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DFT Mechanistic Insights into the Alkyne Insertion Reaction Affording Diiron μ-Vinyliminium Complexes and New Functionalization Pathways

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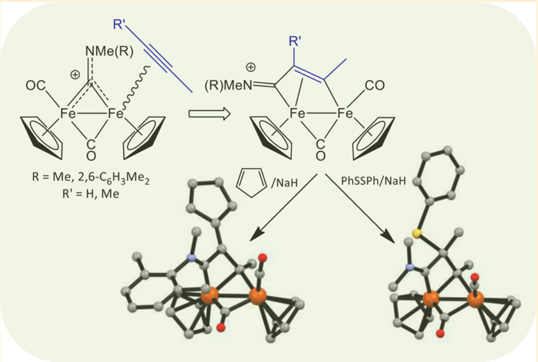
Supporting Information

ABSTRACT: Insertion of propyne or 2-butyne into the Fe−carbyne bond belonging to the fragment $[Fe_2Cp_2(CO)(\mu\text{-}CO)\{\mu\text{-}CNMe(R)\}]^+$ (R = Me or Xyl = 2,6-$C_6H_3Me_2$) was investigated via density functional theory (DFT), and plausible intermediates were identified along the formation of the vinyliminium complexes $[Fe_2Cp_2(CO)(\mu\text{-}CO)\{\mu\text{-}\eta^1:\eta^3\text{-}C(Me)C(R'')CN(Me)(R)\}]SO_3CF_3$, $[\mathbf{2a{-}d}]^+$, thus allowing us to explain regio- and stereochemical features. The X-ray structure of $[\mathbf{2a}]SO_3CF_3$ (R = Me, R″ = H) was determined by single crystal X-ray diffraction. Novel C−C and C−S bond forming pathways involving the vinyliminium ligand were then explored. Thus, $[\mathbf{2b}]SO_3CF_3$ (R = Xyl, R″ = H) reacted with cyclopentadiene (or cyclopentene), triphenylphosphonium methylide, and benzyl bromide, in tetrahydrofuran in the presence of sodium hydride, respectively, to give $[Fe_2Cp_2(CO)(\mu\text{-}CO)\{\mu\text{-}\eta^1:\eta^2\text{-}C(Me)C\{C(CH)_4\}CN(Me)(Xyl)\}]$, **3**, $[Fe_2Cp_2(CO)(\mu\text{-}CO)\{\mu\text{-}\eta^1:\eta^2\text{-}C(Me)C(CH_2)CN(Me)(Xyl)\}]$, **4**, and $[Fe_2Cp_2(CO)(\mu\text{-}CO)\{\mu\text{-}\eta^1:\eta^3\text{-}C(Me)C(CH_2Ph)CN(Me)(Xyl)\}]Br$, $[\mathbf{5}]Br$, in good yields. Unstable complex **4** (detected by IR spectroscopy) readily converted into $[\mathbf{2c}]SO_3CF_3$ (R = Xyl, R″ = Me) upon HSO_3CF_3 protonation of the methylide function. $[\mathbf{5}]Br$ was obtained as *E*/*Z* isomeric mixture, which was then quantitatively converted into the most stable *Z* form, by heating in methanol solution at 50 °C. The reactions of $[\mathbf{2c,d}]SO_3CF_3$ (R = Me, Xyl, R″ = Me) with PhSSPh/NaH selectively yielded the aminoalkylidyne species $[Fe_2Cp_2(SPh)(CO)(\mu\text{-}CO)\{\mu\text{-}CN(Me)(Xyl)\}]$, **6**, and the bis-alkylidene $[Fe_2Cp_2(CO)(\mu\text{-}CO)\{\mu\text{-}\eta^1:\eta^2\text{-}C(Me)C(Me)(SPh)CN(Me)_2\}]$, **7**, respectively, probably via the intermediacy of radical compounds **2c,d**. The structures of **3**−**7** and **2c,d** were elucidated by DFT calculations, and the isolated products were characterized by analytical and spectroscopic methods.



INTRODUCTION

Alkynes are useful and versatile reagents in organometallic chemistry. They can behave as η^2 terminal ligands or occupy bridging sites in polynuclear complexes,[1] and this preliminary coordination may prelude to an impressive variety of reactions pathways.[2] In particular, the intramolecular alkyne insertion into a metal−carbon bond, in di- and trinuclear metal complexes, represents an intriguing strategy to grow various hydrocarbyl fragments stabilized by bridging multisite coordination.[3]

However, $[Fe_2Cp_2(CO)_4]$ is a long time known, easily available and robust compound,[4] previously used as a starting material for pioneering studies to explore new C−C bond coupling reactions and to model the Fischer−Tropsch process.[5] The construction of organometallic motifs supported on the $[Fe_2Cp_2(CO)_x]$ skeleton has witnessed a renewed interest,[6] in view of the current huge effort to develop sustainable synthetic routes based on earth abundant metals,[7] and the awareness that nature uses diiron organometallic units to perform amazingly efficient enzymatic processes.[8]

Diiron compounds $[Fe_2Cp_2(CO)_3(L)]$ are known to undergo alkyne insertion between one Fe atom and the bridging L ligand, the latter being CO[9] or a fragment isolobal to CO (i.e., thiocarbonyl[10] or isocyanide);[11] see Scheme 1. This general reaction requires the preliminary photolytic displacement of one terminal carbonyl ligand, in order to generate a vacant site available to the entrance of the alkyne.

The analogous interaction of alkynes with aminoalkylidyne complexes, $[Fe_2Cp_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}CNMe(R)\}]^+$ (R = Me, $[\mathbf{1a}]^+$; R = Xyl = 2,6-$C_6H_3Me_2$, $[\mathbf{1b}]^+$), benefits from the net cationic charge of the complexes, weakening the terminal CO binding. Therefore, CO elimination is viable with a chemical approach, rather than with the much less selective photochemical method. More precisely, the required vacant site is

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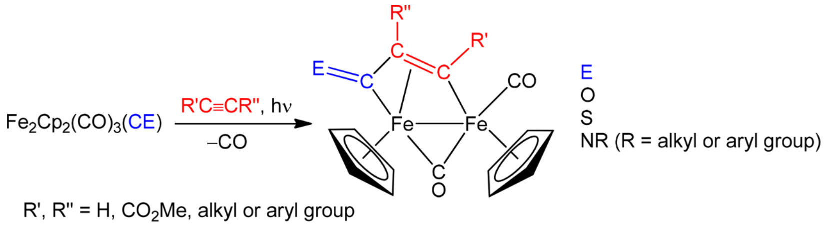
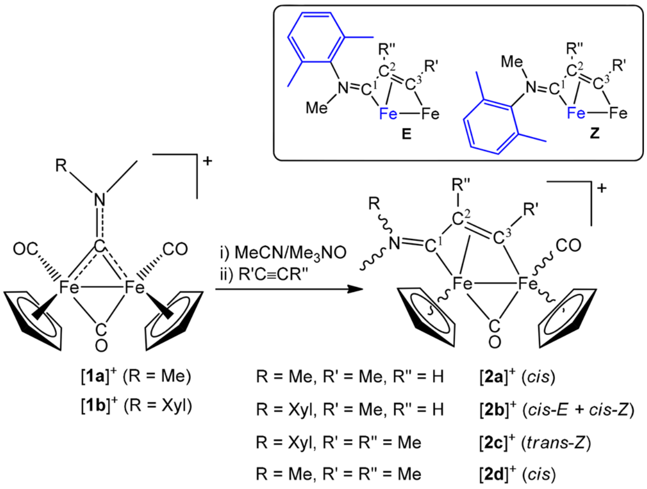
Scheme 1. Insertion Reactions of Alkynes[a]



[a]Into iron–carbonyl (E = O);[9] iron-thiocarbonyl (E = S);[10] iron-isocyanide (E = NR).[11].

conveniently generated removing one carbonyl with trimethylamine-*N*-oxide and can be temporarily occupied by a labile acetonitrile ligand (or chloride, to be abstracted with a silver salt). The subsequent alkyne insertion into iron–carbyne bond, affording vinyliminium complexes, is usually regiospecific, i.e., placing the most hindered alkyne substituent (R′) far from the newly generated iminium moiety.[12] The representative synthesis of [**2a–d**]$^+$ from [**1a–b**]$^+$ and propyne or 2-butyne, respectively, is shown in Scheme 2.

Scheme 2. Synthesis of Vinyliminium Complexes[a]



[a](i) generation of a coordination vacancy and (ii) alkyne insertion into Fe–carbyne bond (Xyl = 2,6-C$_6$H$_3$Me$_2$). Inset: *E*/*Z* geometry around the iminium bond in [**2b–c**]$^+$.

The *μ*-vinyliminium ligand in [**2**]$^+$ displays a rather rare coordination fashion[13] and a rich reactivity, essentially related to the cationic charge of the complex and the cooperative effects provided by the two adjacent iron atoms.[14] Such reactivity ranges from nucleophilic additions,[15] incorporation of small molecular units,[16] and synthesis of unusually functionalized sandwich compounds,[17] or other monoiron species.[18]

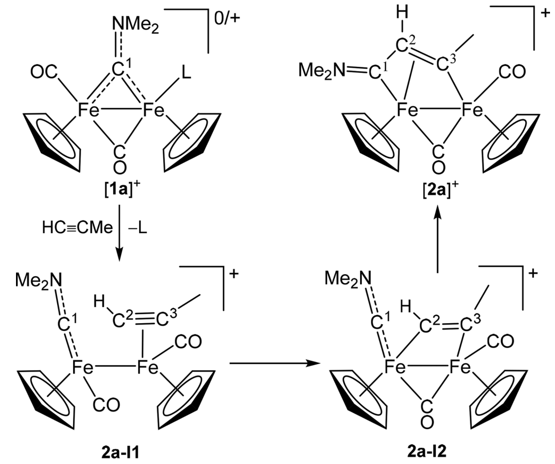
The mechanism of formation of diiron vinyliminium compounds [**2**]$^+$ is not obvious, for at least two reasons. First, iron–alkyne intermediates are likely but elusive[19] and have not been detected experimentally so far. The second point is that the diiron frame seems flexible, from a stereochemical point of view, during the alkyne insertion. Thus, the final products may display both *cis* and *trans* configuration of the Cp ligands (see the specific cases in Scheme 2), while starting complexes [**1a,b**]$^+$ are exclusively *cis*.[20,21] When observed, the *trans* product is a kinetic one and can be quantitatively converted into the more stable *cis* counterpart upon thermal treatment. Moreover, *E*/*Z* isomery can be found in [**2**]$^+$, as a consequence of the two possible spatial orientations adopted by two different N-substituents (Scheme 2, inset).

Herein, we present the results of a density functional theory (DFT) study to give insight into the mechanism of formation of [**2a–c**]$^+$ and to provide explanation for the stereochemistry exhibited by the products. Furthermore, [**2b–d**]SO$_3$CF$_3$ have been selected as starting materials for exploring new synthetic pathways to derivatize the vinyliminium ligand, resulting in unprecedented hydrocarbyl fragments.

■ RESULTS AND DISCUSSION

DFT and Crystallographic Studies. First, the insertion reaction of propyne into the Fe–carbyne bond of [**1a**]$^+$ affording [**2a**]$^{+12a}$ was investigated (Scheme 3). The alkyne is expected to initially coordinate one iron center, although this modality has not been recognized experimentally. In the DFT-optimized geometry of **2a-I1** (Figure 1a), the bridging aminoalkylidyne is migrated to a terminal position, binding one single iron atom (Mayer bond orders[22] for Fe1–C1 and C1–N1 are 1.64 and 1.38, respectively). This rearrangement allows propyne to coordinate the other iron according to a slightly asymmetric η^2-mode (Fe2–C3 = 2.075 Å, Fe2–C4 = 2.101 Å). The two carbonyl ligands occupy terminal sites.

Scheme 3. Proposed DFT Intermediates along the Formation of [2a]$^+$ via Propyne Insertion into Fe–*μ*-Carbyne Bond (L = Cl or NCMe)



Possible intermediate **2a-I1** is 12.0 kcal mol^{-1} less stable than **2a-I2**, wherein the alkyne bridges the two iron centers, and the conversion of the former into the latter requires a small activation energy ($\Delta G^{\ddagger}$ = 1.6 kcal mol^{-1}). In **2a-I2** (Figure

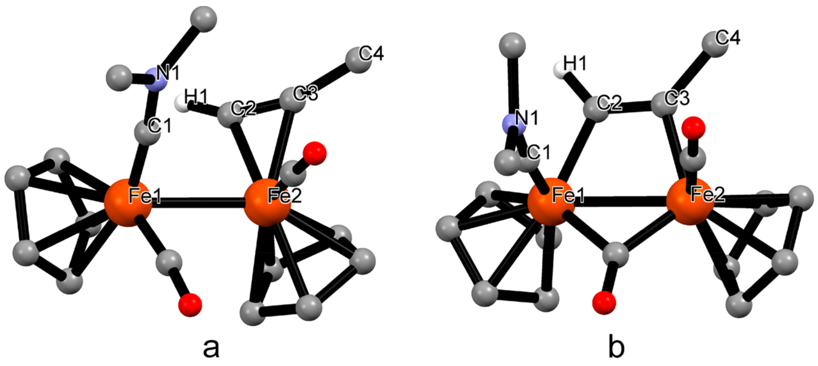


Figure 1. DFT-optimized geometries of **2a-I1** (a) and **2a-I2** (b). Hydrogen atoms (except H1) omitted for clarity. Selected distances (Å) and angles (deg): **2a-I1**: Fe1−Fe2 = 2.745, Fe1−C2 = 3.125, Fe2−C2 = 2.086, Fe2−C3 = 2.110, Fe2−C4 = 3.251, Fe1−C1 = 1.674, C1−N1 = 1.303, C1−C2 = 3.169, C2−C3 = 1.274, H1−C2−C3 = 151.8, C2−C3−C4 = 159.8, Fe1−C1−N1 = 172.9, C1−Fe1−Fe2−C2 = 72.6; **2a-I2**: Fe1−Fe2 = 2.685, Fe1−C2 = 2.010, Fe2−C2 = 2.678, Fe2−C3 = 2.010, Fe1−C1 = 1.655, C1−N1 = 1.304, C1−C2 = 2.458, C2−C3 = 1.326, H1−C2−C3 = 128.6, C2−C3−C4 = 131.2, Fe1−C1−N1 = 173.6.

1b), the orientation of the alkyne Me-substituent minimizes steric repulsions and seems responsible for the observed regiospecificity of the process (see the Introduction and Scheme 2). The distance between the alkyne carbon C2 and the carbyne C1 is 2.458 Å; this configuration is ideal for C1−C2 bond formation (insertion reaction), and **2a-TS2** has been identified as the related transition state. In **2a-TS2**, the C1−C2 distance is shortened to 2.230 Å and the corresponding energy is only 0.4 kcal mol^{-1} higher than that of **2a-I2**.

After insertion, the system collapses to final product [**2a**]$^+$, being 47.8 kcal mol^{-1} more stable than **2a-I2** (a view of the calculated structure of [**2a**]$^+$ is shown in Figure S1). The structure of [**2a**]SO_3CF_3 was experimentally determined by X-ray diffraction: A view of the cation is given in Figure 2, while the salient bonding parameters are reported in Table 1, showing substantial agreement with the corresponding DFT data and with analogous structures previously reported but comprising a xylyl N-substituent.[12]

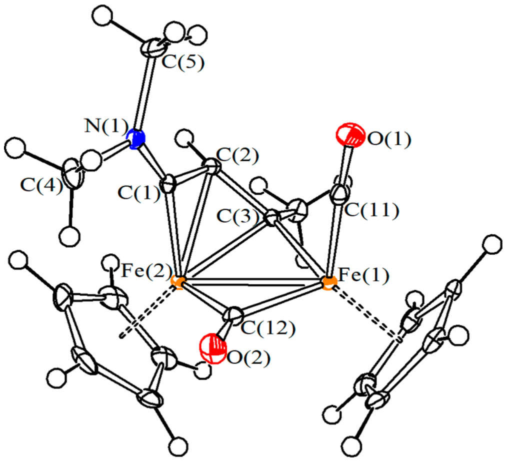


Figure 2. Molecular structure of [**2a**]$^+$ with key atoms labeled. Displacement ellipsoids are at the 30% probability level.

It is interesting to note that in [**2a**]$^+$ (Figure S1) the bonds C1−C2 and C2−C3 exhibit very similar lengths [calculated values: 1.448 (C1−C2) and 1.448 Å (C2−C3); X-ray values: 1.422(2) (C1−C2) and 1.415(2) Å (C2−C3)]. The Mayer bond orders for N−C1, C1−C2, and C2−C3 are 1.38, 1.12, and 1.05, respectively, confirming that the C_3 ligand can be well described as a vinyliminium, with the alkenyl moiety C2−C3 being elongated due to coordination to Fe1. The Mayer bond orders for C1−Fe1, C2−Fe1, C3−Fe1, and C3−Fe2 are 1.01, 0.38, 0.54, and 0.91, respectively.

Table 1. Experimental and Calculated Values for Selected Bond Distances (Å) and Angles (deg) for [2a]$^+$

	X-ray	DFT
Fe(1)−Fe(2)	2.5535(3)	2.538
Fe(1)−C(11)	1.7689(17)	1.728
Fe(1)−C(12)	1.9116(17)	1.894
Fe(2)−C(12)	1.9305(17)	1.928
Fe(1)−C(3)	1.9565(16)	2.062
Fe(2)−C(3)	2.0414(16)	1.954
Fe(2)−C(1)	1.8550(16)	1.844
Fe(2)−C(2)	2.0628(16)	2.103
C(11)−O(1)	1.139(2)	1.194
C(12)−O(2)	1.176(2)	1.217
C(1)−C(2)	1.422(2)	1.448
C(2)−C(3)	1.415(2)	1.448
C(1)−N(1)	1.281(2)	1.317
N(1)−C(4)	1.470(2)	1.490
N(1)−C(5)	1.468(2)	1.493
Fe(1)−C(11)−O(1)	177.18(15)	179.01
Fe(1)−C(12)−Fe(2)	83.30(7)	83.24
Fe(1)−C(3)−Fe(2)	79.36(6)	78.37
Fe(1)−C(3)−C(2)	119.51(12)	120.38
C(3)−C(2)−C(1)	116.06(14)	113.27
C(2)−C(1)−N(1)	133.68(15)	133.78
C(2)−C(1)−Fe(2)	76.76(9)	78.40
C(1)−N(1)−C(4)	121.56(14)	121.56
C(1)−N(1)−C(5)	122.42(14)	122.88
C(4)−N(1)−C(5)	116.02(13)	115.48

The *trans* isomer of [**2a**]$^+$ (experimentally not observed)[12a] could be originated from **2a-I1**, by means of rotation around the Fe−Fe axis affording **2a-I1T** (**2a-I1T** is 30.1 kcal mol^{-1} more stable than **2a-I1**). The transition state for this rotation lies 11.9 kcal mol^{-1} higher than **2a-I1**; therefore, it is expected to be accessible at ambient temperature (**2a-TS**$_{cis-trans}$). Indeed, intramolecular ligand interchanges between *cis*/*trans* and bridging/terminal sites in related diiron systems were previously explained in a similar way (Adams−Cotton mechanism).[23] DFT calculations point that **2a-I1T** has a

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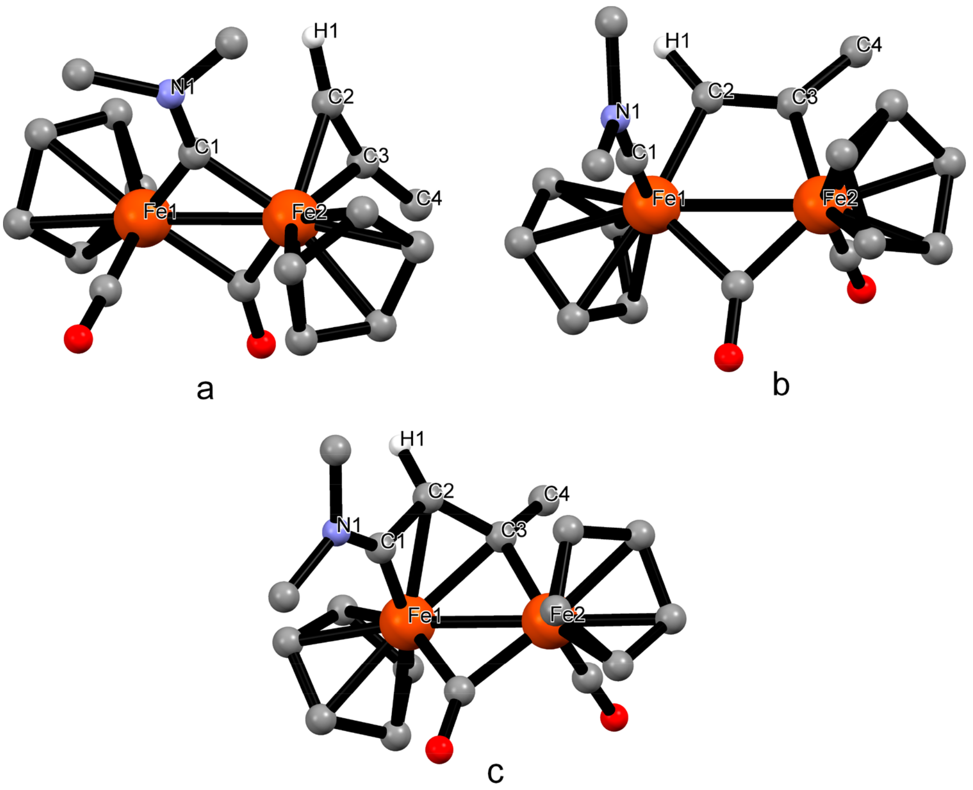


Figure 3. DFT-optimized geometries of **2a-I1T** (a), **2a-I2T** (b), and *trans*-[**2a**]$^+$ (c). Hydrogen atoms (except H1) omitted for clarity. Selected distances (Å) and angles (deg): **2a-I1T**: Fe1−Fe2 = 2.516, Fe1−C1 = 1.852, Fe2−C1 = 1.862, Fe2−C2 = 2.104, Fe2−C3 = 2.148, C1−N1 = 1.328, C2−C3 = 1.270, H1−C2−C3 = 153.5, C2−C3−C4 = 160.1, Fe1−C1−N1 = 136.7; **2a-I2T**: Fe1−Fe2 = 2.685, Fe1−C1 = 1.649, C1−N1 = 1.309, Fe1−C2 = 2.008, Fe2−C3 = 2.014, Fe2−C2 = 2.663, C2−C3 = 1.321, H1−C2−C3 = 129.3, C2−C3−C4 = 131.9, Fe1−C1−N1 = 176.8; *trans*-[**2a**]$^+$: Fe1−Fe2 = 2.529, Fe1−C1 = 1.837, C1−N1 = 1.319, Fe1−C2 = 2.090, Fe1−C2 = 2.059, Fe2−C3 = 1.940, C1−C2 = 1.449, C2−C3 = 1.438, H1−C2−C3 = 121.5, C2−C3−C4 = 119.3, Fe1−C1−N1 = 147.5.

different geometry than **2a-I1**, in that the aminocarbyne bridging coordination is maintained after alkyne binding to one Fe atom (Figure 3a). Nevertheless, further rearrangement to **2a-I2T**, bearing a bridging alkyne (Figure 3b), appears necessary to allow the C1−C2 bond formation. However, the activation energy for the *trans* to *cis* isomerization is much higher than that requested for the formation of **2a-I1**, which makes the whole *trans* path unlikely. The *trans* isomer (Figure 3c) is not favored even on thermodynamic basis, since it is 2.3 kcal mol^{-1} less stable than *cis*-[**2a**]$^+$. A comparative overview of the energy profiles of the calculated pathways leading to *cis*-[**2a**]$^+$ and *trans*-[**2a**]$^+$ is given in Figure 4.

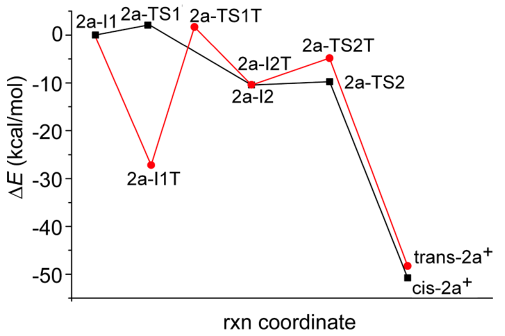


Figure 4. Energy profiles of the pathways leading to *cis*-[**2a**]$^+$ (black line) and *trans*-[**2a**]$^+$ (red line).

Trying to elucidate the synthesis of [**2b**]$^+$,[12a] the picture is qualitatively similar to what discussed for [**2a**]$^+$, but *E* and *Z* isomerism, beyond *cis*/*trans*, is also possible. Indeed the energy difference between (*cis*-*E*)-[**2b**]$^+$ and (*cis*-*Z*)-[**2b**]$^+$ is only 0.8 kcal mol^{-1}, thus justifying the formation of both forms (experimental *E* to *Z* ratio = 2). The obtained product exclusively displays *cis* geometry, which is more stable than the *trans* one by 1.8 kcal mol^{-1}. Views of the calculated structures of (*cis*-*E*)-[**2b**]$^+$ and (*cis*-*Z*)-[**2b**]$^+$ are provided as Figure S2.

Regarding [**2c**]$^+$, the experimental outcome points out that the *trans*-Z isomer (Figure 5) is the kinetic product, converting into the *cis*-*Z* isomer by thermal treatment.[12b] DFT calculations show that the coordination of 2-butyne forces the aminoalkylidyne to shift to one single iron atom (**2c-I1**). This configuration is stabilized by a CH···π weak interaction between the aromatic ring of the xylyl moiety and the methyl belonging to the alkyne. Due to this interaction, which is lost in the TS, the activation barrier for the migration of the alkyne to bridging position (**2c-I2**, $\Delta G = -9.1$ kcal mol^{-1}) is 12.6 kcal mol^{-1} (**2c-TS1**), i.e., higher respect to the case of [**2a**]$^+$. The subsequent insertion step leads to the *cis*-*Z* isomer (ΔG(**2c-TS2**) = −7.5 kcal mol^{-1}; ΔG(*cis*-[**2c**]$^+$) = −47.2 kcal mol^{-1}). The route to the *trans* isomer is more probable: Starting from **2c-I1**, the activation barrier for the rotation around the Fe−Fe bond is 9.9 kcal mol^{-1} (**2c-TS**$_{cis-trans}$), i.e., lower than the activation energy required by **2c-TS1**. The rotation leads to the *trans* isomer, **2c-I1T** (Figure 5), being 29.2 kcal mol^{-1} more stable than **2c-I1**. Then, the alkyne can move to bridging position (ΔG(**2c-TS1**) = 4.7 kcal mol^{-1}, ΔG([**2c-I2T**]$^+$) =

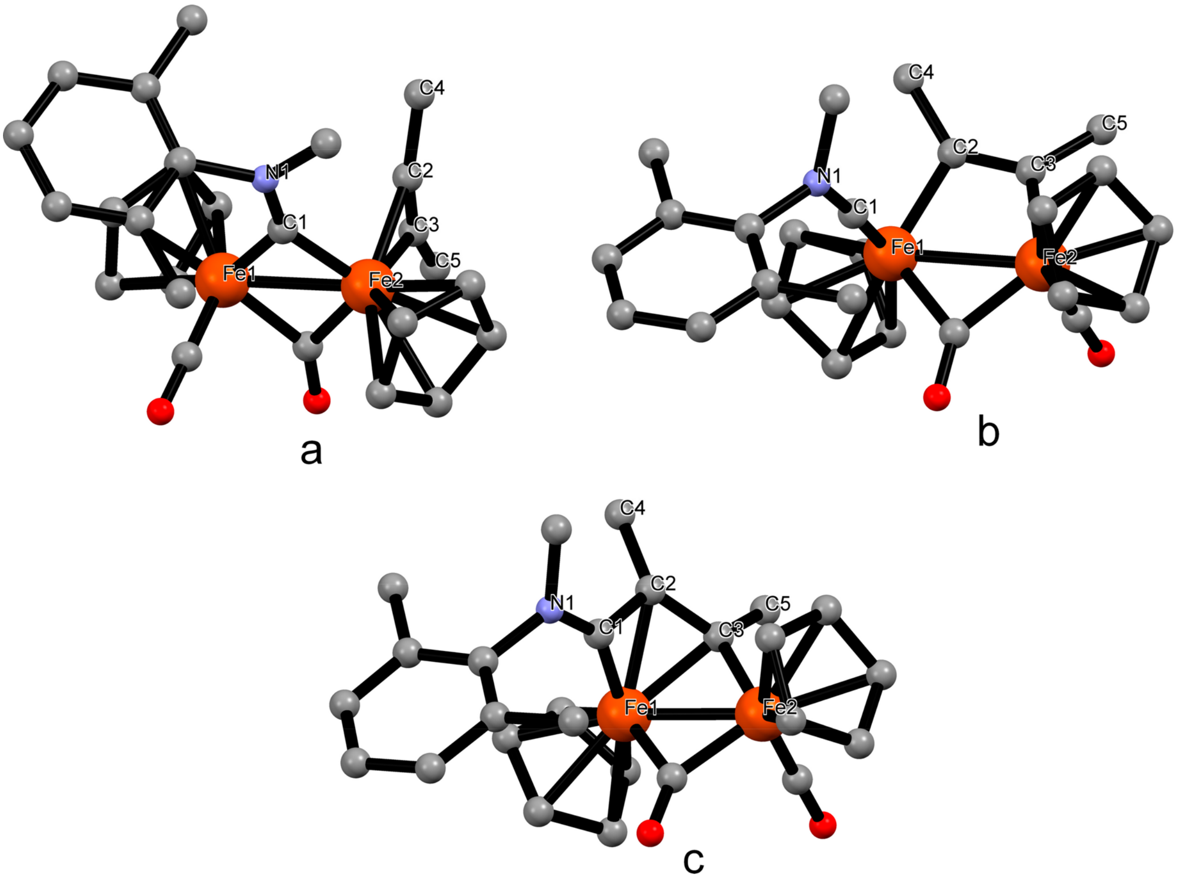


Figure 5. DFT-optimized geometries of **2c-I1T** (a), **2c-I2T** (b) and (*trans*-Z)-[**2c**]$^+$ (c). Hydrogen atoms omitted for clarity. Selected distances (Å) and angles (deg): **2c-I1T**: Fe1−Fe2 = 2.513, Fe1−C1 = 1.870, Fe2−C1 = 1.848, Fe2−C2 = 2.124, Fe2−C3 = 2.140, C1−N1 = 1.337, C1−C2 = 2.742, C2−C3 = 1.271, C2−C4 = 1.483, C4−C2−C3 = 153.0, C2−C3−C5 = 157.5, Fe1−C1−N1 = 134.6; **2c-I2T**: Fe1−Fe2 = 2.651, Fe1−C1 = 1.644, Fe1−C2 = 2.018, Fe2−C2 = 2.703, Fe2−C3 = 2.606, C1−N1 = 1.310, C2−C3 = 1.324, C2−C4 = 1.511, C4−C2−C3 = 131.5, C2−C3−C5 = 130.6, Fe1−C1−N1 = 175.1; (*trans*-Z)-[**2c**]$^+$: Fe1−Fe2 = 2.531, Fe1−C1 = 1.337, Fe1−C2 = 2.123, Fe1−C3 = 2.034, Fe2−C3 = 1.938, C1−N1 = 1.326, C1−C2 = 1.452, C2−C3 = 1.444, C2−C4 = 1.526, C1−C2−C3 = 113.3, N1−C1−C2 = 132.2, C2−C3−C5 = 120.2.

−4.8 kcal mol^{-1}; see Figure 5), and finally, the insertion step takes place almost barrierless (Δ*G*(**2c-TS2**) = −7.7 kcal mol^{-1}), leading to the product (Δ*G*((*cis*-*Z*)-[**2c**]$^+$) = −53.6 kcal mol^{-1}, Figure 6). It is possible that the thermal isomerization of (*trans*-Z)-[**2c**]$^+$ to (*cis*-*Z*)-[**2c**]$^+$.[12b] proceeds through fast de-insertion of the alkyne, thus allowing the system to reach the thermodynamic equilibrium. The calculated structure of (*cis*-*Z*)-[**2c**]$^+$ is shown in Figure S4, while a comparison of calculated and experimental bonding parameters is given in Table S1.

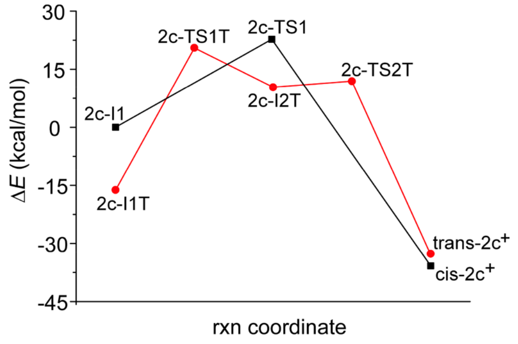
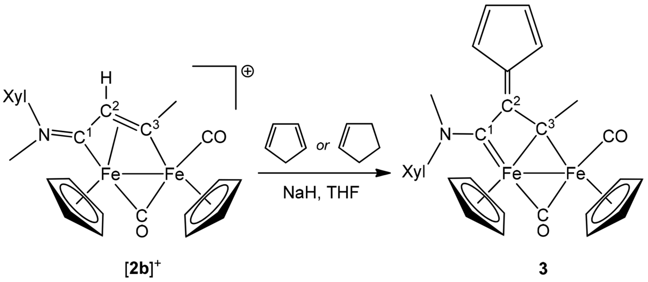


Figure 6. Energy profiles of the pathways leading to (*cis*-*Z*)-[**2c**]$^+$ (black line) and (*trans*-Z)-[**2c**]$^+$ (red line).

C−C Coupling Reactions. The vinyliminium ligand is a useful substrate to generate C−C bonds, and previous reports regarded the addition of cyanide ion,[24] acetylides,[25] and isocyanides.[26] We came interested in the possibility of tethering alkenes to the vinyliminium skeleton upon C^2−H removal. The investigation of the reactivity of [**2a**,**b**]SO_3CF_3 with a series of alkenes did not afford stable products, except in one case. Thus, the reaction of [**2b**]SO_3CF_3 with cyclopentene, in tetrahydrofuran in the presence of sodium hydride, afforded a modest amount of fulvene−bis-alkylidene complex **3**, in admixture with other nonidentified species (Scheme 4).

Scheme 4. Modification of a Vinyliminium Ligand with a Fulvene Moiety via Unusual Activation of Cyclopentadiene/Cyclopentene



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The formation of **3** is notable, since it requires a cycloalkene activation (from cyclopentene to fulvene) almost unknown in the literature. Compound **3** was purified by alumina chromatography and fully characterized by elemental analysis, mass spectrometry, and IR and NMR spectroscopy. Once the structure of **3** had been elucidated, we evaluated that cyclopentadiene could be a more suitable reactant to the synthesis. As a matter of fact, **3** was obtained with an optimized yield of 61% from [**2b**]SO_3CF_3, freshly distilled cyclopentadiene, and sodium hydride (Scheme 4). The formation of **3** appears the result of coupling of dehydrogenated cyclopentadiene with the deprotonated form of $[\mathbf{2b}]^+$, possessing some carbene character (Figure 7).[26] It should be mentioned here that the uncommon cyclopentadiene to fulvene conversion was previously reported upon base-assisted condensation with ketones,[27] but it is unprecedented for an organometallic structure.

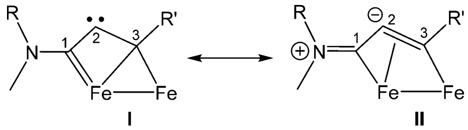


Figure 7. Resonance forms representing the fragment derived from vinyliminium C^2−H deprotonation.

The IR spectrum of **3** (in CH_2Cl_2 solution) displays two bands due to the carbonyl ligands (at 1949 and 1783 cm^{-1}) and an additional absorption at 1551 cm^{-1}, assigned to the coupled vibrations of the $C^1{=}N$ and the $C^2{=}C^3$ bonds by comparison with the calculated IR spectrum (vide infra). The ^1H NMR spectrum (in $CDCl_3$) contains one set of resonances, and the signals related to the fulvene moiety consist of two multiplets at 6.49 and 6.36 ppm, thus indicating free rotation at ambient temperature around the C^2−C bond (vide infra). A NOE experiment by irradiating the Cp resonance at 4.35 ppm resulted in a significant enhancement of the remaining Cp signal at 4.97 ppm, pointing that the two rings are arranged in relative *cis* geometry. However, irradiation of the resonance at 3.27 ppm (NMe) revealed NOE effect with the CH fulvene resonance at 6.49 ppm, but not with any Cp resonance. This outcome clearly indicates that the N-bound methyl group points far from the Fe−Fe axis, the same *Z*-configuration being usually adopted by diiron complexes comprising C^2-substituted vinyliminium and bis-alkylidene ligands.[16a,12b,28]

The ^{13}C resonances related to the C^1 and C^3 carbons fall at typical low fields (247.4 and 195.1 ppm), in agreement with their amino-alkylidene and alkylidene character, respectively.[15b] Several attempts were done to collect X-ray quality crystals of **3**, but unsuccessfully. The structure of **3** (in the *cis-Z* form, as indicated by NMR) was therefore optimized by DFT calculations, and a view of the structure is shown in Figure 8 with calculated bonding parameters reported in the caption.

The Mayer bond orders for N1−C1, C1−C2, C2−C3, and C2−C4 are 1.36, 0.97, 0.83, and 1.24, respectively (the calculated C2−C4 bond length is 1.414 Å). The DFT data suggest some zwitterionic character in the structure of **3**, whose bridging C_3 ligand should be alternatively described as a vinyliminium with the negative charge delocalized on the five-membered substituent (Figure 9). Analogous vinyliminium/bis-alkylidene hybrid structure was revealed by the crystallographic characterization of $[Fe_2Cp_2(CO)(\mu\text{-}CO)\{\mu\text{-}\eta^1{:}\eta^2\text{-}C(Me)C(O)CN(Me)(Xyl)\}]$, differing from **3** in the presence of an oxygen atom in the place of the fulvene moiety.[28] It has to be remarked that the latter two complexes exhibit very close IR spectra and comparable values of ^{13}C NMR chemical shifts for C^1 and C^3.[29] Structure **II** in Figure 9 accounts for the experimentally observed free rotation of the C_5 ring around the C2−C4 bond at ambient temperature (see above).

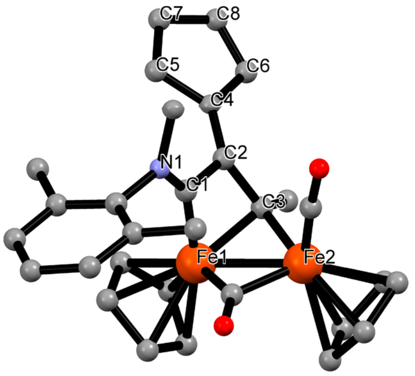


Figure 8. DFT-optimized geometry of **3**. Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (deg): Fe1−Fe2 = 2.503, Fe1−C1 = 1.865, Fe1−C3 = 2.014, Fe1−C2 = 2.403, Fe2−C3 = 1.981, C1−C2 = 1.477, C2−C3 = 1.486, C1−N1 = 1.339, C2−C4 = 1.414, C4−C5 = 1.472, C5−C7 = 1.389, C7−C8 = 1.470, C6−C8 = 1.390, C6−C4= 1.472, C1−C2−C3= 102.5, C2−C1−N1= 127.7, C1−C2−C6 = 125.0, N1−C1−C2−C4 = −48.1.

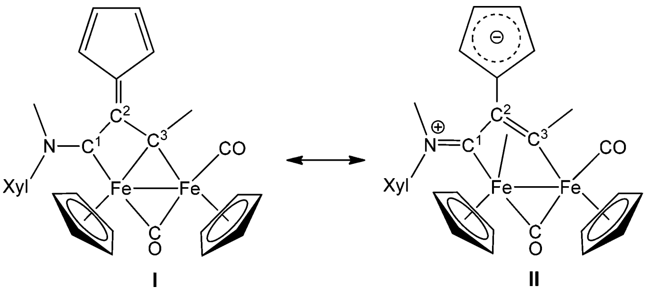
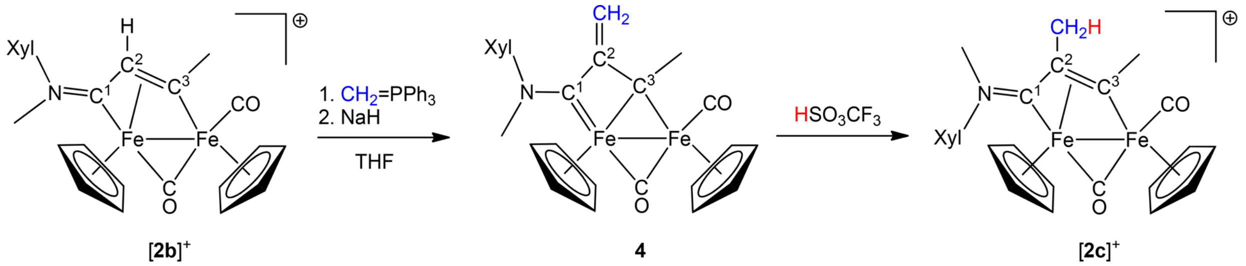


Figure 9. Resonance formulas describing the structure of **3** (compare to Figure 7).

The reaction of [**2b**]SO_3CF_3 with $PPh_3{=}CH_2$/NaH, in tetrahydrofuran, readily proceeded with the clean formation of a neutral product, as suggested by the IR spectrum recorded on the reaction solution after 30 min [ν_{CO} = 1952 and 1773 cm^{-1}]. It is reasonable to assume that the detected compound is bis-alkylidene **4**, analogous to **3** (Figure 9, structure **I**). The formation of **4** might be viewed as the coupling between the carbene moiety belonging to deprotonated $[\mathbf{2b}]^+$ (Figure 7, structure **I**) and the $[CH_2]$ fragment originating from $PPh_3{=}CH_2$. Examples of $[CH_2]$ transfer from $Ph_3P{=}CH_2$ to carbene groups were indeed previously documented.[30] Attempts to isolate **4** were unsuccessful and led to recovery of a small amount of [**2b**]SO_3CF_3. Instead, the treatment of the reaction mixture with HSO_3CF_3 resulted in the fast and clean formation of [**2c**]SO_3CF_3 (Scheme 5), which was isolated in 75% yield after work up and unambiguously identified by elemental analysis, IR, and ^1H NMR spectroscopy.

The structure of **4** was optimized by DFT calculations; the calculated bonding parameters are in well agreement with a bis-alkylidene nature of the bridging C_3 ligand[15b] (Figure 10). On theoretical grounds, the *E* isomer is slightly more stable than the opposite *Z* one (ΔE = 2.0 kcal mol^{-1}), presumably due to attractive forces between the $[CH_2]$ group and the

Scheme 5. Two-Step H^+−CH_3^+ Substitution at a Vinyliminium Ligand



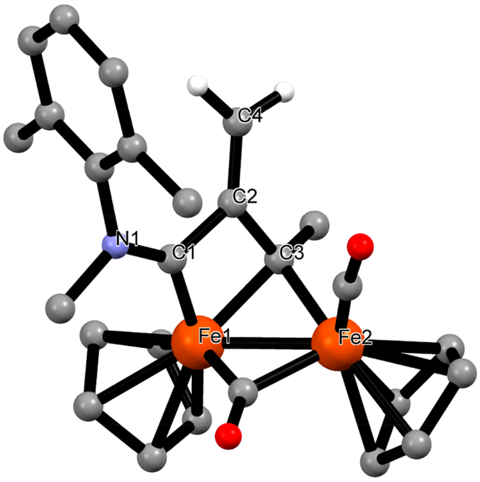


Figure 10. DFT-optimized geometry of *E*-**4**. Hydrogen atoms (except CH_2) omitted for clarity. Selected bond lengths (Å) and angles (deg): Fe1−Fe2 = 2.487, Fe1−C1 = 1.857, Fe1−C2 = 2.514, Fe1−C3 = 1.980, C1−N1 = 1.346, C1−C2 = 1.486, C2−C3 = 1.504, C2−C4 = 1.370, Fe2−C3 = 1.990, C1−C2−C3 = 98.3, C2−C1−N1 = 127.4, C3−C2−C6 = 128.5, N1−C1−C2−C4 = −17.9.

aromatic xylyl ring (CH−π interaction). However, final product [**2c**]$^+$ was recognized in the *Z* form (Scheme 2). This fact indicates that *E* to *Z* conversion must take place on going from [**2b**]$^+$ to [**2c**]$^+$ via **4**, possibly through rotation around the C^1−N axis in **4** (calculated C^1−N distance = 1.346 Å).

With the aim of further exploring the possibility of C−C bond formation, we studied the reaction of [**2b**]SO_3CF_3 with benzyl bromide, in the presence of sodium hydride. This reaction afforded vinyliminium compound [**5**]Br in 55% yield, Scheme 6.

Compound [**5**]Br was purified by quick chromatography through alumina and then characterized by elemental analysis, IR, and NMR spectroscopy. The IR spectrum (in CH_2Cl_2) displays a pattern matching that of analogous complexes bearing alkyl substituents at both C^2 and C^3.[12b] More precisely, the two carbonyl bands are seen at 1986 and 1814 cm^{-1}, while the absorption due to the NC^1C^2 moiety falls at 1603 cm^{-1}. As a comparison, the corresponding values for (*cis-Z*)-[**2c**]-SO_3CF_3 are 1986, 1818, and 1613 cm^{-1}.[12b]

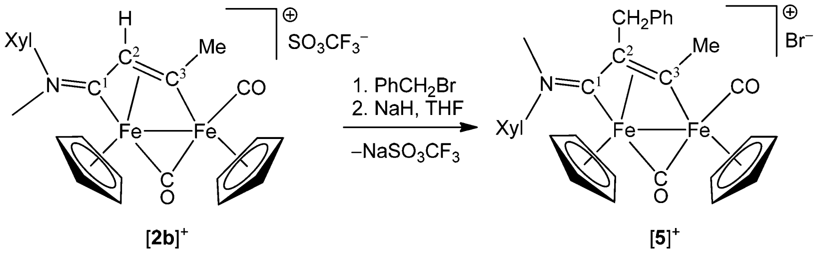
The NMR spectra of [**5**]Br (in $CDCl_3$) evidenced the presence of an isomeric mixture. In general, *E*/*Z* and *cis*/*trans* isomers of diiron vinyliminium complexes can be easily distinguished by ^1H and ^{13}C NMR data (especially the resonances due to Cp and methyl groups).[12] Therefore, in this case the isomers were identified as *cis-E* and *cis-Z* (*E*/*Z* ratio = 2, based on ^1H NMR). The ^{19}F spectrum ruled out the presence of residual triflate anion.

In order to give insight into thermodynamic and structural aspects, we calculated the structures of *E*-[**5**]$^+$ and *Z*-[**5**]$^+$ (Figure 11). The *Z* isomer resulted 2.0 kcal mol^{-1} more stable than the *E* one. In accordance with the DFT outcome, the isomeric mixture was cleanly converted into the most stable *Z* form by heating in methanol solution.

The synthesis of [**5**]$^+$ is formally the result of deprotonation of the parent vinyliminium followed by nucleophilic attack of the resulting zwitterionic species (Figure 7, structure **II**) to the alkyl halide. Despite the tendency of benzyl bromide to be engaged in radical reactions,[31] the possibility of an alternative, radical pathway starting with the NaH-reduction of [**2b**]$^+$ should be ruled out: As a matter of fact, the reaction of [**2b**]SO_3CF_3 with benzyl bromide in the presence of cobaltocene, i.e., a typical mono electron reductant employed in organometallic chemistry,[32] resulted in the formation of a mixture of products not including [**5**]$^+$.

Synthesis of Thiophenolate Compounds. The chemistry of the vinyliminium compounds [**2c**,**d**]SO_3CF_3 is limited by the absence of C^2-bound hydrogen, not allowing the structural modifications otherwise described for [**2a**,**b**]$^+$ (Schemes 4−6). Notwithstanding, it has been documented that C^2-substituted vinyliminium compounds may convert into monoiron species leaving the C^1−C^2−C^3 chain intact, upon reaction with strong reducing agents (NaH or Li^{t}Bu).[33] Sulfur or selenium can be incorporated during the fragmentation process, leading to functionalized metallacycles.[18]

Scheme 6. Derivatization of Vinyliminium Ligand via C−H Cleavage and C−C Coupling



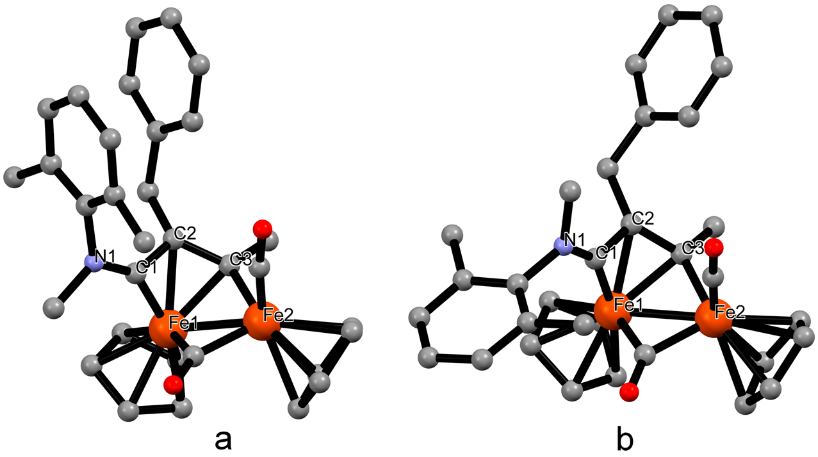
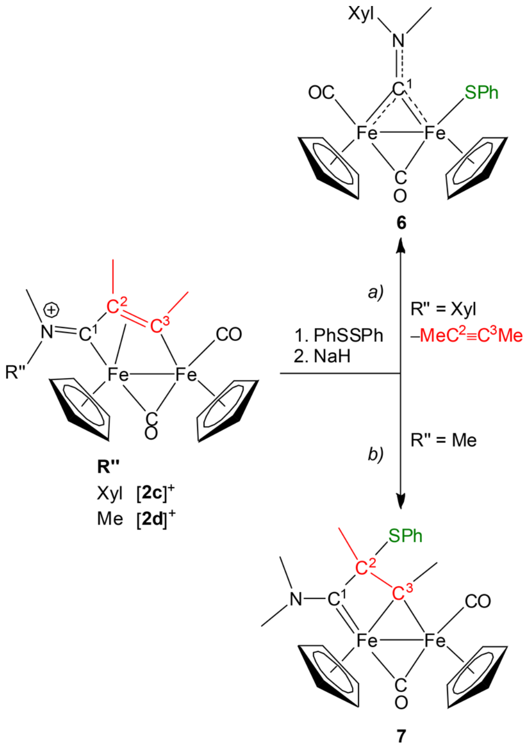


Figure 11. DFT-optimized geometries of (*cis-E*)-[**5**]$^+$ (a) and (*cis-Z*)-[**5**]$^+$ (b). Hydrogen atoms omitted for clarity. Selected distances (Å) and angles (deg): (*cis-E*)-[**5**]$^+$: Fe1−Fe2 = 2.529, Fe1−C1 = 1.845, Fe1−C2 = 2.098, Fe1−C3 = 2.048, Fe2−C3 = 1.952, C1−N1 = 1.322, C1−C2 = 1.447, C2−C3 = 1.452, C1−C2−C3 = 144.5, Fe1−C1−N1 = 144.9; (*cis-Z*)-[**5**]$^+$: Fe1−Fe2 = 2.543, Fe1−C1 = 1.849, Fe1−C2 = 2.104, Fe1−C3 = 2.063, Fe2−C3 = 1.945, C1−N1 = 1.320, C1−C2 = 1.445, C2−C3 = 1.446, C1−C2−C3 = 114.6, Fe1−C1−N1 = 148.3.

We studied the reactivity of [**2c**,**d**]SO_3CF_3 with NaH in the presence of PhSSPh. The reaction involving [**2c**]$^+$ proceeded with alkyne de-insertion and binding of the [SPh] group to one metal center, affording the *μ*-aminocarbyne complex [Fe_2Cp_2(SPh)(CO)(*μ*-CO){*μ*-CN(Me)(Xyl)}], **6**, in 68% yield (Scheme 7a and Figure 12a). The aminocarbyne moiety manifests itself with a diagnostic ^{13}C NMR resonance at characteristic low field (338.5 ppm, $CDCl_3$ solution).[20,34] The IR and NMR features of **6** match those of similar diiron *μ*-aminocarbyne complexes with *cis*-oriented Cp ligands.[34f,g,35]

Scheme 7. Reactions of Vinyliminium Complexes with Diphenyldisulfide in the Presence of Sodium Hydride[a]



[a](a) De-insertion reaction; (b) formation of [SPh]-functionalized bridging ligand.

Interestingly, the reaction of [**2d**]SO_3CF_3 with PhSSPh/NaH revealed a completely different outcome and afforded the bis-alkylidene product [Fe_2Cp_2(CO)(*μ*-CO){*μ*-η^1:η^2-C(Me)-C(Me)(SPh)CN(Me)$_2$}], **7**, in 55% yield (Scheme 7b and Figure 12b).

The IR spectrum of **7** displays carbonyl bands at typically low wavenumbers (1929 and 1752 cm^{-1}), as already found for other diiron complexes containing the bis-alkylidene skeleton.[15b] In the ^1H NMR spectrum, the Cp ligands resonate at 4.61 and 4.39 ppm; these values indicating a *cis* arrangement by comparison with a library of data referring to analogous compounds.[15b] The major NMR features are given by the low field ^{13}C resonances at 251.6 and 177.0 ppm, attributed to the alkylidene carbons C^1 and C^3, respectively. In accordance with the aminocarbene character of C^1, the two N-bound methyl groups are not equivalent due to inhibited rotation around the N−C^1 bond.

The distinct outcomes of the reactions of homologous vinyliminium salts [**2c**,**d**]SO_3CF_3 with PhSSPh/NaH were investigated by DFT calculations. It is reasonable to assume that both reactions proceed with initial electron transfer from sodium hydride to cationic complexes [**2c**,**d**]$^+$ to give **2c**,**d** and subsequent capture of the thiophenolato radical by **2c**,**d**. However, the nucleophilic attack to [**2c**,**d**]$^+$ of the thiophenolate anion, with this anion possibly generated from the interaction of diphenyldisulfide with sodium hydride, was ruled out on the basis of the experimental evidence that the reactions of [**2c**,**d**]SO_3CF_3 with 1−2 equiv of NaSPh in tetrahydrofuran did not produce **6** or **7**. More precisely, [**2d**]SO_3CF_3 revealed to be substantially unreactive, while the addition of NaSPh to [**2c**]SO_3CF_3 led to a mixture of decomposition products. The structures of radical species **2c**,**d** were optimized by DFT (doublet state), resulting rather similar to those of the corresponding parent complexes [**2c**,**d**]$^+$. However, a slight lengthening of the C1−N bond is observable on going from [**2c**,**d**]$^+$ to **2c**,**d** (from 1.317 to 1.337 Å; Mayer bond order from 1.38 to 1.21). The spin density maps related to **2c**,**d** are shown in Figure 13: In both compounds, the spin density has a significant component on the bridging ligand (see Table S2 for details). This favors the SPh attack to the C^2 carbon of **2d** to give **7**. However, the major steric hindrance exerted by the iminium group in **2c** is

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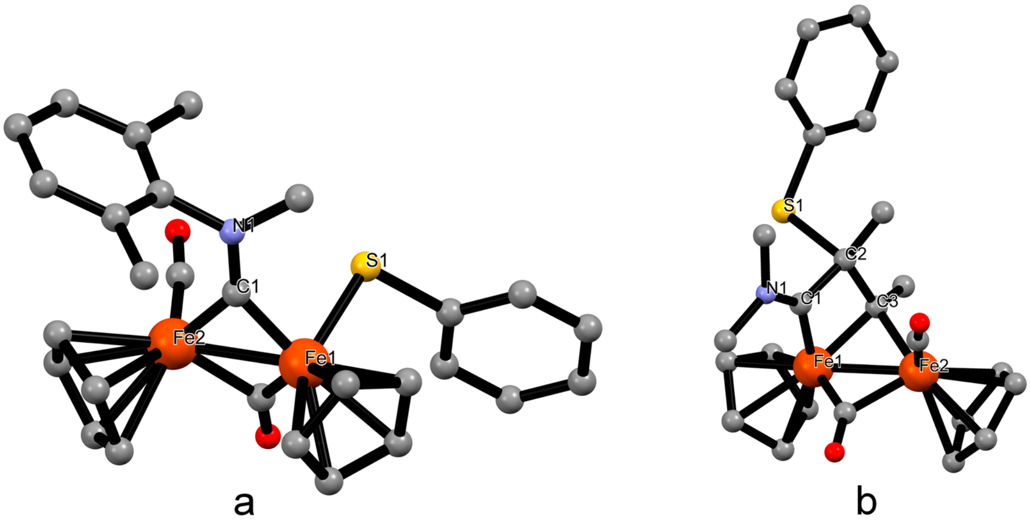
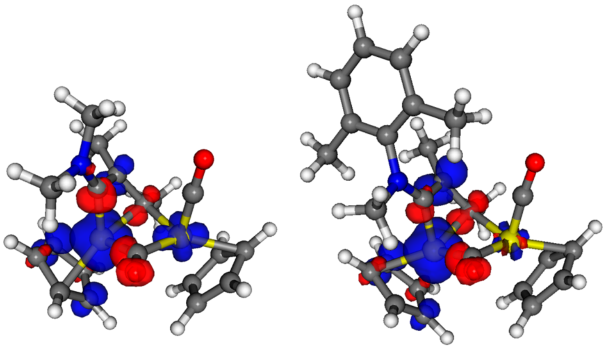


Figure 12. DFT-optimized structures of **6** (a) and **7** (b). Hydrogen atoms omitted for clarity. Selected distances (Å) and angles (deg): **6**: Fe1−Fe2 = 2.473, Fe1−C1 = 1.861, Fe2−C1 = 1.807, C1−N1 = 1.338, Fe2−S1 = 2.371, Fe1−C1−N1 = 137.0, C1−Fe2−S = 85.4, Fe2−S1−C3 = 104.1; **7**: Fe1−Fe2 = 2.484, Fe1−C1 = 1.868, Fe1−C2 = 2.559, Fe1−C3 = 1.957, Fe2−C1 = 3.072, Fe2−C3 = 2.022, C1−C2 = 1.526, C2−C3 = 1.528, C2−S1 = 2.108, C1−N1 = 1.337, Fe1−C1−N1 = 136.8, C1−C2−C3 = 94.4, C1−C2−S1 = 97.8.



2c **2d**

Figure 13. Spin density maps for radical complexes **2c** and **2d**.

presumably responsible for addressing the SPh addition to iron to give **6**.

■ CONCLUSIONS

Vinyliminium ligands in diiron complexes exhibit a rare bridging coordination fashion and a unique reactivity associated with the cooperative effects provided by the two iron centers and the net cationic charge of the compounds. Herein, we have proposed, on the basis of DFT calculations, a mechanistic pathway for the alkyne insertion implicated in the synthesis of the vinyliminium complexes. The described mechanism is in accordance with the regiospecificity of the reaction and the stereochemistry exhibited by the products (*cis*/*trans* and *E*/*Z*), depending on the iminium substituents and the alkyne. These findings may have some general validity and might be extended to analogous alkyne insertion reactions occurring on dimetal frames.[3,9−11] Furthermore, we have described the synthesis of unprecedented organometallic motifs via vinyliminium C−H bond cleavage and subsequent C−C coupling with a variety of organic reactants, including the unusual activation of a cycloalkene. Vinyliminium complexes lacking of appropriate C−H function may be derivatized through one-electron reduction, the resulting radical species incorporating the [SPh] fragment in different ways according to the iminium substituents.

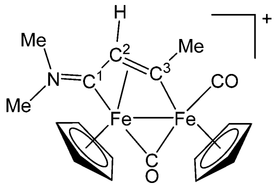
■ EXPERIMENTAL SECTION

Materials and Methods. All the reactions were routinely carried out under nitrogen atmosphere, using standard Schlenk techniques. Organic reactants (Sigma-Aldrich or TCI Europe) were commercial products of the highest purity available. Compounds [**1a**,**b**]SO_3CF_3,[20] triphenylphosphonium methylide (from methyltriphenylphosphonium bromide and LiBu),[36] and [**2c**,**d**]SO_3CF_3[12b] were prepared according to published procedures. Solvents were distilled before use under nitrogen over appropriate drying agents. Once isolated, the metal products were conserved under nitrogen. Chromatography separations were carried out on columns of deactivated alumina (Sigma-Aldrich, 4% w/w water). C, H, and N analyses were performed on a ThermoQuest Flash 1112 Series EA Instrument. The bromide content of [**5**]Br was determined by the Mohr method[37] on a solution prepared by dissolution of the solid in aqueous KOH at boiling temperature, followed by cooling to room temperature and addition of HNO_3 up to neutralization. ESI-MS spectrum was recorded on Waters Micromass ZQ 4000 with the sample dissolved in CH_3CN. Infrared spectra were recorded on liquid samples with a PerkinElmer Spectrum 2000 FT-IR spectrophotometer. NMR spectra were recorded at 298 K on a Mercury Plus 400 instrument. The chemical shifts for ^1H and ^{13}C were referenced to the nondeuterated aliquot of the solvent. The ^1H and ^{13}C NMR spectra were assigned with the assistance of $^1H,^{13}C$ correlation measured through *gs*-HSQC and *gs*-HMBC experiments.[38] NMR signals due to a second isomeric form (where it has been possible to detect them) are italicized. NOE measurements were recorded using the DPFGSE-NOE sequence.[21]

Synthesis of [$Fe_2Cp_2(CO)(\mu\text{-}CO)\{\mu\text{-}\eta^1{:}\eta^3\text{-}C^3(Me)C^2HC^1N(Me)(R)\}$]$SO_3CF_3$ (R = Me, [2a]SO_3CF_3, Chart 1; R = Xyl, [2b]SO_3CF_3, Chart 2). The title compounds were prepared by using a modified literature procedure.[12b]

A solution of [**1a**]SO_3CF_3 (460 mg, 0.866 mmol) in acetonitrile (ca. 10 mL) was treated with Me_3NO (85 mg, 1.13 mmol). The solution turned darker and was stirred at room temperature for 40 min, allowing continuous flux of the produced gas (CO_2) away from the reaction system. Thus, IR spectroscopy indicated the complete conversion of the starting material into [$Fe_2Cp_2(CO)(\mu\text{-}CO)(NCMe)\{\mu\text{-}CNMe_2\}$]$SO_3CF_3$.[20] The volatiles were removed under vacuum. The residue was dissolved in CH_2Cl_2 (20 mL), and a solution of propyne in THF (3.5 mL, ca. 1 mol/L) was added. The resulting mixture was allowed to stir at room temperature for 72 h,

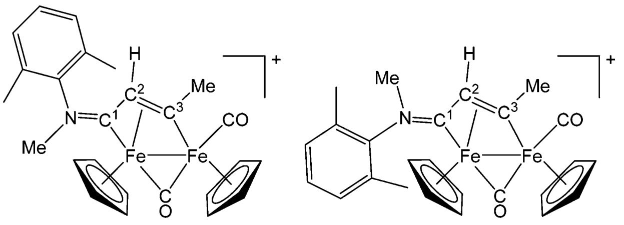
Chart 1. Structure of $[\mathbf{2a}]^{+}$



then charged on an alumina column. After washing with CH_2Cl_2/THF (up to 2:1 v/v) mixtures, the product was collected as a brown fraction using neat MeOH as eluent. A brown solid was obtained upon removal of the solvent under reduced pressure. Yield 451 mg, 96%. Anal. Calcd for $C_{19}H_{20}F_3Fe_2NO_5S$: C, 42.02; H, 3.71; N, 2.58. Found: C, 41.89; H, 3.64; N, 2.68. IR (CH_2Cl_2) $\tilde{\nu}$/cm^{-1} = 1990 vs (CO), 1806 s (μ-CO), 1684 m (C^2C^1N). ^{1}H NMR (dmso-d_6) δ/ppm = 5.48, 5.14 (s, 10 H, Cp); 4.51 (s, 1 H, C^2H); 3.82, 3.77 (s, 6 H, NMe + C^3 Me); 3.18 (s, 6 H, NMe). ^{13}C{^{1}H} NMR (dmso-d_6) δ/ppm = 258.4 (μ-CO); 225.6 (C^1); 211.4 (CO); 208.0 (C^3); 91.2, 88.0 (Cp); 52.1 (C^2); 51.0, 44.8 (NMe_2); 41.7 (C^3 Me). Crystals suitable for X-ray analysis were obtained by slow diffusion of diethyl ether into a dichloromethane solution of $[\mathbf{2a}]SO_3CF_3$ at ambient temperature.

Compound $[\mathbf{2b}]SO_3CF_3$ was obtained using the same procedure employed for the synthesis of $[\mathbf{2a}]SO_3CF_3$, from $[\mathbf{1b}]SO_3CF_3$ (450 mg, 0.724 mmol) and an excess of propyne. Yield 390 mg, 85%. Anal. Calcd for $C_{26}H_{26}F_3Fe_2NO_5S$: C, 49.31; H, 4.14; N, 2.21. Found: C, 49.20; H, 4.22; N, 2.16. IR (CH_2Cl_2) ν/cm^{-1} = 2000 vs (CO), 1815 s (μ-CO), 1632 m (NC^1C^2). ^{1}H NMR ($CDCl_3$) δ/ppm = 7.42–7.09, 6.92 (m, 3 H, $C_6H_3Me_2$); 5.39, 5.28, 5.16, 4.72 (s, 10 H, Cp); 5.23, 3.99 (s, 1 H, C^2H); 4.16, 3.48 (s, 3 H, NMe); 3.99, 3.82 (s, 3 H, C^3 Me); 2.53, 2.28, 1.96, 1.75 (s, 6 H, $C_6H_3Me_2$). *E*/*Z* ratio ≅ 2. ^{13}C{^{1}H} NMR ($CDCl_3$) δ/ppm = 254.6 (μ-CO); 233.4, 230.9 (C^1); 211.6, 211.4 (C^3); 210.6, 209.7 (CO); 144.8, 141.1 (*ipso*-$C_6H_3Me_2$); 134.0, 133.7, 131.6, 129.6, 129.5, 129.3, 129.0 ($C_6H_3Me_2$); 91.0, 90.7, 87.8, 87.6 (Cp); 53.5, 52.7 (C^2); 52.1, 46.0 (NMe); 42.7, 42.3 (C^3Me); 17.9, 17.8, 17.7, 17.2 ($C_6H_3Me_2$).

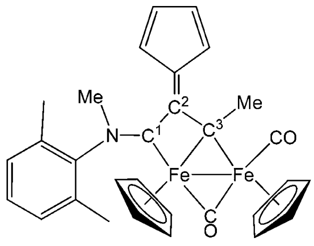
Chart 2. Structure of $[\mathbf{2b}]^{+}$



E Z

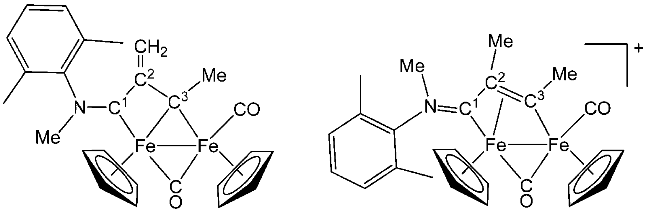
Synthesis of $[Fe_2Cp_2(CO)(\mu\text{-}CO)\{\mu\text{-}\eta^1{:}\eta^2\text{-}C^3(Me)C^2\{C(CH)_4\}C^1N(Me)(Xyl)\}]$, 3 (Chart 3). A solution of $[\mathbf{2b}]SO_3CF_3$ (200 mg, 0.316 mmol) in THF (20 mL) was treated with freshly distilled cyclopentadiene (CpH; 0.18 mL, 2.1 mmol) and then with NaH (23 mg, 0.96 mmol). The resulting mixture was left stirring for 2 h. The final mixture was filtered on a short alumina pad using THF as eluent, and then the volatiles were removed under vacuum. The residue was dissolved in CH_2Cl_2 and charged on an alumina column; after washing with dichloromethane, a dark gray fraction corresponding to **3** was collected using neat THF as eluent. Yield 105 mg, 61%. Anal. Calcd for $C_{30}H_{29}Fe_2NO_2$: C, 65.84; H, 5.34; N, 2.56. Found: C, 65.61; H, 5.40; N, 2.49. IR (CH_2Cl_2) ν/cm^{-1} = 1949 vs (CO), 1783 s (μ-CO), 1551 m (C^1N + $C^2{=}C^3$). ^{1}H NMR ($CDCl_3$) δ/ppm = 7.37–7.22 (3 H, $C_6H_3Me_2$); 6.49, 6.36 (dd, 4 H, CH); 4.97, 4.35 (s, 10 H, Cp); 4.23 (s, 3 H, C^3 Me); 3.27 (s, 3 H, NMe); 2.71, 2.09 (s, 6 H, $C_6H_3Me_2$). ^{13}C{^{1}H} NMR ($CDCl_3$) δ/ppm = 267.2 (μ-CO); 247.4 (C^1); 213.7 (CO); 195.1 (C^3); 142.0 (*ipso*-$C_6H_3Me_2$); 134.9, 134.2, 129.6, 128.8, 128.4 ($C_6H_3Me_2$); 118.5, 118.2 (CH); 95.7 (C^2CCH); 89.3, 88.1 (Cp); 81.2 (C^2); 46.5 (NMe); 45.7 (C^3Me); 20.0, 19.3 ($C_6H_3Me_2$). ESI-MS (ES$^+$) 547 *m*/*z* [M$^+$].

Chart 3. Structure of 3



Reaction of $[2b]SO_3CF_3$ with $Ph_3PCH_2/NaH/CF_3SO_3H$: Formation of $[Fe_2Cp_2(CO)(\mu\text{-}CO)\{\mu\text{-}\eta^1{:}\eta^2\text{-}C^3(Me)C^2(CH_2)C^1N(Me)(Xyl)\}]$, 4, and $[2c]SO_3CF_3$ (Chart 4).[12]. The reaction of $[\mathbf{2b}]SO_3CF_3$ (152 mg, 0.240 mmol) with Ph_3PCH_2 (265 mg, 0.959 mmol) and NaH (17 mg, 0.71 mmol) was carried out by a procedure similar to that described for the synthesis of **3**. After 30 min, the IR spectrum of the mixture cleanly exhibited two bands (1952 vs, 1773 s), assigned to **4**. Every attempt at purification through stationary phases resulted in prevalent decomposition. Thus, the liquid phase was separated and treated with CF_3SO_3H (0.022 mL, 0.249 mmol). Clean formation of *cis*-$[\mathbf{2c}]SO_3CF_3$ was recognized after 5 min by IR spectroscopy. The product was purified by alumina chromatography and finally obtained as a dark-red solid. Yield: 117 mg, 75%. Anal. Calcd for $C_{27}H_{28}F_3Fe_2NO_5S$: C, 50.10; H, 4.36; N, 2.16. Found: C, 49.86; H, 4.28; N, 2.18. IR (CH_2Cl_2) ν/cm^{-1} = 1987 vs (CO), 1819 s (μ-CO), 1610 m (NC^1C^2). ^{1}H NMR ($CDCl_3$) δ/ppm = 7.48–7.00 (3 H, $C_6H_3Me_2$); 5.29, 4.68 (s, 10 H, Cp); 3.88, (s, 3 H, C^3 Me); 3.37 (s, 3 H, NMe); 2.49, 1.99 (s, 6 H, $C_6H_3Me_2$); 2.10 (s, 3 H, C^2 Me).

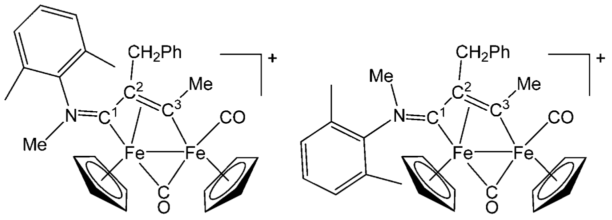
Chart 4. Structures of *E*-4 and *Z*-$[\mathbf{2c}]^{+}$



E-**4** Z-[**2c**]$^+$

Synthesis of $[Fe_2Cp_2(CO)(\mu\text{-}CO)\{\mu\text{-}\eta^1{:}\eta^3\text{-}C^3(Me)C^2(CH_2Ph)C^1N(Me)(Xyl)\}]Br$, [5]Br, and Isomerization Reaction (Chart 5). The synthesis of $[\mathbf{5}]$Br was carried out by a procedure analogous to that described for the synthesis of **3** (reaction time = 24 h). The final mixture was dried under reduced pressure, and the residue was dissolved in dichloromethane and quickly chromatographed through a short alumina pad. After washing with THF, a fraction was collected using neat MeOH as eluent. The title compound was isolated as isomeric mixture (*E*/*Z*) upon removal of the solvent under reduced pressure. Full conversion into the *Z* isomer was achieved by heating a solution of the mixture in MeOH for 40 min at ca. 50 °C. The final product was purified by filtration on a short alumina column and then

Chart 5. Structures of *E*-$[\mathbf{5}]^{+}$ and *Z*-$[\mathbf{5}]^{+}$



E Z

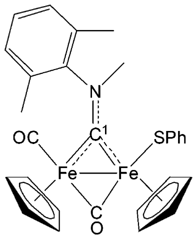
obtained as a crystalline solid upon slow evaporation of the solvent from the methanol solution.

*E-[**5**]Br + Z-[**5**]Br.* Brown solid, from [**2b**]SO_3CF_3 (180 mg, 0.284 mmol), $PhCH_2Br$ (0.31 mL, 2.6 mmol), and NaH (21 mg, 0.88 mmol). Yield 113 mg, 55%. Anal. Calcd for $C_{32}H_{32}BrFe_2NO_2$: C, 58.75; H, 4.93; N, 2.14; Br, 12.21. Found: C, 58.38; H, 4.98; N, 2.26; Br, 11.89. IR (CH_2Cl_2) ν/cm^{-1} = 1986 vs (CO), 1814 s (μ-CO), 1603 m (NC^1C^2), 1586 w (C=C). ^1H NMR ($CDCl_3$) δ/ppm = 7.42−7.05 (8 H, Ph + $C_6\mathit{H}_3Me_2$); 5.49, 5.44, 5.24, 4.99 (s, 10 H, Cp); 4.57, 4.47 (d, 2 H, $^2J_{HH}$ = 19.9 Hz, CH_2); 4.10, 3.15 (s, 3 H, NMe); 3.99, 3.87 (s, 3 H, C^3 Me); 2.57, 2.32, 2.01, 1.74 (s, 6 H, $C_6H_3\mathit{Me}_2$). *E*/*Z* ratio = 2. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ/ppm = 254.7, 254.4 (μ-CO); 233.2, 232.5 (C^1); 211.5, 211.3, 210.5, 209.6 (CO + C^3); 144.6, 140.6 (*ipso*-$C_6H_3Me_2$); 131.5−126.9 (Ph + $C_6H_3Me_2$); 90.9, 90.6, 87.7, 87.4 (Cp); 64.4, 63.8 (C^2); 59.0 (CH_2); 52.1, 46.1 (NMe); 43.0, 42.5 ($C^3\mathit{Me}$); 18.2, 18.1, 17.5, 17.0 ($C_6H_3\mathit{Me}_2$).

*Z-[**5**]Br.* Light brown solid, yield 70%. Anal. Calcd for $C_{32}H_{32}BrFe_2NO_2$: C, 58.75; H, 4.93; N, 2.14; Br, 12.21. Found: C, 58.41; H, 5.03; N, 2.20; Br, 12.04. IR (CH_2Cl_2) ν/cm^{-1} = 1981 vs (CO), 1818 s (μ-CO), 1613 m (NC^1C^2), 1587 w (C=C). ^1H NMR ($CDCl_3$) δ/ppm = 7.43−7.34 (8 H, Ph + $C_6\mathit{H}_3Me_2$); 5.49, 4.99 (s, 10 H, Cp); 4.62, 4.58 (m, 2 H, CH_2); 3.99 (s, 3 H, C^3 Me); 3.15 (s, 3 H, NMe); 2.57, 2.01 (s, 6 H, $C_6H_3\mathit{Me}_2$). $^{13}C\{^1H\}$ NMR (dmso-d_6) δ/ppm = 254.8 (μ-CO); 229.5 (C^1); 212.6 (CO); 206.8 (C^3); 162.6 (*ipso*-Ph); 141.1 (*ipso*-$C_6H_3Me_2$); 138.3, 134.3, 130.0, 129.8, 129.4, 128.0, 127.2 (Ph + $C_6H_3Me_2$); 92.4, 88.8 (Cp); 66.6 (C^2); 58.4 (CH_2); 50.9 (NMe); 38.2 ($C^3\mathit{Me}$); 18.2 ($C_6H_3\mathit{Me}_2$).

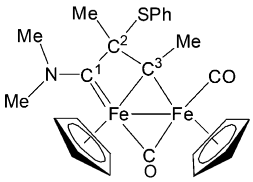
Reaction of [2c]SO_3CF_3 with PhSSPh/NaH: Synthesis of [Fe_2Cp_2(SPh)(CO)(μ-CO){μ-C^1N(Me)(Xyl)}], 6 (Chart 6). To a stirred solution of *cis*-[**2c**]SO_3CF_3 (120 mg, 0.185 mmol) in tetrahydrofuran (15 mL) were added PhSSPh (295 mg, 1.35 mmol) and then NaH (23 mg, 0.96 mmol). The resulting mixture was stirred overnight. Hence, the volatile materials were removed under vacuum. The residue was dissolved in CH_2Cl_2 and filtered through alumina. Compound **6** was recovered as a red microcrystalline powder upon removal of the solvent. Yield 70 mg, 68%. Anal. Calcd for $C_{28}H_{27}Fe_2NO_2S$: C, 60.78; H, 4.92; N, 2.53. Found: C, 60.63; H, 5.01; N, 2.49. IR (CH_2Cl_2) ν/cm^{-1} = 1969 vs (CO), 1791 s (μ-CO), 1512 m (C^1N). ^1H NMR ($CDCl_3$) δ/ppm = 7.49−7.00 (5 H, Ph + $C_6\mathit{H}_3Me_2$); 4.68, 4.26 (s, 10 H, Cp); 4.64 (s, 3 H, NMe); 2.71, 2.25 (s, 6 H, $C_6H_3\mathit{Me}_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ/ppm = 338.5 (C^1); 265.0 (μ-CO); 213.8 (CO); 148.5 (*ipso*-$C_6H_3Me_2$); 137.0−123.2 (Ph + $C_6H_3Me_2$); 87.5, 86.1 (Cp); 51.2 (NMe); 18.5, 17.7 ($C_6H_3\mathit{Me}_2$).

Chart 6. Structure of 6



Reaction of [2d]SO_3CF_3 with PhSSPh/NaH: Synthesis of [Fe_2Cp_2(CO)(μ-CO){μ-η^1:η^2-C^3(Me)C^2(Me)(SPh)C^1N(Me)$_2$}], 7 (Chart 7). To a stirred solution of [**2d**]SO_3CF_3 (130 mg, 0.233 mmol) in THF (15 mL) were added PhSSPh (320 mg, 1.47 mmol) and then NaH (23 mg, 0.96 mmol). The resulting mixture was stirred for 1 h, then filtered on a short alumina pad. Addition of diethyl ether (50 mL) gave a green precipitate which was isolated and dried under vacuum. Yield 66 mg, 55%. Anal. Calcd for $C_{25}H_{27}Fe_2NO_2S$: C, 58.05; H, 5.26; N, 2.71. Found: C, 58.13; H, 5.39; N, 2.66. IR (CH_2Cl_2) ν/cm^{-1} = 1929 vs (CO), 1752 s (μ-CO), 1624 w (C^1N). ^1H NMR ($CDCl_3$) δ/ppm = 7.58−6.84 (5 H, Ph); 4.61, 4.39 (s, 10 H, Cp); 3.71 (s, 3 H, C^3 Me); 3.51, 3.00 (s, 6 H, NMe_2); 1.37 (s, 3 H, C^2 Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ/ppm = 278.4 (μ-CO); 251.6 (C^1); 215.7 (CO); 177.0 (C^3); 152.6 (*ipso*-Ph); 144.7−122.8 (Ph); 87.2, 86.5 (Cp); 84.3 (C^2); 46.3, 45.8 (NMe_2); 43.6 ($C^3\mathit{Me}$); 29.5 ($C^2\mathit{Me}$).

Chart 7. Structure of 7



Computational Studies. All the geometries were optimized with ORCA 4.0.1.2,[39] using the B97 functional[40] in conjunction with a triple-ζ quality basis set (def2-TZVP). The dispersion corrections were taken into account using the Grimme D3-parametrized correction and the Becke−Jonhson damping to the DFT energy.[41] All the structures were confirmed to be local energy minima (no imaginary frequencies) for intermediate species and saddle points (one imaginary frequency) for transition states. In some cases, an unavoidable very low negative frequency is present, correlated to the rotation of the Cp moiety around the Cp−Fe bond axis.

X-ray Crystallography. Crystal data and collection details for [**2a**]SO_3CF_3 are reported in Table S3. Data were recorded on a Bruker APEX II diffractometer equipped with a PHOTON100 detector using Mo Kα radiation. Data were corrected for Lorentz polarization and absorption effects (empirical absorption correction SADABS).[42] The structure was solved by direct methods and refined by full-matrix least-squares based on all data using F^2.[43]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.8b00448.

DFT-optimized geometries of compounds; IR and NMR spectra (PDF)

Computed Cartesian coordinates of all of the compounds reported in this study (XYZ)

Accession Codes

CCDC 1849098 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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