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# Mononuclear Fe(I) and Fe(II) Acetylene Adducts and their Reductive Protonation to Terminal Fe(IV) and Fe(V) Carbynes

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**ABSTRACT:** The activity of nitrogenase enzymes, which catalyze the conversion of atmospheric dinitrogen to bioavailable anmonia, is most commonly assayed by the reduction of acetylene gas to ethylene. Despite the practical importance of acetylene as a substrate, little is known concerning its binding or activation in the iron-rich active site. "Fischer-Tropsch" type coupling of nonnative C<sub>1</sub> substrates to higher-order C<sub>≥2</sub> products is also known for nitrogenase, though potential metal-carbon multiply-bonded intermediates remain underexplored. Here we report the activation of acetylene gas at a mononuclear tris(phosphino)silyl-iron center, (SiP<sub>3</sub>)Fe, to give Fe(I) and Fe(II) side-on adducts, including S = 1/2 Fe<sup>I</sup>( $\eta^2$ -HCCH); the latter is characterized by pulse EPR spectroscopy and DFT calculatoins. Reductive protonation reactions with these compounds converge at stable examples of unusual, formally iron(IV) and iron(V) carbyne complexes, as in diamagnetic (SiP<sub>3</sub>)Fe≡CCH<sub>3</sub> and the paramagnetic cation S = 1/2 [(SiP<sub>3</sub>)Fe≡CCH<sub>3</sub>]<sup>+</sup>. Both alkylcarbyne compounds possess short Fe-C triple bonds (approx. 1.7 Å) trans to the anchoring silane. Pulse EPR experiments, X-band ENDOR and HYSCORE, reveal delocalization of the iron-based spin onto the  $\alpha$ -carbyne nucleus in carbon p-orbitals. Furthermore, isotropic coupling of the distal  $\beta$ -CH<sub>3</sub> protons with iron indicates hyperconjugation with the spin/hole character on the Fe≡C-CH<sub>3</sub> unit. The electronic structures of (SiP<sub>3</sub>)Fe≡CCH<sub>3</sub> and [(SiP<sub>3</sub>)Fe≡N. Such comparisons are germane to the consideration of formally high-valent, multiply-bonded Fe≡C and/or Fe≡N intermediates in synthetic or biological catalysis by iron.

#### INTRODUCTION

Interest in nominally high valent iron nitrides (N<sup>3-</sup>) and imides (NR<sup>2-</sup>) has grown in the past 15-20 years,<sup>1</sup> and has stemmed from a desire to explore their electronic structures and reactivity patterns, especially as they may pertain to important synthetic and biological transformations. For instance, the intermediacy of an Fe=N species has been considered in the context of a distal pathway for biological nitrogen fixation by nitrogenase enzymes (Fe-N<sub>2</sub> + 3 H<sup>+</sup>/e<sup>-</sup>  $\rightarrow$  Fe=N + NH<sub>3</sub>).<sup>2</sup> Relatedly, such an intermediate nitride has been recently characterized within a synthetic iron system that catalyzes N<sub>2</sub>-to-NH<sub>3</sub> conversion.<sup>3</sup>

Nitrogenase enzymes reduce a range of non-native substrates as well, including for example azide (N<sup>3-</sup>), cyanide (CN<sup>-</sup>), CO, CO<sub>2</sub>, and acetylene  $(C_2H_2)$ .<sup>4</sup> Indeed, acetylene reduction to ethylene  $(C_2H_4)$  is the most convenient and hence most common assay for reductive "nitrogenase" activity.<sup>5,6,7</sup> It is perhaps surprising, therefore, that acetylene complexes of iron, and their associated reactivity patterns, have not been well-studied to date. Noting this gap, we undertook a study of the reactivity of acetylene with an iron system supported by a tripodal phosphine ligand, in part for comparison with related studies we and others had undertaken in the context of N<sub>2</sub> chemistry. As a result, we uncovered an unexpectedly rich reactivity profile that links acetylene binding at iron(I) to the ultimate generation of nominally high-valent (+4 and +5) iron carbynes via reductive protonation steps. While these transformations do not appear to model the reactivity profile of acetylene reduction by nitrogenase, they are nevertheless fascinating.

Until recently, iron carbynes of any type had little synthetic precedent.<sup>8,9,10,11,12</sup> Reductive activation of CO and CN<sup>-</sup> at iron recently led to examples of heteroatom-substituted (i.e., Fischer-type) iron carbynes.<sup>10,11</sup> By contrast, the alkylcarbynes featured herein (Fe<sup>IV</sup> $\equiv$ CCH<sub>3</sub> and [Fe<sup>V</sup> $\equiv$ CCH<sub>3</sub>]<sup>+</sup>) are unique in that they are not substituted by heteroatoms. In a broader context, iron complexes featuring strong iron-to-carbon multiple bonds are of continuing interest, especially as they may pertain to intermediates in "Fischer-Tropsch" type C-C coupling pathways exhibited by nitrogenase enzymes in the presence of non-native CO, CO<sub>2</sub>, and CN<sup>-</sup> substrates.<sup>4</sup>

Herein, we describe the following:

(i) The first complexes featuring  $C_2H_2$  bound to a single iron center are characterized, in the formal +1 and +2 oxidation states (i.e.,  $Fe^{I}(C_2H_2)$  and  $Fe^{II}(C_2H_2)^+$ ); the iron(I) derivative is  $S = \frac{1}{2}$ , and pulse EPR data confirm  $n_2$  side-on coordination.

(ii) Well-characterized examples of  $Fe^{IV} \equiv CCH_3$  and  $Fe^{V} \equiv CCH_3^+$  carbynes are presented, including their solid-state X-ray crystal structures and <sup>57</sup>Fe Mössbauer spectra. The  $Fe^{V} \equiv CCH_3^+$  species is  $S = \frac{1}{2}$  and pulse EPR spectroscopy is used to additionally map its electronic structure.

(iii) Mechanistic studies indicate the Fe<sup>I</sup>(C<sub>2</sub>H<sub>2</sub>) species undergoes initial C-H activation, followed by bimolecular H<sub>2</sub> loss, to generate a terminal Fe<sup>II</sup>C≡CH, which can also be independently prepared. The Fe<sup>V</sup>≡CCH<sub>3</sub><sup>+</sup> species is most conveniently accessed by reductive protonation steps from Fe<sup>II</sup>C≡CH.

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The EPR data provided for  $Fe^{I}(C_{2}H_{2})$  and  $Fe^{V} \equiv CCH_{3}^{+}$  could be of value to mechanistic studies employing related EPR techniques of nitrogenases with  $C_{2}H_{2}$ ,<sup>13</sup> or to studies of nonnative  $C_{1}$  substrates that lead to Fischer-Tropsch type C-C couplings.<sup>4</sup>

## RESULTS AND DISCUSSION

## Mononuclear iron-acetylene adducts

Figure 1 outlines the entire reaction manifold discussed herein, where a tris(phosphino)silyl-iron subunit (abbreviated herein as "(SiP<sub>3</sub>)Fe" or "Fe") is common to all of the complexes described. To test the affinity of acetylene for an iron(I) center, the previously reported complex (SiP<sub>3</sub>)Fe<sup>I</sup>N<sub>2</sub> (1) was exposed to acetylene gas. Displacement of N<sub>2</sub> by 1.2 equivalents of acetylene occurs slowly at room temperature in THF to give an unobserved acetylene adduct complex, (SiP<sub>3</sub>)Fe<sup>I</sup>( $\eta^2$ -HCCH) **2** (see below for further characterization at low T), that proceeds to the red, terminal acetylide complex (SiP<sub>3</sub>)Fe<sup>II</sup>CCH **3**, along with liberation of 0.5 equivalents of H<sub>2</sub> (confirmed by GC).



**Figure 1.** Scheme depicting the reaction chemistry discussed herein, along with labeled formal oxidation states and compound numbers.

The acetylide complex **3** can alternatively be prepared by stirring a sodium acetylide slurry with  $(SiP_3)Fe^{II}OTf(4)$  in the presence of tetramethyl ethylenediamine (TMEDA) in 84% yield. The complex has been characterized in solution and the

solid state (see Figure 2) as a trigonal bipyramidal S = 1 iron(II) species featuring the SiP<sub>3</sub> ligand. Complex **3** exhibits a weak C=C vibration (1902 cm<sup>-1</sup>) and a terminal C-H stretch (3277 cm<sup>-1</sup>); isotopic labeling with <sup>13</sup>C<sub>2</sub>-TMED-LiC=CH (see SI for preparation details) gives <sup>13</sup>C<sub>2</sub>-**2** ( $v_{C=C} = 1832$  cm<sup>-1</sup> and  $v_{C-H} = 3262$  cm<sup>-1</sup>;  $\Delta_{C=C} = 70$  cm<sup>-1</sup>;  $\Delta_{C-H} = 15$  cm<sup>-1</sup>; Figure S23). Three other terminal iron-acetylide compounds have previously been crystallographically characterized.<sup>14</sup>



**Figure 2.** Solid-state crystal structures of **3**, **6**, **7**, and **8**, with thermal ellipsoids displayed at 50% probability. The hydrogen atoms of (SiP<sub>3</sub>) and the counter-anions present in the structures for **6** and **7** have been omitted for clarity. A DFT-minimized structure of (SiP<sub>3</sub>)Fe<sup>I</sup>( $\eta^2$ -C<sub>2</sub>H<sub>2</sub>) **2** is also shown, with bond metrics, along with the calculated SOMO orbital and Löwdin spin densities in the primary ligation sphere.

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A thermally stable adduct of acetylene is accessible at the iron(II) state. Accordingly, the light-blue cation  $[(SiP_3)FeN_2]BArF_{24}$  (5)<sup>15</sup>  $(BArF_{24} = [B(3-5-(CF_3)_2-C_6H_3)_4]^{-})$ reacts with one equivalent of acetylene gas in fluorobenzene at 0 °C to afford green [(SiP<sub>3</sub>)Fe(η<sup>2</sup>-HCCH)]BArF<sub>24</sub> (6) (70% isolated yield). The solid-state X-ray structure of the S = 1complex shows the  $\eta^2$ -HCCH ligand bound side-on in the axial position opposite to the silvl anchor (Figure 2). As stated in the introduction, complex  $\mathbf{6}$  is to our knowledge the only example (other than 2, vide infra) of a mononuclear iron complex featuring C<sub>2</sub>H<sub>2</sub> as a ligand.<sup>16</sup> Mononuclear adducts of acetylene are highly uncommon for first row metals in general.<sup>17</sup> Fe-to-acetylene backbonding in **6** is modest (C=C bond length of 1.25 Å; cf. 1.20 Å in free acetylene<sup>18</sup>) and the Fe-P and Fe-Si bond are relatively long, in accord with its S = 1 ground state and side-on accommodation of the acetylene ligand.



**Figure 3.** (a) X-band CW-EPR spectra of  $(SiP_3)Fe(\eta^2-HCCH)$ prepared in 2-MeTHF with natural abundance (top), <sup>13</sup>Cenriched (middle), and <sup>2</sup>H-enriched acetylene (bottom) with simulations using parameters in Table 1 overlaid in red. (b) Derivative spectra of X-band CW-EPR for each isotopologue with simulations overlaid in red. Acquisition parameters: temperature = 77 K; MW frequency = 9.375 GHz; MW power = 2 mW; modulation frequency = 100 kHz; modulation amplitude = 0.1 mT; conversion time = 41 ms.

Because the acetylene adduct  $\text{Fe}^{I}(\eta^{2}\text{-HCCH}) \mathbf{2}$  cannot be observed upon addition of  $C_{2}H_{2}$  to  $\text{Fe}^{I}N_{2} \mathbf{1}$  at room temperature (owing to slow ligand substitution kinetics), we sought its characterization via the low temperature reduction of  $[\text{Fe}^{II}(\eta^{2}\text{-HCCH})]^{+} \mathbf{6}$ . Thus, addition of stoichiometric cobaltocene (Cp<sub>2</sub>Co) to a stirred solution of  $\mathbf{6}$  in 2-MeTHF at -125 °C rapidly generates a new orange species that exhibits first order decay above -80 °C to generate the terminal acetylide Fe<sup>II</sup>CCH  $\mathbf{3}$  (t<sub>1/2</sub>(-40°C)  $\approx$  14 min; monitored by *in situ* UV-visible spectroscopy; Figure S54).

To more thoroughly characterize  $Fe^{I}(\eta^{2}-HCCH)$  **2**, in  ${}^{1}H_{1}$ particular to assess whether alternative "F&CCH aragon Plus Environment

"Fe<sup>III</sup>(H)(CCH)" isomers might be more appropriate, we undertook continuous wave (CW) and pulse EPR experiments of both the natural abundance and deuteron-labeled isotopologue Fe<sup>I</sup>( $\eta^2$ -DCCD) at X-band frequency, coupled with DFT studies. The X-band CW EPR spectrum, shown in Figure 3a,b, exhibits a g-tensor with rhombic symmetry (g = [2.114, 2.040, 2.007]) with coupling evident to three distinct phosphorous nuclei. Simulation of the data indicates that one of the P-donors is coupled more strongly than the other two ( $|A(^{31}P)| = [183, 182, 214]$  MHz, Table 1). These simulated coupling values, and especially the asymmetry with respect to one donor, qualitatively agree with the DFT-predicted <sup>31</sup>P hyperfine tensors calculated from an optimized structure of **2** ( $|A(^{31}P)| = [201, 203, 242]$  MHz; TPSS/def2-TZVP/D3ZERO; see SI for details).

Complementary X-band Electron Nuclear Double Resonance (ENDOR) and Hyperfine Sublevel Correlation (HYSCORE) spectroscopic data allow for further resolution of the coupling of the paramagnetic iron center with NMR active nuclei. Accordingly, hyperfine coupling of the acetylene <sup>1</sup>H nuclei to the spin on iron can be extracted by comparison of the data for  $Fe^{I}(\eta^{2}-HCCH)$  with that for  $Fe^{I}(\eta^{2}-HCCH)$ DCCD). Field-dependent HYSCORE (Figure 4) and <sup>1</sup>H-<sup>2</sup>H ENDOR (Figure 5) spectra show weak <sup>1</sup>H hyperfine couplings to two very similar acetylene-derived protons:  ${}^{1}H_{1}$  (  $A({}^{1}H)$ = [9.4, 20.2, 17.6] MHz, with Euler rotation angles  $[\alpha,\beta,\gamma]$  = [33, 18, -5] relative to the g-tensor and  ${}^{1}\text{H}_{2}(|A({}^{1}\text{H})| = [8.2,$ 18.4, 16.8] MHz, with Euler rotation angles  $[\alpha, \beta, \gamma] = [43, -22, -22]$ 11] These results are also corroborated by the appearance of <sup>2</sup>H features in the HYSCORE data for Fe<sup>I</sup>( $\eta^2$ -DCCD), which are well simulated by scaling these hyperfine tensors by the ratio of the <sup>1</sup>H/<sup>2</sup>H gyromagnetic ratios ( $\gamma^{1}$ H/ $\gamma^{2}$ H = 6.514) (Figures S33-35). These two protons exhibit extremely similar isotropic hyperfine couplings, with  $a_{iso}({}^{1}H_{1}) = 15.7$  MHz and  $a_{iso}({}^{1}H_{2}) = 14.5$  MHz, and are only differentiated by the respective orientations of their hyperfine tensors relative to the molecular g-tensor coordinate frame, which is resolved in the <sup>1</sup>H-<sup>2</sup>H difference ENDOR data acquired near the low-field edge of the EPR spectrum (see Figure 5, top trace). This strongly disfavors assignment as the observation "Fe<sup>III</sup>(H)(CCH)" isomer, as a hydride directly bound to an S =1/2 iron center should exhibit much stronger coupling ( $a_{iso} \approx$ 45 MHz).<sup>19,20</sup>

To distinguish between the Fe<sup>I</sup>( $\eta^2$ -HCCH) and "FeCCH<sub>2</sub>" isomers, we prepared the <sup>13</sup>C-enriched derivative <sup>13</sup>C<sub>2</sub>H<sub>2</sub>-**2**. Consistent fits between the field-dependent <sup>13</sup>C-<sup>12</sup>C difference HYSCORE (Figure 6) and ENDOR spectra (See SI) give two nearly identical, strongly coupled <sup>13</sup>C nuclei <sup>13</sup>C<sub>1</sub>( $|A(^{13}C)| = [17, 24, 8.6], a_{iso} = 16.5$  MHz; <sup>13</sup>C<sub>2</sub>( $|A(^{13}C)| = [24, 16.6, 10.2]$   $a_{iso} = 16.9$  MHz) (Table 1), which also disfavors the "FeCCH<sub>2</sub>" isomer, as such a species would be anticipated to show highly inequivalent <sup>13</sup>C<sub>a</sub> and <sup>13</sup>C<sub>β</sub> couplings, with coupling to C<sub>a</sub> being much larger. Together, these EPR data are fully consistent with a structure for **2** formulated as an  $\eta^2$ -HCCH adduct of iron(I), akin to its one-electron oxidized derivative **6**.

Table 1. Hyperfine coupling constants in MHz determined for  $(SiP_3)Fe(\eta^2\mbox{-}HCCH)$ 

Nucle	eus $A_1$	$A_2$	$A_3$	<i>a</i> <sub>iso</sub>	Euler angles $[\alpha, \beta, \gamma]^{\circ}$
${}^{31}P_1$	183	183	214	193.3	[0, 0, 0]
${}^{31}P_2$	30	28	40	32.7	[0, 0, 0]
${}^{31}P_3$	12	0.5	17	9.8	[0, 0, 0]
${}^{1}\mathrm{H}_{1}$	9.4	20.2	17.6	15.7	[33, 18, -5]
${}^{1}H_{2}$	. 8.2	18.4	16.8	14.5	[43, -22, 11]

$^{13}C_1$	17	24	8.6	16.5	[0, 30, 0]
$^{13}C_2$	24	16.6	10.2	16.9	[0, -30, 0]

Several other side-on adducts of alkynes and alkenes at reduced Fe(I) centers have been reported by Holland and coworkers.<sup>21</sup> These complexes exhibit high-spin S = 3/2 ground state electronic structures and were described with substantial  $\pi$ -backbonding from iron to the coordinated unsaturated ligand. In a study of an  $\alpha$ -70<sup>Val</sup> mutant nitrogenase that is able to accommodate several substituted-acetylene substrates, the S = 3/2 resting state EPR signal is, by contrast, converted to an iron-localized rhombic S = 1/2 doublet in a freeze-quenched experiment using propargyl alcohol (HC=CCH<sub>2</sub>OH) as the substrate.<sup>13</sup> This doublet signal closely matches that of a CO-bound/inhibited state. While <sup>13</sup>C coupling to the doublet signal was measured, it was not possible to distinguish between possible binding modes of the propargyl alcohol.



**Figure 4.** (top) X-band HYSCORE spectrum of natural abundance (SiP<sub>3</sub>)Fe( $\eta^2$ -HCCH) acquired at 338.6 mT (g = 2.058). (bottom) Monochromatic representation of the HYSCORE data with simulations using parameters in Table 1 overlaid: (red) <sup>1</sup>H-1 (blue) <sup>1</sup>H-2, (green) <sup>31</sup>P-3. Acquisition parameters: temperature = 20 K; microwave frequency = 9.751 GHz; MW pulse length ( $\pi/2$ ,  $\pi$ ) = 8 ns, 16 ns;  $\tau$  = 138 ns,  $t_1 = t_2 = 100$  ns;  $\Delta t_1 = \Delta t_2 = 16$  ns; shot repetition time (srt) = 1 ms).

The transformation of  $Fe^{I}(\eta^{2}-HCCH)$  **2** to acetylide  $Fe^{II}CCH$  **3** is interesting to consider further. The available data is insufficient to determine the fate of **2** after its first-order decay. However, two distinct paths seem most plausible to us. In one scenario, which we favor, C-H oxidative addition of the coordinated C<sub>2</sub>H<sub>2</sub> ligand produces "Fe<sup>III</sup>(H)(CCH)", one of the structural isomers considered above. This intermediate then loses half an equivalent of H<sub>2</sub> in a bimolecular step. Relatedly, we recently reported an example of bimolecular H<sub>2</sub> loss from a well-defined Fe<sup>III</sup>-hydride complex that features a sufficiently weak Fe-H bond.<sup>20</sup> Additionally, the oxidative addition pathway (Figure 7) is well precedented for a number of previously characterized alkyne-hydride complexes of Co and Fe.<sup>22</sup> Of note to the present study, we previously reported

reversible activation of phenylacetylene in a structurally related trisphosphine-borane TPBFe system, likely by oxidative addition to a formally Fe(II)-alkyne-hydride/borohydride complex.<sup>23</sup>

Alternatively, another reaction pathway could involve eventual rearrangement of  $Fe^{I}(\eta^{2}-HCCH)$  2 or an intermediate Fe<sup>III</sup>(H)(CCH) to the end-on "FeCCH2" isomer, considered above, again followed by bimolecular H<sub>2</sub> loss. However, transformation by a *unimolecular* 1,2 hydrogen shift of an  $\eta^2$ alkyne adduct to a terminal alkylidene/vinylidene<sup>24</sup> is generally thought to have a high barrier and is therefore difficult without an exogenous acid/base catalysts or high temperature.<sup>25</sup> Berke and coworkers have reported that chromatography on silvlated silica accelerates the formation of terminally stable vinylidene complexes from mixtures of low-valent iron acetylene/alkyne and alkyene-hydride complexes.<sup>22c,26</sup> In the present  $Fe^{I}(\eta^{2}-HCCH)$  2 system, deprotonation by solvent (THF) to produce [FeCCH]<sup>-</sup>, followed by re-protonation to produce FeCCH<sub>2</sub>, seems highly unlikely considering the low acidity expected for 2 in THF. Finally, while we consider it to be unlikely, a bimolecular reaction between  $Fe^{I}(\eta^{2}-HCCH)$  and itself, or with  $Fe^{III}(H)(CCH)$ , could in principle evolve  $H_2$ .



**Figure 5.** Field-dependent X-band <sup>1</sup>H-minus-<sup>2</sup>H Davies ENDOR difference spectra of  $(SiP_3)Fe(\eta^2$ -HCCH) (black) with simulations using parameters in Table 1 overlaid: (red) total <sup>1</sup>H simulation, (blue) <sup>1</sup>H-1, (green) <sup>1</sup>H-2. Acquisition parameters: temperature = 15 K; MW frequency = 9.751 GHz; MW pulse length ( $\pi/2$ ,  $\pi$ ) = 40 ns, 80 ns;  $\tau$  = 260 ns; RF pulse length = 15 µs;  $T_{RF}$  = 2 µs; shot repetition time = 5 ms.

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Figure 6. (top) X-band <sup>13</sup>C-<sup>12</sup>C difference HYSCORE spectrum of  $(SiP_3)Fe(\eta^2-HCCH)$  acquired at 338.6 mT (g = (bottom) Monochromatic representation of the 2.058). HYSCORE data with <sup>13</sup>C simulations using parameters in Table 1 overlaid: (blue)  ${}^{13}C_1$ , (red)  ${}^{13}C_2$ . Acquisition parameters: temperature = 20 K; microwave frequency = 9.751 GHz; MW pulse length  $(\pi/2, \pi) = 8$  ns, 16 ns;  $\tau = 138$ ns,  $t_1 = t_2 = 100$  ns;  $\Delta t_1 = \Delta t_2 = 16$  ns; shot repetition time (srt) = 1 ms).



Figure 7. A qualitative reaction coordinate for the proposed slow substitution of acetylene for N<sub>2</sub> at (SiP<sub>3</sub>)FeN<sub>2</sub>, 1, leading to intermediate (SiP<sub>3</sub>)Fe( $\eta^2$ -HCCH) **2**, which subsequently undergoes sp(C-H)-activation and  $H_2$  release to generate isolable  $(SiP_3)Fe(CCH)$ , **3**. We presume the H<sub>2</sub> elimination step occurs in a bimolecular fashion via two Fe(III)-hydride species. See text for a discussion of other possible pathways.

#### **Terminal iron-carbyne complexes**

The addition of triflic acid (HOTf) to the terminal Feacetylide **3** in diethyl ether at -78°C precipitates [(SiP<sub>3</sub>)Fe=CCH<sub>3</sub>][OTf] (7) as a dark brown solid from solution (40% vield). Use of [H(Et<sub>2</sub>O)<sub>2</sub>][BArF<sub>24</sub>] in place of HOTf affords [(SiP<sub>3</sub>)Fe=CCH<sub>3</sub>][BArF<sub>24</sub>] (Figure 1). The alkylcarbyne cation 7 is a nominally iron(V) complex that, to our knowledge, is the only species of its type, formal or otherwise. The complex exhibits an S = 1/2 ground state (vide infra) and is stable as a solid or in THF or acetonitrile solution at room temperature for extended periods. As stated above, there are a handful of previously characterized, terminal, heteroatom-substituted carbynes of iron.<sup>8,9,10,11,12</sup> There are no prior examples of alkylcarbynes of iron, nor examples where the carbyne is substituted instead by H or aryl for that matter. Additionally, paramagnetic examples of carbyne/alkylidyne complexes are rare,<sup>27,28</sup> and, for first row metals, the only ACS Paragon Plus Environment (HAT) reactions can convert the acetylene

others we know of relate to [(SiP<sub>3</sub>)FeCNH<sub>2</sub>]<sup>+</sup> and [(SiP<sub>3</sub>)FeCNMe<sub>2</sub>]<sup>+</sup>.<sup>11,12</sup>

The solid-state crystal structure of **7** is shown in Figure 2. As required for an S = 1/2 system, the complex deviates slightly from three-fold symmetry (∠P-Fe-P angles 114, 117, 120°). Most noteworthy is a characteristically short  $Fe \equiv C$ -CH<sub>3</sub> bond of 1.70 Å and a Fe=C-CH<sub>3</sub> single bond of 1.42 Å. The Fe-Si bond is long at 2.39 Å, consistent with its position trans to the carbyne ligand. The triflate counter-anion exhibits close contacts with the (SiP<sub>3</sub>)-isopropyl and carbyne C-H positions.

The conversion of (SiP<sub>3</sub>)FeCCH to [(SiP<sub>3</sub>)FeCCH<sub>3</sub>]<sup>+</sup> is a net 2-H<sup>+</sup>/1-e<sup>-</sup> transformation, requiring sacrificial oxidation of half of the starting iron material, for a theoretical 50% yield. Analysis of recovered material shows primarily (SiP<sub>3</sub>)FeOTf 4, indicating the net reducing equivalent is likely derived from the acetylide moiety. The propensity for reaction intermediates to cannibalize themselves en route to 7 is consistent with the observed thermodynamic stability of the terminal product.

It is also noted that protonation of 3 by HOTf does not instead lead to its net oxidation (i.e., to form (SiP<sub>3</sub>)FeCCH<sup>+</sup>) with concomitant loss of 0.5 equivalents of  $H_2$  (eq. 1), especially as the cationic [(SiP<sub>3</sub>)FeCCH]<sup>+</sup> is electrochemically accessible (-0.78 V vs Fc in THF; Figure S58).<sup>29</sup>

FeCCH + HOTf 
$$\rightarrow$$
 [FeCCH]<sup>+</sup> + 0.5 H<sub>2</sub> eq. 1  
(not observed)

Alternatively, protonation of acetylide 3 in ether by the weaker, insoluble acid, imidazolium triflate, to our surprise generates the neutral alkyl carbyne derivative, (SiP<sub>3</sub>)Fe=CCH<sub>3</sub> 8 (25% isolated yield), the product of a net 2 H<sup>+</sup> / 2 e<sup>-</sup> reduction, again requiring some amount of sacrificial oxidation of starting material. The neutral carbyne 8 is thus more favorably synthesized in a heterogeneous mixture of triethylammonium chloride and excess sodium metal to balance the proton-coupled reduction (Figure 1). The Fe=CCH<sub>3</sub><sup>+</sup>/Fe=CCH<sub>3</sub> redox couple between 7 and 8 occurs at -1.00 V vs Fc in THF (Figure S59); chemical oxidation of 8 by ferrocenium  $(Cp_2Fe^+)$  or a strong acid, like [H(Et<sub>2</sub>O)][BArF<sub>24</sub>], cleanly generates 7.

Carbyne 8 is diamagnetic with resolved coupling by  ${}^{1}$ H,  ${}^{31}$ P, and <sup>13</sup>C NMR spectroscopy (Figures S10-16). Isotopic labelling in <sup>13</sup>C<sub>2</sub>-8 reveals a very downfield <sup>13</sup>C resonance for  $C_{\alpha}$  at 348 ppm<sup>30,31</sup> with coupling to  $C_{\beta}$  (48 ppm;  $J_{C(\alpha)-C(\beta)} = 18$ Hz) and three equivalent phosphines (<sup>31</sup>P 107.5 ppm;  $J_{C(\alpha)-P} =$ 18 Hz). By <sup>1</sup>H NMR spectroscopy, the terminal carbyne  $CH_3$ resonance at 2.12 ppm couples to  $C_{\alpha}$  (11 Hz) and  $C_{\beta}$  (127 Hz). The primary ligation of **8** is contracted with respect to  $S = \frac{1}{2}$ [Fe≡CCH<sub>3</sub>]<sup>+</sup> 7, with a Fe≡C bond of 1.68 Å, a 2.33 Å Fe-Si bond, and Fe-P bonds between 2.24-2.26 Å (Figure 2), presumably consistent with increased backbonding upon reduction.

(SiP<sub>3</sub>)Fe≡CCH<sub>3</sub> 8 is quite stable, even in solution at 130°C over a 24 hour time period. Its stability renders it a reaction sink in this system. Indeed, with its diagnostic NMR resonances in hand, it can be identified as a minor side-product of other reactions we have surveyed, including the aforementioned reaction between (SiP<sub>3</sub>)FeOTf and excess sodium acetylide (Figure 1).

The terminal stability of both alkylidyne complexes inspired us to further explore their interconnection with the acetylene complexes, described above, by reductive protonation reactions (Figure 1). Interestingly, net hydrogen

adducts **2** and **6** to the carbynes **7** and **8**. For example, mixing  $[Fe(\eta^2-HCCH)]^+$  **6** with TEMPO-H in 2-MeTHF generates  $Fe\equiv CCH_3^+$  **7**. At -100 °C, a relatively stable orange intermediate **9** can be observed by UV-visible spectroscopy, which then decays to **7** on warming (Figure S55). Our tentative assignment of **9** as a cationic alkenyl complex  $[(SiP_3)Fe(CH=CH_2)]^+$ , if correct, would make it a structurally interesting one. Whereas there is precedent for related, substituted iron alkenyl derivatives,<sup>22g</sup> the Fe-CH=CH<sub>2</sub> subunit is still, to our knowledge, distinct.

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Cationic carbyne 7 can also be generated by the addition of stoichiometric  $[H(Et_2O)_2][BArF_{24}]$  to a 2-MeTHF solution of  $(SiP_3)Fe(\eta^2$ -HCCH) 2 at -125 °C, presumably via 9 as an intermediate (Figure 1). Under similar conditions, the reaction of 2 with TEMPO-H generates the neutral carbyne 8, along with  $(SiP_3)FeCCH 2$  as side product. There thus appears to be a rich reactivity landscape connecting the nascent acetylene adducts and terminal carbynes described herein.

#### Electronic structure of iron-carbyne complexes

The Mössbauer parameters for carbynes 7 and 8 compare well with those of the previously reported and structurally characterized iron carbynes featuring the same (SiP<sub>3</sub>)Fe subunit: (SiP<sub>3</sub>)Fe(COSiMe<sub>3</sub>) and [(SiP<sub>3</sub>)Fe(CNMe<sub>2</sub>)]<sup>0/+</sup> (Table 2). The isomer shifts are relatively close to  $0 \text{ mm s}^{-1}$  across the series, reflecting strong covalency in the short Fe-C triple bond, with Fe=CCH<sub>3</sub><sup>+</sup> 7 and and Fe=CCH<sub>3</sub> 8 having the values.2b,3,32,33,34 smallest δ By comparison,  $[(SiP_3)FeCNMe_2]^+$  has an isomer shift of 0.19 mm s<sup>-1</sup>, indicating less Fe=C covalency, possibly consistent with a  $[Fe=C=NMe_2]^+$  resonance form and its slightly longer Fe-C bond (1.74 Å). The measured quadrupole splittings for this series of carbynes are rather narrow, especially by comparison to the very large  $\Delta E_0$  values reported for other formally highvalent oxide and nitride Fe complexes in  $C_3$ symmetry.1k,2,3,33,34 Frontier orbital manifolds whereby the electrons populate only orbitals of d(xy) and  $d(x^2-y^2)$ parentage, as for the d<sup>4</sup> and d<sup>3</sup> configurations described for the latter systems, is predicted to give large quadrupole splittings, > 5 mm s<sup>-1</sup>, due to the strongly asymmetric, equatorially disposed electric field gradient at Fe.<sup>32</sup> By contrast, the comparatively small  $\Delta E_Q$  values observed for the (SiP<sub>3</sub>)Fecarbyne series reflects the additional presence of substantial electron density along the z-axis (parallel to the Fe=C-Rvector). Inspection of the molecular orbitals of the carbyne series shows that the nominally high-lying Fe-C  $\sigma^*$ antibonding orbital is highly stabilized by mixing with  $Si(\sigma)$ ,<sup>35</sup> resulting in a heavily mixed orbital of a<sub>1</sub> symmetry energetically below the filled, primarily nonbonding orbitals of d(xy) and  $d(x^2-y^2)$  parentage (Figure 8). This observation bears relevance to a contributing resonance structure we have previously considered, with electron density being polarized between a cationic  $R_3Si^+$  anchor and a nominally reduced Fe center (Figure 9).9,36

Table 2. Mössbauer parameters of (SiP<sub>3</sub>)Fe carbynes

Fe≡CX	OSiMe <sub>3</sub> <sup>d</sup>	NMe <sub>2</sub> <sup>e</sup>	$NMe_2^{+e}$	$CH_3$	$\mathrm{CH}_{3}^{+}$	
Fe≡C <sup>a</sup>	1.67	1.71	1.74	1.68	1.70	
Fe-Si <sup>a</sup>	2.30	2.31	2.35	2.33	2.39	
$\delta^{b}$	0.061	0.058	0.19	-0.029	0.0097	
$\Delta E_Q{}^b$	1.12	1.12	1.51	0.72	1.33	
${}^{13}C_{\alpha}{}^{c}$	250.3	279.6		348.4		

<sup>a</sup>approx. measurements in Å. <sup>b</sup>measured in mm s<sup>-1</sup>. <sup>c</sup>measured in ppm in C<sub>6</sub>D<sub>6</sub>. <sup>d</sup>ref. 9. <sup>e</sup>ref. 10.



**Figure 8.** Simplified molecular orbital diagram for the metalligand bonding of a  $(SiP_3)Fe\equiv CR$  carbyne in  $C_{3v}$  symmetry. Approximate orbital energies and compositions shown for  $(SiP_3)FeCCH_3$  (TPSS/Def2-TZVP/D3ZERO). (Inset) DFTpredicted spin density map for  $[(SiP_3)FeCCH_3]^+$  (isovalue:  $0.005 \text{ e}^{-}/\text{Å}^3$ ).



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**Figure 9.** (top) Representative chemical depictions of the related amino- and alkylcarbynes  $(SiP_3)Fe(CNMe_2)^+$  and  $(SiP_3)Fe(CCH_3)^+$ , along with formal iron valence assignments. The true relative state of oxidation at iron is presumed to vary little due to strong covalency. The primary bonding of the carbyne to iron is indicated as  $x_3$ ,  $x_2$ , or L, with backbonds from iron into empty p-orbitals on carbon indicated by the green arrows. Note that a half-arrow is used to indicate hyperconjugation stabilization for the C-centered radical Fe(IV) form of  $(SiP_3)Fe(CCH_3)^+$ . (bottom) DFT-optimized structure of the hypothetical molecule  $(SiP_3)Fe^{IV}(N)$ , with a simplified MO diagram and lobal representations for the Si-Fe-N bonding in  $C_{3v}$  symmetry.



**Figure 10.** X-band CW-EPR spectrum of  $[(SiP_3)FeCCH_3]OTf$ prepared in 7:1 2-MeTHF/MeCN. Acquisition parameters: temperature = 10 K; MW frequency = 9.637 GHz; MW power = 200  $\mu$ W; modulation frequency = 100 kHz; modulation amplitude = 0.4 mT; conversion time = 82 ms.

To further probe the electronic structure of paramagnetic  $[Fe = CCH_3]^+$  7 we undertook CW and pulse EPR studies. The doublet ground state of 7 can only be observed by EPR at very low temperatures due to fast electronic relaxation and line broadening at 77 K. At 10 K, an axial EPR spectrum exhibiting significant anisotropy between g-parallel at 2.61 and g-perpendicular at 1.96-1.93 is resolved (Figure 10), consistent with a largely iron-centered spin. Electron spin inversion recovery experiments show a strong temperature dependence for  $T_1$  spin relaxation (Figure S41). This behavior is likely consistent with a low-lying, thermally populated doublet excited state or efficient electronic relaxation through coupling of low-energy vibrations (< 100 cm<sup>-1</sup>) with the bath. If an Orbach mechanism of electronic relaxation from the excited state is assumed,<sup>37</sup> a small energy difference ( $\Delta$ ) between the ground state and first excited state as low as  $\Delta$  = 24 cm<sup>-1</sup> can be roughly calculated from the temperature dependence of T<sub>1</sub>.<sup>38</sup>

45 EPR analysis of a paramagnetic carbyne/alkylidyne has 46 previously been limited to a tungsten methylidyne cation 47  $([(dmpe)_2(Cl)W^V \equiv CH]^+; g_{iso} = 2.026; |A(^{138}W)| = 221 \text{ MHz};$  $|A(^{31}P)| = 149$  MHz;  $|A(^{13}C)| = 34$  MHz; dmpe = 48 bis(dimethylphosphino)ethane) and to examples with the 49  $(SiP_3)Fe-system$ .<sup>27c,12</sup> Interestingly,  $[(SiP_3)FeCNMe_2]^+$  and 50 [Fe≡CCH<sub>3</sub>]<sup>+</sup> 7 both exhibit nearly identical EPR signatures.<sup>11</sup> 51 Löwdin spin population and spin density analysis of 7 by DFT 52 (TPSS/def2-TZVP/D3ZERO) predicts the majority of 53 unpaired spin on iron (0.99 e<sup>-</sup>), with 0.07 e<sup>-</sup> of opposite spin 54 polarization on  $C_{\alpha}$  (Figure 8) (cf.  $[(SiP_3)FeCNMe_2]^+$ : 0.97 e<sup>-</sup> 55 on Fe, oppositely polarized to 0.03 e<sup>-</sup> on  $C_{\alpha}$  and 0.01 e<sup>-</sup> on  $N_{\beta}$ ). 56 This prediction is in agreement with the large anisotropy 57 between g-parallel and g-perpendicular and the strong 58 temperature dependence observed for T<sub>1</sub> (Figure S41). 59

This predicted spin delocalization compares very well with that for a terminal iron(V)-nitride reported by Smith and coworkers.<sup>33</sup> A follow-up study on this system<sup>39</sup> invoked a dynamic "pseudo Jahn-Teller" distortion for a C<sub>3</sub>-symmetric iron center. Related electronic structure descriptions have been offered for ostensibly low-valent S = 1/2 (SiP<sub>3</sub>)Fe(H<sub>2</sub>) and TPBCo(H<sub>2</sub>) complexes.<sup>40</sup> In Smith's iron(V)-nitride complex, vibronic coupling to a partially filled, degenerate  $d(x^2 - y^2)/d(xy)$  pair gives rise to significant g-anisotropy and mixing with the unfilled d(xz)/d(yz) pair – termed "e-e mixing" - yielding some spin delocalization onto the terminal nitride p-orbitals.<sup>39</sup> The electronic structure of [Fe=CCH<sub>3</sub>]<sup>+</sup> 7 can likely be understood by a similar model: a nearly degenerate S = 1/2 ground state leads to large g-anistropy and mixing of unoccupied d(xz)/d(yz) Fe-C  $\pi^*$ -bond orbitals with partially filled  $d(xy)/d(x^2-y^2)$  orbitals delocalizes modest spin onto  $C_{\alpha}$  of the paramagnetic carbyne (Figure 8).<sup>41</sup>

Table 3. Hyperfine coupling constants in MHz determined for [(SiP<sub>3</sub>)FeCCH<sub>3</sub>]<sup>+</sup> and computed spin densities.

Nucleus	$A_{I}$	$A_2$	$A_3$	<i>a</i> <sub>iso</sub>	Spin density
Fe					0.99
					0.016
<sup>31</sup> P	18	14	25	19.0	0.008
					0.015
$^{13}C_{\alpha}$	18	33	47	32.7	-0.067
$^{13}C_{\beta}$	5.8	5.0	4.0	4.9	-0.006
	96	12.5	06	0.0	-0.004
$^{1}H_{3}C$	0.0	12.5	0.0 6.2	9.9	-0.001
	2.3	0.5	0.5	5.0	-0.0002

As a direct probe of this hypothesis, pulse X-band HYSCORE and ENDOR spectroscopy of 7 was undertaken (Figures 11 and 12). From these complementary methods, comparison of data from  $({}^{13}C_2-7)$  and its natural abundance isotopologue shows hyperfine couplings for the <sup>13</sup>C nuclei of  $C_{\alpha}$  and  $C_{\beta}$  with the spin on iron. Simulation of the data gives an anisotropic hyperfine tensor for  ${}^{13}C_{\alpha} |A({}^{13}C)| = [18, 33,$ 47] MHz;  $a_{iso} = 32.7$  MHz; T = 14.5 MHz) (Table 3), indicative of strong coupling to the  ${}^{13}C_{\alpha}$  nuclear spin. Coupling to  ${}^{13}C_{\beta}$  is weaker and nearly isotropic ( $|A({}^{13}C)| =$ [5.8, 5.0, 4.0] MHz;  $a_{iso} = 4.9$  MHz; T = 0.9 MHz). Following the analysis of Hoffman and coworkers,<sup>39</sup> the  ${}^{13}C_{\alpha}$  hyperfine coupling tensor can be decomposed into isotropic and anisotropic terms; the anisotropic component allows estimation of spin density of approximately 0.06 electrons at  $C_{\alpha}$  in the 2p(x) and 2p(y) orbitals, orthogonal to the  $Fe \equiv C-R$ bond vector. This estimate agrees well with the aforementioned Löwdin spin population analysis.



**Figure 11.** (top) X-band HYSCORE spectrum of  ${}^{13}C_2$ -[(SiP<sub>3</sub>)FeCCH<sub>3</sub>]OTf measured at 280 mT (g = 2.48) (Bottom) Monochromatic representation of the HYSCORE data with simulations of hyperfine couplings overlaid: (green) using simulations parameters in Table 3: (green)  ${}^{31}P$ , (red)  ${}^{13}C_{\alpha}$ , (blue)  ${}^{13}C_{\beta}$ . Acquisition parameters: Acquisition parameters: temperature = 6.5 K; microwave frequency = 9.715 GHz; MW pulse length ( $\pi/2$ ,  $\pi$ ) = 8 ns, 16 ns;  $\tau$  = 168 ns, t<sub>1</sub> = t<sub>2</sub> = 100 ns;  $\Delta t_1 = \Delta t_2 = 16$  ns; shot repetition time (srt) = 1 ms).



**Figure 12.** (A) (black) X-band <sup>13</sup>C-<sup>12</sup>C difference ENDOR spectra of (<sup>13</sup>C<sub>2</sub>-7) and (<sup>12</sup>C<sub>2</sub>-7); (red) <sup>13</sup>C<sub> $\alpha$ </sub> simulated fit; (blue) <sup>13</sup>C<sub> $\beta$ </sub> simulated fit. (B) (black) X-band <sup>1</sup>H-<sup>2</sup>H difference ENDOR spectra of (<sup>1</sup>H<sub>3</sub>C-7) and (<sup>2</sup>H<sub>3</sub>C-7); (red) <sup>1</sup>H<sub>3</sub>C simulated fit 1; (blue) <sup>1</sup>H<sub>3</sub>C simulated fit 2. Acquisition parameters: temperature = 6.5 K; MW frequency = 9.715 ACS Parago

GHz; MW pulse length  $(\pi/2, \pi) = 40$  ns, 80 ns;  $\tau = 190$  ns; RF pulse length = 15 µs; T<sub>RF</sub> = 2 µs; shot repetition time = 5 ms.

Interestingly, despite weak coupling to  $C_{\beta}$ , proton hyperfine coupling to the -CH<sub>3</sub> substituent of [Fe=CCH<sub>3</sub>]<sup>+</sup> **7** is detected by both ENDOR and HYSCORE. Comparison of <sup>2</sup>**H**-**7** with its natural abundance isotopologue and simulation of the ENDOR difference spectrum (Figure 12) provides two hyperfine tensors for <sup>1</sup>H<sub>1</sub>(CH<sub>3</sub>) ( $|A(^{1}H)| = [8.6, 12.5, 8.6]$ MHz;  $a_{iso} = 9.9$  MHz; T = 1.3 MHz) and <sup>1</sup>H<sub>2</sub>(CH<sub>3</sub>) ( $|A(^{1}H)| =$ [2.3, 6.3, 6.3] MHz;  $a_{iso} = 5.0$  MHz; T = 1.3 MHz). Importantly, the isotropic coupling components for the carbyne -*CH*<sub>3</sub> substituent to the unpaired spin are correlated with a "hyperconjugation" interaction between the methyl Hatoms and the spin active Fe and C<sub>a</sub> orbitals.<sup>42,43,44</sup>

A hyperconjugation effect indicates, to some extent, delocalization of spin/hole or cationic character on Fe= $C_{\alpha}$  to the hydrogen s-orbitals on the terminal methyl (see Figure 9 for this and other chemical depictions). This exaggerated resonance description is thus juxtaposed with the electronic structures typically invoked in heteroatom-substituted previously carbyne complexes, like our reported (SiP<sub>3</sub>)FeCOSiMe<sub>3</sub>, (DPB)Fe(COSiMe<sub>3</sub>)<sub>2</sub>.  $[(SiP_3)FeCNMe_2]^{0/+}$ , and  $[(SiP_3)FeCNH_2]^{+20-23}$ . In each of these cases, the Fe-C and C-O/N bonding is qualified by the free "lone pair" on the distal atom, capable of delocalizing bonding across the Fe-C-O/N unit and decreasing the formal valency at iron. The CNR<sub>2</sub> moiety of the amino carbynes are even planar ( $\Sigma \angle \approx 360^{\circ}$ ), consistent with conjugation between nitrogen and the Fe-C  $\pi$ -bond. However, hyperconjugation and delocalization in [(SiP<sub>3</sub>)FeCCH<sub>3</sub>]<sup>+</sup> should be appreciated as a subtle effect, as the spectroscopic data and DFT calculations determine a majority of unpaired spin to be located on iron (Fe: +0.99 e<sup>-</sup> vs.  $C_{\alpha}$ : -0.07 e<sup>-</sup>). Furthermore, the strong similarity between the EPR data for  $[(SiP_3)FeCNMe_2]^+$  and  $[(SiP_3)FeCCH_3]^+$ , the comparably modest calculated spin density across the amino carbyne (Fe: +0.97 e<sup>-</sup> vs  $C_{\alpha}$ : -0.03 e<sup>-</sup> and  $N_{\beta}$ : -0.01 e<sup>-</sup>), and the close congruence between the Mössbauer parameters for all of the (SiP<sub>3</sub>)Fe carbynes, both alkyl- and heteroatom-substituted, suggests that a "Fischer-like" resonance description (the Ltype carbyne donor resonance forms in Figure 9) may in fact be of limited importance to the structural and electronic stabilities of this series of Fe=C triply bonded species.

The latter point speaks to the potential relevance of other hypothetical iron-ligand multiply-bonded species in the namely Fe≡C(H) (SiP<sub>3</sub>)Fe platform, terminal carbide/methylidyne or Fe=N nitride complexes (Figure 9, bottom), the latter possibly arising during the limited nitrogen reduction catalysis mediated by (SiP<sub>3</sub>)FeN<sub>2</sub>;<sup>45</sup> the former have yet to be directly evidenced from cleavage of CO, CN<sup>-</sup>, or C<sub>2</sub>H<sub>2</sub> at iron. We have extensively explored the reactivity and thermochemistry of the early stages of reductive protonation on FeN<sub>2</sub> compounds. In the trisphosphine-borane TPBFeN<sub>2</sub>, the N-N bond is cleaved to yield NH3 and a spectroscopically characterized [(TPB)Fe<sup>IV</sup>≡N]<sup>+</sup> nitride cation.<sup>3</sup> Observation of an iron-N2H4 hydrazine cation46 derived from (SiP3)FeN2 questions the accessibility of any (SiP<sub>3</sub>)Fe=N species through functionalization of dinitrogen. However, the stable bonding in the [(SiP<sub>3</sub>)FeCCH<sub>3</sub>]<sup>+/0</sup> complexes, and the aforementioned implication for the electronic structures of the heteroatomsubstituted relatives, support the potential viability of highvalent, multiply-bonded Fe=C or Fe=N intermediates in the chemistry of this system, and structurally related synthetic or biological iron sites.

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#### CONCLUSION

To close, we have described the activation of acetylene gas at a mononuclear iron site, along with reductive protonation reactions that converge at stable and structurally unusual Fe(IV) and Fe(V) alkylcarbyne complexes. X-rav crystallography, pulse X-band EPR, and other spectroscopies have allowed us to characterize the first Fe(I) and Fe(II) adducts of acetylene, and to discriminate their side-on binding forms from alternative structural isomers (e.g., Fe=CCH<sub>2</sub>). Characterization of their electronic structures, through Mössbauer, DFT, and pulse EPR experiments, reveal strong covalency in the Fe=C triple bonds of the carbyne species and moderate spin delocalization in the cationic S = 1/2 congeners. Congruence between the structural, spectroscopic, and computed parameters of the heteroatom-substituted iron carbynes with those of the newly explored alkylcarbynes described here establishes the viability of a highly covalent Fe-to-C triple bond in trigonal pyramidal symmetry without a requirement for heteroatom resonance stabilization. More generally, the complexes and spectroscopic signatures reported here may guide the ongoing investigation of reactive nitrogenase intermediates with non-native substrates, particularly acetylenic adduct species, or possible carbyne intermediates of Fischer-Tropsch type C-C couplings with C1 substrates.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:

Procedures and characterization data (PDF) X-ray Data (CIF) Computational models (inp)

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#### Notes

The authors declare no competing financial interest.

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