



ALMA MATER STUDIORUM
UNIVERSITÀ DI BOLOGNA

ARCHIVIO ISTITUZIONALE DELLA RICERCA

Alma Mater Studiorum Università di Bologna Archivio istituzionale della ricerca

Cyanide-alkene competition in a diiron complex and isolation of a multisite (cyano)alkylidene-alkene species

This is the final peer-reviewed author's accepted manuscript (postprint) of the following publication:

Published Version:

Cyanide-alkene competition in a diiron complex and isolation of a multisite (cyano)alkylidene-alkene species / Bresciani, Giulio; Schoch, Silvia; Biancalana, Lorenzo; Zacchini, Stefano; Bortoluzzi, Marco; Pampaloni, Guido; Marchetti, Fabio. - In: DALTON TRANSACTIONS. - ISSN 1477-9226. - STAMPA. - 51:(2022), pp. 1936-1945. [10.1039/d1dt03781a]

Availability:

This version is available at: <https://hdl.handle.net/11585/889934> since: 2023-06-09

Published:

DOI: <http://doi.org/10.1039/d1dt03781a>

Terms of use:

Some rights reserved. The terms and conditions for the reuse of this version of the manuscript are specified in the publishing policy. For all terms of use and more information see the publisher's website.

This item was downloaded from IRIS Università di Bologna (<https://cris.unibo.it/>).
When citing, please refer to the published version.

(Article begins on next page)

This is the final peer-reviewed accepted manuscript of:

G. Bresciani, S. Schoch, L. Biancalana, S. Zacchini, M. Bortoluzzi, G. Pampaloni, F. Marchetti, "Cyanide-alkene competition in a diiron complex and isolation of a multisite (cyano)alkylidene-alkene species", *Dalton Trans.*, **2022**, *51*, 1936-1945.

The final published version is available online at:
<https://doi.org/10.1039/D1DT03781A>

Terms of use:

Some rights reserved. The terms and conditions for the reuse of this version of the manuscript are specified in the publishing policy. For all terms of use and more information see the publisher's website.

Cyanide-Alkene Competition at a Diiron Complex and Isolation of Multisite (Cyano)Alkylidene–Alkenyl Ligand

Giulio Bresciani,^{a,d,#} Silvia Schoch,^{a,d,#} Lorenzo Biancalana,^{a,d} Stefano Zacchini,^{b,d} Marco Bortoluzzi,^{c,d,*}
Guido Pampaloni,^{a,d,*} Fabio Marchetti,^{a,d,*}

^a University of Pisa, Department of Chemistry and Industrial Chemistry, Via G. Moruzzi 13, I-56124
Pisa, Italy.

^b University of Bologna, Department of Industrial Chemistry “Toso Montanari”, Viale Risorgimento 4,
I-40136 Bologna, Italy.

^c University of Venezia “Ca’ Foscari”, Department of Molecular Science and Nanosystems, Via Torino
155, I-30170 Mestre (VE), Italy.

^d CIRCC, Via Celso Ulpiani 27, I-70126 Bari, Italy.

[#] Equal contribution

Corresponding Authors

*E-mail addresses: markos@unive.it; fabio.marchetti1974@unipi.it; guido.pampaloni@unipi.it

Abstract

The reaction of the μ -(amino)alkylidyne complex $[\text{Fe}_2\text{Cp}_2(\text{CO})_2(\mu\text{-CO})\{\mu\text{-CNMe}(\text{CH}_2\text{CH}=\text{CH}_2)\}] \text{CF}_3\text{SO}_3$, **[1]** CF_3SO_3 , with NBu_4CN in dichloromethane afforded the μ -(cyano)(amino)alkylidene $[\text{Fe}_2\text{Cp}_2(\text{CO})_2(\mu\text{-CO})\{\mu\text{-C}(\text{CN})\text{N}(\text{Me})(\text{CH}_2\text{CH}=\text{CH}_2)\}]$, **2**, in 91% yield. The decarbonylative reaction of **2** by means of Me_3NO , in acetone at room temperature, gave $[\text{Fe}_2\text{Cp}_2(\text{CO})(\mu\text{-CO})\{\mu\text{-}\eta^1:\eta^3\text{-C}(\text{CN})\text{N}(\text{Me})(\text{CH}_2\text{CH}=\text{CH}_2)\}]$, **3**, containing a rare multisite alkylidene–alkenyl ligand, in admixture with the μ -(amino)alkylidyne-cyanide complex $[\text{Fe}_2\text{Cp}_2(\text{CN})(\text{CO})(\mu\text{-CO})\{\mu\text{-CN}(\text{Me})(\text{CH}_2\text{CH}=\text{CH}_2)\}]$, **4**. The identity of **3** was revealed by X-ray crystallography, and confirmed by mass spectrometry analysis, IR and NMR spectroscopy. Complex **3** is less stable than its geometric isomer **4** by $32.9 \text{ kcal mol}^{-1}$, and full conversion of the former into the latter was achieved upon refluxing a THF solution of **3** for 2 hours. Evidence was collected for the presumable formation of an intermediate *C,N*-coordinated alkylidene, along the route from **4** to **3**. No replacement of alkenyl coordination was observed upon treating **3** with CO or PPh_3 . The reaction of the μ -(amino)alkylidyneimine complex $[\text{Fe}_2\text{Cp}_2(\text{CO})(\mu\text{-CO})(\text{NH}=\text{CPh}_2)\{\mu\text{-CN}(\text{Me})(\text{CH}_2\text{CH}=\text{CH}_2)\}] \text{CF}_3\text{SO}_3$, **[6]** CF_3SO_3 , with NBu_4CN afforded **3** with an optimized yield of 75%. Besides **3**, the unprecedented compounds **2**, **4** and **[6]** CF_3SO_3 were fully characterized by analytical and spectroscopic techniques.

Keywords: diiron complexes; bridging alkylidene; cyanide-alkene competition.

Introduction

Many examples of alkene complexes have been reported for a wide number of transition metals. In general, although isolable species can be normally obtained with simple alkenes, the latter often behave as labile ligands, and their ready substitution represents a feasible strategy to access targeted

derivatives.¹ The possible competition between a single alkene moiety and stronger π -acceptor ligands such as carbon monoxide has been described especially for early metal and group 11 metal complexes.² Otherwise, the binding of alkenes to middle transition metals is relatively weaker, and this feature may be exploited for the construction of chelating ligands with the alkenyl function supplying a hemilabile character useful to catalytic purposes.³

With reference to iron, constituting the focus of the present work, quantitative substitution reactions have been reported with CO and other carbon ligands on several low-valent alkene complexes.⁴ A much stronger coordination of the $\{C=C\}$ function has been achieved on diiron complexes as part of a multidentate ligand, exploiting the stabilizing effect provided by the dimetallic core.^{5,6} Thus, numerous complexes of generic formula $[Fe_2Cp_2(CO)_2\{\mu-\eta^1:\eta^3-C(R)C(R')=C(R'')\}]$, as well as their ruthenium analogues (Figure 1), share a common structural motif based on a robust bridging alkylidene unit and a double carbon-carbon bond tightly coordinating the terminal site of one metal center; these compounds are accessible from diverse synthetic routes and do not show any lability of the alkenyl function.⁵ In particular, displacement of the alkene by carbon monoxide is not viable, unless as a reversible reaction under high gas pressure.⁷ Conversely, only few examples of monoiron $\eta^1:\eta^3$ -alkylidene-alkenyl complexes are available in the literature, displaying a rich reactivity centered on the alkene group.⁸

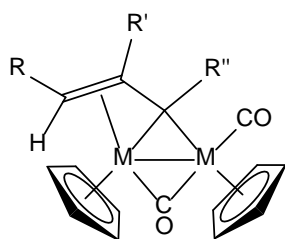
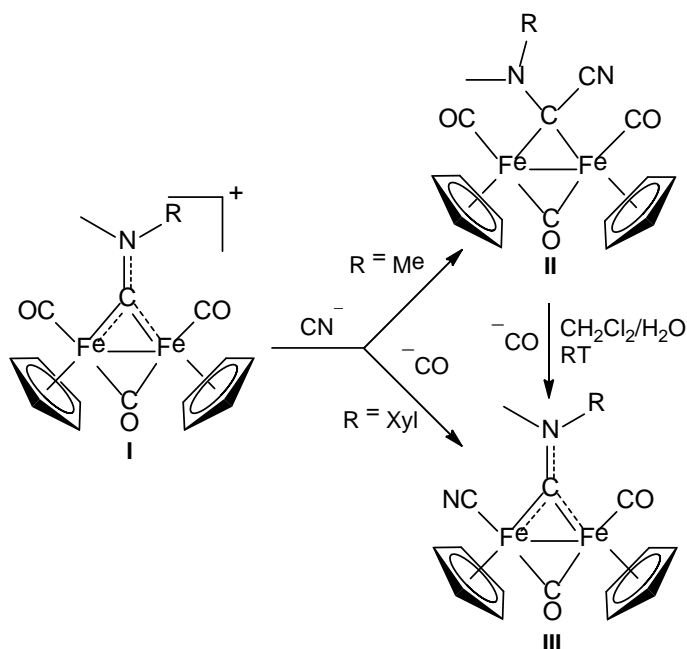


Figure 1. General structure of bridging vinyl-alkylidene ligand supported on the $\{M_2Cp_2(CO)_2\}$ scaffold (M = Fe, Ru; R = alkyl or amino group; R', R'' = alkyl or aryl).

The bridging alkylidene framework is usually accessible via modification of a μ -alkylidyne precursors.⁹ In this regard, the chemistry of cationic diiron bis-cyclopentadienyl complexes with a bridging (amino)alkylidyne ligand (structure I in Scheme 1) has been widely investigated,¹⁰ evidencing

three potential sites for the addition of nucleophiles, i.e. the carbyne, the terminal CO and the Cp ring.^{11,12} Interestingly, cyanide selectively adds to the carbyne center when this is not sterically hindered by the nitrogen substituents, affording a (cyano)(amino)alkylidene moiety (structure **II**).¹³ In correspondence to peculiar electronic factors, cyanide may exchange its position with a CO ligand and thus migrate to terminal site. The bulky xylyl group bound to nitrogen exerts its influence leading to the neutral (amino)alkylidyne **III**.¹¹ Slow cyanide migration from the bridging alkylidene to the iron (conversion from **II** to **III**) was observed in dichloromethane/water mixture.¹¹

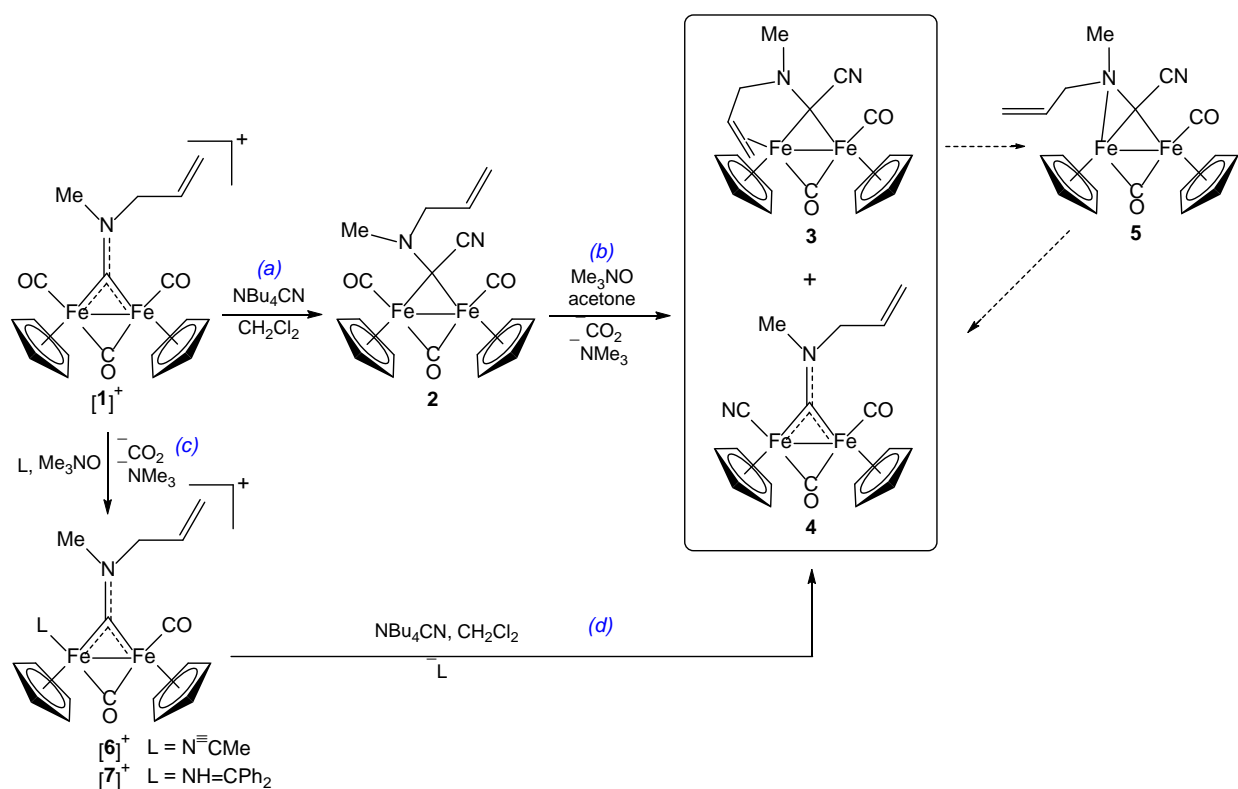


Scheme 1. General structure of diiron μ -aminocarbyne complexes (triflate salts) and cyanide addition (Xyl = 2,6-C₆H₃Me₂).

We became interested in systems analogous to **I-III** comprising an allyl substituent (R) on the nitrogen, with the idea in mind that the {C=C} unit could offer the opportunity for a reversible metal binding, thus opening the doors to catalytic implications. Here, we report the isolation of a rare example of metastable alkylidene-alkenyl species, resulting from the winning competition of an alkenyl moiety with respect to the cyanide ion for iron coordination.

Results and discussion

The (allyl-amino)alkylidyne complex **[1]**CF₃SO₃⁻, synthesized according to a recently published procedure,¹⁴ was treated with tetrabutylammonium cyanide to afford the (cyano)(amino)alkylidene product **2** in a nearly quantitative yield (Scheme 2a). The NMR spectra of **2** (CDCl₃ solution) point out the equivalence of the Cp ligands [$\delta(^1\text{H}) = 4.81$ ppm; $\delta(^{13}\text{C}) = 90.3$ ppm], thus indicating a mutual cis geometry as previously found in homologous compounds.¹³ Moreover, a single set of resonances is detected, indicating that the alkylidene substituents adopt one of the two possible orientations.



Scheme 2. Synthetic routes to allylamino-alkylidene and allylamino-alkylidyne systems differing in the position of a cyano group; CF₃SO₃⁻ is counter anion for cationic complexes. Yields of synthesis of **3** and **4** according to the different methods: (b) 36%, 42%; (d) 16%, 48% (L = NCMe); (d) 75%, 14% (L = NH=CPh₂).

The structure of **2** was optimized by DFT calculations, confirming the higher stability of the cis arrangement of the Cp ligands. The situation of maximum stability was recognized with the bulkier alkylidene substituent (i.e., the amino group) pointing to the other side with respect to the Cp rings (see Figures 2 and S1). The opposite configuration (**2-is2** in Figure S1) is featured by a significantly higher

Gibbs energy ($12.9 \text{ kcal mol}^{-1}$), in accordance with the observation of a single isomeric species in solution.

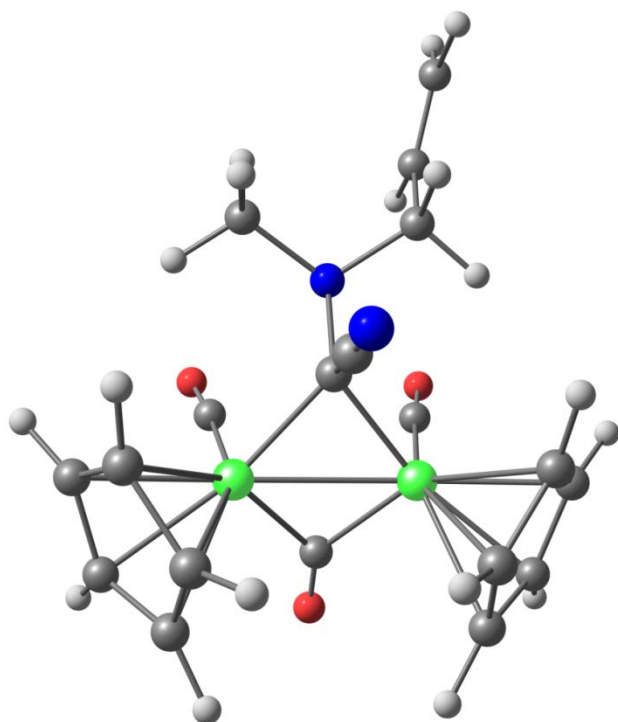


Figure 2. DFT-optimized structure of the most stable isomer of **2**. Color map: Fe, green; N, blue; O, red; C, gray; H, white. Selected bond lengths (Å): Fe-Fe, 2.508; Fe-C (alkylidene) 1.979 (average); Fe-C (CO) 1.753 (average); Fe-C (μ -CO) 1.897 (average); Fe-C (Cp) 2.122 (average).

We noticed that a new set of signals appeared when **2** was kept in CDCl_3 overnight. The new set was finally attributed to the CO-released derivative **3**. To efficiently obtain this targeted complex, an acetone solution of **2** was treated with Me_3NO to facilitate the elimination of one carbonyl ligand as carbon dioxide. Hence, a mixture of two products was afforded from this reaction, i.e. **3** and its (amino)alkylidyne-cyanide isomer **4** (Scheme 2b), which were separated via column chromatography on alumina and isolated in 36% and 42% yields, respectively.

The spectroscopic features of **4** resemble those for the homologous compounds previously reported (see structure **III** in Scheme 1);^{11,13} in particular, the shift of the ^{13}C resonance from 160.4 to ca. 332 ppm accounts for the conversion of the bridging (amino)alkylidene ligand (**2**) to bridging (amino)alkylidyne (**4**). Two *cis*-species for **4** were detected in solution by NMR in comparable

amounts, due to E/Z isomerism arising from inhibited rotation around the carbyne-N bond (Figure S2). This kind of isomerism was previously recognized in many other diiron aminocarbyne complexes of general formula $[\text{Fe}_2\text{Cp}_2(\text{CO})(\text{X})(\mu\text{-CO})\{\mu\text{-CN}(\text{Me})(\text{Y})\}]^{0/+}$ (X = anionic or neutral ligand \neq CO; Y \neq Me).^{5b,15}

Complex **3** was unambiguously identified by means of single crystal X-ray diffraction, mass spectrometry and IR and NMR spectroscopy. The structure of **3** is composed of a *cis*- $\text{Fe}_2\text{Cp}_2(\text{CO})(\mu\text{-CO})$ core coordinated to the $\{\mu\text{-}\eta^1\text{:}\eta^3\text{-C}(\text{CN})\text{N}(\text{Me})(\text{CH}_2\text{CH}=\text{CH}_2)\}$ alkylidene–alkenyl ligand. Due to the low quality of the crystals and twinning, the precision on the bonding parameters is not very high. Nonetheless, the Fe(1)-C(4) [2.02(2) Å] and Fe(2)-C(4) [1.99(2) Å] distances are typical for a bridging alkylidene ligand on a diiron framework [ref: EJIC 2007, 1799-1807; JOMC 2005, 690, 837-846; OM 2008, 27, 5058-5066; OM 2010, 29, 1797-1805; OM 2011, 30, 4115-4122; OM 2007, 26, 3577-3584; OM 2004, 23, 3348-3354; K. H. Trylus, U. Kernbach, I. Brüdgam, W. P. Fehlhammer, ICA 1999, 291, 266-278]. The C(1)-C(2) contact [1.37(4) Å] displays a double bond character [ref: (a) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans.* **1987**, S1. (b) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1.], and the Fe(2)-C(1) [2.14(2) Å] and Fe(2)-C(2) [2.13(3) Å] bonding distances are comparable to those found in other Fe-(olefin) complexes [ref: E. O. Changamu, H. B. Friedrich, M. Rademeyer, JOMC 2008, 693, 164-168; A. Casitas, H. Krause, S. Lutz, R. Goddard, E. Bill, A. Fürstner, OM 2018, 37, 729-739; A. Fürstner, R. Martin, H. Krause, G. Seidel, R. Goddard, C. W. Lehmann, JACS, 2008, 130, 8773-8787; K. Ferré, P. Le Mignot, S. Sinbandhit, L. Toupet, V. Guerschais, Chem. Commun., 2000, 1405-1406; R. Schobert, W. Förtsch, F. Hampel, JOMC, 1996, 526, 169-174; R. S. Bly, M. M. Hossain, L. Lebioda, JACS, 1985, 107, 5549-5550; Y.-R. Hu, T. W. Leung, S.-C. H. Su, A. Wojcicki, OM 1985, 4, 1001-1005]. Even though the alkenyl and terminal CO ligands on Fe(2) and Fe(1), respectively, have very different σ/π characters, the $\mu\text{-CO}$ ligand is almost perfectly symmetrical [Fe(1)-C(12) 1.91(3) Å; Fe(2)-C(12) 1.90(3) Å]. The core composed of Fe(1), Fe(2) and the two bridging carbons, C(4) and C(12), is almost planar [mean deviation from the least square plane 0.0841 Å]. The amine nitrogen N(1) displays a considerable pyramidalization [sum angles at N(1) 344(3)°] in view of its sp^3 hybridization, and the three N(1)-C(3) [1.42(3) Å], N(1)-C(4) [1.42(3) Å] and N(1)-C(6) [1.42(3) Å] bonding distances are identical within experimental precision, in keeping with their $\text{N}(\text{sp}^3)\text{-C}(\text{sp}^3)$ nature. The cyano group C(5)N(2) shows the expected triple bond

character [1.14(3) Å] and the C(4)-C(5)-N(2) [177(2) °] angle is almost linear in keeping with sp hybridization of C(5).

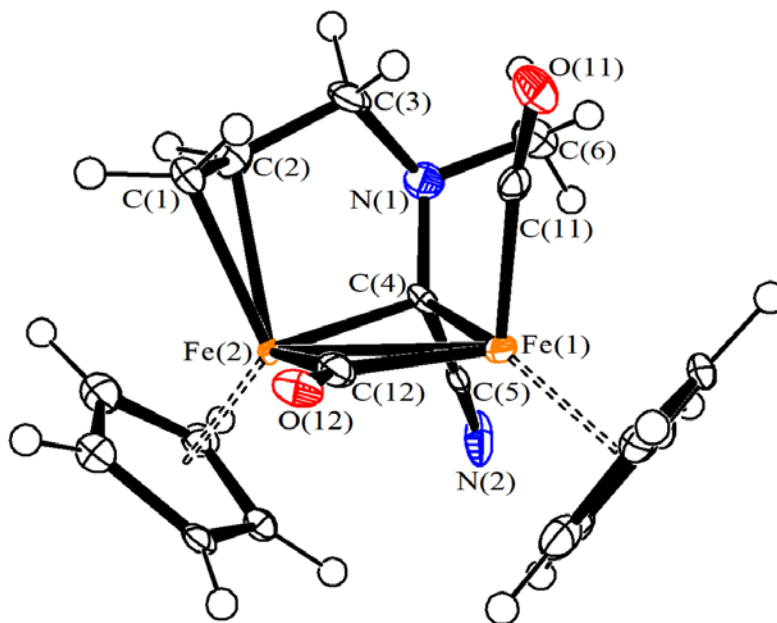


Figure 3. View of the molecular structure of $[\text{Fe}_2\text{Cp}_2(\text{CO})(\mu\text{-CO})\{\mu\text{-}\eta^1\text{:}\eta^2\text{-C}(\text{CN})\text{N}(\text{Me})(\text{CH}_2\text{CH}=\text{CH}_2)\}]$, **3**. Displacement ellipsoids are at the 50% probability level. Main bond distances (Å) and angles (°): Fe(1)-Fe(2) 2.535(3), Fe(1)-C(11) 1.79(2), Fe(1)-C(12) 1.91(3), Fe(2)-C(12) 1.90(3), Fe(1)-C(4) 2.02(2), Fe(2)-C(4) 1.99(2), Fe(2)-C(1) 2.14(2), Fe(2)-C(2) 2.13(3), C(1)-C(2) 1.37(4), C(2)-C(3) 1.45(3), C(3)-N(1) 1.42(3), N(1)-C(4) 1.42(3), N(1)-C(6) 1.42(3), C(4)-C(5) 1.43(3), C(5)-N(2) 1.14(3), C(11)-O(11) 1.12(3), C(12)-O(12) 1.17(2), Fe(1)-C(11)-O(11) 165(2), Fe(1)-C(12)-Fe(2) 83.4(8), Fe(1)-C(4)-Fe(2) 78.3(7), C(1)-C(2)-C(3) 123(2), C(2)-C(3)-N(1) 109.4(19), C(3)-N(1)-C(4) 110.3(18), C(3)-N(1)-C(6) 117.0(19), C(6)-N(1)-C(4) 116.7(19), N(1)-C(4)-C(5) 107.8(19), C(4)-C(5)-N(2) 177(2).

The mass spectrum exhibits the peak corresponding to the ion $[\mathbf{3}+\text{H}]^+$ at 407.0140 m/z, confirming the loss of one CO with respect to **2**. The IR spectrum of **3** (CH_2Cl_2 solution) in the 2300-1500 cm^{-1} region contains three main absorptions due to the cyano moiety (2169 cm^{-1}), one terminal carbonyl (1938 cm^{-1}) and one bridging carbonyl (1775 cm^{-1}). Compared to the parent complex **2**, in the ^1H NMR spectrum of **3** (CDCl_3 solution) the allyl resonances are strongly shielded and the $\{\text{NCH}_2\}$ protons become nonequivalent, suggesting a ring closure with engagement of the alkenyl moiety in metal coordination [δ/ppm (**3**) = 4.35 (CH=), 3.17, 0.85 (NCH₂), 3.10, 0.96 (=CH₂); δ/ppm (**2**) = 5.74 (CH=), 3.75 (NCH₂), 5.21, 5.06 (=CH₂)]. Accordingly, a parallel phenomenon is evident from the ^{13}C NMR spectrum, especially for the alkenic carbons [δ/ppm (**3**) = 68.2 (CH=), 56.8 (=CH₂); δ/ppm (**2**) = 136.3 (CH=),

116.9 (=CH₂)]. Ongoing from **2** to **3**, the ¹³C resonance for the aminocarbene center shifts from 160.4 to 211.7 ppm.¹⁶

DFT calculations allowed to assess the relative stability of **3** with respect to its geometric isomers. Thus, the bridging coordination of the alkylidene ligand is favored over the terminal coordination, and the cis mutual geometry of the Cp ligands is more stable than the trans one. On the other hand, **3** is unstable with respect to its conversion into the amino-alkylidyne species **4**, resulting from **3** via cyanide migration: this reaction is featured by computed $\Delta G = -32.9 \text{ kcal mol}^{-1}$, and was achieved quantitatively by heating a THF solution of **3** at reflux temperature for 2 hours.

The formation of **4** from **3** consists in the migration of the cyanide anion from the bridging alkylidene to the terminal coordination site occupied by the alkene moiety. We carried out a DFT study aimed to detect possible intermediates along the pathway from **3** to **4**. We identified the isomer **5** as a plausible intermediate, being $15.3 \text{ kcal mol}^{-1}$ more stable than **3** (Scheme 2 and Figure S4). Complex **5** comprises a bridging (cyano)(amino)alkylidene ligand filling the coordination sphere of one iron center by the lone pair belonging to the amino group; the DFT-optimized structure of **5** features cis-configuration of the Cp rings. The peculiar nature of the bridging ligand in **5** finds some confirmation in the literature. First, few examples of firm coordination of amine groups to iron in systems based on the {Fe₂Cp₂(CO)₂} skeleton were previously reported by some of us.¹⁷

Second, a quite similar situation concerns the species [Fe₂Cp₂(CO)(μ -CO){ μ - κ C,S-C(CN)SMe}], wherein the bridging thioalkylidene ligand forms a {Fe-C-S} triangle analogous to that in **5**.¹⁸

We made several attempts with the purpose to isolate **5** along the route from **3** into **4**. Interestingly, when a very small amount of **3** was stored in the solid state at room temperature for 1 month, a clean transformation of the solid was detected by IR and ¹H NMR spectroscopy, suggesting the formation of **5**. The IR spectrum (CH₂Cl₂) of this product is quite different from that of **3**, and indicates the presence of a carbon-bound cyano group (at 2194 cm⁻¹), a terminal and a bridging carbonyl. In particular, a

considerable shift to higher frequency is noticed for the terminal CO stretching vibration (from 1938 to 1969 cm^{-1}). Coherently with the structure of **5**, the ^1H NMR spectrum of the isolated product reveals hindered rotation around the N-CH₂ bond (two distinct resonances at 3.65 and 2.18 ppm) and the alkenyl unit free from coordination, with a substantial downfield shift of the related signals with respect to the situation in **3** [in **3**: $\delta = 4.35(\text{CH}=\), 3.10, 0.96 (=CH_2)$ ppm; in **5**: $\delta = 5.91(\text{CH}=\), 5.22 (=CH_2)$ ppm].

To test the lability of the alkenyl moiety, complex **3** was treated with, respectively, an excess of CO and PPh₃ in dichloromethane solution at room temperature for 8 hours, but no variation was detected in the IR/ ^{31}P NMR spectra. This outcome rules out the hemilabile character of the alkylidene-alkenyl ligand.

We explored different strategies with the aim of improving the synthesis yield of **3**. We reckoned that cyanide addition to a cationic derivative of [1]CF₃SO₃ containing a suitable terminal ligand (L) could lead to **3**, via nucleophilic attack to the carbyne center followed by L displacement by the alkenyl moiety (Scheme 2c-d). When L was acetonitrile, i.e., compound [6]CF₃SO₃ was employed to this purpose, **3** and **4** were isolated in 16% and 48% yields, respectively. Subsequently, we sought for a ligand L more tightly bonded with respect to acetonitrile, to limit the degree of L/cyanide substitution and thus favor cyanide attack to the carbyne. We identified a commercial imine as appropriate in this regard, and we prepared the new benzophenone imine complex [7]CF₃SO₃. The reaction of this latter with NBu₄CN finally provided an optimal yield of 75% for the kinetic product **3**, Scheme 2d, L = Ph₂C=NH.

Conclusions

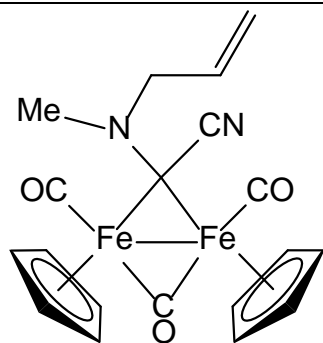
.....

Experimental

Materials and methods. Reactants and solvents were purchased from Alfa Aesar, Merck, Strem or TCI Chemicals, and were of the highest purity available. Complex $[\text{Fe}_2\text{Cp}_2(\text{CO})_2(\mu\text{-CO})\{\mu\text{-CNMe}(\text{CH}_2\text{CH}=\text{CH}_2)\}]\text{CF}_3\text{SO}_3$, **[1]** CF_3SO_3 , was prepared according to the literature.¹⁴ Reactions were conducted under N_2 atmosphere using standard Schlenk techniques, and products were conserved under N_2 once isolated. Dichloromethane, tetrahydrofuran, and diethyl ether were dried with the solvent purification system mBraun MB SPS5. Chromatography separations were carried out on columns of deactivated alumina (Merck, 4% w/w water) using bottle solvents. IR spectra of solutions were recorded using a CaF_2 liquid transmission cell ($2300\text{-}1500\text{ cm}^{-1}$) on a Perkin Elmer Spectrum 100 FT-IR spectrometer. IR spectra were processed with Spectragryph software.¹⁹ NMR spectra were recorded at 298 K on a Bruker Avance II DRX400 instrument equipped with a BBFO broadband probe. Chemical shifts (expressed in parts per million) are referenced to the residual solvent peaks.²⁰ NMR spectra were assigned with the assistance of ^1H - ^{13}C (*gs*-HSQC and *gs*-HMBC) correlation experiments.²¹ NMR signals due to secondary isomeric forms (where it is possible to detect them) are italicized. Elemental analyses were performed on a Vario MICRO cube instrument (Elementar). HPLC-MS analysis was performed with a API3000 instrument (SCIEX) equipped with ESI(+) source and a quadrupole detector.

Synthesis and characterization of $[\text{Fe}_2\text{Cp}_2(\text{CO})_2(\mu\text{-CO})\{\mu\text{-C}(\text{CN})\text{N}(\text{Me})(\text{CH}_2\text{CH}=\text{CH}_2)\}]\text{CF}_3\text{SO}_3$, **2 (Chart 1).**

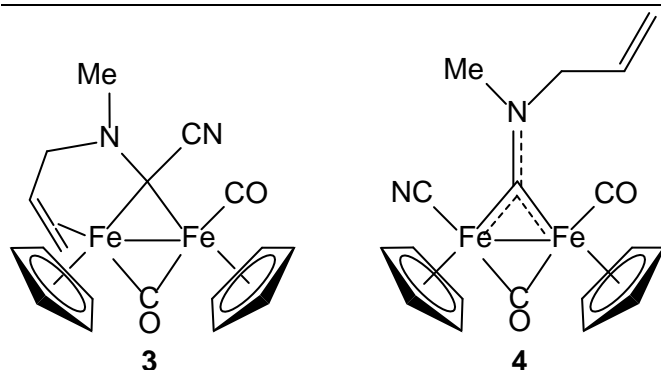
Chart 1. Structure of **2**.



A solution of **[1]**CF₃SO₃ (83.0 mg, 0.150 mmol) in CH₂Cl₂ (10 mL) was treated with tetrabutylammonium cyanide (44.0 mg, 0.164 mmol), and the mixture was stirred at room temperature for 1 hours. Then volatiles were evaporated under reduced pressure, the residue was dissolved in Et₂O/CH₂Cl₂ (10:1 v/v), and the solution was charged on top of an alumina column. Diethyl ether was eluted to remove impurities, then a brown-red fraction corresponding to **2** was separated with dichloromethane. The solution was dried under vacuum, thus affording a red solid. Yield 59 mg, 91%. Anal. calcd. for C₁₉H₁₈Fe₂N₂O₃: C, 52.58; H, 4.18; N, 6.45. Found: C, 52.73; H, 4.24; N, 6.50. IR (CH₂Cl₂): $\tilde{\nu}/\text{cm}^{-1}$ = 2146m (C≡N), 2004vs (CO), 1969m (CO), 1798s (μ-CO). ¹H NMR (CDCl₃): δ/ppm = 5.74 (m, 1 H, CH=); 5.21, 5.06 (m, 2 H, =CH₂); 4.81 (s, 10 H, Cp); 3.75 (d, 2 H, ³J_{HH} = 6.0 Hz, NCH₂); 2.76 (s, 3 H, NMe). ¹³C{¹H} NMR (CDCl₃): δ/ppm = 267.0 (μ-CO); 209.3 (CO); 160.4 (μ-C); 136.3 (CH=); 127.9 (C≡N); 116.9 (=CH₂); 90.3 (Cp); 65.2 (NCH₂); 45.7 (NMe). A minor amount of **3** (approximately 20%) was detected in the NMR spectrum.

Decarbonylation reaction of 2: synthesis and characterization of [Fe₂Cp₂(CO)(μ-CO){μ-η¹:η²-C(CN)N(Me)(CH₂CH=CH₂)}], 3, and [Fe₂Cp₂(CN)(CO)(μ-CO){μ-CN(Me)(CH₂CH=CH₂)}], 4 (Chart 2).

Chart 2. Structures of 3 and 4.



A mixture of **2** (70 mg, 0.16 mmol) and Me₃NO (24 mg, 0.32 mmol) in deaerated acetone (7 mL) was stirred at room temperature for 24 hours, with the released gas (CO₂) allowed to flux out. The final mixture was dried under reduced pressure, the residue was dissolved in diethyl ether and this solution was charged on top of an alumina column. Diethyl ether and dichloromethane were eluted to remove impurities, then a red fraction corresponding to **3** was collected with CH₂Cl₂/THF mixture (9/1 v/v). A green fraction corresponding to **4** was subsequently collected with MeCN/MeOH mixture (20/1 v/v). The title compounds were isolated upon removal under vacuum of the solvent from each solution. Crystals of **3** suitable for X-ray analysis were collected by slow diffusion of XX into a solution of the compound in xx, at -30 °C.

3: Brown powder, yield 22 mg (36%). Anal. calcd. for C₁₈H₁₈Fe₂N₂O₂: C, 53.24; H, 4.47; N, 6.90. Found: C, 53.30; H, 4.49; N, 6.86. IR (CH₂Cl₂): $\tilde{\nu}/\text{cm}^{-1}$ = 2169m (C≡N), 1938vs (CO), 1775s (μ-CO). ¹H NMR (CDCl₃): δ/ppm = 4.75, 4.47 (s, 10 H, Cp); 4.35 (m, 1 H, CH=); 3.17 (dd, ²J_{HH} = 11.8, ³J_{HH} = 6.1 Hz, 1 H, NCH₂); 3.10 (dd, ³J_{HHcis} = 7.9 Hz, ²J_{HH} = 1.2, 1 H, =CH₂); 2.76 (s, 3 H, NMe); 0.96 (dd, ³J_{HHtrans} = 12.7 Hz, ²J_{HH} = 0.7, 1 H, =CH₂); 0.85 (dd, ²J_{HH} = 12.0, ³J_{HH} = 9.3 Hz, 1 H, NCH₂). ¹³C{¹H} NMR (CDCl₃): δ/ppm = 277.5 (μ-CO); 213.8 (CO); 211.7 (μ-C); 135.3 (C≡N); 90.7, 89.4 (Cp); 68.2 (CH=); 58.5 (NCH₂); 56.8 (=CH₂); 42.7 (NMe). HPLC-MS(+): m/z found 407.0140 [**3**+H]⁺, calcd. for C₁₈H₁₉Fe₂N₂O₂ 407.0145.

4: Green powder, yield 27 mg (42%). Anal. calcd. for C₁₈H₁₈Fe₂N₂O₂: C, 53.24; H, 4.47; N, 6.90. Found: C, 53.18; H, 4.39; N, 6.86. IR (CH₂Cl₂): $\tilde{\nu}/\text{cm}^{-1}$ = 2092m (C≡N), 1981vs (CO), 1804s (μ-CO).

^1H NMR (CDCl_3): $\delta/\text{ppm} = 6.27, 6.09$ (m, 1 H, $\text{CH}=\text{}$); $5.56\text{-}5.45$ (m, 2 H, $=\text{CH}_2$); $5.36\text{-}5.06, 4.41\text{-}4.34$ (m, 2H, NCH_2); $4.83, 4.80, 4.77, 4.73$ (s, 10 H, Cp); $4.15, 3.99$ (s, 3 H, NMe). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): $\delta/\text{ppm} = 332.7, 332.3$ ($\mu\text{-C}$); $262.2, 261.8$ ($\mu\text{-CO}$); $211.4, 211.1$ (CO); 135.8 ($\text{C}\equiv\text{N}$); $132.8, 131.8$ ($\text{CH}=\text{}$); $119.5, 119.2$ ($=\text{CH}_2$); $87.1, 87.0, 86.7, 86.6$ (Cp); $68.8, 68.7$ (NCH_2); $49.7, 49.3$ (NMe). Isomer ratio= 55:45.

Stability studies on complex 3.

A) Quantitative isomerization to 4.

A solution of **3** (0.050 mmol) in THF (10 mL) was heated at reflux temperature. After 2 hours, an aliquot of the solution was withdrawn and dried under vacuum; subsequent IR spectrum of the residue in CH_2Cl_2 showed the complete disappearance of the bands related to the starting material and the clean formation of **4**.

B) Formation of an intermediate product.

A solid sample of **3** (ca. 15 mg) was stored at ca. $25\text{ }^\circ\text{C}$ for 1 month. The resulting red solid was dissolved in the minimum volume of dichloromethane and this solution was passed through a short alumina pad, then the solvent was removed under vacuum. Anal. calcd. for $\text{C}_{18}\text{H}_{18}\text{Fe}_2\text{N}_2\text{O}_2$: C, 53.24; H, 4.47; N, 6.90. Found: C, 52.90; H, 4.61; N, 6.82. IR (CH_2Cl_2): $\tilde{\nu}/\text{cm}^{-1} = 2194\text{m}$ ($\text{C}\equiv\text{N}$), 1969vs (CO), 1784s ($\mu\text{-CO}$). ^1H NMR (CDCl_3): $\delta/\text{ppm} = 5.91$ (m, 1 H, $\text{CH}=\text{}$); 5.22 (m, 2 H, $=\text{CH}_2$); $4.55, 4.52$ (s, 10 H, Cp); $3.65, 2.18$ (d, 2 H, $^3J_{\text{HH}} = 6.0$ Hz, NCH_2). NMe not assigned.

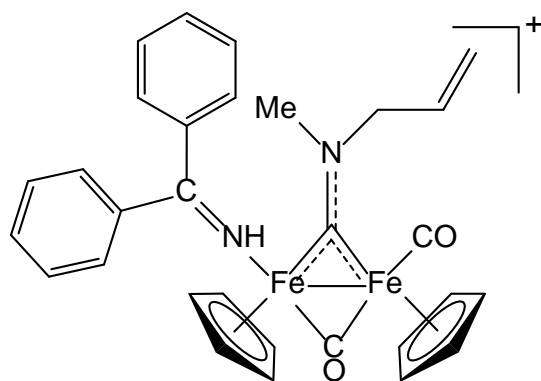
Reaction of $[\text{Fe}_2\text{Cp}_2(\text{CO})(\mu\text{-CO})(\text{NCMe})\{\mu\text{-CN}(\text{Me})(\text{CH}_2\text{CH}=\text{CH}_2)\}]\text{CF}_3\text{SO}_3$, $[\text{6}]\text{CF}_3\text{SO}_3$, with NBu_4CN .

A solution of $[\text{1}]\text{CF}_3\text{SO}_3$ (110 mg, 0.197 mmol) in MeCN (8 mL) was treated with Me_3NO (24 mg, 0.32 mmol). The resulting mixture was stirred for 1 hour, during which time progressive color

darkening occurred. The complete conversion of the starting material into the corresponding acetonitrile adduct $[6]CF_3SO_3$ was checked by IR spectroscopy [IR (CH_2Cl_2): $\tilde{\nu}/cm^{-1} = 1987vs$ (CO), 1818s (μ -CO), 1568w (μ -CN)]. The volatiles were removed under vacuum to afford a dark-brown residue which was dissolved in dichloromethane (7 mL). Hence, tetrabutylammonium cyanide (53 mg, 0.20 mmol) was added, and the resulting mixture was stirred for 1 hour at room temperature. The final solution was charged on top of an alumina column, and dichloromethane was used as eluent to remove impurities. Then, the red fraction corresponding to **3** was collected with CH_2Cl_2/THF mixture (9/1 v/v). The subsequent green fraction corresponding to **4** was collected with MeCN/MeOH (20/1 v/v). The title compounds were isolated upon removal under vacuum of the solvent from the solutions, and then identified by IR and 1H NMR spectroscopy. Yields: **3**, 13 mg (16%); **4**, 38 mg (48%).

Synthesis and characterization of $[Fe_2Cp_2(CO)(\mu-CO)(NH=CPh_2)\{\mu-CN(Me)(CH_2CH=CH_2)\}]CF_3SO_3$, $[7]CF_3SO_3$ (Chart 3).

Chart 3. Structure of $[7]^+$.



A mixture of $[1]CF_3SO_3$ (140 mg, 0.251 mmol), Me_3NO (38 mg, 0.51 mmol) and benzophenone imine (0.150 mL, 0.90 mmol) in THF (7 mL) was stirred at room temperature for 3 hours. Afterwards, volatiles were evaporated under reduced pressure, the resulting residue was dissolved in the minimum volume of dichloromethane, and this solution was charged on top of an alumina column. Dichloromethane/tetrahydrofuran mixtures were eluted to remove impurities, then a brown fraction

corresponding to [7]CF₃SO₃ was collected with THF/MeOH (20/1 v/v). The obtained solution was dried under vacuum, and the residue was suspended in Et₂O (20 mL), filtered, and washed with Et₂O (2 x 5 mL). The resulting brown solid was dried under vacuum. Yield 130 mg, 73%. Anal. calcd. for C₃₁H₂₉F₃Fe₂N₂O₅S: C, 52.42; H, 4.11; N, 3.94; S, 4.51. Found: C, 52.48; H, 4.15; N, 3.88; S, 4.48. IR (CH₂Cl₂): $\tilde{\nu}/\text{cm}^{-1}$ = 1977vs (CO), 1813s (μ -CO). ¹H NMR (acetone-d₆): δ/ppm = 7.78-7.34, 6.98-6.81 (m, 11 H, Ph + NH); 6.69, 6.44 (m, 1H, CH=); 5.90-5.67(m, 2 H, =CH₂); 5.54, 5.37 (m, 2H, NCH₂); 5.22, 5.20, 4.81, 4.74 (s, 10 H, Cp); 4.95, 4.46 (s, 3 H, NMe). ¹³C{¹H} NMR (acetone-d₆): δ/ppm = 336.0 (μ -C); 267.2, 266.7 (μ -CO); 213.9, 213.5 (CO); 193.2, 193.0 (C=N); 139.8, 1.37.7, 137.6, 134.2, 133.2, 132.8, 132.7, 131.7, 131.6, 130.3, 130.2, 129.6, 129.5, 129.4, 128.2, 128.0 (C₆H₄ + CH=); 121.0, 119.9 (=CH₂); 90.0, 89.9, 88.0, 87.7 (Cp); 71.1, 69.6 (NCH₂); 52.6, 50.6 (NMe). Isomer ratio = 54:46.

Reaction of [7]CF₃SO₃ with NBu₄CN.

A solution of [7]CF₃SO₃ (89.0 mg, 0.125 mmol) in CH₂Cl₂ (7 mL) was treated with tetrabutylammonium cyanide (37.0 mg, 0.138 mmol), and the resulting mixture was stirred at room temperature for 1 hour. The final solution was charged on top of an alumina column, and chromatographic separation was performed as described above for the reaction of [6]CF₃SO₃ with NBu₄CN. Products were isolated upon removal of the solvent under vacuum and identified by IR and ¹H NMR spectroscopy. Yields: **3**, 38 mg (75%); **4**, 7.1 mg (14%).

X-ray crystallography

Crystal data and collection details for **3** are reported in Table 1. Data were recorded on a Bruker APEX II diffractometer equipped with a PHOTON2 detector using Mo-K α radiation. The structure was solved by direct methods and refined by full-matrix least-squares based on all data using F^2 .²² Hydrogen atoms were fixed at calculated positions and refined using a riding model. The crystals are

racemically twinned with refined Flack parameter of 0.12(12) [H. D. Flack, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 1983, **39**, 876-881]

Table 1. Crystal data and measurement details for **3**.

3	
Formula	C ₁₈ H ₁₈ Fe ₂ N ₂ O ₂
FW	406.04
T, K	100(2)
λ , Å	0.71073
Crystal system	Monoclinic
Space group	Cc
<i>a</i> , Å	9.0058(12)
<i>b</i> , Å	24.672(3)
<i>c</i> , Å	7.7615(11)
β , °	114.513(5)
Cell Volume, Å ³	1569.1(4)
Z	4
<i>D_c</i> , g·cm ⁻³	1.719
μ , mm ⁻¹	1.862
F(000)	832
Crystal size, mm	0.18×0.12×0.09
θ limits, °	1.651-25.090
Reflections collected	7929
Independent reflections	2636 [<i>R_{int}</i> = 0.0725]
Data / restraints / parameters	2636 / 248 / 219
Goodness on fit on F ²	1.242
<i>R</i> ₁ (<i>I</i> > 2 σ (<i>I</i>))	0.0847
<i>wR</i> ₂ (all data)	0.2166
Largest diff. peak and hole, e Å ⁻³	1.243 / -0.967

DFT calculations

The ground- and transition state structures were optimized using the hybrid B3PW91 DFT functional²³ in combination with Ahlrichs' split-valence-polarized basis set.²⁴ The C-PCM implicit solvation model was added to ω B97X calculations, considering acetonitrile as continuous medium.²⁵ The stationary points were characterized by IR simulations (harmonic approximation), from which zero-point

vibrational energies and thermal corrections ($T = 25^{\circ}\text{C}$) were obtained. The software used was Gaussian 09.²⁶ Cartesian coordinates of the DFT-optimized structures are collected in a separated .xyz file.

Acknowledgements

We thank the University of Pisa for financial support (Fondi di Ateneo 2020).

Supporting Information Available

DFT calculated structures; NMR and IR spectra of products; mass spectrum of **3**. Cartesian coordinates of the DFT-optimized structures are also collected in a separated .xyz file. CCDC reference number XXXXXXXX (**3**) contains the supplementary crystallographic data for the X-ray study reported in this work. These data are available free of charge at <http://www.ccdc.cam.ac.uk/structures>.

References

-
- 1 a) Crabtree, R. H.; Mingos, D. M. P. *Comprehensive Organometallic Chemistry*, Elsevier, III Edition, 2007. b) Elschenbroich, C. *Organometallics*. Wiley, III Ed., 2003. c) Weding, N.; Hapke, M. Preparation and synthetic applications of alkene complexes of group 9 transition metals in [2+2+2] cycloaddition reactions. *Chem. Soc. Rev.*, 2011, 40, 4525–4538.
- 2 Selected references: (a) Pampaloni, G.; Peloso, R.; Graiff, C.; Tiripicchio, A. Synthesis, characterization and olefin/CO exchange reactions of pyrazolylborato complexes of copper(I). *Dalton Trans.* 2006, 3576-3583. (b) Capracotta, M. D.; Sullivan, R. M.; Martin, J. D. Sorptive reconstruction of CuMCl_4 (M = Al, Ga) upon small molecule binding and the competitive binding of CO and ethylene. *J. Amer. Chem. Soc.*, 2006, 128, 13463-13473. (c) Pampaloni, G.; Peloso, R.; Graiff, C.; Tiripicchio, A. Synthesis, Characterization, and Olefin/CO Exchange Reactions on copper(I) Derivatives containing bidentate oxygen ligands, *Organometallics*, 2005, 24, 4475-4482. (d) Calderazzo, F.; Guelfi, M.; Pampaloni, G. Olefin and CO competition for bis(cyclopentadienyl)vanadium(II). *Organometallics*, 2004, 23, 1519-1524.
- 3 Corberan, R.; Sanau, M.; Peris, E. $\text{Cp}^*\text{Ir(III)}$ Complexes with Hemicleaveable Ligands of the Type N-Alkenyl Imidazolin-2-ylidene. Reactivity and Catalytic Properties. *Organometallics* 2007, 26, 3492-3498.
- 4 See for instance: (a) Schneider, J. J.; Czap, N.; Bläser, D.; Boese, R. Metal Atom Synthesis of $(\eta^6\text{-Toluene})(\eta^2\text{-ethene})\text{iron}(\sigma^1\text{-stannandiyls})$: Unusual Iron(0) Complexes. *J. Am. Chem. Soc.* 1999, 121, 1409–1410. (b) Wang, L.; Cheng, J.; Ma, Y.; Chen, Q.; Leng, X.; Deng, L. Three-coordinate Bis(N-heterocyclic carbene)iron(0) complexes with alkene and alkyne ligation: Synthesis and characterization. *Polyhedron* 2021, 197, 115054. (c) Zenneck, U.; Frank, W. Bis($\eta^2\text{-ethene})(\eta^6\text{-toluene})\text{iron}$. *Angew. Chem. Int. Ed.* 1986, 25, 831-833. (d) Burcher, B.; Sanders, K. J.; Benda, L.; Pintacuda, G.; Jeanneau, E.; Danopoulos, A. A.; Braunstein, P.; Olivier-Bourbigou, H.; Breuil, P.-A. R. Straightforward Access to Stable, 16-Valence-Electron Phosphine Stabilized Fe0 Olefin Complexes and Their Reactivity. *Organometallics* 2017, 36, 605–613.

This item was downloaded from IRIS Università di Bologna (<https://cris.unibo.it/>)

When citing, please refer to the published version.

-
- 5 Mazzoni,R.; Salmi,M.; Zanotti,V. C-C Bond Formation in Diiron Complexes. *Chem. Eur. J.* 2012, 18, 10174-10194.
- 6 (a) Lawrence, J. D.; Li, H.; Rauchfuss, T. B. Beyond Fe-only hydrogenases: N-functionalized 2-aza-1,3-dithiolates $\text{Fe}_2[(\text{SCH}_2)_2\text{NR}](\text{CO})_x$ ($x = 5, 6$). *Chem. Commun.*, 2001, 1482–1483. (b) Renili,F.; Marchetti,F.; Zacchini,S.; Zanotti,V. Assembly and incorporation of a CO_2Me group into a bridging vinyliminium ligand in a diiron complex. *J. Organomet. Chem.* 2011, 696, 1483-1486. (c)
- 7 Angermund,H.; Grevels,F.-W.; Moser,R.; Benn,R.; Krüger,C.; Romão,M. *J. Organometallics*, 1988, 7, 1994-2004.
- 8 Schobert, R.; Förtsch, W.; Hampel, F. Chemistry of metallacyclic alkenylcarbene complexes: Synthesis, structure and $\text{SN},2'$ -type reactions of a chelated iron (η^2 -olefin) dioxocarbene. *J. Organomet. Chem.* 1996, 526, 169-174.
- 9 (a) Casey, C. P.; Konings, M. S.; Marder, S. R. Addition of nucleophiles to cationic diiron p-vinylcarbyne complexes; synthesis of functionalized diiron alkenylidene complexes. *J. Organomet. Chem.* 1988, 345, 125-134. (b) Casey, C. P.; Woo, L. K.; Fagan, P. J.; Palermo, R. E.; Adams, B. R. Reactions of Acetylenes with a Cationic Bridging Methylidyne Diiron Complex. *Organometallics* 1987,6,447-454.
- 10 a) Biancalana, L.; Marchetti, F. Aminocarbyne Ligands in Organometallic Chemistry. *Coord. Chem. Rev.*, in press. b) Marchetti,F. Constructing Organometallic Architectures from Aminoalkylidyne Diiron Complexes. *Eur. J. Inorg. Chem.* 2018, 3987–4003.
- 11 Agonigi,G.; Bortoluzzi,M.; Marchetti,F.; Pampaloni,G.; Zacchini,S.; Zanotti,V. Regioselective Nucleophilic Additions to Diiron Carbonyl Complexes Containing a Bridging Aminocarbyne Ligand: A Synthetic, Crystallographic and DFT Study. *Eur. J. Inorg. Chem.* 2018, 960–971.
- 12 Albano, V. G.; Busetto, L.; Camiletti, C.; Castellari, C.; Monari, M.; Zanotti, V. Selective C-C bond formation at diiron μ -aminocarbyne complexes. *J. Chem. Soc. Dalton Trans.*, 1997, 4671–4676.
- 13 Zanotti,V.; Bordoni,S.; Busetto,L.; Carlucci,L.; Palazzi,A.; Serra,R.; Albano,V. G.; Monari,M.;Prestopino,F.; Laschi,F.; Zanello, P.Diiron Aminoalkylidene Complexes. *Organometallics* 1995, 14, 5232-5241.
- 14 Biancalana,L.; De Franco,M.; Ciancaleoni,G.; Zacchini,S.; Pampaloni,G.; Gandin,V.; Marchetti,F.Easily Available, Amphiphilic Diiron Cyclopentadienyl Complexes Exhibit in Vitro

This item was downloaded from IRIS Università di Bologna (<https://cris.unibo.it/>)

When citing, please refer to the published version.

Anticancer Activity in 2D and 3D Human Cancer Cells through Redox Modulation Triggered by CO Release. *Chem. Eur. J.* 2021, 27, 10169-10185.

- 15 Albano, V. G.; Busetto, L.; Marchetti, F.; Monari, M.; Zacchini, S.; Zanotti, V. Synthesis and Characterization of New Diiron and Diruthenium μ -Aminocarbonyl Complexes Containing Terminal S-, P- and C-Ligands. *Z. Naturforsch.* 2007, 62b, 427-438.
- 16 Albano, V. G.; Bordoni, S.; Braga, D.; Busetto, L.; Palazzi, A.; Zanotti, V. Dinuclear Cyanoalkylidene Complexes of Iron, *Angew. Chem. Int. Ed.* 1991, 30, 847-849.
- 17 (a) De Palo, A.; Zacchini, S.; Pampaloni, G.; Marchetti, F. Construction of a Functionalized Selenophene-Allylidene Ligand via Alkyne Double Action at a Diiron Complex. *Eur. J. Inorg. Chem.* 2020, 3268–3276. (b) Marchetti, F.; Zacchini, S.; Zanotti, V. Amination of Bridging Vinyliminium Ligands in Diiron Complexes: C-N Bond Forming Reactions for Amidine-Alkylidene Species. *Organometallics* 2018, 37, 107–115. (c) Busetto, L.; Marchetti, F.; Renili, F.; Zacchini, S.; Zanotti, V. Addition of Alkynes to Zwitterionic μ -Vinyliminium Diiron Complexes: New Selenophene (Thiophene) and Vinyl Chalcogenide Functionalized Bridging Ligands. *Organometallics* 2010, 29, 1797–1805.
- 18 Busetto, L.; Zanotti, V. Thiocarbonyl, thiocarbonyl and thiocarbene ligands in di- and polynuclear complexes. *Inorg. Chim. Acta* 2008, 361, 3004–3011.
- ¹⁹ Menges, F. "Spectragryph - optical spectroscopy software", Version 1.2.5, @ 2016-2017, <http://www.ffmpeg2.de/spectragryph>.
- ²⁰ Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. NMR Chemical Shifts of Trace Impurities: Common Laboratory Solvents, Organics, and Gases in Deuterated Solvents Relevant to the Organometallic Chemist. *Organometallics* 2010, 29, 2176–2179.
- 21 Willker, W.; Leibfritz, D.; Kerssebaum, R.; Bermel, W. Gradient selection in inverse heteronuclear correlation spectroscopy. *Magn. Reson. Chem.* 1993, 31, 287-292.
- 22 Sheldrick, G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr. C*, 2015, 71, 3-8.
- 23 (a) Becke, A. D. Density-Functional Exchange-Energy Approximation with Correct Asymptotic Behavior. *Phys. Rev.* 1988, A38, 3098–3100. (b) Becke, A. D., Density-Functional Thermochemistry. 3. The Role of Exact Exchange. *J. Chem. Phys.* 1993, 98, 5648–5652.

This item was downloaded from IRIS Università di Bologna (<https://cris.unibo.it/>)

When citing, please refer to the published version.

-
- 24 Weigend, F.; Ahlrichs, R. Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. *Phys. Chem. Chem. Phys.* 2005, 7, 3297–3305.
- 25 (a) Cossi, M.; Rega, N.; Scalmani, G.; Barone, V. Energies, structures, and electronic properties of molecules in solution with the C-PCM solvation model. *J. Comput. Chem.* 2003, 24, 669–681. (b) Barone, V.; Cossi, M. Quantum Calculation of Molecular Energies and Energy Gradients in Solution by a Conductor Solvent Model. *J. Phys. Chem. A* 1998,102, 1995–2001.
- 26 (a) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V. Cioslowski, J. and Fox, D. J. Gaussian 09, Revision C.01, Gaussian Inc., Wallingford, CT, 2010.

This item was downloaded from IRIS Università di Bologna (<https://cris.unibo.it/>)

When citing, please refer to the published version.