Published in final edited form as:

J Am Chem Soc. 2013 August 28; 135(34): 12580–12583. doi:10.1021/ja406874k.

A CO-derived Fe 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, CA 91125, United States

Abstract

An Fe diphosphineborane platform that was previously reported to facilitate a high degree of N₂ functionalization is herein shown to effect reductive CO coupling. Disilylation of an Fe dicarbonyl precursor furnishes a structurally unprecedented Fe 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 Fe dicarbyne at ambient temperature and 1 atm H₂ results in release of a CO-derived olefin.

Reductive coupling of CO to C₂₊-containing products has been a longstanding focus in organometallic chemistry primarily motivated by the goal of developing homogeneous alternatives to Fischer-Tropsch reactions.¹ In addition, it was recently discovered that nitrogenases, best known for effecting N₂ reduction to NH₃, also reduce CO to higher-order hydrocarbons.² 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.³ To this end, Lippard and coworkers previously described the disilylation of Na[(dmpe)₂M(CO)₂] (M = V, Nb, or Ta; dmpe = Me₂PCH₂CH₂PMe₂) complexes to form CO-derived ²-alkyne ligands⁴ which can undergo subsequent hydrogenation to release an olefin.^{4c, 5} Although dicarbyne⁶ intermediates were proposed in these reactions,⁷ such species were not detected. Similarly, Mayr and coworkers reported the transformation of W(CO)₆ to a nucleophilic *cis*-acyl-carbyne complex which, upon further elaboration of the acyl group, undergoes C–C coupling to form an ²-alkyne ligand;⁸ a W dicarbyne intermediate was proposed but not observed. In the related context of isocyanide reductive coupling, Philippou and Pombeiro have studied the synthesis⁹ and C–C coupling reactivity^{9a–c} of bis(aminocarbyne) Mo and W complexes. In this report, we describe the preparation of an unprecedented mononuclear Fe dicarbyne complex that is derived from CO. Structural, spectroscopic, and theoretical characterization of the Fe dicarbyne as well as several related species permits a comparative analysis of the bonding in these highly covalent complexes. Moreover, exposure of the featured dicarbyne to H₂ (1 atm) results in the facile release of a *Z*-olefin product at room temperature (RT).

The CO reduction chemistry described herein utilizes the (DPB)Fe platform¹⁰ (DPB:¹¹ PhB(*o*-⁴Pr₂PC₆H₄)₂) which has been recently shown to facilitate a high degree of N₂

Corresponding Author. jpeters@caltech.edu.

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>.

functionalization. In Fe complexes of this ligand, the polyhaptic BPh moiety can function as a donor and/or an acceptor, thereby making this framework well suited for multi-electron, 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_2 complex¹⁰ **1** results in initial formation of red-orange (DPB)Fe(CO)₂ **2** followed by paleyellow (DPB)Fe(CO)₃ **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*-^{*i*}Pr₂PC₆H₄)₃)).¹² The asymmetry in the solid-state structure of **2** is maintained in solution as evidenced by the presence of two sharp peaks in its ³¹P NMR spectrum at 90.6 and 54.6 ppm (²*J*_{PP} = 65.3 Hz). Given previous work with Fe and Ni complexes of this ligand class,^{10, 13} we anticipated that the ³-BCC interaction in **2** could be hemilabile and participate in an E–H bond activation process. Accordingly, colorless (DPB–H)Fe(H)(CO)₂ **4** is formed quantitatively over the course of minutes upon exposure of **2** to 1 atm H₂ at RT. Its ¹H NMR spectrum shows the presence of a terminal Fe–H signal at –7.73 ppm (1H, dt, ²*J*_{HP} = 54.4 Hz, ²*J*_{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⁺ (see SI), prompting us to pursue one- and two-electron chemical reductions.¹⁴ Accordingly, mono- and dianions **5** and **6** were prepared by reduction with K and isolated with [K(benzo-15-crown-5)₂] counteranions. 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 between trigonal bipyramidal (TBP) and square pyramidal ($\tau = 0.44$)¹⁵ with a wide (P–Fe–P) = 142.71(2)° whereas dianion **6** is TBP ($\tau = 0.93$) with a contracted (P–Fe–P) = 120.60(1)°. The wide (P–Fe–P) 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 ν_{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 backbonding rather than increased Fe–B backbonding.

Complexes **3** and **6** as well as the first reported Fe–borane complex, (4-B(mim^{*t*}Bu)₃)Fe(CO)₂ **7** (mim^{*t*}Bu = 2-mercapto-1-*tert*-butylimidazolyl),¹⁶ are all 18-electron Fe polycarbonyl complexes, and therefore constitute an informative set for comparison of their Fe–B bonding (Chart 1). Compared with **6**, complex **3** has a longer Fe–B distance (2.5263(6) vs. 2.4099(9) Å), a less pyramidalized B center (τ (C–B–C)) = 342° vs. 330°, and a less upfield-shifted ¹¹B 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 ML₅Z complexes¹⁷ and their Fe centers could therefore be considered divalent (assuming strong Fe–B bonding) or zero-valent (assuming weak Fe–B bonding).¹⁸ 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 may also be a contributing factor). Whereas the B atom in **3** has three C substituents and conjugates into the π system of the phenyl group, the B atom in **7** has three electronegative N substituents that contribute little π donation owing to the orthogonal orientation of the pyrrolyl groups with respect to the B 2p_z 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 zero-valent, akin to that of $\text{Fe}(\text{CO})_5$.

Interestingly, 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^{-1})¹⁹ which have been assigned to one or more formyl and/or bridging carbonyl ligand(s). The similarly low-energy bands in **6** demonstrate that highly charged, reduced complexes featuring terminal CO ligands may also give rise to such signals.

In addition, the low-energy CO stretches in **6** suggest the possibility that the O atoms may be functionalized with an electrophilic reagent.²⁰ In situ reduction of **2** with excess K and addition to a -78°C solution of 2.2 equiv trimethylsilyltriflate (TMSOTf) results in silylation of both O atoms to give the dicarbyne **8** (eq. 1). Since only two terminal Fe carbynes have been reported^{20b, 21} and **8** is a unique example of an Fe 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.

(1)

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 avg.) are similar to the Fe–C distance of 1.671(2) Å reported for $(\text{SiP}_3)\text{Fe}(\text{COTMS})$ ^{20b} (SiP_3 : $(\alpha\text{-Pr}_2\text{PC}_6\text{H}_4)_3\text{Si}$) 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) of 151° (avg.), compared with 171° (avg.) for (Fe–C1–O1). In solution, the two carbyne ligands in ^{13}C -labeled samples are further differentiated by their ^{13}C NMR resonances at 230.2 ppm (d, $^2J_{\text{CC}} = 3.2$ Hz) and 261.9 ppm (dt, $^2J_{\text{CP}} = 9.0$ Hz, $^2J_{\text{CC}} = 3.2$ 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 $(\text{SiP}_3)\text{Fe}(^{13}\text{COTMS})$ is 250.3 ppm (q, $^2J_{\text{CP}} = 16.4$ Hz).²² 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 ^{11}B NMR signal (6.4 ppm). In addition, the Mössbauer isomer shift of **8** ($\delta = -0.200$ mm s^{-1}) is substantially more negative than that of **2** ($\delta = 0.087$ mm s^{-1}), 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 dblock metal does not have enough orbitals to form four independent bonds (as in **8C**);^{3a, 9d} however, **8C** may be a valid resonance contributor if either three-center hyperbonding²³ or mixing with Fe 4p orbitals²⁴ 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,²⁵ 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 η -agostic alkylidenes:²⁶ 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 η -agostic alkylidenes feature attenuated—but significant— $^1J_{\text{CH}}$ values,²⁶ no ^{11}B – ^{13}C coupling is resolved in the ^{13}C signal corresponding to C2, suggesting that $^1J_{\text{BC}}$ is low (< 2 Hz, compared with $^1J_{\text{BC}} = 49.5$ Hz for NaBPh₄).²⁷ 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^2 hybridization; however, the B–C2 distance is ~0.2 Å (avg.) longer than the other B–C sp2 distances (1.65 Å (avg.)). In addition, the average Fe–C distance of all structurally-characterized O-substituted Fischer-type Fe carbenes is 1.90 Å,²⁸ which is >0.2 Å (avg.) longer than the Fe–C2 distance observed in **8**. Given the low value of $^1J_{\text{BC2}}$ 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, (PMe₃)₂Fe(COSiH₃)₂ **9** were optimized and studied using DFT (M06L/6–311+g(d)). The five highest-filled MOs of **9** (Figure 4) include one essentially non-bonding orbital with some degree of Fe–P backbonding (HOMO) as well as four highly covalent orbitals with significant Fe–C bonding (HOMO-1 through HOMO-4). Thus, **9** may be regarded as isoelectronic to known compounds of the form (PR₃)₂Fe(NO)₂.²⁹ 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 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)₂M(η^2 -(TMSO)C $\equiv$ C(OTMS))]⁺ complexes (M = V, Nb, and Ta) which feature C–C-coupled η^2 -alkyne ligands (*vide supra*).⁴ Nevertheless, facile C–C coupling is achieved upon RT addition of 1 atm H₂ to solutions of **8**, which results in liberation of olefin **10** in moderate yield (43%, avg. 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 ^{12}C - and ^{13}C -labeled **8** gives only $^{12}\text{C}^{12}\text{C}$ and $^{13}\text{C}^{13}\text{C}$ olefin with no $^{12}\text{C}^{13}\text{C}$ 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 ^1H NMR spectroscopy. Previous examples of reductive CO coupling using Fe are few,³⁰ 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 [(dmpe)₂M(η^2 -(TMSO)C $\equiv$ C(OTMS))]⁺ complexes to release **10** occurs either at elevated H₂ pressures (~8 atm H₂ for M = V)^{4c} or with the aid of a hydrogenation catalyst (1 atm H₂ and 5% Pd/C for M = Ta).⁵ By comparison, hydrogenation of **8** occurs within minutes at 1 atm H₂.

(2)

In summary, we have shown that the (DPB)Fe platform, which was previously studied in the context of N₂ functionalization,¹⁰ also facilitates CO functionalization to furnish a structurally unique Fe dicarbyne complex. Like the Fe aminoimide intermediate in (DPB)Fe-mediated N₂ functionalization, the Fe 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. Ongoing studies to map additional details regarding the release of **10** from **8** and to develop conditions for catalytic reductive CO coupling are underway.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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

Funding Sources

No competing financial interests have been declared.

REFERENCES

1. West NM, Miller AJM, Labinger JA, Bercaw JE. *Coord. Chem. Rev.* 2011; 255:881–898.
2. (a) Lee CC, Hu Y, Ribbe MW. *Science*. 2010; 329:642–642. [PubMed: 20689010] (b) Yang ZY, Dean DR, Seefeldt LC. *J. Biol. Chem.* 2011; 286:19417–19421. [PubMed: 21454640] (c) Hu Y, Lee CC, Ribbe MW. *Science*. 2011; 333:753–755. [PubMed: 21817053]
3. (a) Wilker CN, Hoffmann R, Eisenstein O. *Nouv. J. Chim.* 1983; 7:585. (b) Mayr A, Bastos CM. *Prog. Inorg. Chem.* 1992; 40:1–98.
4. (a) Bianconi PA, Williams ID, Engeler MP, Lippard SJ. *J. Am. Chem. Soc.* 1986; 108:311–313. (b) Bianconi PA, Vrtis RN, Rao CP, Williams ID, Engeler MP, Lippard SJ. *Organometallics*. 1987; 6:1968–1977. (c) Protasiewicz JD, Lippard SJ. *J. Am. Chem. Soc.* 1991; 22:6564–6570. (d) Carnahan EM, Protasiewicz JD, Lippard SJ. *Acc. Chem. Res.* 1993; 26:90–97.
5. Vrtis RN, Bott SG, Rardin RL, Lippard SJ. *Organometallics*. 1991; 10:1364–1373.
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 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 Fe dicarbyne complex in this report is a unique structure regardless of how many independent Fe–C bonds it contains. See McNaught AD, Wilkinson A. *IUPAC Compendium of Chemical Terminology* (2nd Ed.). 1997 Oxford Blackwell Scientific Publications. Compiled by
7. (a) Protasiewicz JD, Masschelein A, Lippard SJ. *J. Am. Chem. Soc.* 1993; 115:808–810. (b) Protasiewicz JD, Bronk BS, Masschelein A, Lippard SJ. *Organometallics*. 1994; 13:1300–1311.
8. McDermott GA, Mayr A. *J. Am. Chem. Soc.* 1987; 109:580–582.
9. (a) Filippou AC, Grünleitner W, Völkl C, Kiprof P. *Angew. Chem. Int. Ed.* 1991; 30:1167–1169. (b) Filippou AC, Völkl C, Grünleitner W, Kiprof P. *J. Organomet. Chem.* 1992; 434:201–223. (c) Wang Y, Da Silva JJF, Pombeiro AJ, Pellinghelli MA, Tiripicchio A, Henderson RA, Richards RL. *J. Chem. Soc. Dalton Trans.* 1995:1183–1191. (d) Filippou AC, Hofmann P, Kiprof P, Schmid HR, Wagner C. *J. Organomet. Chem.* 1993; 459:233–247.
10. Suess DLM, Peters JC. *J. Am. Chem. Soc.* 2013; 135:4938–4941.
11. Bontemps S, Gornitzka H, Bouhadir G, Miqueu K, Bourissou D. *Angew. Chem. Int. Ed.* 2006; 45:1611–1614.

12. Moret M-E, Peters JC. *Angew. Chem. Int. Ed.* 2011; 50:2063–2067.
13. Harman WH, Peters JC. *J. Am. Chem. Soc.* 2012; 134:5080–5082. [PubMed: 22380492]
14. A recent Fe(CO)₂ charge series: Tondreau AM, Milsmann C, Lobkovsky E, Chirik PJ. *Inorg. Chem.* 2011; 50:9888–9895. [PubMed: 21667935]
15. Addison AW, Rao TN, Reedijk J, van Rijn J, Verschoor GC. *J. Chem. Soc. Dalton Trans.* 1984:1349.
16. Figueroa JS, Melnick JG, Parkin G. *Inorg. Chem.* 2006; 45:7056–7058. [PubMed: 16933903]
17. Green MLH. *J. Organomet. Chem.* 1995; 500:127–148.
18. (a) Hill AF. *Organometallics*. 2006; 25:4741–4743. (b) Parkin G. *Organometallics*. 2006; 25:4744–4747. (c) Sircoglou M, Bontemps S, Mercy M, Saffon N, Takahashi M, Bouhadir G, Maron L, Bourissou D. *Angew. Chem. Int. Ed.* 2007; 46:8583–8586. (d) Suess DLM, Tsay C, Peters JC. *J. Am. Chem. Soc.* 2012; 134:14158–14164. [PubMed: 22891606] (e) Anderson JS, Moret M-E, Peters JC. *J. Am. Chem. Soc.* 2013; 135:534–537. [PubMed: 23259776]
19. (a) Thorneley, R.; George, SJ. *Prokaryotic Nitrogen Fixation: A Model System for Analysis of a Biological Process*. Wymondham, UK: Horizon Scientific Press; 2000. p. 81 (b) Yan L, Dapper CH, George SJ, Wang H, Mitra D, Dong W, Newton WE, Cramer SP. *Eur. J. Inorg. Chem.* 2011; 2011:2064–2074.
20. (a) Peters JC, Odom AL, Cummins CC. *Chem. Commun.* 1997:1995. (b) Lee Y, Peters JC. *J. Am. Chem. Soc.* 2011; 133:4438–4446. [PubMed: 21375250]
21. Fischer EO, Schneider J, Neugebauer D. *Angew. Chem. Int. Ed.* 1984; 23:820–821.
22. Caution should be exercised when interpreting these ¹³C shifts since transition metal carbyne and carbene ligands can assume a wide range of chemical shift values.
23. Landis CR, Weinhold F. *J. Comput. Chem.* 2006; 28:198–203. [PubMed: 17063478]
24. Moret M-E, Zhang L, Peters JC. *J. Am. Chem. Soc.* 2013; 135:3792–3795. [PubMed: 23418750]
25. Haaland A. *Angew. Chem. Int. Ed.* 1989; 28:992–1007.
26. (a) Schultz AJ, Williams JM, Schrock RR, Rupprecht GA, Fellmann JD. *J. Am. Chem. Soc.* 1979; 101:1593–1595. (b) Schrock RR. *Chem. Rev.* 2002; 102:145–180. [PubMed: 11782131]
27. Weigert FJ, Roberts JD. *J. Am. Chem. Soc.* 1969; 91:4940–4941.
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 MJ, Graham W, Smith RA, Stewart RP. *J. Am. Chem. Soc.* 1973; 95:1684–1686. (b) Wong A, Atwood JD. *J. Organomet. Chem.* 1980; 199:C9–C12. (c) Okazaki M, Ohtani T, Inomata S, Tagaki N, Ogino H. *J. Am. Chem. Soc.* 1998; 120:9135–9138. (d) Sazama GT, Betley TA. *Organometallics*. 2011; 30:4315–4319.

Figure 1. Displacement ellipsoid (50%) representations of (left) **2** and (right) **3**. P^iPr_2 groups are truncated and H atoms are omitted for clarity.

Figure 2.
Displacement ellipsoid (50%) representations of (left) **5** and (right) **6**. P^iPr_2 groups are truncated and H atoms, solvent molecules, and counterions are omitted for clarity.

Figure 3. Displacement ellipsoid (50%) representation of one of the two crystallographically-independent molecules of **8** (left). PR_2 groups are truncated. Relevant resonance structures of **8** (right).

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 $0.05 \text{ e}^- \text{ \AA}^{-3}$ level.

Scheme 1.

3

Fe-B = 2.5263(6) Å
 $\Sigma\angle(\text{C-B-C}) = 342^\circ$

$[\text{K}(\text{benzo-15-c-5})_2]_2$

6

Fe-B = 2.4099(9) Å
 $\Sigma\angle(\text{C-B-C}) = 330^\circ$

7: Parkin (2006)

Fe-B = 2.108(6) Å
 $\Sigma\angle(\text{N-B-N}) = 327^\circ$

Chart 1.
 Selected Fe-BR₃ complexes.

Table 1

Selected bond lengths (Å), angles (°), and IR bands (cm⁻¹)

	Fe-CO (avg.)	Fe-P (avg.)	Fe-B	(C-B-C)	CO(sym,asym)
2	1.745	2.212	2.3080(15)	342	1908, 1863
5	1.756	2.212	2.4192(15)	330	1857, 1791
6	1.727	2.156	2.4099(9)	330	1738, 1659