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Coupling of Isocyanide and μ-Aminocarbyne Ligands in Diiron Complexes Promoted by Hydride Addition

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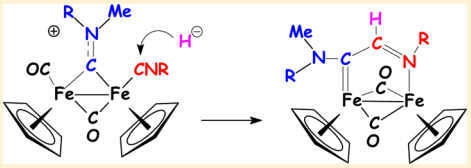
Supporting Information

ABSTRACT: The diiron μ-aminocarbyne complexes $[Fe_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)(CNR')(Cp)_2][SO_3CF_3]$ (R = R′ = Xyl, **2a**; R = Xyl, R′ = Me, **2b**; R = Xyl, R′ = Bu^t, **2c**; R = Xyl, R′ = *p*-$C_6H_4CF_3$, **2d**; R = Me, R′ = Xyl, **2e**; Xyl = 2,6-$Me_2C_6H_3$), containing an isocyanide ligand, have been obtained via CO replacement with the appropriate CNR′ ligand from $[Fe_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)_2(Cp)_2][SO_3CF_3]$ (R = Xyl, **1a**; R = Me, **1b**). Compound **2a**, upon treatment with $NaBH_4$ and heating at reflux temperature in THF solution, is transformed into the aminocarbene−aldimine $[Fe_2\{\mu\text{-}\eta^1(C):\eta^1(N)\text{-}CN(Me)(Xyl)CH{=}N(Xyl)\}(\mu\text{-}CO)_2(Cp)_2]$ (**3**) in moderate yield. The reactions occurs via formation of the formimidoyl complex $[Fe_2\{\mu\text{-}CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)\{C(H){=}NXyl\}(Cp)_2]$ (**4a**), which has been isolated by reacting **2a** with $NaBH_4$ at 0 °C. Likewise, the formimidoyl complex $[Fe_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)\{C(H){=}NR'\}(Cp)_2]$ (R = Xyl, R′ = Me, **4b**; R = Me, R′ = Xyl, **4c**) have been obtained from **2b**,**e**, respectively, upon reaction with $NaBH_4$, but these complexes do not convert into the aminocarbene−aldimine complexes analogous to **3**. Reactions of **2a** with other nucleophiles have been investigated, without obtaining any product similar to **3**. Complex **2a** reacts with NaCN or with $LiPPh_2$, resulting in isocyanide displacement and formation of $[Fe_2\{\mu\text{-}CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)(CN)(Cp)_2]$ (**5**) and $[Fe_2\{\mu\text{-}CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)(PPh_2)(Cp)_2]$ (**6**), respectively. Addition of the organocopper reagent $Li_2CuCNMe_2$ to **2a** affords the acyl complex $[Fe_2\{\mu\text{-}CN(Me)(Xyl)\}(\mu\text{-}CO\{C(O)Me\}(CNXyl)(Cp)_2]$ (**7**). The thiocarbyne complex $[Fe_2\{\mu\text{-}CSMe\}(\mu\text{-}CO)(CO)(CNXyl)(Cp)_2][SO_3CF_3]$ (**8**), which shows analogies with **2a**, reacts with $NaBH_4$, affording the carbene derivative $[Fe_2\ \mu\text{-}\{C(SMe)(H)\}(\mu\text{-}CO)(CO)(CNXyl)(Cp)_2]$ (**9**). The molecular structures of **2a** and **3** have been determined by X-ray diffraction studies.



INTRODUCTION

Isocyanides are extremely valuable building blocks for the construction of complex molecular structures and, in particular, of heterocycles. Ever since the Passerini and Ugi reactions were discovered, multicomponent reactions (MCRs) based on isocyanides have had a continuous development.[1] In addition, the past decade has witnessed a remarkable growth of interest for transition-metal-promoted isocyanide insertion, providing further possibilities for the use of isocyanides as C1 synthons.[2] This field has been so far dominated by palladium,[3] but it is reasonable to assume that there is potential for expanding metal-promoted isocyanide transformations. This is suggested by the fact that isocyanides have long proved to be both excellent ligands and reactive species in a variety of transition-metal complexes.[4]

Our specific interest concerns diiron complexes and is aimed at finding new reactions, based on Fe, potentially able to replace, or provide alternatives to, the use of rare, expensive, or toxic metals.[5] Indeed, examples of isocyanide insertion into Fe−C bonds are known,[6] but catalytic applications are very limited.[7] On the other hand, diiron complexes with isocyanide ligands have long been known, and these ligands, like carbonyls, can assume both bridging and terminal coordination.[8] More recently, interest toward diiron isocyanide complexes has resurged as a consequence of the fact that these compounds can be regarded as models for the active site of [FeFe]ase natural enzymes.[9] We have previously published two different approaches to C−C bond formation involving diiron complexes and isocyanides. One method (Scheme 1a) consists of alkyne insertion into the Fe−C bond of a bridging isocyanide.[10] The second example pertains to the addition of isocyanide to a bridging vinyliminium, affording a ketenimine (Scheme 1b).[11] In this case metal activation concerns the bridging organic frame and isocyanide is used as a reagent rather than a ligand.

In light of these results, we decided to extend studies to diiron complexes of the type $[Fe_2\{\mu\text{-}CN(R)Me\}(\mu\text{-}CO)(CO)(CNR')(Cp)_2]^+$ (R = Me, Xyl; Xyl = 2,6-$Me_2C_6H_3$) containing both isocyanide (as a terminally bound ligand) and activated bridging ligands. In particular, we investigated μ-aminocarbyne ligands in that they exhibit a remarkable electrophilic character which, in theory, should be exploited to promote assembly with terminally bound ligands. For example, we have previously reported that the aminocarbyne diiron complexes $[Fe_2(\mu\text{-}CNMe_2)(\mu\text{-}CO)(CO)(L)(Cp)_2][SO_3CF_3]$ (L = nitriles,[12] imines[13]) undergo attack by acetylides (LiCCR) at the unsaturated L ligands, which consequently rearrange and undergo coupling with the bridging aminocarbyne. In these

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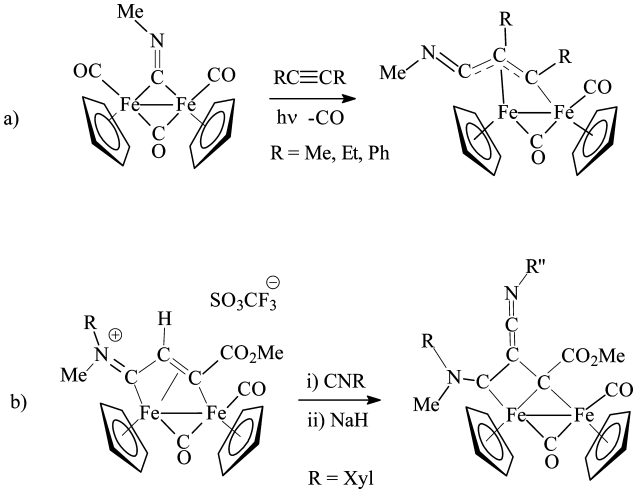
Scheme 1. Examples of Isocyanide Incorporation into Bridging Ligands



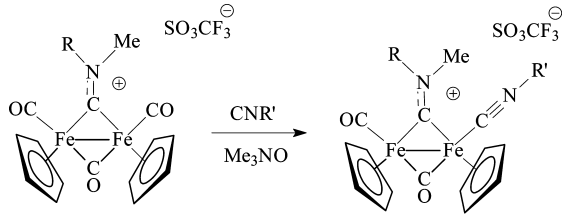
examples, assembly of three components (aminocarbyne, acetylide, and unsaturated N-containing ligands) gave rise to the formation of a more complex molecular fragment, bridging the two Fe atoms.[12,13]

Here, we report on the results obtained with a similar approach, aimed at assembling isocyanides and bridging ligands, initiated by nucleophilic addition. The final target is to find out new C−C bond forming reactions assisted by iron.

RESULT AND DISCUSSION

As a first step, we synthesized a few diiron μ-aminocarbyne complexes containing a terminally bound isocyanide ligand (see Scheme 2, complexes **2a**−**e**). To the best of our knowledge,

Scheme 2. CO Displacement by Isocyanides



	R	R'	
1a	Xyl	Xyl	**2a**
1a	Xyl	Me	**2b**
1a	Xyl	Bu^t	**2c**
1a	Xyl	*p*-$C_6H_4CF_3$	**2d**
1b	Me	Xyl	**2e**

complexes **2a**−**e** have been not reported in the literature, in spite of the fact that the analogous $[Fe_2(\mu\text{-}CNMe_2)(\mu\text{-}CO)(CO)(CNMe)(Cp)_2]^+$ has been described by Manning and co-workers several years ago.[14] Therefore, their preparation and properties are detailed in the Experimental Section. Complexes **2a**−**e** have been conveniently obtained from their aminocarbyne precursors **1a** upon replacement of CO with the appropriate isocyanide, using Me_3NO to favor CO displacement (Scheme 2).

All of the compounds have been characterized by IR and NMR spectroscopy and elemental analysis. The structure of **2a** has been ascertained by X-ray diffraction studies (Figure 1 and Table 1). The Cp ligands adopt a cis geometry relative to the

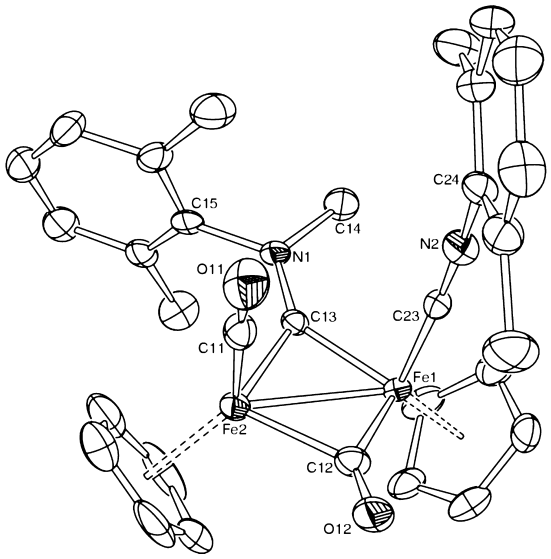


Figure 1. Molecular structure of **2a**, with key atoms labeled (the counteranion $SO_3CF_3^-$ and all H atoms have been omitted). Displacement ellipsoids are at the 30% probability level.

$Fe_2(\mu\text{-}C)_2$ plane, as previously found for analogous diiron and diruthenium complexes. Moreover, the bulky Xyl group in the bridging ligand μ-CN(Me)(Xyl) points toward the opposite side of the terminal CNXyl ligand, in order to minimize steric repulsions.

The IR spectra of **2a**−**e** (in CH_2Cl_2 solution) exhibit the usual ν(CO) pattern consisting of terminal and bridging carbonyl absorptions (e.g., for **2b** at 1989 and 1823 cm^{-1}, respectively). Complexes **2** should, in theory, display different isomeric forms: *cis*,*trans*, due to the mutual position of the Cp ligands with respect to the Fe−Fe bond, and *E*,*Z*, associated with the different orientations that the N substituents Me and Xyl (Xyl = 2,6$Me_2C_6H_3$) can assume with respect to the nonequivalent Fe atoms, as a consequence of the double-bond character of the μ-C−N interaction. Usually, complexes of the type $[Fe_2\{\mu\text{-}CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)(L)(Cp)_2]$ (L = halides, cyanides, alkyl, acyl, etc.) in chlorinated solvents preferentially adopt the *cis* isomeric form with *E* configuration, which is the same observed in the solid state for **2a**.[15,13] NMR data show that the isomeric composition of the isocyanide complexes **2a**−**d** is consistent with that usually found in analogous diiron complexes. In particular, ^{1}H NMR spectra and NOE experiments indicate that **2c**,**d** are formed exclusively as *cis* isomers with the isocyanide ligand and the *N*-methyl on the same side (*E* configuration). Conversely, complexes **2a**,**b** exist in both *E* and Z forms, but the *E* isomer is more abundant. ^{13}C NMR spectra of **2a**−**e** show the typical low-field resonance due to the aminocarbyne center (e.g., at δ 332.4 ppm for **2b**) and the signal due to the isocyanide carbon (at δ 116.3 ppm for **2b**).

Having obtained and characterized the new complexes **2a**−**e**, we then investigated their reactions with nucleophiles, aimed at transforming the isocyanide ligands into more reactive species, potentially able to further rearrange and undergo coupling with the bridging aminocarbyne. This strategy, which implies multicomponent assembly of isocyanide, aminocarbyne, and nucleophile, was successfully accomplished only in one case. Indeed, treatment of **2a** with an excess of $NaBH_4$ (or $LiHBEt_3$) in THF solution at room temperature leads to the consumption of **2a** (monitored by IR spectroscopy) and the formation of

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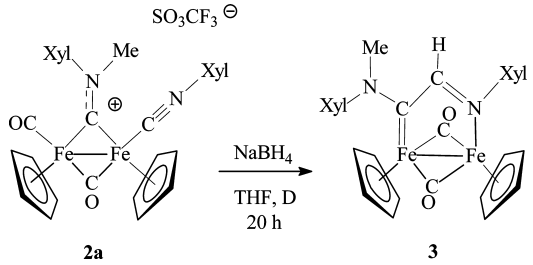
Table 1. Selected Bond Lengths (Å) and Angles (deg) for 2a

Fe(1)−Fe(2)	2.5260(16)	C(11)−O(11)	1.137(9)
Fe(2)−C(11)	1.754(10)	C(12)−O(12)	1.157(9)
Fe(1)−C(12)	1.888(8)	C(13)−N(1)	1.303(9)
Fe(2)−C(12)	1.981(8)	N(1)−C(14)	1.487(10)
Fe(1)−C(13)	1.866(7)	N(1)−C(15)	1.450(10)
Fe(2)−C(13)	1.884(7)	C(23)−N(2)	1.162(9)
Fe(1)−C(23)	1.812(9)	N(2)−C(24)	1.428(11)
Fe(1)−C(12)−Fe(2)	81.5(3)	Fe(1)−C(23)−N(2)	176.2(7)
Fe(1)−C(13)−Fe(2)	84.7(3)	C(23)−N(2)−C(24)	166.0(8)

products which, upon heating in THF at reflux temperature for about 20 h, afforded the complex **3** in moderate yield (Scheme 3).

Scheme 3. Hydride Addition and Rearrangement



2a **3**

Complex **3** has been characterized by spectroscopy and X-ray diffraction: the ORTEP molecular diagram is shown in Figure 2, whereas relevant bond angles and distances are reported in

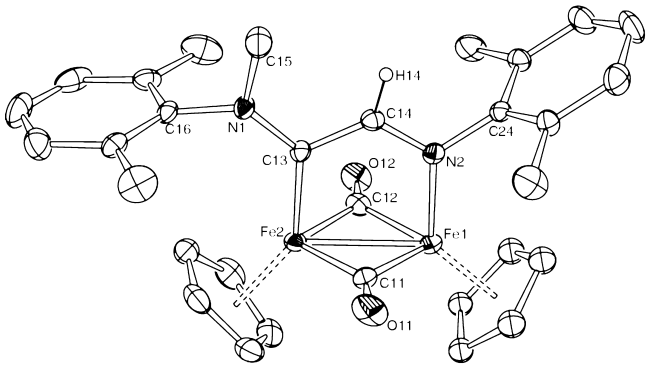


Figure 2. Molecular structure of **3**, with key atoms labeled (all H atoms, except H(14), have been omitted). Displacement ellipsoids are at the 30% probability level. Only the main image of the disordered Cp ring bonded to Fe(1) is reported.

Table 2. The molecule contains the bridging aminocarbene−aldimine ligand μ-η^1:η^1-CN(Me)(Xyl)C(H)=N(Xyl) coordinated to a $Fe_2(\mu\text{-}CO)_2(Cp)_2$ unit, with the Cp ligands in *cis* positions with respect to the $Fe_2(\mu\text{-}CO)_2$ plane. The Fe(2)−C(13) distance (1.911(6) Å) is comparable with the values found in analogous diiron complexes which contain a terminal two-electron-donor aminocarbene ligand,[16] even though the C(13)−N(1) interaction (1.386(7) Å) shows some elongation; nonetheless, N(1) presents the expected sp^2 hybridization (sum of angles 359.5(8)°), suggesting a π interaction between the nitrogen and the carbene carbon. The Fe(1)−N(2) distance (1.864(5) Å) is one of the shortest found for an iron−imine nitrogen interaction[17] and is, for instance, 0.1 Å shorter than that in the diiron imino complex $[Fe_2\{\mu\text{-}C\{N(Me)(Xyl)\}(\mu\text{-}CO)(CO)\{N(H)C(C{\equiv}CTol)CMe_3\}(Cp)_2]$ which contains a pure σ-Fe−N(imine) interaction (1.964(3) Å).[13] The shortening of the Fe−N interaction in **3** can be explained by assuming that a strong bond is formed due to extensive overlap which develops between metal and nitrogen orbitals when the nitrogen is in the delocalized electron system of the ligand. Moreover, the bond can be further strengthened by back-donation from iron to the antibonding π-orbital of the imine. In agreement with this, the C(14)−N(2) interaction (1.326(8) Å) is considerably elongated in comparison to a normal C=N bond. The strong π character of the Fe(1)−N(2) interaction is also evidenced by the asymmetry of both μ-CO bridges (Fe(1)−C(11), 1.912(7) Å; Fe(2)−C(11), 1.865(7) Å; Fe(1)−C(12), 1.919(7) Å; Fe(2)−C(12), 1.888(6) Å), which show shorter contacts to the more electron rich Fe(2) center. Finally, the C(13)−C(14) interaction (1.422(8) Å) presents some double-bond character, indicating delocalization between the aminocarbene and the imino termini of the bridging ligand.

The ^{1}H NMR spectrum of **3** shows two sets of resonances, which indicate the presence of the two isomeric forms. These are associated with the presence of the aminocarbene ligand and with the different orientation that the N substituents (Me and Xyl) can adopt. The most relevant features in the NMR spectra include the ^{1}H NMR resonances attributable to the C−H in the bridging C_3 frame (at 6.79 and 5.72 ppm, for the two isomers, respectively) and the ^{13}C NMR resonances of the aminocarbene and the iminium carbon (at about 230 and 160 ppm, respectively).

The formation of **3** exhibits some peculiar features that deserve to be underlined. First, the reaction is a unique example of coupling of isocyanide and aminocarbyne ligands, initiated by hydride addition. It affords an aminocarbene ligand containing an imidoyl group. Analogies can be envisaged with reductive coupling of two isocyanide ligands in the dimolybdenum complex $[Mo_2Cp_2(\mu\text{-}SMe)_3(XylNC)_2][BF_4]$ reported by Petillon, Schollhammer and co-workers.[18] Also in that case, a coupling reaction was initiated by a nucleophile (the hydrosulfide anion) and occurred via C−C bond formation, yielding the aminocarbene derivative $[Mo_2Cp_2(\mu\text{-}SMe)_3\{\mu\text{-}\eta^1(C)$:$\eta^1(C)\text{-}C(NHXyl)C(NXyl)\}]$. However, both the ligand and the coordination mode are different from those observed in **3**.

A second observation concerns the reaction mechanism, which presumably proceeds via hydride addition at the isocyanide ligand to generate a formimidoyl intermediate. Indeed, it has been relatively easy to isolate and characterize such an intermediate by performing the reaction of **2a** with $NaBH_4$ (or $LiHBEt_3$) in THF solution at 0 °C. Compound **4a** (Scheme 4) has been purified by chromatography and fully characterized by IR and NMR spectroscopy and elemental analysis. Details are reported in the Experimental Section. The

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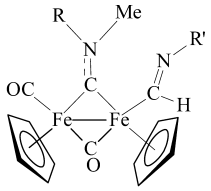
Table 2. Selected Bond Lengths (Å) and Angles (deg) for 3

Fe(1)−Fe(2)	2.5056(13)	C(11)−O(11)	1.209(8)
Fe(1)−C(11)	1.912(7)	C(12)−O(12)	1.189(8)
Fe(2)−C(11)	1.865(7)	C(13)−N(1)	1.386(7)
Fe(1)−C(12)	1.919(7)	C(13)−C(14)	1.422(8)
Fe(2)−C(12)	1.888(6)	C(14)−N(2)	1.326(8)
Fe(1)−N(2)	1.864(5)	N(1)−C(16)	1.429(7)
Fe(2)−C(13)	1.911(6)	N(2)−C(24)	1.428(7)
		N(1)−C(15)	1.464(8)
Fe(1)−C(11)−Fe(2)	83.1(3)	C(13)−N(1)−C(15)	123.4(5)
Fe(1)−C(12)−Fe(2)	82.3(3)	C(13)−N(1)−C(16)	124.0(5)
Fe(2)−C(13)−C(14)	117.4(4)	C(15)−N(1)−C(16)	112.1(5)
Fe(2)−C(13)−N(1)	130.9(4)	C(14)−N(2)−Fe(1)	122.5(4)
N(1)−C(13)−C(14)	111.7(5)	C(14)−N(2)−C(24)	114.1(5)
C(13)−C(14)−N(2)	122.8(5)	Fe(1)−N(2)−C(24)	123.4(4)

Scheme 4. Formimidoyl Complexes



R	R'	
Xyl	Xyl	**4a**
Xyl	Me	**4b**
Me	Xyl	**4c**

reaction also affords, as a minor product, the bridging hydride complex $[Fe_2\{\mu\text{-CN(Me)(Xyl)}\}(\mu\text{-H})(CO)_2(Cp)_2]$, which is presumably formed by hydride displacement of the isocyanide and has been identified by comparison of its spectroscopic data with those reported in the literature.[19]

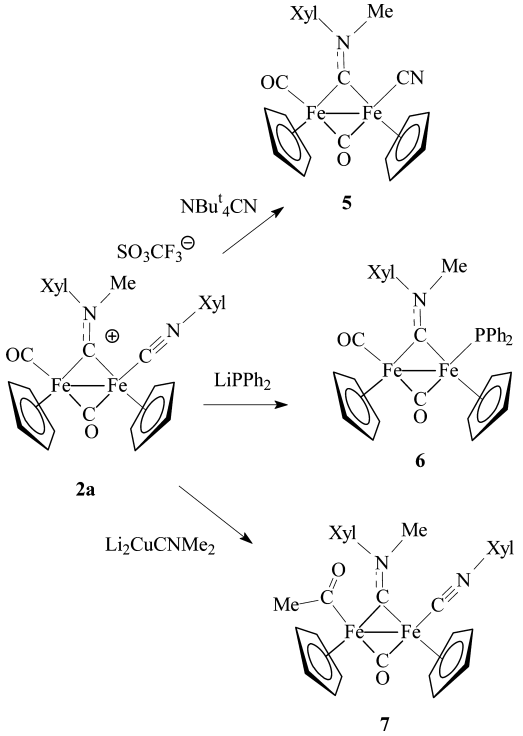
Interestingly, other complexes of type **2** (namely **2b,e**) undergo hydride addition to form the corresponding formimidoyl complexes **4b,c** (Scheme 4).

In order to demonstrate that the formimidoyl complex **4a** really corresponds to an intermediate step in the formation of **3**, a sample of pure **4a** has been treated in THF at reflux temperature for 20 h. The reaction afforded **3** in good yelds (about 80%). Conversely, analogous treatment of **4b,c** gave extensive decomposition and failed to produce compounds analogous to **3**.

The formation of **4a−c** is interesting in that both dinuclear[20] and trinuclear[21] formimidoyl complexes are normally obtained by reaction of isocyanides with μ-hydride complexes, via isocyanide insertion into metal−hydride bonds, whereas the complementary route (i.e., hydride addition to isocyanide ligands) is less common.[22] A further point of interest is that formimidoyl ligands usually adopt a bridging coordination in dinuclear complexes, acting as three-electron donors via C and N coordination.[20,21] Conversely, **4a−c** exhibit a σ-coordinated formimidoyl, which is normally observed only in mononuclear complexes.[23] In our case, this is most probably a consequence of coordinative saturation, which does not provide access to bridging coordination. Indeed, IR spectra of **4a−c** show the usual ν(CO) band pattern consistent with the presence of one terminally bonded and one bridging CO. Moreover, NMR spectra indicate the presence of the bridging aminocarbyne ligand (e.g., ^{13}C NMR resonance of the μ-carbyne carbon at δ 337.6 for **4a**) and of the two Cp ligands as well. Thus, ancillary ligands and the diiron frame remain unchanged upon hydride addition and do not allow bridging coordination of the formimidoyl.

As mentioned above, the formation of **3** was unique in that only hydride, among the nucleophiles investigated, initiates the observed rearrangement and assembly. Reactions of **2a** with NaCN or with $LiPPh_2$ resulted in the displacement of the isocyanide, affording the complexes **5** and **6**, respectively (Scheme 5). In contrast, the reaction of **2a** with $Li_2CuCNMe_2$ afforded the acyl derivative $[Fe_2\{\mu\text{-CN(Me)(Xyl)}\}(\mu\text{-CO})\{C(O)Me\}(CNXyl)(Cp)_2]$ (**7**) (Scheme 5).

Scheme 5. Reactions with Nucleophiles



Selective nucleophilic addition at the CO is consistent with previously reported reactions of the analogous aminocarbyne complex $[Fe_2\{\mu\text{-CN(Me)(Xyl)}\}(\mu\text{-CO})(CO)_2(Cp)_2][SO_3CF_3]$ with organocopper reagents, which also afforded acyl derivatives.[24] Complex **2a** resulted unreactive toward other nucleophiles such as MeOH, NH_2Bu^n, and NaN_3, whereas

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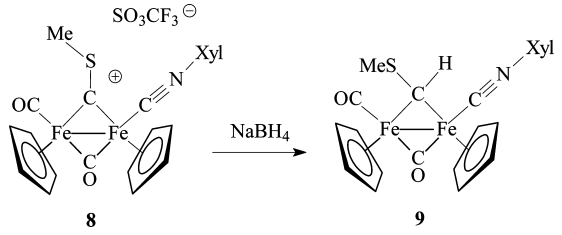
reactions with MeLi and PhLi produced extensive decomposition.

Complexes **5**–**7** have been characterized by spectroscopy and elemental analysis. Complex **5** has been identified by comparison of its spectroscopic properties with those reported in the literature.[19] Details are reported in the Experimental Section. It has to be remarked that complex **6** exists, in solution, as mixture of *E* and Z isomers, with prevalence of the former, whereas the ^{1}H NMR spectrum of **7** exhibits a single set of resonances. NOE investigations performed on **7** have evidenced a significant NOE effect between the resonance related to the *N*-methyl group (at δ 4.29 ppm) and the resonance attributed to the equivalent methyls of the terminal CNXyl moiety (at 2.05 ppm), indicating that these groups are placed on the same side (as shown in Scheme 5).

Finally, we have investigated the reactivity of the thiocarbyne complex $[Fe_2\{\mu\text{-CSMe}\}(\mu\text{-CO})(CO)(CNXyl)(Cp)_2][SO_3CF_3]$ (**8**), which differs from **2a** in that it displays the bridging thiocarbyne ligand μ-CSMe in place of the aminocarbyne μ-CN(Me)(Xyl). It has been shown that μ-thiocarbyne and μ-aminocarbyne diiron complexes exhibit a few similarities but also some distinct features.[25] Here, we have found that **8** reacts with $NaBH_4$, but neither the isocyanide nor the CO undergoes nucleophilic attack. In this case, hydride addition takes place selectively at the carbyne carbon, yielding the bridging thiocarbene complex $[Fe_2\{\mu\text{-C(SMe)(H)}\}(\mu\text{-CO})(CO)(CNXyl)(Cp)_2]$ (**9**) (Scheme 6).

Scheme 6. Hydride Addition at the Thiocarbyne Complex



Complex **9** closely resembles the thiocarbene $[Fe_2\{\mu\text{-C(SMe)(H)}\}(\mu\text{-CO})(CO)_2(Cp)_2]$, which was analogously obtained by treatment of the cationic thiocarbyne $[Fe_2(\mu\text{-CSMe})(\mu\text{-CO})(CO)_2(Cp)_2]^+$ with $NaBH_4$.[26]

Compound **9** was characterized by IR and NMR spectroscopy and elemental analysis. The IR spectrum of **9** (in CH_2Cl_2 solution) exhibits absorptions due to terminal and bridging carbonyls (at 1944 and 1758 cm^{-1}) and an absorption attributable to the C≡N group (2075 cm^{-1}). The ^{1}H NMR spectrum shows a unique set of resonances: the μ-CH proton resonates at low field (δ 11.63 ppm), as expected for a bridging thiocarbene ligand. The SMe protons resonate at 2.82 ppm, whereas the methyl protons of the Xyl group give rise to a single resonance at 2.28 ppm. The thiocarbene carbon resonates at 166.7 ppm in the ^{13}C NMR spectrum, whereas the resonance of the isocyanide carbon is found at 176.0 ppm.

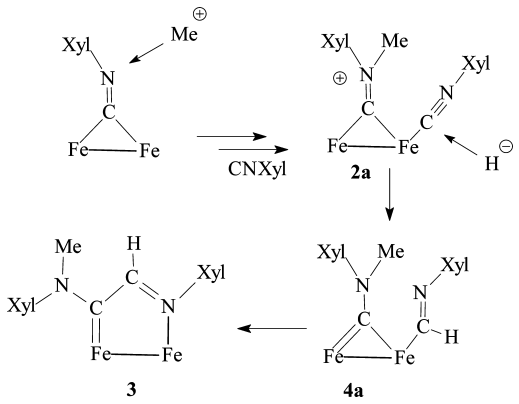
No reaction was observed between the isocyanide and the bridging carbene ligand upon thermal treatment of **9** (in THF at reflux) for 20 h.

CONCLUSIONS

Assembly of bridging carbyne and isocyanide ligands, in the complex $[Fe_2\{\mu\text{-CN(Me)(Xyl)}\}(\mu\text{-CO})(CO)(C{\equiv}NR')(Cp)_2][SO_3CF_3]$ (**2a**), has been obtained upon hydride addition and thermal treatment. The reaction proceeds via hydride attack at the isocyanide to yield a formimidoyl, which subsequently undergoes coupling with the bridging carbyne ligand. The resulting fragment acts as a bridging aminocarbene–aldimine ligand, coordinated through the carbene carbon and imine nitrogen.

Considering that the μ-aminocarbyne is simply obtained by methylation (with $MeSO_3CF_3$) of a isocyanide ligand, the observed aminocarbyne–formimidoyl coupling can be regarded as the assembly of two isocyanide ligands, via C–C coupling, provided that one isocyanide has been activated by electrophilic addition (transformation into aminocarbyne) and the other has been activated by nucleophilic addition (transformation into formimidoyl) (Scheme 7). This "double activation" is a multistep process, significantly different from the "reductive coupling" of isocyanides, which is so far the major approach to the metal-mediated assembly of isocyanides.[16,27]

Scheme 7. Sequential Steps in Isocyanide Activation[a]



[a]Ancillary ligands have been omitted for clarity.

Unfortunately the reaction does not have a general character, in that other nucleophiles (NaCN, $LiPPh_2$ $Li_2CuCNMe_2$) do not give addition at the isocyanide and fail to induce the "double activation" mentioned above. Nevertheless, the reaction offers an unprecedented example of C–C bond formation promoted by diiron complexes.

EXPERIMENTAL SECTION

General Data. All reactions were routinely carried out under a nitrogen atmosphere, using standard Schlenk techniques. Solvents were distilled immediately before use under nitrogen from the appropriate drying agents. Chromatography separations were carried out on columns of deactivated alumina (4% w/w water). Glassware was oven-dried before use. Infrared spectra were recorded on a PerkinElmer Spectrum 2000 FT-IR spectrophotometer, and elemental analyses were performed on a ThermoQuest Flash 1112 Series EA instrument. NMR spectra were recorded on a Mercury Plus 400 instrument. Unless otherwise stated, NMR spectra were recorded at 298 K. Chemical shifts for ^{1}H and ^{13}C were referenced to internal TMS. Spectra were fully assigned via DEPT experiments and ^{1}H,^{13}C correlation measured through gs-HSQC and gs-HMBC experiments. NOE measurements were recorded using the DPFGSE-NOE sequence. NMR signals due to the minor isomeric form (where it has been possible to detect) are italicized. All of the reagents were commercial products (Aldrich) of the highest purity available and were used as received. $[Fe_2(CO)_4(Cp)_2]$ was purchased from Strem and used as received. The compounds $[Fe_2\{\mu\text{-CN(Me)(R)}\}(\mu\text{-CO})(CO)_2(Cp)_2][SO_3CF_3]$ (R = Xyl, **1a**; R = Me, **1b**)[14a,28] and $[Fe_2(\mu$-

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CSMe)(μ-CO)(CO)$_2$(Cp)$_2$][SO$_3$CF$_3$][29] were prepared as described in the literature.

Synthesis of [Fe$_2${μ-CN(Me)(R)}(μ-CO)(CO)(CNR′)(Cp)$_2$][SO$_3$CF$_3$] (2a−e). A solution of [Fe$_2${μ-CN(Me)(Xyl)}(μ-CO)(CO)$_2$(Cp)$_2$][CF$_3$SO$_3$] (**1a**; 100 mg, 0.161 mmol), in THF (15 mL), was treated with CNXyl (23 mg, 0.175 mmol) and then with Me$_3$NO (16 mg, 0.213 mmol). The mixture was stirred for 3 h. Solvent removal under reduced pressure gave a solid residue which was dissolved in CH_2Cl_2 and chromatographed on alumina. Elution with MeCN afforded a red-brown band corresponding to **2a** (R = R′ = Xyl) (yield 104 mg, 90%; *E*/*Z* ratio 3/1, determined by integration of NMR signals) Crystals of *E*-**2a** suitable for X-ray analysis were obtained by a CH_2Cl_2 solution layered with diethyl ether at −20 °C. Anal. Calcd for $C_{32}H_{31}F_3Fe_2N_2O_5S$: C, 53.06; H, 4.31; N, 3.87. Found: C, 53.12; H, 4.22; N, 3.99. IR (CH_2Cl_2) ν(C≡N) 2120 (vs), ν(CO) 1991 (vs), 1824 (s), cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.37−7.01 (m, 6 H, Me$_2$C$_6$*H*$_3$); 5.33, 5.29, 4.69, 4.65 (s, 10 H, Cp); 4.54, 4.41 (s, 3 H, NMe); 2.74, 2.70, 2.07, 1.88 (s, 6 H, μ-CN*Me*$_2$C$_6$H$_3$); 2.27, 2.10 (s, 6 H, CN*Me*$_2$C$_6$H$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 332.0, 330.9 (μ-CN); 258.8, 259.2 (μ-CO); 210.5, 210.2 (CO); 167.3, 166.9 (CN); 148.0, 147.8 (C$_{ipso\text{-}Xyl}$); 134.8−127.9 (C$_{arom}$); 89.4, 89.1, 88.5, 88.4 (Cp); 54.9, 54.8 (NMe); 18.6, 17.4 18.4, 17.3 (*Me*$_2$C$_6$H$_3$).

Complexes **2b−e** were prepared by the same procedure described for **2a** by reacting **1a,b** with the appropriate isocyanide CNR′, respectively.

2b: R = Xyl, R′ = Me; yield 72%. Anal. Calcd for $C_{25}H_{25}F_3Fe_2N_2O_5S$: C, 47.34; H, 3.97; N, 4.42. Found: C, 47.41; H, 4.02; N, 4.33. Data for **2b** are as follows. IR (CH_2Cl_2): ν(C≡N) 2182 (vs), ν(CO) 1989 (vs), 1823 (s), cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.38−7.26 (m, 3 H, Me$_2$C$_6$*H*$_3$); 5.22, 5.16, 4.50, 4.29 (s, 10 H, Cp); 4.56 4.46 (s, 3 H, μ-CNMe); 3.20, 3.11 (s, 3 H, CNMe); 2.46, 2.39, 2.13, 2.12 (s, 6 H, *Me*$_2$C$_6$H$_3$). *E*/*Z* ratio 3/1. ^{13}C{^{1}H} NMR ($CDCl_3$) δ 334.0, 332.4 (μ-CN); 259.6, 258.4 (μ-CO); 210.9, 208.9 (CO); 148.6, 147.7 (C$_{ipso\text{-}Xyl}$); 134.0−128.9 (C$_{arom}$); 122.5, 119.3 (CN); 90.5, 89.1, 88.0, 87.8 (Cp); 55.0, 54.6 (μ-CN*Me*); 31.1 30.8 (CN*Me*); 18.6, 18.5, 18.2, 17.2 (*Me*$_2$C$_6$H$_3$).

2c: R = Xyl, R′ = Bu^t; yield 85%. Anal. Calcd for $C_{28}H_{31}F_3Fe_2N_2O_5S$: C, 49.73; H, 4.62; N, 4.14. Found: C, 49.81; H, 4.55; N, 4.10. Data for **2c** are as follows. IR (CH_2Cl_2): ν(C≡N) 2149 (vs), ν(CO) 1988 (vs), 1822 (s), cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 7.54−7.23 (m, 3 H, Me$_2$C$_6$*H*$_3$); 5.24, 4.64 (s, 10 H, Cp); 4.50 (s, 3 H, NMe); 2.72, 2.16 (s, 6 H, *Me*$_2$C$_6$H$_3$); 1.29 (s, 9 H, C*Me*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 332.4 (μ-CN); 259.1 (μ-CO); 210.8 (CO); 147.7 (C$_{ipso\text{-}Xyl}$); 133.1, 131.5, 129.7, 128.9, 128.8 (C$_{arom}$); 116.3 (CN); 88.4, 88.0 (Cp); 58.8 (NMe); 49.7 (*C*Me$_3$); 30.0 (C*Me*$_3$); 18.6, 17.2 (*Me*$_2$C$_6$H$_3$).

2d: R = Xyl, R′ = p-C$_6$H$_4$CF$_3$; yield 72%. Anal. Calcd for $C_{31}H_{26}F_6Fe_2N_2O_5S$: C, 48.72; H, 3.43; N, 3.67. Found: C, 48.70; H, 3.31; N, 3.80. Data for **2d** are as follows. IR (CH_2Cl_2): ν(C≡N) 2119 (vs), ν(CO) 1985 (vs), 1824 (s), cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 7.71−7.13 (m, 7 H, Me$_2$C$_6$*H*$_3$ and C$_6$*H*$_4$CF$_3$); 5.27, 4.63 (s, 10 H, Cp); 4.36 (s, 3 H, NMe); 2.68, 1.99 (s, 6 H, *Me*$_2$C$_6$H$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 330.3 (μ-CN); 257.5 (μ-CO); 209.6 (CO); 168.9 (CN); 147.9 (C$_{ipso\text{-}Xyl}$); 133.3−118.6 (C$_{arom}$); 115.4 (CF$_3$); 89.2, 88.5 (Cp); 52.0 (μ-CN*Me*); 18.4, 18.1 (*Me*$_2$C$_6$H$_3$).

2e: R = Me, R′ = Xyl; yield 85%. Anal. Calcd for $C_{25}H_{25}F_3Fe_2N_2O_5S$: C, 47.34; H, 3.97; N, 4.42. Found: C, 47.30; H, 3.99; N, 4.21. Data for **2e** are as follows. IR (CH_2Cl_2): ν(C≡N) 2119 (vs), ν(CO) 1987 (vs), 1819 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 7.07−6.98 (m, 3 H, Me$_2$C$_6$*H*$_3$); 5.21, 5.18 (s, 10 H, Cp); 4.37, 4.27 (s, 6 H, NMe); 2.18 (s, 6 H, *Me*$_2$C$_6$H$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 322.1 (μ-CN); 260.8 (μ-CO); 210.1 (CO); 167.7 (CN); 134.5, 128.5, 127.9 (C$_{arom}$); 88.8, 88.6 (Cp); 53.7 (NMe); 18.4 (*Me*$_2$C$_6$H$_3$).

Synthesis of [Fe$_2${μ-CN(Me)(Xyl)C(H)═N(Xyl)}(μ-CO)$_2$(Cp)$_2$] (3). Complex **2a** (150 mg, 0.207 mmol) in THF (20 mL) was treated with NaBH$_4$ (40 mg, 1.05 mmol) at reflux for 20 h. Then, the solvent was removed and the residue was dissolved in Et$_2$O and filtered through an alumina pad. Solvent removal and chromatography of the residue on an alumina column with a mixture (1/1 v/v) of CH_2Cl_2 and Et$_2$O as eluent gave a red-violet band containing **3**. Yield: 64 mg, 54%. Crystals suitable for X-ray analysis were obtained by a Et$_2$O/*n*-pentane (1/3) solution, at −20 °C. Anal. Calcd for $C_{31}H_{32}Fe_2N_2O_2$: C, 64.61; H, 5.60; N, 4.86. Found: C, 64.62; H, 5.55; N, 4.78. Data for **3** are as follows. IR (CH_2Cl_2): ν(CO) 1734 (vs) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.30, 7.28, 7.04, 6.88, 6.87 (s, 6 H, Me$_2$C$_6$*H*$_3$); 6.79, 5.72 (s, 1 H, CH); 5.13, 4.41, 4.36, 4.23 (s, 10 H, Cp); 3.52, 2.76 (s, 3 H, NMe); 2.30, 2.21, 1.99, 1.95 (s, 6 H, *Me*$_2$C$_6$H$_3$). *E*/*Z* ratio 13/10. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 291.2, 290.3 (μ-CO); 232.0, 229.2 (C$_{carbene}$); 162.7, 159.6 (*C*H═NXyl); 149.6, 148.0, 144.0, 141.8 (C$_{ipso\text{-}Xyl}$); 135.9, 133.2, 129.6−125.1 (C$_{arom}$); 89.2, 88.9, 88.4, 88.3 (Cp); 47.2, 43.8 (NMe); 18.4, 17.9, 17.7, 17.6 (*Me*$_2$C$_6$H$_3$).

Synthesis of [Fe$_2${μ-CN(Me)(R)}(μ-CO)(CO){C(H)═NR′}(Cp)$_2$][SO$_3$CF$_3$] (4a−c). Complex **2a** (150 mg, 0.207 mmol) was dissolved in THF (15 mL) and treated with NaBH$_4$ (40 mg, 1.05 mmol) at 0 °C. The solution was stirred for 30 min, and then the mixture was warmed to room temperature and was filtered on an alumina pad. The solvent was removed, and the residue, dissolved in CH_2Cl_2, was chromatographed on alumina. A first band, corresponding to the complex [Fe$_2${μ-CN(Me)(Xy)}(μ-H)(CO)$_2$(Cp)$_2$], was obtained in low yield (23 mg, 25%). Then, complex **4a** was isolated as a green fraction by using THF as eluent. Yield: 79 mg, 66%. Anal. Calcd for $C_{31}H_{32}Fe_2N_2O_2$: C, 64.61; H, 5.60; N, 4.86. Found: C, 64.55; H, 5.51; N, 4.93. Data for **4a** (R = R′ = Xyl) are as follows. IR (CH_2Cl_2): ν(CO) 1955 (vs), 1785 (s), ν(C═N) 1538 (s), cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 9.08, 8.49 (s, 1 H, CH); 7.30−6.67 (m, 6 H, Me$_2$C$_6$*H*$_3$); 4.95, 4.92, 4.38, 4.35 (s, 10 H, Cp); 4.30, 4.21 (s, 3 H, NMe); 2.65, 2.60, 2.18 (s, 6 H, *Me*$_2$C$_6$H$_3$); 2.00, 1.91 (s, 6 H, *Me*$_2$C$_6$H$_3$). *E*/*Z* ratio 6/1. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 337.6 (μ-CN); 271.2 (μ-CO); 215.2 (CO); 208.6 (CN); 147.9 (C$_{ipso\text{-}Xyl}$); 134.1−121.3 (C$_{arom}$); 90.0, 89.6, 88.3, 86.1 (Cp); 52.3, 51.6 (NMe); 18.9, 18.6, 18.5, 18.0, 17.7 (*Me*$_2$C$_6$H$_3$).

Compounds **4b,c** were prepared by the same procedure described for **4a**, by reacting NaBH$_4$ with **2b,e**, respectively.

4b: R = Xyl, R′ = Me; yield 45%. Anal. Calcd for $C_{24}H_{26}Fe_2N_2O_2$: C, 59.29; H, 5.39; N, 5.76. Found: C, 59.30; H, 5.48; N, 5.61. Data for **4b** are as follows. IR (CH_2Cl_2): ν(CO) 1952 (vs), 1762 (s), ν(C═N) 1590 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 8.01 (br, 1 H, CH); 7.50−7.13 (m, 3 H, Me$_2$C$_6$*H*$_3$); 4.89, 4.33 (s, 10 H, Cp); 4.20, 4.08 (s, 6 H, NMe); 2.61, 2.14 (s, 6 H, *Me*$_2$C$_6$H$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 336.7 (μ-CN); 269.9 (μ-CO); 257.5 (CN); 216.5 (CO); 147.9 (C$_{ipso\text{-}Xyl}$); 133.1, 133.0, 129.8, 128.3, 128.2 (C$_{arom}$); 87.9, 86.2 (Cp); 50.2 (μ-CN*Me*); 41.5 (CN*Me*); 18.3, 17.4 (*Me*$_2$C$_6$H$_3$).

4c: R = Me, R′ = Xyl; yield 49%. Anal. Calcd for $C_{24}H_{26}Fe_2N_2O_2$: C, 59.29; H, 5.39; N, 5.76. Found: C, 59.40; H, 5.22; N, 5.74. Data for **4c** are as follows. IR (CH_2Cl_2): ν(CO) 1927 (vs), 1746 (s), ν(C═N) 1586 (s), cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 9.62 (s, 1 H, CH); 7.11, 6.91 (m, 3 H, Me$_2$C$_6$*H*$_3$); 4.56, 4.51 (s, 10 H, Cp); 3.77, 3.08 (s, 6 H, NMe); 2.39 (s, 6 H, *Me*$_2$C$_6$H$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 331.4 (μ-CN); 264.3 (μ-CO); 214.9 (CO); 207.5 (CN); 145.6 (C$_{ipso\text{-}Xyl}$); 138.5, 127.9, 121.7 (C$_{arom}$); 87.4, 85.4 (Cp); 53.8, 44.9 (NMe); 19.0 (*Me*$_2$C$_6$H$_3$).

Synthesis of [Fe$_2${μ-CN(Me)(Xyl)}(μ-CO)(CO)(CN)(Cp)$_2$] (5). Complex **2a** (95 mg, 0.130 mmol) was dissolved in THF (15 mL) and treated with NBu$^t_4$CN (42 mg, 0.157 mmol). The solution was heated to reflux temperature for 30 min, and then it was filtered on an alumina pad. Solvent removal gave complex **5** as a green powder. Yield: 42 mg, 68%.

Synthesis of [Fe$_2${μ-CN(Me)(Xyl)}(μ-CO)(CO)(PPh$_2$)(Cp)$_2$] (6). Complex **2a** (95 mg, 0.130 mmol), was dissolved in THF (15 mL) and treated at room temperature with LiPPh$_2$ (0.18 mmol) in THF solution (2.0 mL). The solution was stirred for 20 min, and then the solvent was removed under reduced pressure. Chromatography of the residue on an alumina column with a mixture of THF and MeOH (9/1 v/v) as eluent gave an emerald green band corresponding to **6**. Yield: 56 mg, 68%. Anal. Calcd for $C_{34}H_{32}Fe_2NO_2P$: C, 64.89; H, 5.13; N, 2.23. Found: C, 64.92; H, 5.06; N, 2.15. Data for **6** are as follows. IR (CH_2Cl_2): ν(CO) 1981 (vs), 1786 (s), cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.72−7.22 (m, 16 H, Me$_2$C$_6$*H*$_3$ and PPh$_2$); 4.95, 4.71, 4.42, 4.25 (s, 10 H, Cp); 4.67 (s, 3 H, NMe); 2.69, 2.64, 2.23 (s, 6 H, Me$_2$C$_6$H$_3$). *E*/*Z* ratio: 5/1. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 333.0 (μ-C); 267.6 (μ-CO);

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213.1, 212.0 (CO); 151.0−125.6 (C_{arom}); 89.0, 87.4, 87.3, 87.0 (Cp); 51.4 (NMe); 18.6, 18.5, 18.4, 18.2 ($Me_2C_6H_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 34.7, 33.6.

Synthesis of [Fe_2(μ-CN(Me)(Xyl)}(μ-CO){C(O)Me}(CNXyl)($Cp)_2$] (7). Complex **2a** (250 mg, 0.345 mmol) was dissolved in THF (22 mL) and treated at −50 °C with $Li_2CuCNMe_2$ (0.40 mmol) in THF solution (2.5 mL), freshly prepared by reacting CuCN and MeLi in a 1/2 ratio. The resulting mixture was stirred for 50 min, and then the solvent was removed under reduced pressure. The solid residue was dissolved in CH_2Cl_2 and filtered on alumina. Solvent removal gave **7** as a green microcrystalline solid. Yield: 153 mg, 75%. Anal. Calcd for $C_{32}H_{34}Fe_2N_2O_2$: C, 65.11; H, 5.81; N, 4.75. Found: C, 65.04; H, 5.88; N, 4.62. Data for **7** are as follows. IR (CH_2Cl_2): ν(C≡N) 2071 (vs), ν(CO) 1749 (s), 1591 (ms) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.25−6.89 (m, 6 H, $Me_2C_6H_3$); 4.80, 4.19 (s, 10 H, Cp); 4.29 (s, 3 H, NMe); 2.63, 2.26 (s, 6 H, $Me_2C_6H_3$); 2.32 (s, 3 H, MeCO); 2.05 (s, 6 H, $Me_2C_6H_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 340.2 (μ-C); 277.4 (MeCO); 274.0 (μ-CO); 178.9 (C≡N); 148.5 ($C_{ipso\text{-}Xyl}$); 135.3, 134.0, 133.7, 129.4, 127.8, 127.5, 157.4, 125.8 (C_{arom}); 88.1, 85.3 (Cp); 51.4 (NMe); 46.5 (*Me*CO); 18.7, 18.4, 17.4 ($Me_2C_6H_3$).

Synthesis of [Fe_2{μ-CSMe}(μ-CO)(CO)(CNXyl)($Cp)_2$][SO_3CF_3] (8). Complex [Fe_2{μ-CSMe}(μ-CO)$(CO)_2(Cp)_2$][SO_3CF_3] (300 mg, 0.562 mmol), in THF solution (15 mL), was treated with C≡NXyl (81 mg, 0.618 mmol) and with Me_3NO (51 mg, 2.13 mmol). The mixture was stirred for 1 h, and then the solvent was removed. The residue was subsequently chromatographed on alumina, and elution with MeOH gave a dark red band corresponding to **8**. Yield: 286 mg, 80%. Anal. Calcd for $C_{24}H_{22}F_3Fe_2NO_5S_2$: C, 45.23; H, 3.48; N, 2.20. Found: C, 45.20; H, 3.35; N, 2.19. IR (CH_2Cl_2): ν(C≡N) 2132 (vs), ν(CO) 2002 (vs), 1833 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.29−6.65 (m, 3 H, $Me_2C_6H_3$); 5.33, 5.24 (s, 10 H, Cp); 3.63 (s, 3 H, SMe); 2.16 (s, 6 H, $Me_2C_6H_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 411.1 (μ-C); 260.9 (μ-CO); 208.6 (CO); 167.5 (*C*NXyl); 143.9 ($C_{ipso\text{-}Xyl}$); 134.9, 134.2, 128.2, 128.0 (C_{arom}); 90.5, 90.0 (Cp); 36.9 (SMe); 18.4 ($Me_2C_6H_3$).

Synthesis of [$Fe_2(Cp)_2$(CO)(μ-CO)(CNXyl){C(SMe)(H)}] (9). A solution of **8** (200 mg, 0.314 mmol) in THF (15 mL) was treated with $NaBH_4$ (36 mg, 0.952 mmol). The mixture was stirred for 30 min and then it was filtered through an alumina pad. Solvent removal and chromatography of the residue on an alumina column with CH_2Cl_2 as eluent afforded **9**. Yield: 115 mg, 75%. Anal. Calcd for $C_{23}H_{23}Fe_2NO_2S$: C, 56.47; H, 4.74; N, 2.86. Found: C, 56.58; H, 4.68; N, 2.96. IR (CH_2Cl_2): ν(C≡N) 2075 (vs), ν(CO) 1944 (vs), 1758 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 11.63 (s, 1 H, μ-CH); 7.15−6.69 (m, 3 H, $Me_2C_6H_3$); 4.70, 4.66 (s, 10 H, Cp); 2.82 (s, 3 H, SMe); 2.28 (s, 6 H, $Me_2C_6H_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 279.2 (μ-CO); 212.6 (CO); 176.0 (C≡N); 166.7 (μ-CH); 139.1 ($C_{ipso\text{-}Xyl}$); 134.5−126.3 (C_{arom}); 86.4, 86.1 (Cp); 27.1 (SMe); 19.1, 18.7 ($Me_2C_6H_3$).

X-ray Crystallography. Crystal data and collection details for **2a** and **3** are reported in Table S1 in the Supporting Information. The diffraction experiments were carried out on a Bruker SMART 2000 diffractometer equipped with a CCD detector using Mo Kα radiation. Data were corrected for Lorentz−polarization and absorption effects (empirical absorption correction SADABS).[30] Structures were solved by direct methods and refined by full-matrix least squares on the basis of all data using F^2.[31] Non-H atoms were refined anisotropically, unless otherwise stated. H atoms were placed in calculated positions, except H(14) in **4**, which was located in the Fourier map and refined with the C(14)−H(14) distance restrained to 0.93 Å. H atoms were treated isotropically using the 1.2-fold U_{iso} value of the parent atom, except for methyl protons, which were assigned the 1.5-fold U_{iso} value of the parent C atom. The crystals of **3** appeared to be racemically twinned with a refined Flack parameter of 0.66(3).[32] One Cp ligand in **3** is disordered. Disordered atomic positions were split and refined isotropically using similar distances and similar U restraints and one occupancy parameter per disordered group. The crystals of **2a** are very small and of low quality, although different attempts at recrystallization have been made. While the overall connectivity of **2a** is certain, structural parameters, however, should be taken with caution.

■ ASSOCIATED CONTENT

Supporting Information

A table, figures, and CIF files giving NMR spectra for all new compounds and crystal data for **2a** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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