

# A CO-Derived Iron Dicarbyne That Releases Olefin upon Hydrogenation

Daniel L. M. Suess and Jonas C. Peters\*

Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, United States

**S** Supporting Information

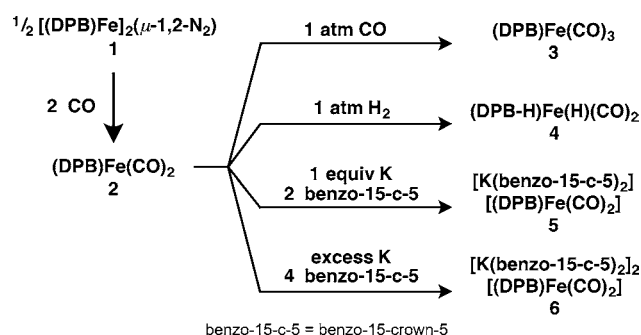
**ABSTRACT:** An iron diphosphineborane platform that was previously reported to facilitate a high degree of N<sub>2</sub> functionalization is herein shown to effect reductive CO coupling. Disilylation of an iron dicarbonyl precursor furnishes a structurally unprecedented iron dicarbyne complex. Several complexes related to this process are also characterized which allows for a comparative analysis of their respective Fe–B and Fe–C bonding. Facile hydrogenation of the iron dicarbyne at ambient temperature and 1 atm H<sub>2</sub> results in release of a CO-derived olefin.

Reductive coupling of CO to C<sub>2+</sub>-containing products has been a longstanding focus in organometallic chemistry primarily motivated by the goal of developing homogeneous alternatives to Fischer–Tropsch reactions.<sup>1</sup> In addition, it was recently discovered that nitrogenases, best known for effecting N<sub>2</sub> reduction to NH<sub>3</sub>, also reduce CO to higher-order hydrocarbons.<sup>2</sup> As such, studies of metal complexes that mediate reductive CO coupling remain of high interest in the dual contexts of improving syngas conversion technologies as well as modeling biological carbon fixation.

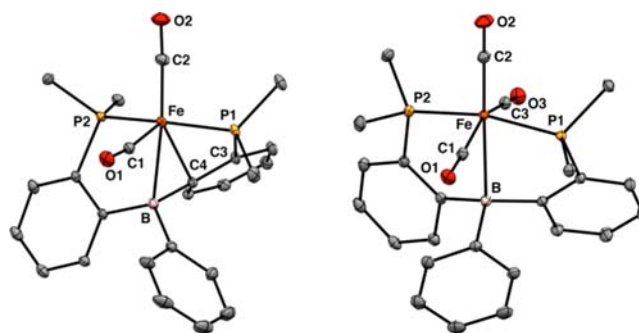
One approach to C–C bond formation from CO-derived ligands is coupling of two carbynes at a single metal site.<sup>3</sup> To this end, Lippard and co-workers previously described the disilylation of Na[(dmpe)<sub>2</sub>M(CO)<sub>2</sub>] (M = V, Nb, or Ta; dmpe = Me<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PMe<sub>2</sub>) complexes to form CO-derived η<sup>2</sup>-alkyne ligands<sup>4</sup> which can undergo subsequent hydrogenation to release an olefin.<sup>4c,5</sup> Although dicarbyne<sup>6</sup> intermediates were proposed in these reactions,<sup>7</sup> such species were not detected. Similarly, Mayr and co-workers reported the transformation of W(CO)<sub>6</sub> to a nucleophilic *cis*-acyl-carbyne complex which, upon further elaboration of the acyl group, undergoes C–C coupling to form an η<sup>2</sup>-alkyne ligand;<sup>8</sup> a tungsten dicarbyne intermediate was proposed but not observed. In the related context of isocyanide reductive coupling, Filippou and Pombeiro have studied the synthesis<sup>9</sup> and C–C coupling reactivity<sup>9a–c</sup> of bis-(aminocarbyne) Mo and W complexes.

In this report, we describe the preparation of a mononuclear iron dicarbyne complex that is derived from CO. Structural, spectroscopic, and theoretical characterization of the iron dicarbyne as well as several related species permits a comparative analysis of the bonding in these highly covalent complexes. Exposure of the featured dicarbyne to H<sub>2</sub> (1 atm) results in the facile release of a Z-olefin product at room temperature.

## Scheme 1



The CO reduction chemistry described herein utilizes a (DPB)Fe system<sup>10</sup> (DPB<sup>11</sup> = PhB(*o*-iPr<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>) which has been recently shown to facilitate a high degree of N<sub>2</sub> functionalization. In iron complexes of this ligand, the polyhaptic BPh moiety can function as a donor and/or an acceptor, thereby making this framework well suited for multielectron, reductive transformations. For the purposes of CO coupling, we targeted (DPB)Fe complexes with >1 CO ligand. Addition of 1 atm CO to the previously described diiron bridging N<sub>2</sub> complex<sup>10</sup> 1 results in initial formation of red-orange (DPB)Fe(CO)<sub>2</sub> 2 followed by pale-yellow (DPB)Fe(CO)<sub>3</sub> 3 (Scheme 1). Prolonged photolysis of solutions of 3 results in loss of CO and regeneration of 2. This conversion is accompanied by binding of a phenylene linker in 2 (Figure 1) to give a geometrical motif similar to that observed in the isoelectronic complex (TPB)Fe(CO) (TPB = B(*o*-iPr<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>).<sup>12</sup> The asymmetry in



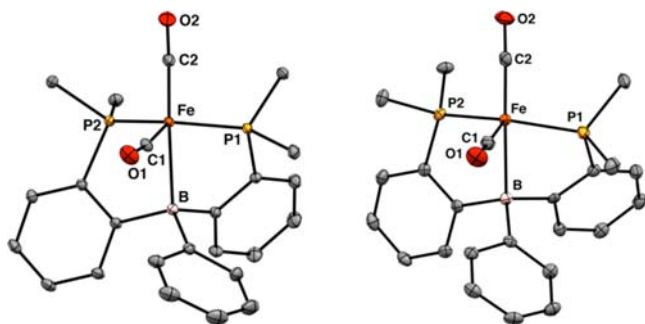
**Figure 1.** Displacement ellipsoid (50%) representations of (left) 2 and (right) 3. P<sup>i</sup>Pr<sub>2</sub> groups are truncated, and H atoms are omitted for clarity.

Received: July 5, 2013

Published: August 9, 2013

the solid-state structure of **2** is maintained in solution as evidenced by the presence of two sharp peaks in its  $^{31}\text{P}$  NMR spectrum at 90.6 and 54.6 ppm ( $^2J_{\text{PP}} = 65.3$  Hz). Given previous work with Fe and Ni complexes of this ligand class,<sup>10,13</sup> we anticipated that the  $\eta^3\text{-BCC}$  interaction in **2** could be hemilabile and participate in an E–H bond activation process. Accordingly, colorless (DPB–H)Fe(H)(CO)<sub>2</sub> **4** is formed quantitatively over the course of minutes upon exposure of **2** to 1 atm H<sub>2</sub> at room temperature. Its  $^1\text{H}$  NMR spectrum shows the presence of a terminal Fe–H signal at –7.73 ppm (1H, dt,  $^2J_{\text{HP}} = 54.4$  Hz,  $^2J_{\text{HH}} = 7.6$  Hz) and a bridging Fe–H–B signal at –17.0 ppm (1H, br); XRD analysis establishes its *cis*-dihydride stereochemistry (see SI).

Complex **2** exhibits two quasireversible waves in its cyclic voltammogram at –1.94 and –2.70 V vs Fc/Fc<sup>+</sup> (see SI), prompting us to pursue one- and two-electron chemical reductions.<sup>14</sup> Accordingly, mono- and dianions **5** and **6** were prepared by reduction with K and isolated with [K(benzo-15-crown-5)]<sub>2</sub> counteranions (benzo-15-crown-5 is abbreviated as benzo-15-c-5). Structural characterization by XRD analysis shows that both **5** and **6** lack the phenylene interaction that is present in **2** (Figure 2). Monoanion **5** adopts a geometry



**Figure 2.** Displacement ellipsoid (50%) representations of (left) anion **5** and (right) dianion **6**. PPr<sub>2</sub> groups are truncated and H atoms, solvent molecules, and counteranions are omitted for clarity.

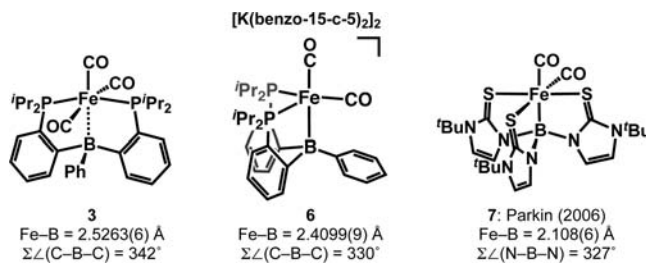
between trigonal bipyramidal (TBP) and square pyramidal ( $\tau = 0.44$ )<sup>15</sup> with a wide  $\angle(\text{P–Fe–P})$  angle of 142.71(2)° whereas dianion **6** is TBP ( $\tau = 0.93$ ) with a contracted  $\angle(\text{P–Fe–P})$  angle of 120.60(1)°. The wide  $\angle(\text{P–Fe–P})$  angle in **5** suggests that the unpaired electron resides in an orbital in the P–Fe–P plane; both the rhombic X-band EPR signal and the calculated spin density of **5** support this assignment (see SI). The Fe–B distances in **5** and **6** are nearly equivalent at 2.4192(15) and 2.4099(9) Å, respectively, while the average Fe–P and Fe–C(O) distances contract upon reduction from **5** to **6** (Table 1). A marked decrease in  $\nu_{\text{CO}}$  upon reduction of **2** to **5** and **5** to **6** is also observed (Table 1). Taken together, these data suggest that the extra electron density in **6** is absorbed largely by increased Fe–CO and Fe–P  $\pi$  backbonding rather than increased Fe–B  $\sigma$  backbonding.

**Table 1.** Selected Bond Lengths (Å), Angles (°), and Infrared Bands (cm<sup>–1</sup>)

	Fe–CO (avg.)	Fe–P (avg.)	Fe–B	$\sum\angle(\text{C–B–C})$	$\nu_{\text{CO}}(\text{sym,asym})$
<b>2</b>	1.745	2.212	2.3080(15)	342	1908, 1863
<b>5</b>	1.756	2.212	2.4192(15)	330	1857, 1791
<b>6</b>	1.727	2.156	2.4099(9)	330	1738, 1659

Complexes **3** and **6** as well as the first reported iron–borane complex, ( $\kappa^4\text{-B}(\text{mim}^{\text{tBu}})_3$ )Fe(CO)<sub>2</sub> **7** ( $\text{mim}^{\text{tBu}} = 2\text{-mercapto-1-tert-butylimidazolyl}$ ),<sup>16</sup> are all 18-electron iron polycarbonyl complexes, and therefore constitute an informative set for comparison of their Fe–B bonding (Chart 1). Compared with **6**,

**Chart 1.** Selected Fe–BR<sub>3</sub> Complexes



complex **3** has a longer Fe–B distance (2.5263(6) vs 2.4099(9) Å), a less pyramidalized B center ( $\sum\angle(\text{C–B–C}) = 342^\circ$  vs  $330^\circ$ ), and a less upfield-shifted  $^{11}\text{B}$  NMR signal (20.3 vs 14.1 ppm). These data indicate somewhat stronger Fe–B bonding in **6** compared with **3**, which may be rationalized by the dianionic charge and more electron-releasing Fe center in the former.

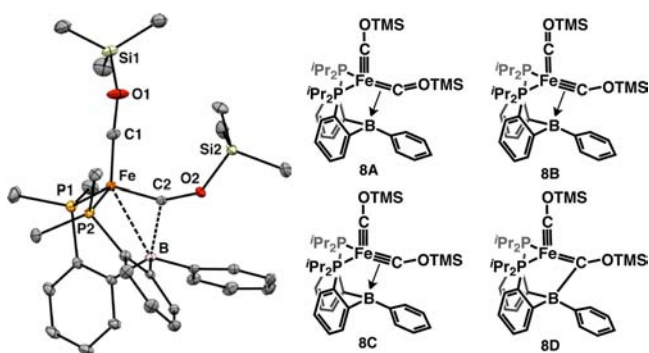
Both **3** and **7** are nominally isoelectronic ML<sub>5</sub>Z complexes<sup>17</sup> and their Fe centers could therefore be considered divalent (assuming strong Fe–B bonding) or zerovalent (assuming weak Fe–B bonding).<sup>18</sup> The most striking contrast between **3** and **7** is that the Fe–B distance in **7** is 2.108(6) Å—ca. 0.4 Å shorter than that in **3**. We attribute this difference primarily to the greater Lewis acidity of the B center of **7** (though the relative electron richness of the Fe centers is a contributing factor). Whereas the B atom in **3** has three C substituents and conjugates into the  $\pi$  system of the phenyl group, the B atom in **7** has three comparatively electronegative N substituents that contribute little  $\pi$  donation owing to the orthogonal orientation of the pyrrolyl groups with respect to the B 2p<sub>z</sub> orbital. The Lewis acidity of the B atom in **7** is therefore expected to be much greater than that of the B atom in **3**. Accordingly, while the Fe center in **7** may be formulated as divalent, the Fe center in **3** is in our view more usefully considered zerovalent, akin to that of Fe(CO)<sub>5</sub>.

We note that the C–O stretching frequencies of **6** are reminiscent of some low-energy bands that have been observed for nitrogenases in the presence of CO (between 1679 and 1715 cm<sup>–1</sup>)<sup>19</sup> which have been assigned to one or more formyl and/or bridging carbonyl ligand(s). In addition, the low-energy C–O stretches in **6** suggest the possibility that the O atoms may be functionalized with an electrophilic reagent.<sup>20</sup> In situ reduction of **2** with excess K and addition to a –78 °C solution of 2.2 equiv of trimethylsilyl triflate (TMSOTf) results in silylation of both O atoms to give the dicarbyne **8** (eq 1). Since only two terminal



iron carbynes have been reported<sup>20b,21</sup> and **8** is a unique example of an iron dicarbyne, its molecular and electronic structures are of particular interest. Although **8** reverts to **2** in solution over several days, the rate of this decomposition is sufficiently slow to allow for solid- and solution-state characterization.

Single crystals of **8** contain two molecules in the asymmetric unit and were studied by XRD analysis (Figure 3). The very short Fe–C distances of 1.639 Å (Fe–C1 avg.) and 1.676 Å (Fe–C2



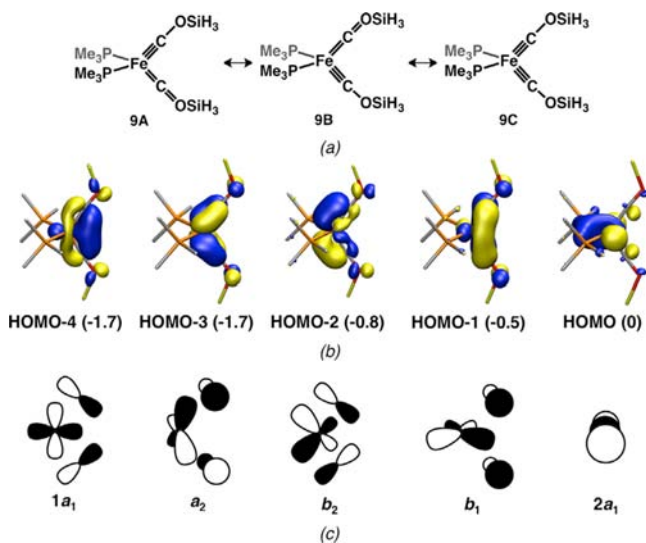
**Figure 3.** (Left) Displacement ellipsoid (50%) representation of one of the two crystallographically independent molecules of **8**. P<sup>i</sup>PR<sub>2</sub> groups are truncated, and H atoms are omitted for clarity. (Right) Relevant resonance structures of **8**.

avg.) are similar to the Fe–C distance of 1.671(2) Å reported for (SiP<sub>3</sub>)Fe(COTMS)<sup>20b</sup> (SiP<sub>3</sub>: (o-<sup>i</sup>Pr<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>Si) and indicate Fe–C multiple-bond character for both carbyne ligands. The C2 carbyne ligand is distinguished by a long, yet non-negligible B–C2 interaction (1.86 Å (avg.)) and a contracted ∠(Fe–C2–O2) angle of 151° (avg.), compared with 171° (avg.) for the ∠(Fe–C1–O1) angle. In solution, the two carbyne ligands in <sup>13</sup>C-labeled samples are further differentiated by their <sup>13</sup>C NMR resonances at 230.2 ppm (d, <sup>2</sup>J<sub>CC</sub> = 3.2 Hz) and 261.9 ppm (dt, <sup>2</sup>J<sub>CP</sub> = 9.0 Hz, <sup>2</sup>J<sub>CC</sub> = 3.2 Hz), assigned to C1 and C2, respectively, on the basis of DFT calculations (see SI). For reference, the chemical shift corresponding to the carbyne ligand in (SiP<sub>3</sub>)Fe(<sup>13</sup>COTMS) is 250.3 ppm (q, <sup>2</sup>J<sub>CP</sub> = 16.4 Hz).<sup>22</sup> The B atom in **8** is pyramidalized in both the solution and solid states as indicated by the low ∑∠(C–B–C) = 328° (avg.) and upfield-shifted <sup>11</sup>B NMR signal (6.4 ppm). In addition, the Mössbauer isomer shift of **8** (δ = –0.200 mm s<sup>–1</sup>) is substantially more negative than that of **2** (δ = 0.087 mm s<sup>–1</sup>), indicating a greater degree of Fe–L covalent bonding in **8** (see SI). Taken together, these XRD, NMR, and Mössbauer data suggest that extensive Fe–C multiple bonding and additional C2–B bonding should be considered when assessing the valence bonding in **8**.

To account for these features, we propose several possible resonance structures for **8** (Figure 3). Structures **8A**, **8B**, and **8C** have two dicarbyne ligands, one of which exhibits dative bonding to the pendant borane. Structures **8A** and **8B** emphasize that a d-block metal does not have enough orbitals to form four independent π bonds (as in **8C**);<sup>3a,9d</sup> however, **8C** may be a valid resonance contributor if either three-center hyperbonding<sup>23</sup> or mixing with Fe 4p orbitals<sup>24</sup> is invoked. Resonance form **8D** is distinguished from **8A/B/C** in that the B atom in **8D** is bonded to one of the carbynes by a two-center “normal” covalent bond,<sup>25</sup> thereby rendering that fragment a zwitterionic Fischer-type carbene with a formal negative charge on the B atom. The Fe–C(OR)–B bonding in **8** may be compared to the M–C(R)–H bonding in α-agostic alkylidenes:<sup>26</sup> analogously to **8**, the latter class of compounds is characterized by M–C–R angles between 120° and 180°, short M–C distances, and long C–H distances. Whereas α-agostic alkylidenes feature attenuated—but significant—<sup>1</sup>J<sub>CH</sub> values,<sup>26</sup> no <sup>11</sup>B–<sup>13</sup>C coupling is resolved in the <sup>13</sup>C signal corresponding to C2, suggesting that <sup>1</sup>J<sub>BC</sub> is low (<2 Hz, compared with <sup>1</sup>J<sub>BC</sub> = 49.5 Hz for NaBPh<sub>4</sub>).<sup>27</sup> Structurally, a boratocarbene ligand as depicted in **8D** would be expected to display four B–C bonds of similar length since each C substituent would have sp<sup>2</sup> hybridization; however, the B–C2 distance is ~0.2 Å (avg.) longer than the other B–C<sub>sp<sup>2</sup></sub> distances

(1.65 Å (avg.)). In addition, the average Fe–C distance of all structurally characterized O-substituted Fischer-type iron carbenes is 1.90 Å,<sup>28</sup> which is >0.2 Å (avg.) longer than the Fe–C2 distance observed in **8**. Given the low value of <sup>1</sup>J<sub>BC2</sub> and these structural metrics, we weight resonance contributors **8A/B/C** more heavily than **8D**.

In order to gain further insight into the bonding in **8**, the structures of **8** and a hypothetical, simplified model, (PMe<sub>3</sub>)<sub>2</sub>Fe(COSiH<sub>3</sub>)<sub>2</sub> **9** were optimized and studied using DFT (M06L/6-311+g(d)). The five highest-filled MOs of **9** (Figure 4) include



**Figure 4.** (a) Resonance structures of **9**. (b) Calculated valence MOs of **9**. (c) Atomic orbital representations of the calculated MOs. Orbital energies (relative to the HOMO) are given in parentheses, and isosurfaces are shown at the 0.05 e<sup>–</sup>Å<sup>–3</sup> level.

one essentially nonbonding orbital with some degree of Fe–P backbonding (HOMO) as well as four orbitals with significant Fe–C π bonding (HOMO–1 through HOMO–4). Thus, **9** may be regarded as isoelectronic to known compounds of the form (PR<sub>3</sub>)<sub>2</sub>Fe(NO)<sub>2</sub>.<sup>29</sup> Although the filled MOs of **8** are more complex than those of **9** owing to the lower overall symmetry of **8** as well as mixing with aryl π orbitals, the shapes and ordering of the valence orbitals for the two molecules correlate with good fidelity (see SI). These calculations suggest that the electronic structures of **8** and **9** are largely analogous and that the electronic structure of **8**, which includes the additional borane–carbyne interaction, may be considered as a perturbation of that of **9**.

The stability of the dicarbyne form of **8** with respect to C–C coupling is in marked contrast to the analogous [(dmpe)<sub>2</sub>M(η<sup>2</sup>-(TMSO)C≡C(OTMS))] + complexes (M = V, Nb, and Ta) which feature C–C-coupled η<sup>2</sup>-alkyne ligands (*vide supra*).<sup>4</sup> Nevertheless, facile C–C coupling is achieved upon room temperature addition of 1 atm H<sub>2</sub> to solutions of **8**, which results in liberation of olefin **10** in moderate yield (43%, average of three runs; eq 2). The hydrogenation of **8** is highly stereoselective,



furnishing *Z*-olefin **10** without any detected *E* isomer. Performing the hydrogenation with a mixture of <sup>12</sup>C<sup>12</sup>C- and <sup>13</sup>C<sup>13</sup>C-labeled **8** gives only <sup>12</sup>C<sup>12</sup>C and <sup>13</sup>C<sup>13</sup>C olefin with no <sup>12</sup>C<sup>13</sup>C



olefin, which indicates that the C–C coupling process occurs at a single metal site. Although we have not yet been able to fully characterize the resulting Fe-containing product, there appears to be only one Fe-containing species, which is a paramagnet as indicated by  $^1\text{H}$  NMR spectroscopy. Previous examples of reductive CO coupling using Fe are few,<sup>30</sup> and, to our knowledge, the release of an olefin by a hydrogenative CO reductive coupling pathway has not been previously reported for Fe. The aforementioned hydrogenation of  $[(\text{dmpe})_2\text{M}(\eta^2\text{-(TMSO)-C}\equiv\text{C(OTMS)})]^+$  complexes to release **10** occurs either at elevated  $\text{H}_2$  pressures ( $\sim 8$  atm  $\text{H}_2$  for  $\text{M} = \text{V}$ )<sup>4c</sup> or with the aid of a hydrogenation catalyst (1 atm  $\text{H}_2$  and 5% Pd/C for  $\text{M} = \text{Ta}$ ).<sup>5</sup> By comparison, hydrogenation of **8** occurs within minutes at 1 atm  $\text{H}_2$ .

In summary, we have shown that the (DPB)Fe platform, which was previously studied in the context of  $\text{N}_2$  functionalization,<sup>10</sup> also facilitates CO functionalization to furnish a structurally unique iron dicarbyne complex. Like the iron aminoimide intermediate in (DPB)Fe-mediated  $\text{N}_2$  functionalization, the iron dicarbyne complex in this report features extensive Fe–L multiple bonding. Initial reactivity studies of this species reveal that it undergoes hydrogenative C–C coupling to furnish a CO-derived olefin.

## ■ ASSOCIATED CONTENT

### Supporting Information

Experimental and computational details, spectra, and XRD tables. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

### Corresponding Author

[jpeters@caltech.edu](mailto:jpeters@caltech.edu)

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

We acknowledge the NIH (GM070757) and the Beckman Institute for funding and thank Lawrence Henling for assistance with XRD studies.

## ■ REFERENCES

- (1) West, N. M.; Miller, A. J. M.; Labinger, J. A.; Bercaw, J. E. *Coord. Chem. Rev.* **2011**, *255*, 881.
- (2) (a) Lee, C. C.; Hu, Y.; Ribbe, M. W. *Science* **2010**, *329*, 642. (b) Yang, Z. Y.; Dean, D. R.; Seefeldt, L. C. *J. Biol. Chem.* **2011**, *286*, 19417. (c) Hu, Y.; Lee, C. C.; Ribbe, M. W. *Science* **2011**, *333*, 753.
- (3) (a) Wilker, C. N.; Hoffmann, R.; Eisenstein, O. *Nouv. J. Chim.* **1983**, *7*, 585. (b) Mayr, A.; Bastos, C. M. *Prog. Inorg. Chem.* **1992**, *40*, 1.
- (4) (a) Bianconi, P. A.; Williams, I. D.; Engeler, M. P.; Lippard, S. J. *J. Am. Chem. Soc.* **1986**, *108*, 311. (b) Bianconi, P. A.; Vrtis, R. N.; Rao, C. P.; Williams, I. D.; Engeler, M. P.; Lippard, S. J. *Organometallics* **1987**, *6*, 1968. (c) Protasiewicz, J. D.; Lippard, S. J. *J. Am. Chem. Soc.* **1991**, *22*, 6564. (d) Carnahan, E. M.; Protasiewicz, J. D.; Lippard, S. J. *Acc. Chem. Res.* **1993**, *26*, 90.
- (5) Vrtis, R. N.; Bott, S. G.; Rardin, R. L.; Lippard, S. J. *Organometallics* **1991**, *10*, 1364.
- (6) Dicarbyne complexes have also been referred to as “carbene-carbyne” or “bis-carbene” complexes to reflect the fact that d-block metals do not have enough orbitals to form four independent  $\pi$  bonds. However, since the carbon centers in “...CR” ligands are monovalent, we refer to these ligands as carbynes and the species in question as dicarbyne complexes. In addition to being consistent with current IUPAC definitions, this allows for carbene ligands (which have divalent

carbon centers) to be distinguished from carbyne ligands. Nevertheless, it should be emphasized that the iron dicarbyne complex in this report is a unique structure regardless of how many independent Fe–C  $\pi$  bonds it contains. See: McNaught, A. D.; Wilkinson, A. *IUPAC Compendium of Chemical Terminology*, 2nd ed.; Blackwell Scientific Publications: Oxford, 1997.

- (7) (a) Protasiewicz, J. D.; Masschelein, A.; Lippard, S. J. *J. Am. Chem. Soc.* **1993**, *115*, 808. (b) Protasiewicz, J. D.; Bronk, B. S.; Masschelein, A.; Lippard, S. J. *Organometallics* **1994**, *13*, 1300.
- (8) McDermott, G. A.; Mayr, A. *J. Am. Chem. Soc.* **1987**, *109*, 580.
- (9) (a) Filippou, A. C.; Grünleitner, W.; Völk, C.; Kiprof, P. *Angew. Chem., Int. Ed.* **1991**, *30*, 1167. (b) Filippou, A. C.; Völk, C.; Grünleitner, W.; Kiprof, P. *J. Organomet. Chem.* **1992**, *434*, 201. (c) Wang, Y.; Da Silva, J. J. F.; Pombeiro, A. J.; Pellinghelli, M. A.; Tiripicchio, A.; Henderson, R. A.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1995**, 1183. (d) Filippou, A. C.; Hofmann, P.; Kiprof, P.; Schmid, H. R.; Wagner, C. *J. Organomet. Chem.* **1993**, *459*, 233.
- (10) Suess, D. L. M.; Peters, J. C. *J. Am. Chem. Soc.* **2013**, *135*, 4938.
- (11) Bontemps, S.; Gornitzka, H.; Bouhadir, G.; Miqueu, K.; Bourissou, D. *Angew. Chem., Int. Ed.* **2006**, *45*, 1611.
- (12) Moret, M.-E.; Peters, J. C. *Angew. Chem., Int. Ed.* **2011**, *50*, 2063.
- (13) Harman, W. H.; Peters, J. C. *J. Am. Chem. Soc.* **2012**, *134*, 5080.
- (14) A recent Fe(CO)<sub>2</sub> charge series: Tondreau, A. M.; Milsmann, C.; Lobkovsky, E.; Chirik, P. J. *Inorg. Chem.* **2011**, *50*, 9888.
- (15) Addison, A. W.; Rao, T. N.; Reedijk, J.; van Rijn, J.; Verschoor, G. C. *J. Chem. Soc., Dalton Trans.* **1984**, 1349.
- (16) Figueroa, J. S.; Melnick, J. G.; Parkin, G. *Inorg. Chem.* **2006**, *45*, 7056.
- (17) Green, M. L. H. *J. Organomet. Chem.* **1995**, *500*, 127.
- (18) (a) Hill, A. F. *Organometallics* **2006**, *25*, 4741. (b) Parkin, G. *Organometallics* **2006**, *25*, 4744. (c) Sircoglou, M.; Bontemps, S.; Mercy, M.; Saffon, N.; Takahashi, M.; Bouhadir, G.; Maron, L.; Bourissou, D. *Angew. Chem., Int. Ed.* **2007**, *46*, 8583. (d) Suess, D. L. M.; Tsay, C.; Peters, J. C. *J. Am. Chem. Soc.* **2012**, *134*, 14158. (e) Anderson, J. S.; Moret, M.-E.; Peters, J. C. *J. Am. Chem. Soc.* **2013**, *135*, 534.
- (19) (a) Thorneley, R.; George, S. J. *Prokaryotic Nitrogen Fixation: A Model System for Analysis of a Biological Process*; Horizon Scientific Press: Wymondham, UK, 2000; p 81. (b) Yan, L.; Dapper, C. H.; George, S. J.; Wang, H.; Mitra, D.; Dong, W.; Newton, W. E.; Cramer, S. P. *J. Inorg. Chem.* **2011**, *2011*, 2064.
- (20) (a) Peters, J. C.; Odom, A. L.; Cummins, C. C. *Chem. Commun.* **1997**, 1995. (b) Lee, Y.; Peters, J. C. *J. Am. Chem. Soc.* **2011**, *133*, 4438.
- (21) Fischer, E. O.; Schneider, J.; Neugebauer, D. *Angew. Chem., Int. Ed.* **1984**, *23*, 820.
- (22) Caution should be exercised when interpreting these  $^{13}\text{C}$  shifts since transition metal carbyne and carbene ligands can assume a wide range of chemical shift values.
- (23) Landis, C. R.; Weinhold, F. *J. Comput. Chem.* **2006**, *28*, 198.
- (24) Moret, M.-E.; Zhang, L.; Peters, J. C. *J. Am. Chem. Soc.* **2013**, *135*, 3792.
- (25) Haaland, A. *Angew. Chem., Int. Ed.* **1989**, *28*, 992.
- (26) (a) Schultz, A. J.; Williams, J. M.; Schrock, R. R.; Rupprecht, G. A.; Fellmann, J. D. *J. Am. Chem. Soc.* **1979**, *101*, 1593. (b) Schrock, R. R. *Chem. Rev.* **2002**, *102*, 145.
- (27) Weigert, F. J.; Roberts, J. D. *J. Am. Chem. Soc.* **1969**, *91*, 4940.
- (28) Data from a CSD search including the May 2013 update.
- (29) Harrison, W.; Trotter, J. *J. Chem. Soc., A* **1971**, 1542.
- (30) (a) Bennett, M. J.; Graham, W.; Smith, R. A.; Stewart, R. P. *J. Am. Chem. Soc.* **1973**, *95*, 1684. (b) Wong, A.; Atwood, J. D. *J. Organomet. Chem.* **1980**, *199*, C9. (c) Okazaki, M.; Ohtani, T.; Inomata, S.; Tagaki, N.; Ogino, H. *J. Am. Chem. Soc.* **1998**, *120*, 9135. (d) Sazama, G. T.; Betley, T. A. *Organometallics* **2011**, *30*, 4315.