Regioselective Nucleophilic Additions to Diiron Carbonyl Complexes Containing a Bridging Aminocarbyne Ligand: a Synthetic, Crystallographic and DFT Study

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Abstract. Diiron μ-aminocarbyne compounds, **1a-e**, were prepared in two steps from $Fe_2Cp_2(CO)_4$, negating the need of difficult purification procedures of intermediate species, and efficiently isolated by alumina chromatography. Minor amounts of μ-aminocarbyne aryl-isocyanide compounds, **2a-c**, were obtained as side products. The structures of the cations in **1a,c,e** were DFT calculated, and the carbyne carbon was generally predicted to be the thermodynamic site of hydride addition, in agreement with a previous experimental finding concerning **1a**. Accordingly, the reaction of **1e** with $NaBH_4$ afforded a bridging aminocarbene complex, **4**, in 85% yield. Otherwise the reaction of **1c** with $NaBH_4$ yielded the aminocarbyne-cyclopentadiene derivative **3** (70%), presumably as a consequence of the steric protection exerted by the xylyl-methyl groups towards

the carbyne moiety. The sequential treatment of **1a,c** with $Li_2CuCNMe_2$ and $MeSO_3CF_3$ afforded **5a-5b**, comprising both aminocarbyne and alkoxycarbene ligands. In accordance with DFT calculations, the alkoxycarbene moiety in **5a** resulted to be the most favourable site of nucleophilic attack. Thus the reactions of **5a** with NH_2R (R = Et, ^iPr) and NBu_4CN respectively gave aminocarbyne-aminocarbene complexes, **6a-6b**, and the aminocarbyne-α-cyanoalkyl **7**. All the products were fully characterized by spectroscopic and analytical methods, moreover the structures of **1a**, **1d**, **6a** and **7** were elucidated by single crystal X-ray diffraction studies.

Introduction

Since its early preparation by Cotton and Wilkinson in the fifties,[1] the easily available and rugged compound $[Fe_2Cp_2(CO)_4]$ has become a "battle horse" of organometallic chemistry.[2] It has been employed in homogeneous catalytic processes,[3] as a convenient precursor to iron nanoparticles,[4] and as a starting material to access a huge variety of mono-[5] and dinuclear[6] derivatives. As a preliminary step, both thermal[7] and photochemical methods[8] have been proposed for carbon monoxide/isocyanide substitution, however these reactions generally afford mixtures of poly-substituted products. This is true especially when aryl-isocyanides are involved, in view of their greater ability to replace CO ligands, with respect to alkyl-isocyanides.[7b] The isolation of mono-isocyanide species, $[Fe_2Cp_2(CO)_3(CNR)]$ (R = alkyl or aryl group), is therefore a difficult task, and their clear spectroscopic identification is further complicated by the fact that they exist as mixtures of isomers.[9] The preparation of some of the compounds $[Fe_2Cp_2(CO)_3(CNR)]$ has been better accomplished by alternative and more elaborated routes.[7b,10] The selective formation of $[Fe_2Cp_2(CO)_3(CNR)]$ is desired in that it represents the first, crucial step to the synthesis of versatile mono-aminocarbyne complexes, $[Fe_2Cp_2(CO)_3(\mu\text{-CNRR'})]^+$,[11] obtained from the isocyanide precursors by addition of strong alkylating agents.[12] Some reactivity of N-alkyl aminocarbyne complexes, and in particular $[Fe_2Cp_2(CO)_3(\mu\text{-CNMe}_2)][SO_3CF_3]$ (**1a**), with anionic nucleophiles was elucidated in the past. Addition reactions usually occur in a selective manner depending on the nature of the reactant, and are directed to the carbyne carbon,[13] a terminal carbonyl ligand,[14] or a Cp moiety (Scheme 1).[14] Conversely, the parallel chemistry of $[Fe_2Cp_2(CO)_3\{\mu\text{-CN(Me)(Xyl)}\}][SO_3CF_3]$ (**1c**, Xyl = 2,6-$C_6H_3Me_2$)[8] has been barely explored, despite the fact that the aryl substituent is expected to provide important steric and electronic effects.[15]
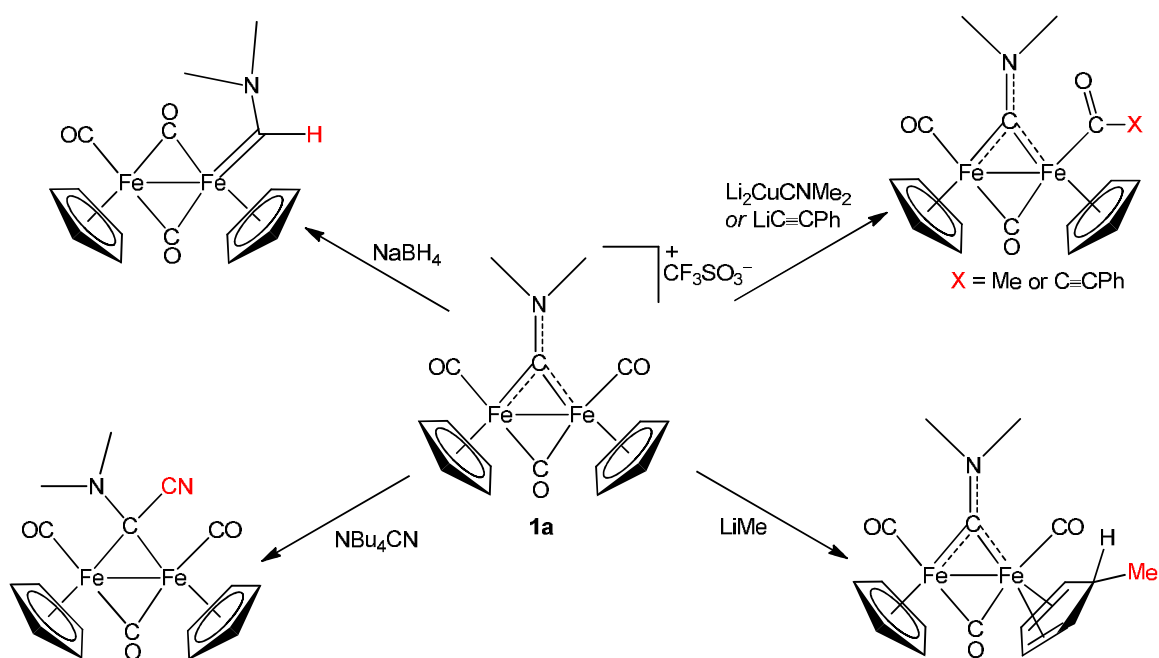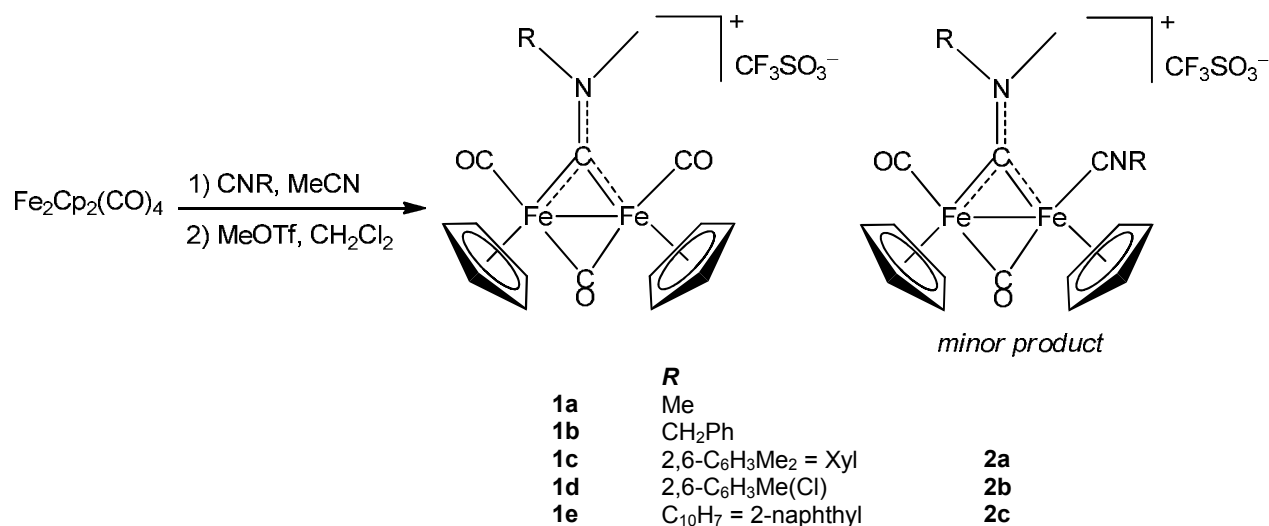
Scheme 1. Regioselective additions of nucleophiles to the diiron aminocarbyne complex **1a**.

Herein, we describe an optimized procedure to obtain diiron aminocarbyne compounds of general formula $[Fe_2Cp_2(CO)_3(\mu\text{-}CNMeR)][SO_3CF_3]$, from $[Fe_2Cp_2(CO)_4]$ and isocyanides. The reactions of some of the products with a series of nucleophiles will be discussed, with the assistance of DFT calculations giving insight into thermodynamic and structural features.

Results and discussion

The commercial compound $[Fe_2Cp_2(CO)_4]$ was allowed to react with the appropriate isocyanide, in ca. 3:2 molar ratio, in acetonitrile solution.[16] The reactions with alkyl-isocyanides were conducted at reflux conditions, whereas the reactions with aryl-isocyanides proceeded at room temperature. The resulting mixtures were dried under vacuum and the residues were dissolved in dichloromethane and then treated with methyl triflate, thus affording the μ-aminocarbyne complexes **1a-e** (Scheme 2). The difficult isolation of the mono-isocyanide intermediates (see Introduction) is unnecessary. The final products **1a-e** were efficiently purified by alumina chromatography and then isolated as microcrystalline, air stable compounds in 65-92% yields. The synthesis of **1c-e** is accompanied by the side formation of minor products derived from di-isocyanide species, **2a-c**. Compounds **2a-c** were recovered by the chromatography in 3-12% yields, **2a** being formerly reported as obtained by a different route.[11c] The chromatography allowed to recover unreacted $[Fe_2Cp_2(CO)_4]$, too.

	R	
1a	Me	
1b	CH_2Ph	
1c	2,6-C_6H_3Me_2 = Xyl	**2a**
1d	2,6-C_6H_3Me(Cl)	**2b**
1e	C_10H_7 = 2-naphthyl	**2c**

Scheme 2. Synthesis of diiron μ-aminocarbyne complexes.

The new products **1d-e** and **2b-c** were characterized by elemental analysis, IR and NMR spectroscopy. The full NMR characterization of the already known **1a-c** is supplied here for the first time. The carbyne nature of the bridging [CN] moiety in **1a-e** is manifested by a strongly deshielded ^{13}C NMR resonance (e.g., at 327.8 ppm in the case of **1c** in CDCl_3 solution).[11,17] **1d** exists in

solution as two isomeric forms in comparable ratio, the two isomers presumably differing in the orientation of the aryl-substituents (i.e., Me and Cl) respect to the Fe–Fe axis. No change in the isomer composition was detected by heating **1d** in isopropanol solution at reflux temperature for 24 h. Crystals of **1a** and **1d** suitable for X-ray diffraction analysis could be obtained. A view of the respective cations is given in Figures 1 and 2, whereas relevant bonding parameters are listed in Tables 1 and 2. The structures of **1a** and **1d** closely resemble those previously reported for analogous diiron μ-aminocarbyne compounds for what concern the geometry and the bonding parameters.[12,18] Thus, they consist of a $Fe_2(CO)_2Cp_2$ unit in *cis* configuration and two bridging ligands, i.e. a carbon monoxide and the aminocarbyne group. The latter can be alternatively described as an iminium: in fact, the C-N distance [1.297(4) in **1a** and 1.295(5) Å in **1d**] falls within the range of double bonds.[19] The structure of **1d** exhibits the chlorine atom pointing to the opposite side respect to the Cp rings.
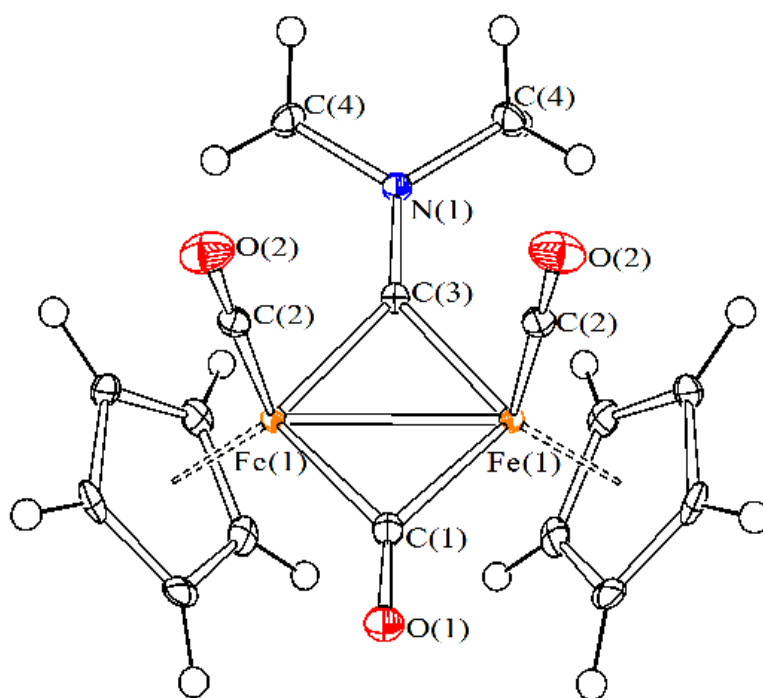

Figure 1. View of the structure of the cation within **1a**. Displacement ellipsoids are at the 30% probability level.

Table 1.Selected bond distances (Å) and angles (°) for the cation within **1a**.

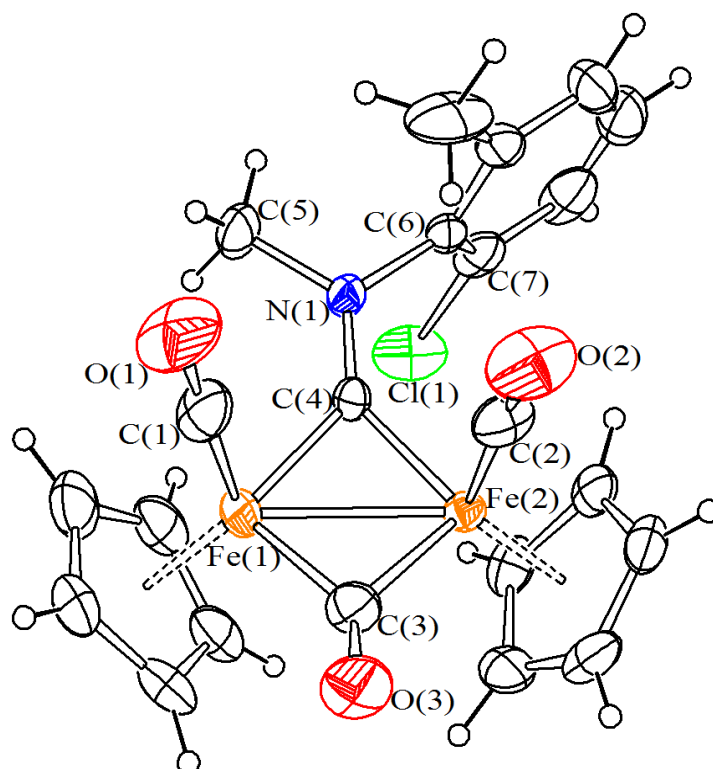|			
Fe(1)−Fe(1)	2.5218(7)	Fe(1)−C(2)	1.775(2)
Fe(1)−C(1)	1.933(3)	Fe(1)−C(3)	1.875(2)
C(1)−O(1)	1.177(4)	C(2)−O(2)	1.138(3)
C(3)−N(1)	1.297(4)	C(4)−N(1)	1.471(3)
Fe(1)−Cp$_{average}$	2.113(4)		
Fe(1)−C(1)−Fe(1)	81.41(13)	Fe(1)−C(3)−Fe(1)	84.53(13)
Fe(1)−C(2)−O(2)	179.4(2)	Sum at N(1)	360.0(2)

Figure 2. View of the structure of the cation within **1d**. Displacement ellipsoids are at the 30% probability level.

Table 2.Selected bond distances (Å) and angles (°) for the cation within **1d**.

Fe(1)−Fe(2)	2.504(2)	Fe(1)−C(1)	1.754(6)
Fe(1)−C(3)	1.933(5)	Fe(2)−C(3)	1.939(4)
Fe(1)−C(4)	1.871(4)	Fe(2)−C(4)	1.875(4)
Fe(2)−C(2)	1.760(5)	C(3)−O(3)	1.154(5)
C(1)−O(1)	1.143(7)	C(2)−O(2)	1.134(6)
C(4)−N(1)	1.295(5)	C(5)−N(1)	1.486(5)

C(6)−N(1)	1.450(5)	C(7)−Cl(1)	1.749(6)
Fe(1)−Cp$_{average}$	2.12(2)	Fe(2)−Cp$_{average}$	2.104(9)
Fe(1)−C(3)−Fe(2)	80.61(17)	Fe(1)−C(4)−Fe(3)	83.92(15)
Fe(1)−C(1)−O(1)	176.8(5)	Fe(2)−C(2)−O(2)	176.3(5)
Sum at N(1)	360.0(5)		

In order to compare the electrophilic behaviour of **1a** (see Introduction and Scheme 1) with that of the aryl-substituted homologues, we studied the reactions of **1c** and **1e** with NaBH$_4$. The reaction involving the naphthyl-derivative **1e** afforded a bridging aminocarbene group (Scheme 3, compound **4**), thus resembling the previous result obtained with **1a** (Scheme 1).[13] On the other hand, the hydride attack to **1c** selectively occurred at the Cp ligand, resulting in the formation of a cyclopentadiene (Scheme 3, compound **3**). The new complexes **3** and **4** were purified by alumina chromatography and characterized by elemental analysis and IR and NMR spectroscopy. The IR spectrum of **3** (in CH$_2$Cl$_2$) shows three absorptions related to one bridging (1771 cm^{-1}) and two terminal (1960, 1925 cm^{-1}) carbonyl ligands. A ^{13}C NMR resonance at 333.6 (CDCl$_3$ solution) represents clear evidence that the aminocarbyne group is not involved in the reaction. Two isomers were NMR detected for **3** (approximate ratio = 1.5), probably originating by the different orientations that the N-substituents can assume with respect to the non equivalent Fe atoms, as a consequence of the double-bond character of the µ-C−N interaction (E/Z isomers). Complexes of the type [Fe$_2${µ-CN(R)(R')}(µ-CO)(CO)(L)Cp$_2$] (R ≠ R', L = halide, CN, Ph), in chlorinated solvents, preferentially adopt the E configuration, with the Cp ligands in mutual *cis* position.[11c,e,20]

The most salient spectroscopic features of **4** are the NMR resonances related to the newly formed carbene centre, at 13.11 (^{1}H) and 182.4 (^{13}C) ppm. The bridging coordination of the carbene is indicated by the IR spectrum, consisting of one absorption ascribable to a bridging CO (1765 cm^{-1}) and other two absorptions due to terminal carbonyls (1955, 1925 cm^{-1}).
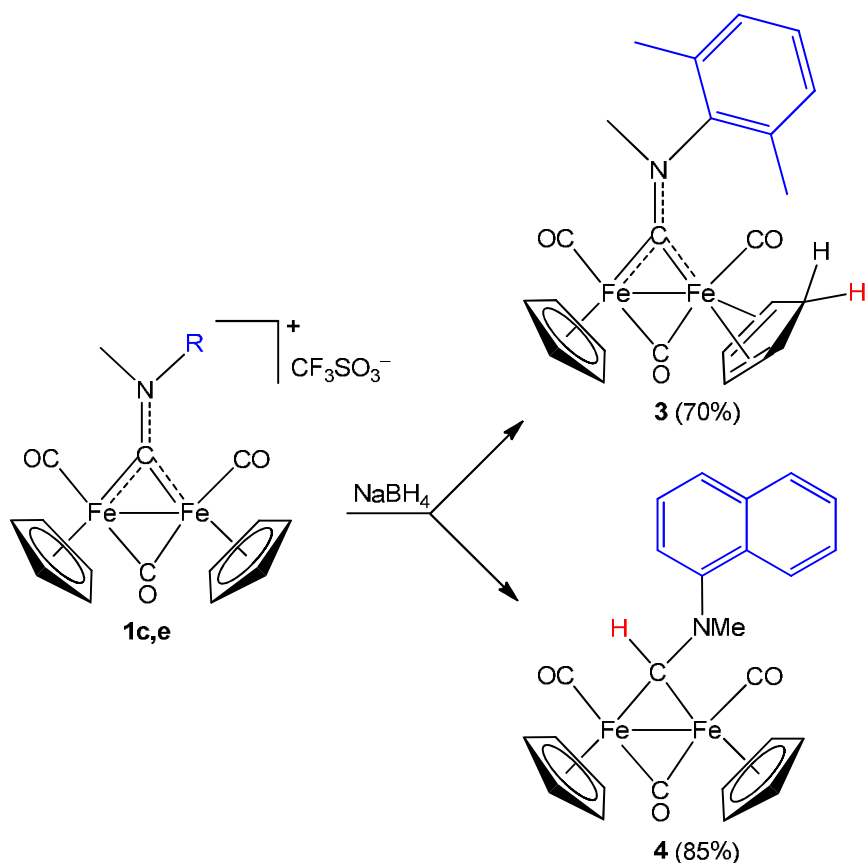
Scheme 3. Regioselective hydride additions to aryl-substituted μ-aminocarbyne complexes.

The DFT-optimized geometries of **3** and **4** are shown in Figure 3. Concerning **3**, the structure displaying the xylyl on the same side respect to the cyclopentadiene ligand resulted only slightly more stable than the alternative form with opposite configuration of the N-substituents (Figure S2), in agreement with the NMR observation in solution of two isomers in comparable amount (see above).
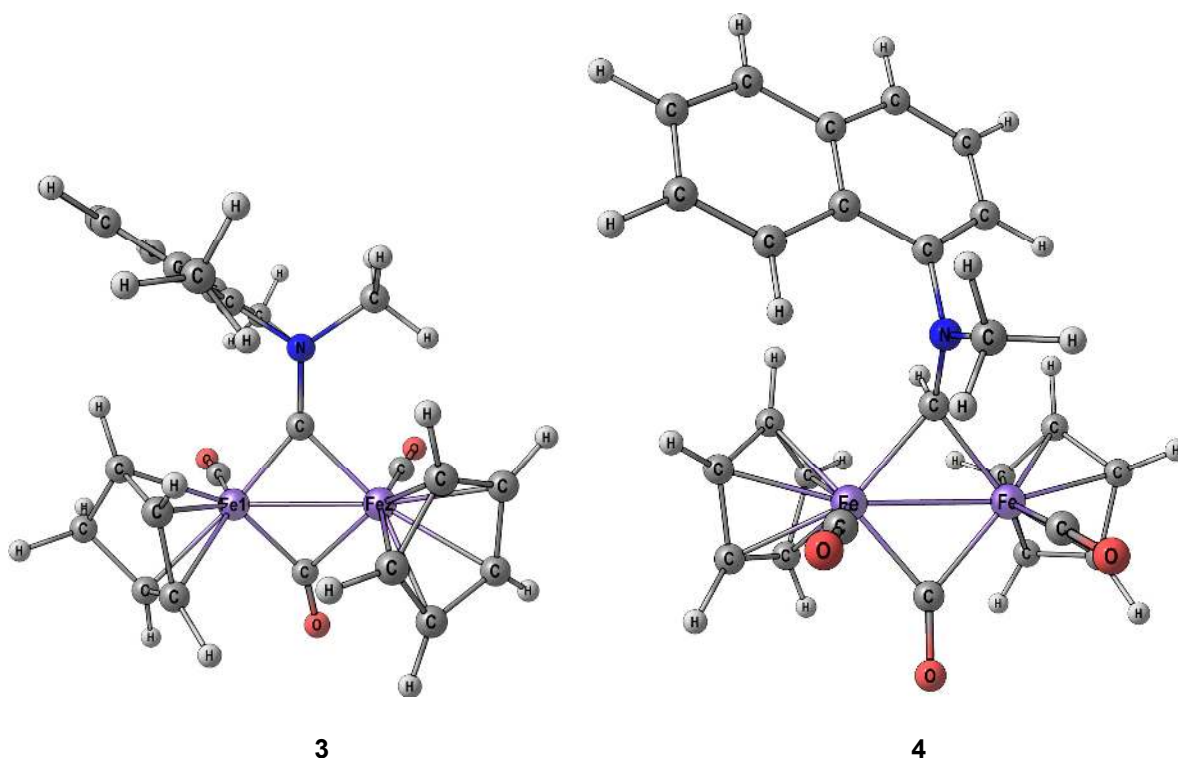
3

4

Figure 3. DFT-optimized structures of **3** and **4** (ωB97X functional). Selected computed bond lengths (Å) for **3**: Fe1−C(cyclopentadiene) 2.028, 2.039, 2.083, 2.111, 2.657; Fe1-C(aminocarbyne) 1.840; Fe1−C(μ-CO) 1.833; Fe1−C(CO) 1.762; Fe2-C(Cp) 2.075, 2.093, 2.105, 2.111, 2.112; Fe2−C(aminocarbyne) 1.874; Fe2−C(μ-CO) 2.055; Fe2−C(CO) 1.764; Fe−Fe 2.530; C−N 1.319. Selected computed bond lengths (Å) for **4**: Fe1−C(Cp) 2.079, 2.091, 2.115, 2.120, 2.128; Fe1−C(aminocarbene) 1.964; Fe1−C(μ-CO) 1.918; Fe1−C(CO) 1.764; Fe2−C(Cp) 2.083, 2.089, 2.117, 2.129, 2.129; Fe2−C(aminocarbene) 2.012; Fe2−C(μ-CO) 1.877; Fe2−C(CO) 1.759; Fe−Fe 2.537; C−N 1.390.

In order to give insight into the different outcomes of the reactions of **1a,c,e** with NaBH$_4$, we considered all the potential products and compared their energies in the distinct cases (see Figures S1-S3 supplied as Supporting Information). In general, the attack to the aminocarbyne carbon appears to be largely favourable from a thermodynamic point of view;[21] the resulting aminocarbene ligand may occupy either a bridging or a terminal site, the two sites bearing comparable energies.[13] The aminocarbene frame in **4** adopts the bridging coordination mode, possibly also due to the lack of a convenient activation barrier pathway needed to allow the exchange between the bridging, hindered aminocarbene and a terminal carbon monoxide.

The charge distribution on the aminocarbyne moiety was calculated for compounds **1a**, **1c** and **1e** (Figure 4), and seems in alignment with the thermodynamic considerations: it is negligibly affected by the nature of the N-substituents, thus suggesting the absence of conjugation between the [CN]

unit and the aromatic ring in **1c,e**. Based on these observations, it is presumable that the favourable hydride attack to the aminocarbyne carbon of **1c** (see above) is inhibited due to steric protection exerted towards that carbon centre by the methyl substituents situated on the aryl ring, and not for electronic reasons.[15] A view of the electron density surface of **1c** is given in <mark>Figure S5</mark>. We tested the thermal stability of **3** in various solvents, with the aim of promoting intramolecular H-migration from the cyclopentadiene ligand to the carbyne carbon, suggested by the theoretical considerations. Unfortunately, these experiments resulted in the formation of complicated mixtures of products.
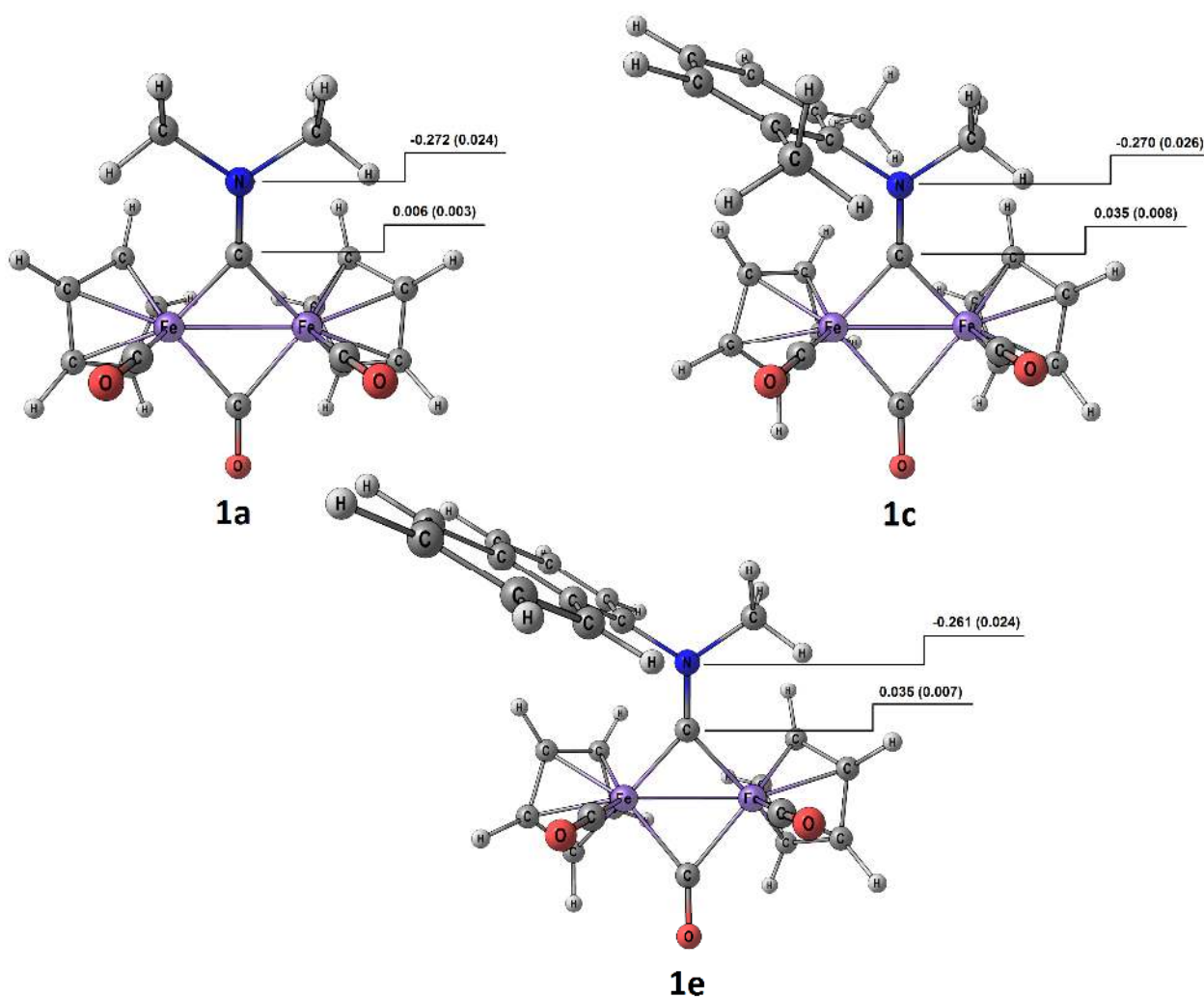

Figure 4. DFT-optimized geometries of selected cations within aminocarbyne complexes (ωB97X functional), with Mulliken partial charges (a.u.) on the μ-aminocarbyne moiety. Data from Hirshfeld population analyses are in parenthesis. Selected computed bond lengths and angles are compared in Table S1, while Cartesian coordinates are collected in a separated .xyz file.

The inertness of the xylyl-aminocarbyne moiety of **1c** respect to nucleophilic addition is manifested also in the reaction with NBu$_4$CN, proceeding with direct carbon monoxide/cyanide substitution to give in 84% yield the complex [Fe$_2${μ-CN(Me)(Xyl)}(μ-CO)(CO)(CN)(Cp)$_2$] (Scheme 4). This complex were previously prepared by replacement of the labile acetonitrile ligand from [Fe$_2${μ-CNMe(R)}(μ-CO)(CO)(NCMe)Cp$_2$][SO$_3$CF$_3$] (R = Me, Xyl; Scheme 4).[22] It should be remarked that the reaction of **1a** with NBu$_4$CN at room temperature selectively results in carbyne-cyanide coupling to give the aminocarbene [Fe$_2${μ-CN(Me)$_2$(CN)}(μ-CO)(CO)$_2$(Cp)$_2$] (see also Scheme 1). On the other hand, the reaction of [Fe$_2${μ-CNMe$_2$}(μ-CO)(CO)$_2$Cp$_2$][I] with KCN in solution of ethanol at reflux conditions was previously reported to give [Fe$_2${μ-CN(Me)$_2$}(μ-CO)(CO)(CN)(Cp)$_2$].[23] Moreover, we observed that [Fe$_2${μ-CN(Me)$_2$(CN)}(μ-CO)(CO)$_2$(Cp)$_2$], upon contact with water for prolonged time in an attempt to test air/water stability, converted into [Fe$_2${μ-CN(Me)$_2$}(μ-CO)(CO)(CN)(Cp)$_2$] (Scheme 4). These observations suggest that the replacement of a CO ligand by cyanide is a favourable process, which may proceed through the intermediate attack to the aminocarbyne carbon. The steric hindrance around this forces the direct formation of the thermodynamic product.
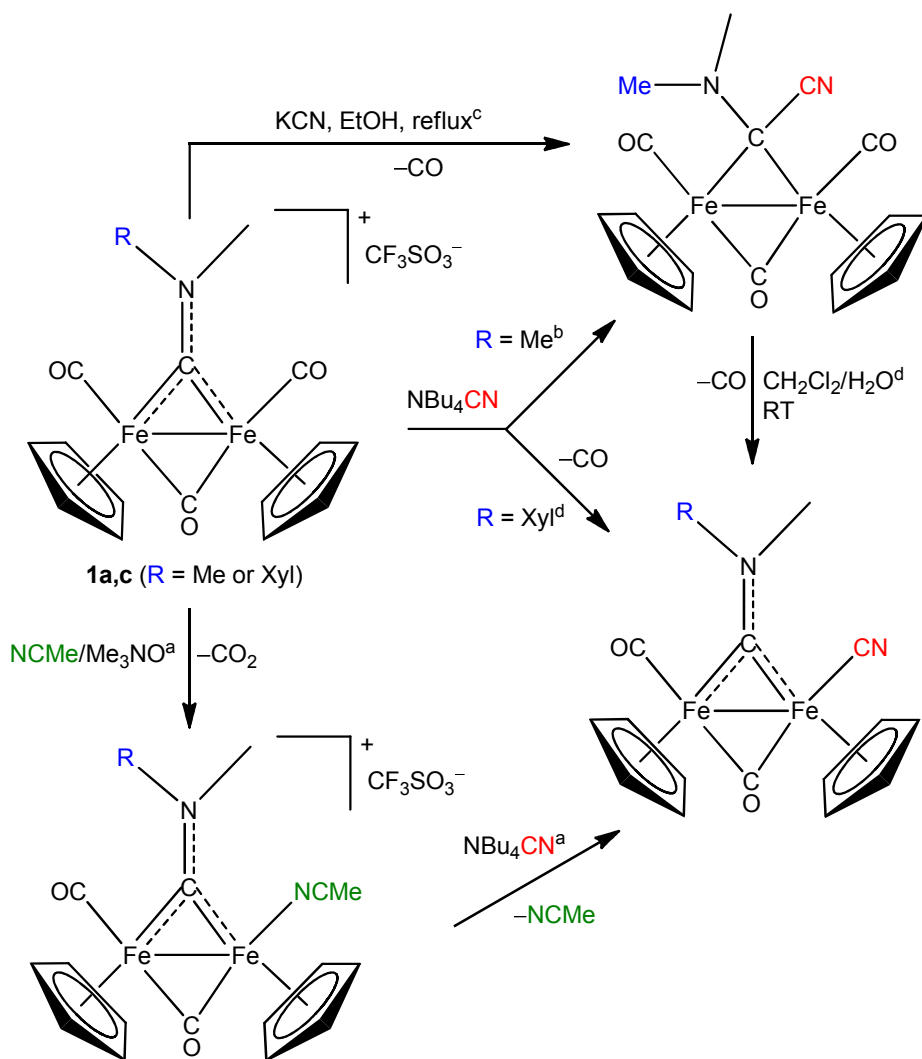
Scheme 4. Overview of the reactivity of diiron μ-aminocarbyne complexes with the cyanide ion [[a] ref. 22; [b] ref.13; [c] ref. 23; [d] present work].

In order to introduce a further carbene functionality in **1a,c**, the compounds [Fe$_2${μ-CN(Me)(R)}(μ-CO)(CO){C=O)Me}Cp$_2$] (R = Me,[14] Xyl [20]) were preliminarily prepared. These were allowed to react with methyl triflate in dichloromethane, thus affording [Fe$_2${μ-CN(Me)(R)}(μ-CO)(CO){C(OMe)Me}Cp$_2$][SO$_3$CF$_3$] (R = Me, **5a**; R = Xyl, **5b**) in 80-85% yields, Scheme 5.
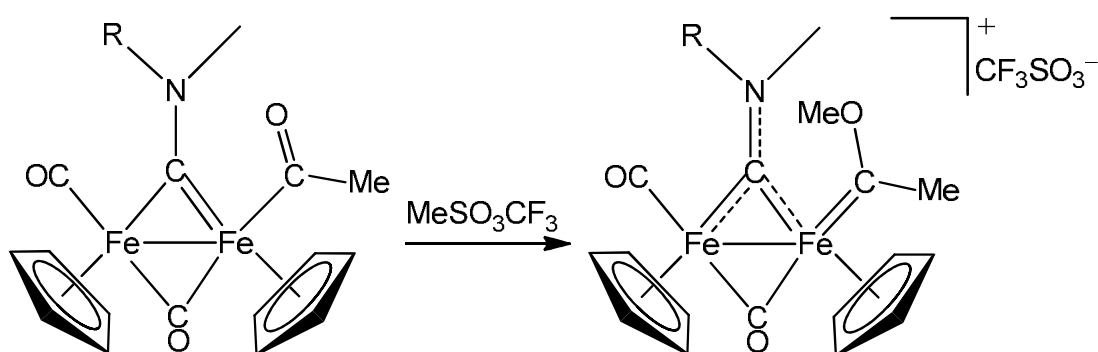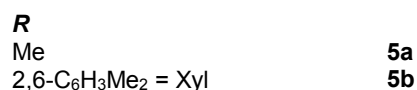
Scheme 5. Synthesis of diiron complexes with μ-aminocarbyne and alkoxycarbene ligands.

The new aminocarbyne-alkoxycarbene [24] complexes **5a-b** were purified by filtration through celite, and then characterized by elemental analysis and IR and NMR spectroscopy. The NMR spectra exhibit the expected resonance due to the aminocarbyne centre (*e.g.* at 325.4 ppm in the case of **5a**). In accord with the significant accumulation of positive charge on the alkoxycarbene moiety (see below), even the carbene carbon resonates at unusual low fields (e.g. at 330.7 ppm in the case of **5a**). The structure of **5a** was DFT calculated, and the electronic features were investigated (Figure 5). Population analyses, the Hirshfeld one in particular, evidenced the greater electrophilicity of the alkoxycarbene function with respect to the aminocarbyne. Accordingly, the plot of the squared LUMO suggests that such empty orbital is mainly localized on the carbene, thus rendering this site accessible to nucleophiles.
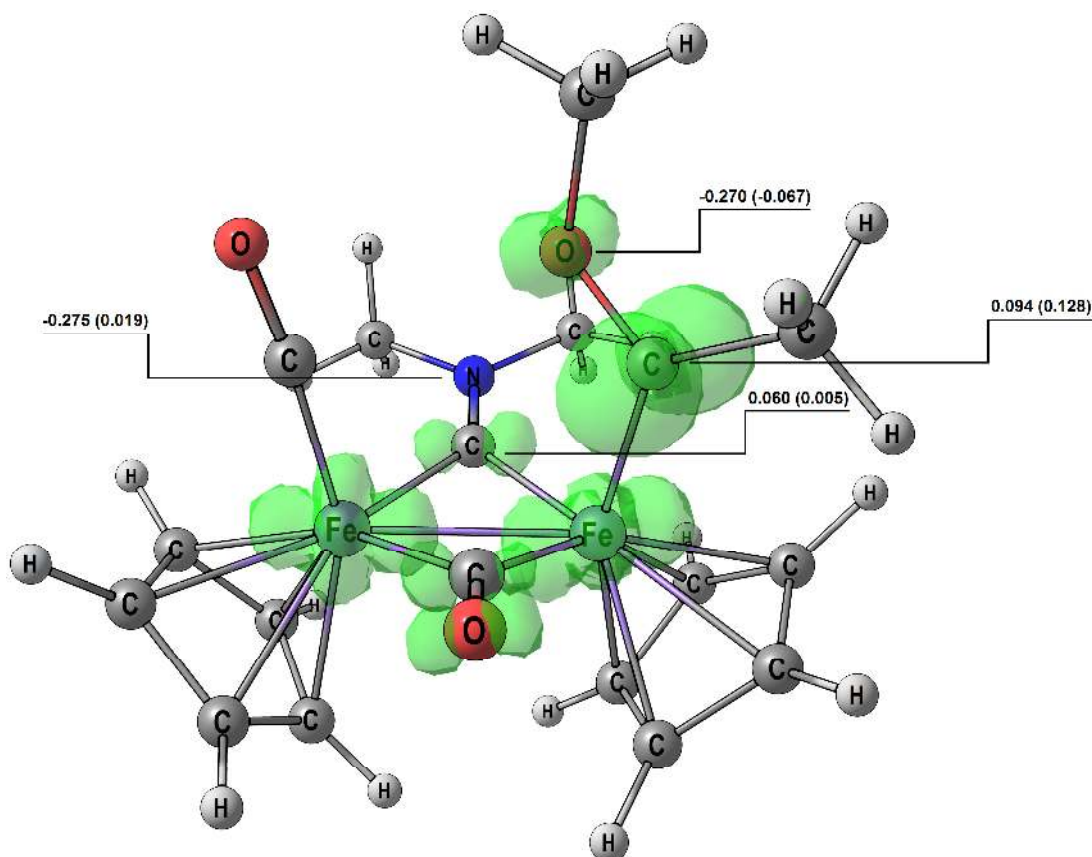
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The reactivity of **5a** with a small selection of nucleophiles was studied (Scheme 6).
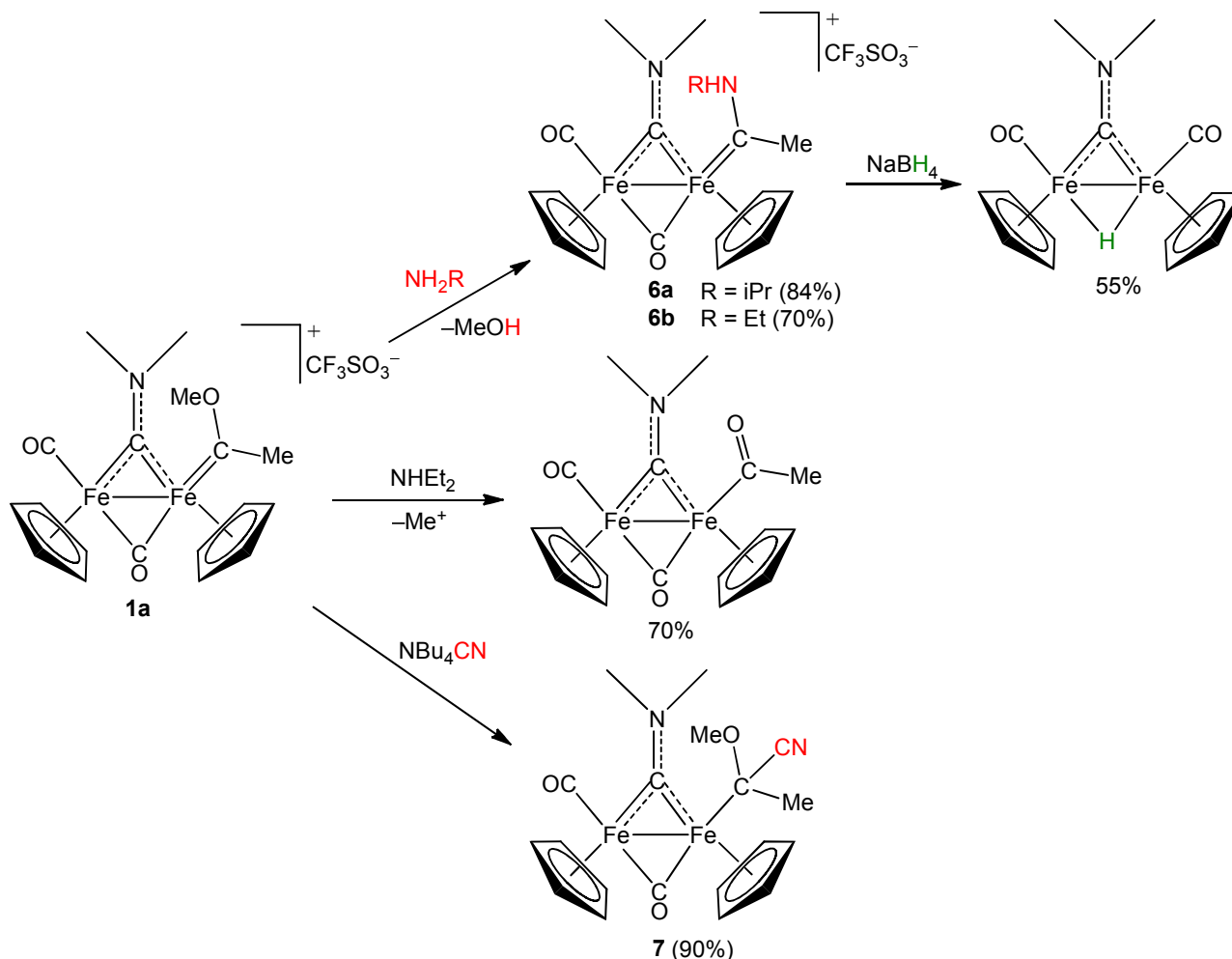
Scheme 6. Additions of nucleophiles to the alkoxycarbene moiety in diiron complexes containing additional μ-aminocarbyne ligand.

The reactions of **5a** with primary amines resulted in selective aminolysis, to afford the new aminocarbyne-aminocarbene complexes [Fe$_2$(μ-CNMe$_2$)(μ-CO)(CO){C(Me)NH(R)}(Cp)$_2$][SO$_3$CF$_3$] (R = ^{i}Pr, **6a**; R = Et, **6b**), in good to high yields.[25] Instead NHEt$_2$ acted as a base towards **5a**, and demethylation effectively occurred to regenerate the parent compound [Fe$_2${μ-CN(Me)$_2$}(μ-CO)(CO){C=O)Me}Cp$_2$] (Scheme 5). When **6b** was treated with

NaBH$_4$, the aminocarbene unit was dissociated and the bridging hydride complex [Fe$_2$(μ-CNMe$_2$)(μ-H)(CO)$_2$(Cp)$_2$] was obtained as the prevalent product.[22]

Compounds **6a-b** were purified by alumina chromatography, and then fully spectroscopically characterized. In **6a**, the resonances related to the aminocarbyne and aminocarbene carbons have been detected at 330.4 and 261.2 ppm, respectively. The structure of **6a** was ascertained by X-ray diffraction (Figure 6, Table 3): its geometry and bonding parameters closely resemble to those previously reported for analogous cationic diiron aminocarbyne-aminocarbene species with miscellaneous substituents.[11] In particular, the Fe(2)−C(16) interaction [1.927(4) Å] shows a considerable π-character, and the C(16)−N(2) distance [1.291(5) Å] also indicates some π-bond between the carbene carbon and N(2). An intra-molecular H-bond involving the N(2)-H(2n) group and N(1) is present [N(2)-H(2n) 0.869(19) Å, H(2n)···N(1) 2.55(3) Å, N(2)···N(1) 3.252(4) Å, <N(2)H(2n)N(1) 138(4)°].

Figure 6. View of the structure of **6a**. Displacement ellipsoids are at the 30% probability level.

Table 3.Selected bond distances (Å) and angles (°) for **6a**.

Fe(1)−Fe(2)	2.5017(9)		
Fe(1)−C(11)	1.750(4)	Fe(2)−C(16)	1.927(4)
Fe(1)−C(12)	1.974(3)	Fe(2)−C(12)	1.879(4)
Fe(1)−C(13)	1.909(3)	Fe(2)−C(13)	1.843(3)
C(11)−O(11)	1.143(5)	C(12)−O(12)	1.169(4)
C(13)−N(1)	1.284(4)	C(14)−N(1)	1.472(5)
C(15)−N(1)	1.477(5)	C(16)−C(17)	1.499(5)
C(16)−N(2)	1.292(5)	N(2)−C(18)	1.499(9)
Fe(1)−Cp$_{average}$	2.111(11)	Fe(2)−Cp$_{average}$	2.122(11)
Fe(1)-C(12)−Fe(2)	80.95(14)	Fe(1)−C(13)−Fe(2)	83.62(14)
Fe(1)−C(11)−O(11)	177.2(4)	Sum at N(1)	359.9(5)
Fe(2)−C(16)−N(2)	125.5(3)	Fe(2)-C(16)−C(17)	119.1(3)
N(2)−C(16)−C(17)	115.4(4)	C(16)−N(2)−C(18)	133.5(5)

The reaction of **5a** with NBu$_4$CN, performed in dichloromethane, afforded the α-cyano-methoxyalkyl complex [Fe$_2$\{μ-CN(Me)$_2$\}(μ-CO)(CO)\{C(CN)(OMe)Me\}Cp$_2$], **7**, in 90% yield. The X-ray structure of **7** (Figure 7 and Table 4) resembles that of [Fe$_2$\{μ-CN(Me)(Xyl)\}(μ-CO)(CO)\{C(CN)(OMe)(C≡CPh)\}Cp$_2$], for what concerns the bonding parameters and overall geometry.[24a] In particular, the Fe(1)-C(6) distance [2.075(4) Å] is that of a pure Fe-C(sp^3) σ-bond and is similar to that found in the cyano-methyl complex [Fe$_2$\{μ-CN(Me)$_2$\}(μ-CO)(CO)(CH$_2$CN)Cp$_2$].[26]
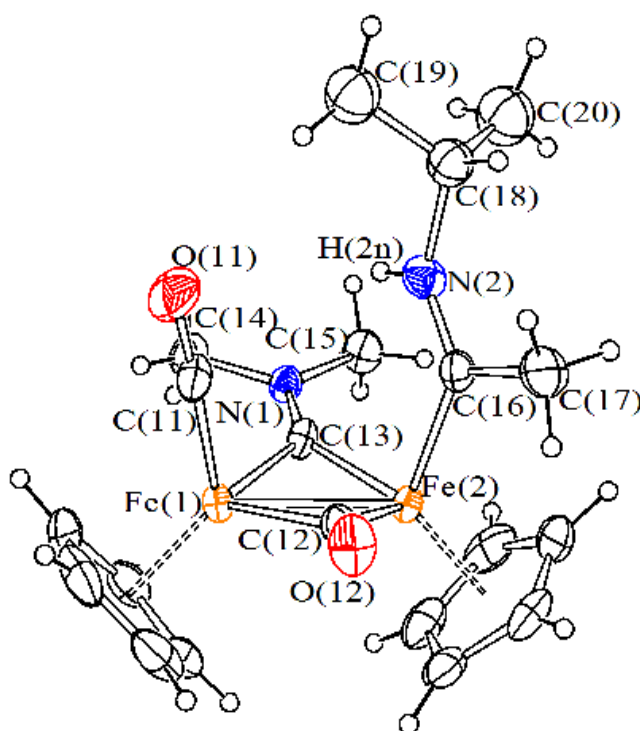
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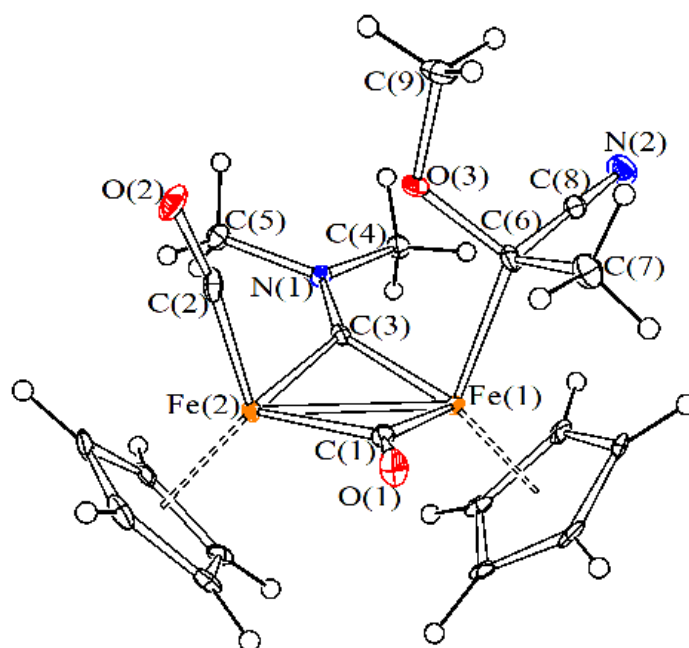
Figure 7. View of the structure of **7**. Displacement ellipsoids are at the 30% probability level.

Table 4.Selected bond distances (Å) and angles (°) for **7**.

Fe(1)-Fe(2)	2.5012(7)		
Fe(1)-C(1)	1.866(4)	Fe(2)-C(1)	1.992(4)
Fe(1)-C(6)	2.075(4)	Fe(2)-C(2)	1.756(4)
Fe(1)-C(3)	1.845(4)	Fe(2)-C(3)	1.887(4)
C(1)-O(1)	1.166(5)	C(2)-O(2)	1.142(5)
C(3)-N(1)	1.294(5)	C(4)-N(1)	1.462(5)
C(5)-N(1)	1.469(5)	C(6)-C(7)	1.532(5)
C(6)-C(8)	1.470(6)	N(2)-C(8)	1.148(5)
C(6)-O(3)	1.440(5)	O(3)-C(9)	1.417(5)
Fe(1)-Cp$_{average}$	2.121(9)	Fe(2)-Cp$_{average}$	2.115(9)
Fe(1)-C(1)-Fe(2)	80.75(15)	Fe(1)-C(3)-Fe(2)	84.14(16)
Fe(1)-C(2)-O(2)	171.7(3)	Sum at N(1)	360.0(5)
C(6)-O(3)-C(9)	116.5(3)	C(6)-C(8)-C(2)	178.7(4)

Complex **7** is a racemate, due to the presence of a stereogenic carbon centre. The IR spectrum (in CH$_2$Cl$_2$) shows the absorption accounting for the cyanide group at 2180 cm^{-1}, while the ^{13}C NMR resonance due to the Fe-bound alkyl carbon has been found at 57.0 ppm. We extended the reactivity of **5a** also to the reaction with NaBH$_4$, but this resulted non selective and a complicated mixture of products was obtained.

Conclusions

The synthetic procedure to access cationic diiron aminocarbyne compounds starting from the easily available [Fe$_2$Cp$_2$(CO)$_4$] has been optimized, negating the need of difficult purification procedures of intermediate species. The electrophilic behaviour of aminocarbyne complexes has been investigated, and according to DFT results the aminocarbyne function is the privileged site of hydride addition, irrespective of the nature of the N-substituents. Nevertheless, the steric protection exerted by a N-bound xylyl group on the adjacent carbyne centre is responsible for deviating the hydride attack to one Cp ligand, and also to avoid carbyne-cyanide coupling. The introduction of a terminal alkoxycarbene ligand, beside the bridging aminocarbyne, has allowed to ascertain the higher electrophilicity of the former function respect to the latter, in accordance with computational outcomes. Diiron aminocarbyne complexes are versatile starting materials to obtain a large variety of highly functionalized hydrocarbyl ligands, that are not accessible by conventional organic chemistry;[15,27] the present results indicate that a fine control of regiochemistry is viable by an accurate choice of nitrogen substituents and co-ligands.

Experimental section

General experimental details: All the reactions were routinely carried out under nitrogen atmosphere, using standard Schlenk techniques. Solvents were purchased from Sigma Aldrich and distilled before use under nitrogen from appropriate drying agents. Deuterated solvents and organic reactants were commercial products (Sigma Aldrich) of the highest purity available and used as

received. [Fe$_2$(CO)$_4$Cp$_2$] was purchased from Strem and used as received. CNMe,[28] Li$_2$Cu(CN)Me$_2$,[29] [Fe$_2$\{μ-C(CN)NMe$_2$\}(μ-CO)(CO)$_2$Cp$_2$] [13] and [Fe$_2$\{μ-CN(Me)(R)\}(μ-CO)(CO)\{C=O\}Me\}Cp$_2$] (R = Me,[22] Xyl [20]) were prepared according to published procedures. Once isolated, the metal products were conserved under nitrogen. Chromatography separations were carried out on columns of deactivated alumina (4% *w/w* water) or celite. The reaction vessels were oven dried at 140°C prior to use, evacuated (10^{-2} mmHg) and then filled with nitrogen. NMR spectra were recorded at 298 K on either a Mercury Plus 400 instrument or a Bruker Avance II DRX400 instrument equipped with a BBFO broadband probe. The chemical shifts for ^{1}H and ^{13}C were referenced to the non-deuterated aliquot of the solvent. NMR signals related to a secondary isomeric form (where it has been possible to detect/resolve it) are italicized. The ^{1}H and ^{13}C NMR spectra were assigned with assistance of ^{1}H,^{13}C correlation measured through *gs*-HSQC and *gs*-HMBC experiments.[30] Infrared spectra were recorded on a Perkin-Elmer Spectrum 2000 FT-IR spectrophotometer. Elemental analyses were performed on a ThermoQuest Flash 1112 Series EA Instrument.

Synthesis and characterization of [Fe$_2$\{μ-CNMe(R)\}(μ-CO)(CO)$_2$Cp$_2$][SO$_3$CF$_3$] [R = Me, 1a; R = CH$_2$Ph, 1b; R = 2,6-C$_6$H$_3$Me$_2$ (Xyl), 1c; R = 2,6-C$_6$H$_3$(Me)(Cl), 1d; R = C$_{10}$H$_7$, 1e].

[Fe$_2$\{μ-CNMe$_2$\}(μ-CO)(CO)$_2$Cp$_2$][SO$_3$CF$_3$], 1a.[12c] A solution of [Fe$_2$Cp$_2$(CO)$_4$] (38.0 g, 0.107 mol) in acetonitrile (ca. 80 mL) was treated with freshly synthesized methyl isocyanide (2.94 g, 0.0716 mol), and the resulting solution was heated at reflux temperature for 6 hours. The volatiles were then removed under reduced pressure. The dark brown residue was dissolved into dichloromethane (ca. 100 mL) and CH$_3$SO$_3$CF$_3$ (8.9 mL, 0.0786 mol) was added dropwise to the stirred solution. The mixture was allowed to stir at room temperature for further 6 hours, and finally charged on an alumina column. Elution with CH$_2$Cl$_2$ allowed to recover unreacted [Fe$_2$(Cp)$_2$(CO)$_4$], then **1a** was eluted by using neat methanol. Slow evaporation of the solvent afforded air stable, dark red crystals of **1a** suitable for X-ray analysis. Yield 26.4 g, 69% (respect to isocyanide). Anal.

Calcd. for $C_{17}H_{16}F_3Fe_2NO_6S$: C, 38.45; H, 3.04; N, 2.64. Found: C, 38.12; H, 3.07; N, 2.59. IR (CH_2Cl_2): ν_{CO} = 2022 (vs), 1990 (w), 1835 (m), ν_{CN} = 1604 (m) cm^{-1}. ^{1}H NMR (dmso-d6): δ = 5.49 (s, 10 H, Cp); 4.17 ppm (s, 3 H, NMe). ^{13}C{^{1}H} NMR (dmso-d6): δ = 315.5 (μ-CN); 257.6 (μ-CO); 209.3 (CO); 90.8 (Cp); 54.6 ppm (NMe).

[Fe_2{μ-CNMe(CH_2Ph)}(μ-CO)(CO)_2Cp_2][SO_3CF_3], 1b.[12c] This compound was obtained as an air stable red solid by a procedure similar to that described for the synthesis of **1a**, from $[Fe_2Cp_2(CO)_4]$ (4.53 g, 12.8 mmol), benzyl isocyanide (1.00 g, 8.54 mmol) and methyl trifluoromethanesulfonate (1.06 mL, 9.4 mmol). Yield 4.51 g, 87% (respect to isocyanide). Anal. Calcd. for $C_{23}H_{20}F_3Fe_2NO_6S$: C, 45.50; H, 3.32; N, 2.31. Found: C, 45.70; H, 3.25; N, 2.36. IR (CH_2Cl_2): ν_{CO} = 2021 (vs), 1990 (w-m), 1836 (s), ν_{CN} = 1605 (m-s), ν_{CC} = 1591 (m), 1578 (m) cm^{-1}. ^{1}H NMR (dmso-d6): δ = 7.53, 7.46 (m, 5 H, Ph); 5.77, 5.76 (m, 2 H, CH_2); 5.57, 5.48 (s, 10 H, Cp); 3.98 ppm (s, 3 H, NMe). ^{13}C{^{1}H} NMR (dmso-d6): δ = 320.0 (μ-CN); 256.8 (μ-CO); 209.2 (CO); 134.7 (*ipso*-Ph); 129.7, 129.0, 127.9 (Ph); 91.1, 91.0 (Cp); 71.2 (CH_2); 51.8 ppm (NMe).

[Fe_2{μ-CNMe(Xyl)}(μ-CO)(CO)_2Cp_2][SO_3CF_3], 1c.[8] A solution of 2,6-dimethylphenyl isocyanide (1.00 g, 7.62 mmol) in acetonitrile (15 mL) was added dropwise along 20 minutes into a solution of $[Fe_2Cp_2(CO)_4]$ (4.05 g, 11.4 mmol) in acetonitrile (50 mL). The mixture was left stirring at room temperature for 18 h, then the volatiles were removed under reduced pressure. The red-brown residue was dissolved into dichloromethane (70 mL) and $CH_3SO_3CF_3$ (0.95 mL, 8.4 mmol) was added dropwise to the stirred solution. The mixture was allowed to stir at room temperature for further 6 hours, and finally charged on an alumina column. Elution with CH_2Cl_2 allowed to recover unreacted $[Fe_2(Cp)_2(CO)_4]$, then **2a** was separated using THF (vide infra), and **1c** was finally eluted with neat methanol. The solvent was removed under reduced pressure, then CH_2Cl_2 (10 mL) and petroleum ether (70 mL) were added to the residue in the order given. The mixture was dried under vacuum, thus **1c** was afforded as an air stable red powder. Yield 4.35 g, 92% (respect to isocyanide). Anal. Calcd. for $C_{24}H_{22}F_3Fe_2NO_6S$: C, 46.40; H, 3.57; N, 2.25. Found: C, 46.26; H,

3.68; N, 2.37. IR (CH$_2$Cl$_2$): ν_{CO} = 2024 (vs), 1992 (m), 1840 (s), ν_{CN} = 1606 (w), ν_{CC} = 1547 (w), 1530 (m) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 7.34-7.28 (m, 3 H, C$_6$H$_3$Me$_2$); 5.44, 4.78 (s, 10 H, Cp); 4.42 (s, 3 H, NMe); 2.66, 2.10 ppm (s, 6H, C$_6$H$_3$Me$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 327.8 (μ-CN); 253.9 (μ-CO); 208.6 (CO); 133.7-129.8 (C$_6$H$_3$Me$_2$); 91.1, 91.3 (Cp); 56.3 (NMe); 19.3, 18.1 ppm (C$_6$H$_3$Me$_2$).

[Fe$_2$\{μ-CNMe(2,6-C$_6$H$_3$MeCl)\}(μ-CO)(CO)$_2$Cp$_2$][SO$_3$CF$_3$], 1d. This compound was obtained as an air stable red solid by a procedure similar to that described for the synthesis of **1c**, from [Fe$_2$Cp$_2$(CO)$_4$] (3.75 g, 10.6 mmol), 2-chloro-6-methylphenyl isocyanide (1.00 g, 6.60 mmol) and methyl trifluoromethanesulfonate (0.90 mL, 8.0 mmol). Yield 3.30 g, 78% (respect to isocyanide). Crystals suitable for X-ray analysis were collected by slow diffusion of diethyl ether into a dichloromethane solution of **1d**, at −30 °C. Anal. Calcd. for C$_{23}$H$_{19}$ClF$_3$Fe$_2$NO$_6$S: C, 43.06; H, 2.98; N, 2.18. Found: C, 42.70; H, 3.06; N, 2.21. IR (CH$_2$Cl$_2$): ν_{CO} = 2030 (vs), 1998 (m), 1841 (m) cm^{-1}; ν_{CN} = 1606 (w), ν_{CC} = 1544 (w), 1522 (w) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 7.58-7.43 (3 H, C$_6$H$_3$MeCl); 5.47, *5.46*, 4.87, *4.81* (s, 10 H, Cp); 4.46, *4.45* (s, 3 H, NMe); *2.77*, 2.17 ppm (s, 3 H, C$_6$H$_3$MeCl). Isomer ratio 3:2. ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 331.5 (μ-CN); *253.2*, 251.0 (μ-CO); *208.1*, 207.2 (CO); 145.6, 136.1, 134.8, 132.9, 131.6, 130.9, 130.7, 130.4, 129.4, 129.1, 128.5 (C$_6$H$_3$MeCl); 90.7, 89.9, *89.6* (Cp); 55.7, *55.4* (NMe); 19.0, *17.7* ppm (C$_6$H$_3$MeCl).

[Fe$_2$\{μ-CNMe(C$_{10}$H$_7$)\}(μ-CO)(CO)$_2$Cp$_2$][SO$_3$CF$_3$], 1e. This compound was obtained as an air stable red solid by a procedure similar to that described for the synthesis of **1c**, from [Fe$_2$Cp$_2$(CO)$_4$] (3.70 g, 10.5 mmol), 2-naphthyl isocyanide (1.00 g, 6.53 mmol) and methyl trifluoromethanesulfonate (0.88 mL, 7.8 mmol). Yield 2.73 g, 65% (respect to isocyanide). Anal. Calcd. for C$_{26}$H$_{20}$F$_3$Fe$_2$NO$_6$S: C, 48.55; H, 3.13; N, 2.18. Found: C, 48.40; H, 3.11; N, 2.25. IR (CH$_2$Cl$_2$): ν_{CO} = 2021 (vs), 1989 (w-m), 1836 (m) cm^{-1}; ν_{CN} = 1605 (w), ν_{CC} = 1565 (w-m), 1548 (w), 1539 (w) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 8.11, 7.98, 7.65 (m, 7 H, C$_{10}$H$_7$); 5.50, 4.71 (s, 10 H, Cp); 4.67 ppm (s, 3 H, NMe). ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 324.5 (μ-CN); 254.4 (μ-CO); 208.8,

207.7 (CO); 147.5 (ipso-$C_{10}H_7$); 133.4, 132.8, 130.8, 129.0, 127.9, 127.8, 124.2, 122.6 ($C_{10}H_7$); 90.4, 90.1 (Cp); 57.4 ppm (NMe).

Isolation and characterization of [Fe$_2$\{μ-CNMe(R)\}(μ-CO)(CO)(CNR)Cp$_2$][SO$_3$CF$_3$], [R = 2,6-C$_6$H$_3$Me$_2$ (Xyl), 2a;[11c] R = 2,6-C$_6$H$_3$(Me)(Cl), 2b; R = C$_{10}$H$_7$, 2c]. These compounds were obtained as side products of the reactions leading to **1c-e**, and separated by chromatography using tetrahydrofuran as eluent. The solvent was removed under reduced pressure, then CH$_2$Cl$_2$ (5-10 mL) and petroleum ether (40-60 mL) were added to the residue in the order given. The mixture was dried under vacuum, thus **2a-c** were afforded as air stable powders.

[Fe$_2$\{μ-CNMe(Xyl)\}(μ-CO)(CO)\{CN(Xyl)\}Cp$_2$][SO$_3$CF$_3$], 2a.[11c] Dark brown solid. Yield 166 mg, 3% (respect to xylyl isocyanide). Anal. Calcd. for C$_{32}$H$_{31}$F$_3$Fe$_2$N$_2$O$_5$S: C, 53.06; H, 4.31; N, 3.87. Found: C, 53.23; H, 4.30; N, 3.78. IR (CH$_2$Cl$_2$): ν_{CO} = 1991 (vs), 1824 (s), ν_{CN} = 2120 (vs) cm^{-1}.

[Fe$_2$\{μ-CNMe(2,6-C$_6$H$_3$MeCl)\}(μ-CO)(CO)\{CN(2,6-C$_6$H$_3$MeCl)\}Cp$_2$][SO$_3$CF$_3$], 2b. Black solid. Yield 505 mg, 10% (respect to 2-chloro-6-methylphenyl isocyanide). Anal. Calcd. for C$_{30}$H$_{25}$Cl$_2$F$_3$Fe$_2$N$_2$O$_5$S: C, 47.09; H, 3.29; N, 3.66. Found: C, 46.80; H, 3.16; N, 3.81. IR (CH$_2$Cl$_2$): ν_{CO} = 1997 (s), 1829 (m), ν_{CN} = 2117 (vs) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 7.56-7.04 (C$_6$H$_3$MeCl); 5.46, 5.41, 5.34, 5.32, 4.86, 4.82, 4.79, 4.73 (s, Cp); 4.54, 4.46 (s, NMe); 2.35, 2.28, 2.22, 2.17 ppm (s, C$_6$H$_3$MeCl). Isomer ratio 2:1.5:2:1.

[Fe$_2$\{μ-CNMe(C$_{10}$H$_7$)\}(μ-CO)(CO)\{CN(C$_{10}$H$_7$)\}Cp$_2$][SO$_3$CF$_3$], 2c. Dark brown solid. Yield 200 mg, 12% (respect to 2-naphthyl isocyanide). Anal. Calcd. for C$_{36}$H$_{27}$F$_3$Fe$_2$N$_2$O$_5$S: C, 56.27; H, 3.54; N, 3.65. Found: C, 56.48; H, 3.48; N, 3.70. IR (CH$_2$Cl$_2$): ν_{CO} = 1987 (s), 1826 (m), ν_{CN} = 2115 (s), 1507 (w) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 8.11-7.08 (C$_{10}$H$_7$); 5.48, 5.39, 5.38, 4.70, 4.66 (s, Cp); 4.64, 4.62, 4.52 ppm (s, NMe). Isomer ratio ca. 1:1:1.

Reactions of 1b,c with NaBH$_4$. Synthesis and characterization of [Fe$_2${μ-CNMe(Xyl)}(μ-CO)(CO)$_2$Cp(η^4-C$_5$H$_6$)], 3, and [Fe$_2${μ-CHNMe(C$_{10}$H$_7$)}(μ-CO)(CO)$_2$Cp$_2$], 4.

[Fe$_2${μ-CNMe(Xyl)}(μ-CO)(CO)$_2$Cp(η^4-C$_5$H$_6$)], 3. A solution of **1c** (200 mg, 0.322 mmol) in tetrahydrofuran (10 mL) was treated with NaBH$_4$ (65 mg, 1.7 mmol), and the resulting mixture was allowed to stir at room temperature for 20 min. Then the liquid was filtered through an alumina column using tetrahydrofuran as eluent. The volatiles were removed from the filtered solution under reduced pressure. The residue was dissolved into diethyl ether and charged on an alumina column. A red band corresponding to **3** was collected by using neat diethyl ether as eluent. The product was obtained as a red powder upon removal of the solvent under vacuum. Yield 107 mg, 70%. Anal. Calcd. for C$_{23}$H$_{23}$Fe$_2$NO$_3$: C, 58.39; H, 4.90; N, 2.96. Found: C, 58.50; H, 4.97; N, 3.02. IR (CH$_2$Cl$_2$): ν_{CO} = 1960 (vs), 1925 (m), 1771 (m), ν_{CN} = 1551 (w) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 7.15-7.01 (m, 3 H, C$_6$H$_3$Me$_2$); 4.80, *4.70* (s, 5 H, Cp); 4.56, 4.49, 4.11, 3.20 (m, 4 H, C$_5$H$_4$); 4.32, 4.14 (s, 3 H, NMe); 3.05, 2.79 (d, 2 H, ^{2}J$_{HH}$ = 12 Hz, CH$_2$); 2.44, *2.37, 2.33,* 2.28 ppm (s, 6 H, C$_6$H$_3$Me$_2$). Isomer ratio 3:2. ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 333.6 (μ-CN); 276.4 (μ-CO); 223.1, *218.4,* 213.6 (CO); 148.0 (*ipso*-C$_6$H$_3$Me$_2$); 134.6, 133.8, 132.8, 132.7, 129.9, 129.2, 128.3, 127.9, 127.8, 127.5, 125.6 (C$_6$H$_3$Me$_2$); 85.0, *82.3* (Cp); 90.0, 87.5, 85.0, 81.7, 64.5, 62.0 (C$_5$H$_4$); 52.7, *52.6* (NMe); 45.4 (CH$_2$); 18.2, 18.1, 17.8, 17.7 ppm (C$_6$H$_3$Me$_2$).

[Fe$_2${μ-CHNMe(C$_{10}$H$_7$)}(μ-CO)(CO)$_2$Cp$_2$], 4. This product was obtained by using a procedure closely resembling that described for **3**, from **1e** (200 mg, 0.311 mmol) and NaBH$_4$ (60 mg, 1.6 mmol). Dark green solid. Yield 131 mg, 85%. Anal. Calcd. for C$_{25}$H$_{21}$Fe$_2$NO$_3$: C, 60.64; H, 4.28; N, 2.83. Found: C, 60.38; H, 4.16; N, 2.90. IR (CH$_2$Cl$_2$): 1955 (vs, ν_{CO}), 1925 (m, ν_{CO}), 1765 (m, ν_{CO}), 1625 (w), 1597 (w), 1508 (w) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 13.11 (μ-CH); 7.94-7.02 (7 H, C$_{10}$H$_7$); 4.79, 4.72 (s, 10 H, Cp); 3.18 ppm (s, 3 H, NMe). ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 277.1 (μ-CO); 213.8 (CO); 182.4 (μ-CN); 148.2 (*ipso*-Ph); 134.5, 129.2, 128.9, 127.6, 127.3, 126.8, 124.0, 118.8, 112.0 (C$_{10}$H$_7$); 88.5, 87.3 (Cp); 40.4 ppm (NMe).

Reactions of 1a,c with NBu₄CN.

A) Synthesis of [Fe₂{μ-CN(Me)(Xyl)}(μ-CO)(CO)(CN)(Cp)₂].[22]

NBu₄CN (43 mg, 0.16 mmol) was added to a solution of **1c** (90 mg, 0.15 mmol) in CH_2Cl_2 (12 mL). The mixture was allowed at room temperature for 6 hours, then it was filtered on an alumina column by using neat dichloromethane as eluent. The product was isolated as an air stable green powder upon removal of the solvent under vacuum. Yield 59 g, 84%. Anal. Calcd. for $C_{23}H_{22}Fe_2N_2O_2$: C, 58.76; H, 4.72; N, 5.96. Found: C, 58.58; H, 4.82; N, 5.90. IR (CH_2Cl_2): ν_{CO} = 1981 (vs), 1804 (s), $\nu_{C\equiv N}$ = 2091 (w) cm^{-1}. ^{1}H NMR (CDCl₃): δ = 7.3 (3 H, C₆*H*₃Me₂); 5.07, 4.22 (s, 10 H, Cp); 4.46 (s, 3 H, NMe); 2.65, 2.45 ppm (s, 6 H, C₆H₃*Me*₂).[22]

B) Study of the stability of [Fe₂{μ-C(CN)NMe₂}(μ-CO)(CO)₂Cp₂].[13]

The air- and water-stability of the title compound was monitored via IR spectroscopy. The compound appeared almost stable after ten days in contact with air. A portion of the compound (0.50 mmol) was dissolved into CH_2Cl_2 (2 mL), and the solution was diluted with H_2O (5 mL). After 10 days, CH_2Cl_2 (10 mL) was added, then the organic phase was charged on an alumina column. Elution with neat dichloromethane allowed to collect a green band corresponding to [Fe₂{μ-CN(Me)₂}(μ-CO)(CO)(CN)Cp₂],[22,23] which was isolated upon removal of the volatiles under vacuum. Yield 137 mg, 72%. Anal. Calcd. for $C_{16}H_{16}Fe_2N_2O_2$: C, 50.57; H, 4.24; N, 7.37. Found: C, 50.46; H, 4.15; N, 7.46. IR (CH_2Cl_2): ν_{CO} = 1981 (vs), 1804 (s), ν_{CN} = 2091 (w), 1578 (w) cm^{-1}. ^{1}H NMR (CDCl₃): δ = 4.83, 4.79 (s, 10 H, Cp); 4.28, 4.14 ppm (s, 6 H, NMe).[23]

Synthesis and characterization of [Fe₂{μ-CN(Me)(R)}(μ-CO)(CO){C(OMe)Me}Cp₂][SO₃CF₃] (R = Me, 5a; R = Xyl, 5b).

[Fe₂{μ-CN(Me)₂}(μ-CO)(CO){C(OMe)Me}Cp₂][SO₃CF₃], 5a. A solution of [Fe₂{μ-CN(Me)₂}(μ-CO)(CO){C=O)Me}Cp₂] (150 mg, 0.378 mmol) in tetrahydrofuran (15 mL) was

treated with methyl trifluoromethanesulfonate (0.047 mL, 0.42 mmol). The mixture was allowed to stir at room temperature for one hour, then it was filtrated on a celite pad. Addition of diethyl ether (50 mL) to the filtrated solution resulted in precipitation of an air stable red powder. Yield 178 mg, 84%. Crystals suitable for X-ray analysis were obtained from a CH_2Cl_2/diethyl ether mixture, stored at −20 °C. Anal. Calcd. for $C_{19}H_{22}F_3Fe_2NO_6S$: C, 40.67; H, 3.95; N, 2.50. Found: C, 40.82; H, 3.87; N, 2.59. IR (CH_2Cl_2): ν_{CO} = 1986 (vs), 1808 (s), ν_{CN} = 1586 (m) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ = 5.04, 5.02 (s, 10 H, Cp); 4.10, 4.04 (s, 6 H, NMe); 3.74 (s, 3 H, OMe); 2.65 ppm (s, 3 H, Fe=CMe). ^{13}C$\{^1$H$\}$ NMR (CD_2Cl_2): δ = 330.7 (Fe=C); 325.4 (μ-C); 262.2 (μ-CO); 211.8 (CO); 91.1, 88.4 (Cp); 62.2 (OMe); 52.9, 52.6 (NMe); 42.2 ppm (Fe=C*Me*).

[Fe₂{µ-CN(Me)(Xyl)}(µ-CO)(CO){C(OMe)Me}Cp₂][SO₃CF₃], 5b. This product was obtained by the same procedure as that described for the synthesis of **5a**, from [Fe₂{µ-CN(Me)(Xyl)}(µ-CO)(CO){C=O)Me}Cp₂] (170 mg, 0.349 mmol) and methyl trifluoromethanesulfonate (0.043 mL, 0.38 mmol). Red solid. Yield 186 mg, 82%. Anal. Calcd. for $C_{26}H_{28}F_3Fe_2NO_6S$: C, 47.95; H, 4.33; N, 2.15. Found: C, 48.08; H, 4.20; N, 2.28. IR (CH_2Cl_2): ν_{CO} = 1987 (vs), 1809 (s), ν_{CN} = 1522 (m) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ = 7.5-7.2 (3 H, C$_6$*H*$_3$Me$_2$); 5.19, 4.43 (s, 10 H, Cp); 4.35 (s, 3 H, NMe); 3.94 (s, 3 H, OMe); 2.90, 2.54, 2.35 ppm (s, 9 H, Fe=CMe + C$_6$H$_3$*Me*$_2$). ^{13}C$\{^1$H$\}$ NMR (CD_2Cl_2): δ = 333.3, 333.0 (μ-C + Fe=C); 262.0 (μ-CO); 212.1 (CO); 147.4 (*ipso*-C$_6$H$_3$Me$_2$); 132.9, 132.8, 130.2, 128.9, 128.9 (C$_6$H$_3$Me$_2$); 91.8, 88.0 (Cp); 63.3 (OMe); 55.0 (NMe); 43.6 (Fe=C*Me*); 18.6, 17.2 ppm (C$_6$H$_3$*Me*$_2$).

Reactions of 5a with amines. Synthesis and characterization of [Fe₂(µ-CNMe₂)(µ-CO)(CO){C(Me)NH(R)}(Cp)₂][SO₃CF₃] (R = ^{i}Pr, 6a; R = Et, 6b). A solution of **5a** (88 mg, 0.157 mmol) in tetrahydrofuran (12 mL) was treated with NH₂^{i}Pr (0.10 mL, 1.16 mmol). The mixture was stirred for 2 hours, then the volatile materials were removed under vacuum. The resulting residue was dissolved into CH_2Cl_2 (5 mL) and charged on an alumina column. A red band

corresponding to **6a** was collected by using methanol as eluent, then the product was isolated as a red solid after removal of the solvent under vacuum. Yield 78 mg, 84%. Anal. Calcd. for $C_{21}H_{27}F_3Fe_2N_2O_5S$: C, 42.88; H, 4.63; N, 4.76. Found: C, 43.06; H, 4.66; N, 4.67. IR (CH_2Cl_2): ν_{CO} = 1973 (vs), 1795 (s), ν_{CN} = 1570 (m) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 4.82, 4.61 (s, 10 H, Cp); 4.24, 4.04 (s, 6 H, NMe$_2$); 3.66 (septet, $^3J_{HH}$ = 6.4 Hz, 1 H, C*H*Me$_2$); 1.95 (s, 3 H, Fe=CMe); 0.94, 0.90 ppm (d, $^3J_{HH}$ = 6.4 Hz, 6 H, CH*Me$_2$*). ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 330.4 (μ-CN); 271.6 (μ-CO); 261.2 (Fe=*C*); 211.7 (CO); 88.6, 88.3 (Cp); 53.9, 52.1 (NMe$_2$); 50.8 (*C*HMe$_2$); 32.8 (Fe=C*Me*); 21.6, 21.4 ppm (CH*Me$_2$*).

To obtain **6b**, a large excess of NH$_2$Et was bubbled into a solution of **5a** (130 mg, 0.232 mmol) in CH$_2$Cl$_2$ (20 mL), then the mixture was allowed to stir at room temperature for 45 min. The final solution was charged on al alumina column, and a red band corresponding to **6b** was eluted using neat CH$_2$Cl$_2$ as eluent. The product was isolated as a red powder upon removal of the solvent under vacuum. Yield 93 mg, 70%. Anal. Calcd. for $C_{20}H_{25}F_3Fe_2N_2O_5S$: C, 41.84; H, 4.39; N, 4.88. Found: C, 41.65; H, 4.47; N, 4.95. IR (CH$_2$Cl$_2$): ν_{CO} = 1975 (vs), 1796 (s), ν_{CN} = 1566 (m) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 8.46 (s, 1 H, NH); 4.98, 4.84 (s, 10 H, Cp); 4.46, 4.28 (s, 6 H, NMe$_2$); 3.34, 3.26 (m, 2 H, C*H$_2$*CH$_3$); 2.23 (s, 3 H, Fe=CMe); 1.01 ppm (t, $^3J_{HH}$ = 7.34, 6.60 Hz, 3 H, CH$_2$C*H$_3$*). ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 329.1 (μ-CN); 269.1 (μ-CO); 261.7 (Fe=*C*); 211.9 (CO); 89.0, 88.2 (Cp); 54.3, 52.9 (NMe$_2$); 44.0 (*C*H$_2$); 33.5 (Fe=C*Me*); 13.8 ppm (*C*H$_3$).

The reaction of **5a** (0.80 mmol) with NHEt$_2$ (0.80 mmol) was carried out by a procedure similar to that described for the synthesis of **6a**. Compound [Fe$_2${μ-CN(Me)$_2$}(μ-CO)(CO){C=O)Me}Cp$_2$] [14] was finally recovered in ca. 70% yield after alumina chromatography.

Reaction of 5a with NBu$_4$CN: synthesis and characterization of [Fe$_2${μ-CN(Me)$_2$}(μ-CO)(CO){C(CN)(OMe)Me}Cp$_2$], 7. A solution of **5a** (120 mg, 0.214 mmol) in dichloromethane (15 mL) was treated with NBu$_4$CN (69 mg, 0.26 mmol). The mixture was stirred for 1 hour, then

the resulting solution was charged on an alumina column. The band corresponding to **7** was collected by using neat dichloromethane as eluent, then the product was isolated as a dark red solid upon removal of the solvent under vacuum. Yield 84 mg, 90%. Crystals suitable for X ray analysis were collected by a CH_2Cl_2 solution layered with petroleum ether and stored at −30 °C. Anal. Calcd. for $C_{19}H_{22}Fe_2N_2O_3$: C, 52.09; H, 5.06; N, 6.39. Found: C, 52.20; H, 4.99; N, 6.44. IR (CH_2Cl_2): $\nu_{C\equiv N}$ = 2180 (w), ν_{CO} = 1965 (vs), 1774 (s), ν_{CN} = 1561 (m) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 4.74, 4.54 (s, 10 H, Cp); 4.44, 4.06 (s, 6 H, NMe$_2$); 2.71 (s, 3 H, OMe); 1.43 ppm (s, 3 H, FeCMe). ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 332.8 (μ-CN); 270.7 (μ-CO); 215.4 (CO); 130.2 (C≡N); 89.2, 86.6 (Cp); 57.0 (Fe*C*Me); 53.0, 50.0 (NMe$_2$); 50.3 (OMe); 27.1 ppm (Fe*CMe*).

X-ray crystallography.

Crystal data and collection details for **1a**, **1d**·CHCl$_3$, **6a** and **7** are reported in Table 6. The diffraction experiments were carried out on a Bruker SMART 2000 (**6a**) and Bruker APEX II (**1a**, **1d**·CHCl$_3$, and **7**) diffractometer, equipped with a CCD (**6a**) or CMOS (**1a**, **1d, 7**) detector using Mo-Kα radiation. Data were corrected for Lorentz polarization and absorption effects (empirical absorption correction SADABS).[31] Structures were solved by direct methods and refined by full-matrix least-squares based on all data using F^2.[32] Hydrogen atoms were fixed at calculated positions and refined by a riding model, except N-bonded hydrogens of **6a**, which were located in the Fourier map. All non-hydrogen atoms were refined with anisotropic displacement parameters, unless otherwise stated. Crystals of **1a** contain half of the cation and half of the anion located on *m*. Crystals of **6a** contain two independent molecules, with similar structures and bonding parameters. One Cp ligand, the Me and Cl bonded to the aromatic ring in the cation, the [CF$_3$SO$_3$]$^-$ anion and the CHCl$_3$ molecule of **1d**·CHCl$_3$ are disordered, as well as the ^{i}Pr group of **6a**. Disordered atomic positions were split and refined using one occupancy parameter per disordered group.

Table 6. Crystal data and measurement details for **1a**, **1d**·CHCl$_3$, **6a** and **7**.

	1a	1d·CHCl₃	6a	7
Formula	$C_{17}H_{16}F_3Fe_2NO_6S$	$C_{24}H_{20}Cl_4F_3Fe_2NO_6S$	$C_{21}H_{27}F_3Fe_2N_2O_5S$	$C_{19}H_{22}Fe_2N_2O_3$
FW	531.07	760.97	588.20	438.08
T, K	100(2)	295(2)	293(2)	100(2)
λ, Å	0.71073	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Triclinic	Triclinic	Orthorhombic
Space group	$Pnma$	$P\bar{1}$	$P\bar{1}$	$P2_12_12_1$
a, Å	15.0150(14)	8.6653(7)	13.562(3)	8.3837(7)
b, Å	10.0255(9)	13.3677(13)	13.585(3)	13.0412(10)
c, Å	13.0438(12)	14.6970(12)	15.886(3)	16.6589(13)
α, °	90	70.288(3)	102.20(3)	90
β, °	90	73.740(2)	109.69(3)	90
γ °	90	71.215(2)	107.32(3)	90
Cell Volume, Å³	1963.5(3)	1489.0(2)	2467.6(11)	1821.4(3)
Z	4	2	4	4
D_c, g·cm⁻³	1.796	1.697	1.583	1.598
μ, mm⁻¹	1.647	1.462	1.317	1.614
F(000)	1072	764	1208	904
Crystal size, mm	0.19×0.16×0.12	0.19×0.16×0.12	0.22×0.19×0.14	0.19×0.13×0.12
θ limits, °	2.068–26.999	1.672–25.499	1.451–27.485	1.983–25.875
Reflections collected	25914	18616	27089	13635
Independent reflections	2264 [R_{int} = 0.0609]	5539 [R_{int} = 0.0279]	11334 [R_{int} = 0.0431]	3494 [R_{int} = 0.0569]
Data / restraints /parameters	2264 / 0 / 149	5539 / 470 / 474	11334 / 241 / 629	3494 / 42 / 240
Goodness of fit on F²	1.139	1.051	1.027	1.085
R_1 ($I > 2\sigma(I)$)	0.0356	0.0567	0.0493	0.0304
wR_2 (all data)	0.0691	0.1621	0.1407	0.0583
Largest diff. peak and hole, e Å⁻³	0.501 / –0.475	1.409 / –0.921	0.845 / –0.365	0.293 / –0.316

Computational studies. The electronic structures of the compounds were optimized using the range-separated ωB97X DFT functional [33] in combination with Ahlrichs' split-valence polarized basis set. [34] The "restricted" formalism was applied in all cases. The stationary points were

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characterized by IR simulations (harmonic approximation), from which zero-point vibrational energies and thermal corrections (T= 298.15 K) were obtained. [35] Partial charges were obtained from the Mulliken and Hirshfeld population analyses. [36] The software used was Gaussian 09. [37]

Supporting Information. CCDC reference numbers 1575217 (**1a**), 1575218 (**1d**·CHCl$_3$), 1575219 (**6a**) and 1575220 (**7**) contain the supplementary crystallographic data for the X-ray studies reported in this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [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].

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