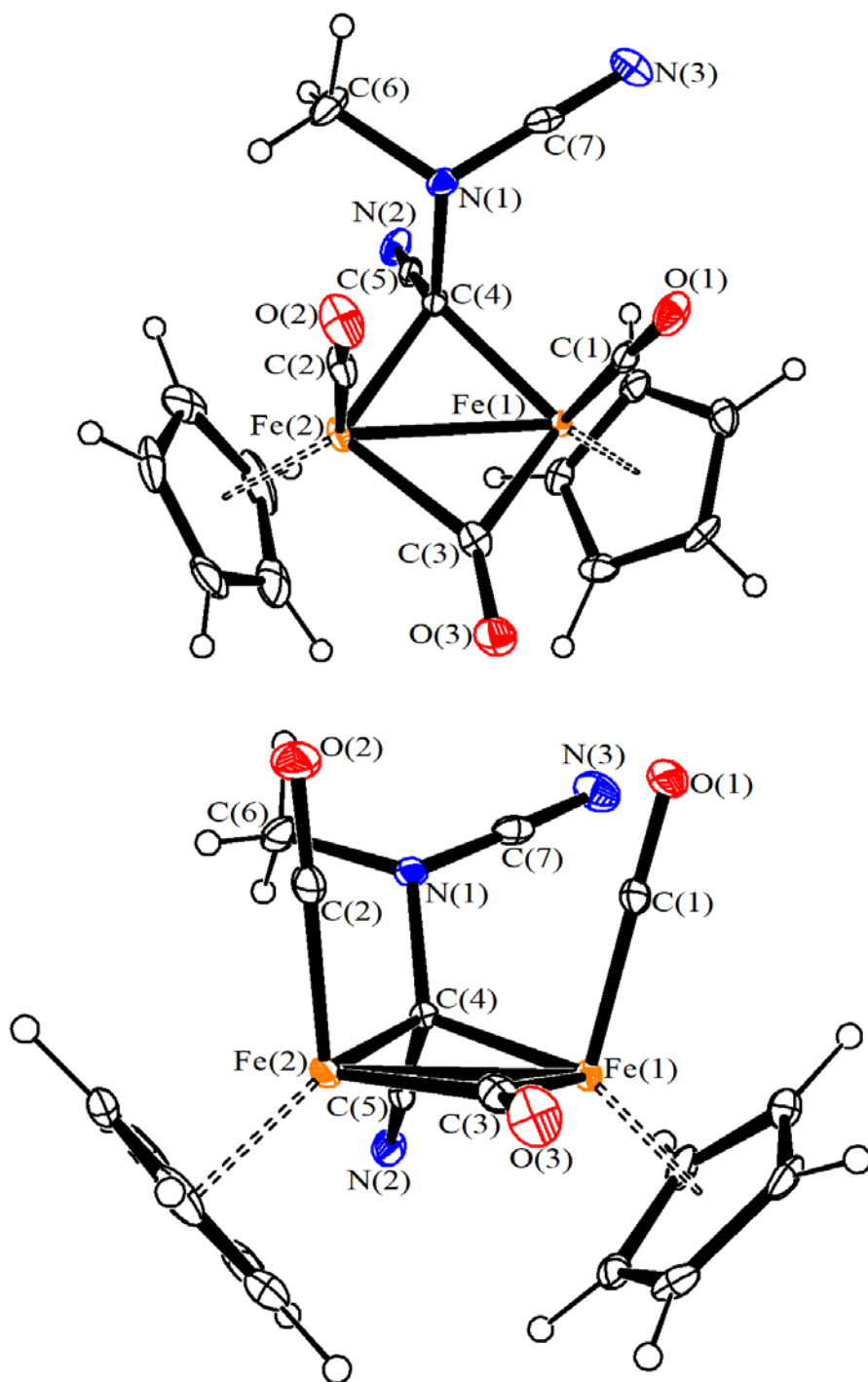
**Scheme 2.** Formation of diiron and monoiron derivatives from the nonselective reaction of cyanogen bromide with diiron mono-isocyanide complex ( $1^{\text{Me}}$ , shown as isocyanide-bridging isomer): isolated products (a), proposed reaction sequence for the formation of **3**, via (ciano)aminoalkylidyne  $[2^{\text{Me}, \text{CN}}]^+$  (b).

The formation of **3** from **1**<sup>Me</sup> and BrCN implies the action of BrCN as a source of both CN<sup>+</sup> and CN<sup>-</sup> [11c, 17, 18, <sup>24</sup>]. The reaction sequence presumably involves the initial formation of the targeted aminoalkylidene complex [**2**<sup>Me,CN</sup>]<sup>+</sup> which, due to its high reactivity towards nucleophiles (vide infra), readily undergoes cyanide addition at the carbyne center (Scheme 2b). In accord with this hypothesis, a reaction between **1**<sup>Me</sup>, BrCN and Na[CF<sub>3</sub>SO<sub>3</sub>] (1:1.2:1.3 eq.) allowed to detect a new IR band at 1856 cm<sup>-1</sup> which could be tentatively assigned to [**2**<sup>Me,CN</sup>]<sup>+</sup> (Figure S2). Besides, it was previously reported that aminoalkylidene compounds of type **2** (Scheme 1) are susceptible to cyanide addition from [Bu<sub>4</sub>N]CN, that is selectively directed to the carbyne [<sup>25</sup>].

The identity of **3** was ascertained by single crystal X-ray diffraction analysis (Figure 1 and Table 1). The molecular structure of **3** is composed of a *cis*-[Fe<sub>2</sub>Cp<sub>2</sub>(CO)<sub>2</sub>(μ-CO)] unit [7, 12, <sup>26</sup>] bonded to an unprecedented bridging {μ-C(CN)N(CN)Me} N-methylcyanamido-(cyano)alkylidene ligand. Both the bridging μ-CO [Fe(1)-C(3) 1.919(4) Å, Fe(2)-C(3) 1.921(4) Å] and {μ-C(CN)N(CN)Me} [Fe(1)-C(4) 1.972(4) Å, Fe(2)-C(4) 1.971(4) Å] ligands display a perfectly symmetric coordination to the iron centers, since the latter are both bonded to terminal CO ligands. The Fe-C bond distances to the {μ-C(CN)N(CN)Me} ligand substantially match those previously reported for related cyano-alkylidene diiron complexes [<sup>27</sup>]. The C(4)-N(1) [1.501(5) Å], N(1)-C(6) [1.489(5) Å] and C(4)-C(5) [1.455(5) Å] distances suggest the presence of almost pure single bonds [<sup>28</sup>], whereas C(5)-N(2) [1.144(5) Å] and C(7)-N(3) [1.141(6) Å] are typical triple bonds. The amido center N(1) displays a significant pyramidalization [sum angles 345.4(5)° instead of 360°] in view of the lack of conjugation with C(4) and C(6). The N(1)-C(7) contact [1.341(6) Å] is in keeping with a single N(sp<sup>3</sup>)-C(sp) bond [<sup>29</sup>].







**Figure 1.** View of the molecular structure of **3**. Displacement ellipsoids are at the 30% probability level.

**Table 1.** Selected bond lengths (Å) and angles (°) for **3**.

Fe(1)-Fe(2)	2.5187(7)	Fe(1)-C(1)	1.771(4)
Fe(2)-C(2)	1.784(4)	Fe(1)-C(3)	1.919(4)
Fe(2)-C(3)	1.921(4)	Fe(1)-C(4)	1.972(4)
Fe(2)-C(4)	1.971(4)	C(1)-O(1)	1.133(5)

C(2)-O(2)	1.132(5)	C(3)-O(3)	1.165(5)
C(4)-C(5)	1.455(5)	C(4)-N(1)	1.501(5)
C(5)-N(2)	1.144(5)	N(1)-C(6)	1.489(5)
N(1)-C(7)	1.341(6)	C(7)-N(3)	1.141(6)
Fe(1)-C(1)-O(1)	178.4(4)	Fe(2)-C(2)-O(2)	178.7(4)
Fe(1)-C(3)-Fe(2)	81.98(16)	Fe(1)-C(4)-Fe(2)	79.41(15)
C(4)-C(5)-N(2)	176.9(4)	C(4)-N(1)-C(6)	116.4(3)
C(4)-N(1)-C(7)	114.4(3)	C(6)-N(1)-C(7)	114.6(4)
N(1)-C(7)-N(3)	176.9(5)	C(5)-C(4)-N(1)	106.2(3)

To the best of our knowledge, **3** contains the first example of structurally characterized aminoalkylidene ligand with a cyano substituent on the nitrogen.

Complex **3** was further characterized by IR and NMR spectroscopy. The IR spectrum (in CH<sub>2</sub>Cl<sub>2</sub>) shows diagnostic bands at 2202 and 2162 cm<sup>-1</sup>, ascribable to the cyanamido and cyano moieties, respectively. Moreover, the two terminal and the bridging CO ligands give rise to a typical three-bands pattern (2013, 1978 and 1813 cm<sup>-1</sup>). The IR spectrum of the related complex [Fe<sub>2</sub>Cp<sub>2</sub>(CO)<sub>3</sub>{μ-C(CN)N(Ph)Me}] in dichloromethane exhibited absorptions at 2000, 1963 (terminal CO), 1799 (bridging CO) and 2146 (C≡N) cm<sup>-1</sup> [25a]. A comparative view of data suggests that the N-methylcyanamido unit in **3** exerts a significant electron withdrawing effect, contributing to a weakened iron to carbonyl back-donation.

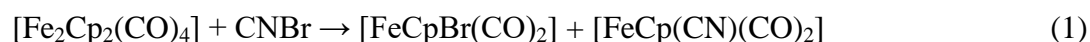
The <sup>1</sup>H and <sup>13</sup>C NMR spectra of **3** (CDCl<sub>3</sub> solution, Figures S5-S6) reveal a single, sharp set of signals. Therefore, it can be concluded that the C-C bond coupling converting **2**<sup>Me,CN</sup> into **3** (Scheme 2) is stereospecific, placing the amino group far away from the Cp rings, as recognized in the X-ray structure of **3** and coherently with previous crystallographic and computational findings on analogous compounds [25b, 11c]. The resonances of the cyclopentadienyls and terminal carbonyls are isochronous in **3** [δ(<sup>1</sup>H) = 4.93 ppm (Cp); δ(<sup>13</sup>C) = 207.9 (CO), 90.9 ppm (Cp)], confirming the cis arrangement observed in the solid state.

The alkylidene carbon appears significantly shielded (δ = 141 ppm) with respect to what found in related aminoalkylidene complexes of generic formula [Fe<sub>2</sub>Cp<sub>2</sub>(CO)<sub>3</sub>{μ-C(CN)NR<sub>2</sub>}] (δ ≈ 160 ppm)

[25a]; instead, the carbene-bound cyanide and the nitrogen-bound cyanide in **3** resonate at 128 and 119 ppm, in the typical range for alkylidene-cyanide [25a] and organic nitrile groups [<sup>30</sup>, <sup>31</sup>].

On the other hand, the formation of the monoiron by-products witnesses the oxidizing activity of BrCN, on considering that such complexes contain a Fe<sup>II</sup> center, whereas **1**<sup>Me</sup>, **2**<sup>Me,CN</sup> and **3** are [Fe<sup>I</sup>Fe<sup>I</sup>] complexes. Accordingly, [FeCpBr(CO)(CNMe)] was previously obtained by oxidative cleavage of **1**<sup>Me</sup> with either Br<sub>2</sub>, Ag<sup>I</sup> salts in CHBr<sub>3</sub> or RSnBr<sub>3</sub> [<sup>32</sup>]. The formation of [Fe<sub>2</sub>Cp<sub>2</sub>(CO)<sub>4</sub>] might be the consequence of one-electron oxidation of [Fe<sub>2</sub>Cp<sub>2</sub>(CO)<sub>3</sub>(CNMe)] and subsequent fragmentation [32b, <sup>33</sup>].

When BrCN was allowed to react with [Fe<sub>2</sub>Cp<sub>2</sub>(CO)<sub>4</sub>], the organic reagent exclusively acted as an overall two-electron oxidant, affording a mixture of iron(II) piano-stool compounds (Equation 1, see Figure S3 and Experimental for details).



We worked to extend the cyanylating process shown in Scheme 2 to other [Fe<sub>2</sub>Cp<sub>2</sub>(CO)<sub>3</sub>(CNR)] complexes (R = C<sub>6</sub>H<sub>11</sub>, 4-C<sub>6</sub>H<sub>4</sub>OMe); nonetheless, the reactions of these complexes with cyanogen bromide, carried out under different conditions, always led to mixtures of CpFe<sup>II</sup> products and no evidence for C-CN bond formation was found.

## Conclusions

In the framework of our interest in the building of uncommon hydrocarbyl ligands stabilized by bridging coordination in dinuclear group 8 metal complexes [2, 10, <sup>34</sup>], here we report the formation of a rare N-cyano substituted  $\mu$ -aminoalkylidene ligand in a diiron complex, obtained by CN<sup>+</sup> addition to coordinated isocyanide via intermediate formation of a reactive N-cyano aminoalkylidyne. Despite competitive reactions arising from the oxidizing/brominating power of cyanogen bromide were

responsible for the low-yield isolation of the product, the cyanylating process described herein is unprecedented. The structural characterization of the novel  $\mu$ -aminoalkylidene species did not evidence appreciable charge delocalization within the  $\{C_{\text{carbene}}-\text{N}-\text{C}\equiv\text{N}\}$  skeleton.

### 3. Experimental

#### 3.1. General experimental details

$[\text{Fe}_2\text{Cp}_2(\text{CO})_4]$  (99%) was purchased from Strem Chemicals, other reactants and solvents were obtained from Merck, Apollo Scientific or TCI Chemicals and were of the highest purity available. Cyanogen bromide was stored at 4 °C. Contaminated labware was treated with NaOH/bleach ( $\text{BrCN}$ ) or  $\text{HCl}/\text{EtOH}$  (isocyanides). Complex  $[\text{Fe}_2\text{Cp}_2(\text{CO})_3(\text{CNMe})]$ , **1<sup>Me</sup>**, and related isocyanide complexes were prepared according to the literature [35]; an improvement in the workup of **1<sup>Me</sup>** is herein described. All reactions were carried out under dry  $\text{N}_2$  using standard Schlenk techniques and anhydrous solvents stored over 3 Å MS; MeCN was distilled from  $\text{CaH}_2$ ,  $\text{CHCl}_3$  from  $\text{P}_2\text{O}_5$ ,  $\text{CH}_2\text{Cl}_2$  was obtained from SPS 5 solvent purifier (MBraun). The purification of **1<sup>Me</sup>** and all chromatographic separations were carried out under a nitrogen atmosphere using neutral alumina columns and non-anhydrous solvents. The other operations were conducted under air with common laboratory glassware. NMR spectra were recorded on JEOL YH JNM-ECZ400S or JNM-ECZ500R instruments equipped with broadband probes. Solutions for NMR analyses were prepared under  $\text{N}_2$  using  $\text{CDCl}_3$  stored in the dark over  $\text{K}_2\text{CO}_3$ . Chemical shifts are referenced to the residual solvent peaks ( $^1\text{H}$ ,  $^{13}\text{C}$ ) [36].  $^1\text{H}$  and  $^{13}\text{C}$  spectra were assigned with the assistance of  $^1\text{H}$ - $^{13}\text{C}$  *gs*-HSQC and *gs*-HMBC experiments. IR spectra of solid samples (650-4000  $\text{cm}^{-1}$ ) were recorded on a Perkin Elmer Spectrum One FT-IR spectrometer equipped with a UATR sampling accessory; IR spectra of solutions were recorded on a Perkin Elmer Spectrum 100 FT-IR spectrometer using a  $\text{CaF}_2$  liquid transmission cell (1300-2600  $\text{cm}^{-1}$ ). IR spectra were processed with Spectragryph software [37]. Carbon, hydrogen and nitrogen analyses were

performed on a Vario MICRO cube instrument (Elementar). *Caution: cyanogen bromide is an extremely toxic chemical which can be easily absorbed through skin; it must be used only in a well-ventilated fumehood while wearing protective gloves; contaminated tools should be treated with bleach.*

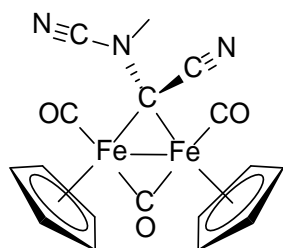
### 3.2. Synthesis and characterization of compounds

#### 3.2.1. Purification of $[\text{Fe}_2\text{Cp}_2(\text{CO})_3(\text{CNMe})]$ , $\mathbf{1}^{\text{Me}}$ , by protonation/deprotonation sequence.

The reaction of  $[\text{Fe}_2\text{Cp}_2(\text{CO})_4]$  and freshly-prepared methyl isocyanide was carried out according to the published procedure [35]. Following volatiles removal under vacuum, a portion of the crude reaction mixture (2.35 g) was suspended in  $\text{Et}_2\text{O}$  (50 mL) and treated with 48% w/w  $\text{HBF}_4$  (aq. solution; 0.65 mL, 5.0 mmol). The dark red suspension was maintained under vigorous stirring for 2 h and the scarlet red solid was triturated to avoid its clumping. Next, the mixture was moved on top of an alumina column (h 4.5 cm, d 2.3 cm). A red-brown band, containing  $[\text{Fe}_2\text{Cp}_2(\text{CO})_4]$ , was eluted with  $\text{Et}_2\text{O}$ . Then a 5 %  $\text{Et}_3\text{N}$  solution in  $\text{CH}_2\text{Cl}_2$  allowed to collect a red-violet band, containing  $\mathbf{1}^{\text{Me}}$ . Volatiles were removed under vacuum and the resulting red-violet solid was dried under vacuum and stored under nitrogen. Yield: 1.365 g, *ca.* 86 % (with respect to methyl isocyanide; rescaled from the mass fraction of the raw material).

#### 3.2.2. Reactivity of $[\text{Fe}_2\text{Cp}_2(\text{CO})_3(\text{CNMe})]$ with cyanogen bromide: synthesis and characterization of $[\text{Fe}_2\text{Cp}_2(\text{CO})_3\{\mu\text{-C}(\text{CN})\text{N}(\text{CN})\text{Me}\}]$ , $\mathbf{3}$ (Figure 2).

**Figure 2.** Structure of  $\mathbf{3}$ .



In a 50 mL Schlenk tube, a dark-red solution of  $[\text{Fe}_2\text{Cp}_2(\text{CO})_3(\text{CNMe})]$ , **1**<sup>Me</sup> (360 mg, 0.981 mmol), in MeCN (7 mL) was treated with cyanogen bromide (126 mg, 1.19 mmol, 1.2 equivalents) and heated at 60 °C for 2.5 h. IR analysis indicated complete conversion of **1**. The final mixture was moved through a short alumina column (h 2 cm, d 2.3 cm) to remove a rusty-brown solid. The dark blood red eluate was dried under vacuum. The residue was suspended in Et<sub>2</sub>O (10 mL), adding a small amount of CH<sub>2</sub>Cl<sub>2</sub> to achieve complete solubilization, then moved on top of alumina column (h 4 cm, d 3.4 cm). A dark red band containing a mixture of  $[\text{Fe}_2\text{Cp}_2(\text{CO})_4]$  and  $[\text{FeCpBr}(\text{CO})_2]$  was eluted with Et<sub>2</sub>O. Then, a brown tailed band containing  $[\text{FeCpBr}(\text{CO})(\text{CNMe})]$  was eluted using CH<sub>2</sub>Cl<sub>2</sub>. Finally, a red-violet band containing **3** was eluted with CH<sub>2</sub>Cl<sub>2</sub>/MeCN 10:1 v/v. Volatiles were removed under vacuum. The residues containing  $[\text{FeCpBr}(\text{CO})(\text{CNMe})]$  or **3** were triturated in a Et<sub>2</sub>O/hexane 1:1 v/v mixture and the suspensions were filtered on a G4 sintered glass filter. The solids were washed with hexane, dried under vacuum (40 °C) and stored under inert atmosphere before characterization.

*Reaction optimization.* Decreasing the amount of BrCN, down to 1.0 equivalents, leads to incomplete conversion of **1**<sup>Me</sup> while increasing its amount, up to 2.0 equivalents, promotes the formation of CpFe<sup>II</sup>by-products at the expense of **3**. The formation of **3** was also observed in refluxing CHCl<sub>3</sub> (1.2 eq. BrCN) while it was completely inhibited when the reaction was carried out CH<sub>2</sub>Cl<sub>2</sub> at room temperature or using the milder cyanylating agent [DMAP-CN]Br instead of BrCN [21].

**$[\text{Fe}_2\text{Cp}_2(\text{CO})_3\{\mu\text{-C}(\text{CN})\text{N}(\text{CN})\text{Me}\}]$ , **3**.** Red solid, yield 35 mg (9%). Soluble in MeOH, MeCN, CH<sub>2</sub>Cl<sub>2</sub>, sparingly soluble in Et<sub>2</sub>O, insoluble in hexane, water. The solutions are stable when exposed to air for relatively short times; formation of a brown solid occurs after several hours. X-ray quality crystals of **3** were collected from a THF solution layered with Et<sub>2</sub>O and settled aside at – 20 °C. Anal. Calcd. for C<sub>17</sub>H<sub>13</sub>Fe<sub>2</sub>N<sub>3</sub>O<sub>3</sub>: C, 48.73; H, 3.13; N, 10.03. Found: C, 47.47; H, 2.96; N, 9.76. IR (solid state):  $\tilde{\nu}/\text{cm}^{-1}$  = 3124w, 3104w, 2198m (NC≡N), 2160w (CC≡N); 2007s, 1994s, 1972s, 1938w-sh (CO); 1797s, 1761w-sh (μ-CO); 1467w, 1445w, 1421w, 1359w, 1248w (N-CN) [<sup>38</sup>], 1118w, 1104w, 1061w, 1000m, 974m, 949w-sh, 869w-sh, 878m, 861m, 850m, 826m-sh, 716s. IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\tilde{\nu}/\text{cm}^{-1}$  =

2202w (NC≡N), 2162w (CC≡N), 2013s (CO), 1978w-sh (CO), 1813m (μ-CO). IR (MeCN):  $\tilde{\nu}/\text{cm}^{-1}$  = 2202w (NC≡N), 2162w (CC≡N), 2008s (CO), 1971w-sh (CO), 1812m (μ-CO).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta/\text{ppm}$  = 4.93 (s, 10H, Cp), 3.35 (s, 3H,  $\text{NCH}_3$ ). The spectrum was recorded with recycle delay (d1) of 10 sec.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta/\text{ppm}$  = 261.6 (μ-CO), 207.9 (CO), 140.8 (μ-CN), 129.6 (CCN), 119.0 (NCN), 90.9 (Cp), 43.5 ( $\text{NCH}_3$ ).

**[FeCpBr(CO)(CNMe)].** This compound was previously reported[32]: Red-brown solid, yield 26 mg (10%). Soluble in  $\text{CH}_2\text{Cl}_2$ , less soluble in  $\text{Et}_2\text{O}$ , insoluble in hexane; the solutions are stable when exposed to air for relatively short times. Anal. Calcd. for  $\text{C}_8\text{H}_8\text{BrFeNO}$ : C, 35.60; H, 2.99; N, 5.19. Found: C, 35.79; H, 2.75; N, 5.04. IR (solid state):  $\tilde{\nu}/\text{cm}^{-1}$  = 3099w, 3086w, 2937w; 2198s-sh, 2180s (CN); 1966s-sh, 1956s (CO); 1445w-sh, 1421m-sh, 1407m, 1357w, 1248-1212w, 1155w, 1114w, 1000w, 866w-sh, 836m, 825m. IR ( $\text{CH}_2\text{Cl}_2$ ):  $\tilde{\nu}/\text{cm}^{-1}$  = 2191s (CN), 1985s (CO), 1425w-sh, 1416w.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta/\text{ppm}$  = 4.73 (s, 5H, Cp); 3.58 (s, 3H,  $\text{NCH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta/\text{ppm}$  = 217.2 (CO), 158.7 (CN), 82.1 (Cp), 31.4 ( $\text{NCH}_3$ ).

### 3.2.4. Reaction of $[\text{Fe}_2\text{Cp}_2(\text{CO})_4]$ with cyanogen bromide.

In a 50 mL Schlenk tube, a dark-red solution of  $[\text{Fe}_2\text{Cp}_2(\text{CO})_4]$  (286 mg, 0.809 mmol) in  $\text{CHCl}_3$  (10 mL) was treated with cyanogen bromide (172 mg, 1.62 mmol, 2.0 equivalents) and heated at reflux for 3 h. IR analysis indicated the formation of  $[\text{FeCpBr}(\text{CO})_2]$ ,  $[\text{FeCp}(\text{CN})(\text{CO})_2]$  and a minor amount of unreacted  $[\text{Fe}_2\text{Cp}_2(\text{CO})_4]$ . The mixture was moved through a short alumina column (h 2 cm, d 2.3 cm) and the red-brown eluate was dried under vacuum. IR analysis indicated the disappearance of  $[\text{FeCp}(\text{CN})(\text{CO})_2]$  and formation of other unidentified products. The residue was suspended in  $\text{Et}_2\text{O}$  and moved on top of an alumina column. Elution with  $\text{Et}_2\text{O}$  allowed to collect a red band containing  $[\text{Fe}_2\text{Cp}_2(\text{CO})_4]$  and  $[\text{FeCpBr}(\text{CO})_2]$ . IR data are given below.



$[\text{Fe}_2\text{Cp}_2(\text{CO})_4] + [\text{FeCpBr}(\text{CO})_2]$  [39]. IR ( $\text{CH}_2\text{Cl}_2$ ):  $\tilde{\nu}/\text{cm}^{-1} = 2049\text{s}, 2004\text{s}, 1959\text{m}, 1774\text{m}$ . IR (hexane):  $\tilde{\nu}/\text{cm}^{-1} = 2051\text{s}, 2010\text{s}, 1962\text{m}, 1794\text{m}$ .  $[\text{FeCp}(\text{CN})(\text{CO})_2]$  [22]. IR (MeCN):  $\tilde{\nu}/\text{cm}^{-1} = 2117\text{m}$  (CN), 2062s (CO), 2020s (CO). IR ( $\text{CH}_2\text{Cl}_2$ ):  $\tilde{\nu}/\text{cm}^{-1} = 2121\text{w}$  (CN), 2058s (CO), 2011s (CO).

Reaction optimization. A significantly lower conversion was observed with 1.0 equivalents of BrCN in refluxing  $\text{CHCl}_3$  (2 h). A reaction carried out with in refluxing MeCN with a lesser amount of BrCN (1.2 eq) resulted in the formation of additional products (IR bands at 2210, 2163, 2140  $\text{cm}^{-1}$ ).

### 3.3. X-Ray crystallography.

Crystal data and collection details for **3** are reported in Table 2. 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) [40]. The structure was solved by direct methods and refined by full-matrix least-squares based on all data using  $F^2$  [41]. Hydrogen atoms were fixed at calculated positions and refined by a riding model. All non-hydrogen atoms were refined with anisotropic displacement parameters.

**Table 2.** Crystal data and measurement details for **3**.

	<b>3</b>
Formula	$\text{C}_{17}\text{H}_{13}\text{Fe}_2\text{N}_3\text{O}_3$
FW	419.00
T, K	100(2)
$\lambda$ , Å	0.71073
Crystal system	Monoclinic
Space group	$P2_1$
$a$ , Å	7.7127(3)
$b$ , Å	13.0194(5)
$c$ , Å	8.9353(4)
$\beta$ , °	114.9410(10)
Cell Volume, Å <sup>3</sup>	813.56(6)
Z	2
$D_c$ , $\text{g}\cdot\text{cm}^{-3}$	1.710
$\mu$ , $\text{mm}^{-1}$	1.804
F(000)	424

Crystal size, mm	0.16×0.183×0.09
$\theta$ limits, °	2.514–26.999
Reflections collected	11981
Independent reflections	3542 [ $R_{int} = 0.0296$ ]
Data / restraints / parameters	3542 / 7 / 228
Goodness on fit on $F^2$	1.106
$R_1$ ( $I > 2\sigma(I)$ )	0.0270
$wR_2$ (all data)	0.0639
Absolute structure parameter	0.06(2)
Largest diff. peak and hole, e Å <sup>-3</sup>	0.522 / –0.293

**Supplementary Materials.** IR and NMR spectra. CCDC reference number 2177579(3) contains the supplementary crystallographic data for the X-ray study reported in this paper. These data can be obtained free of charge at <https://www.ccdc.cam.ac.uk/structures/> (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

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**Conflicts of Interest.** The authors declare no conflict of interest.

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