Organometallics 1992, *11*, 2613–2622

δ 6.42 (m, 2 H, Cp), 6.25 (m, 2 H, Cp), 6.18 (m, 2 H, Cp), 6.11 (m, 2 H, Cp), 2.12 (s, 6 H, $CpCH_3$). Anal. Calcd (found) for $C_{12}H_{14}Cl_8Hg_2NbO$: C, 15.1 (14.4); H, 1.5 (1.5); Hg, 42.1 (42.2). Single crystals of **10** for X-ray analysis were obtained from acetone/hexane at −10 °C after several weeks.

Reaction of 1 with Me_3SiCl: $Cp'_2Nb(Cl)O$ (11). To a stirred dichloromethane solution of **1** (38.2 mg, 0.10 mmol) was added $ClSiMe_3$ (10.8 mg, 0.10 mmol); the solution became yellow immediately. After the mixture was stirred for 30 min, the solvent was removed at reduced pressure. Trituration of the residue with toluene, followed by cooling of the toluene extracts at −10 °C, gave yellow crystals of $Cp'_2Nb(Cl)O$ (52%) (**11**). IR (KBr, cm^{-1}) ν 3075 (w), 2922 (w), 1505 (s), 1453 (s), 1359 (m), 1220 (s), 1088 (m), 1023 (vs), 777 (m), 853 (s), 816 (vs), 617 (m); ^1H NMR (300 MHz, $CDCl_3$) δ 6.08 (m, 4 H, Cp), 5.99 (m, 2 H, Cp), 5.96 (m, 2 H, Cp), 2.19 (s, 6 H, Cp); MS (EI, 12 eV, DIP) *m/e* 301.9 (M^+, 24.4), 265.9 (M^+ − Cl, 27.7), 223.8 (M^+ − MeCp, 100). These data are in agreement with those reported previously.[17]

X-ray Structure Determinations of 3, 8, and 11. Single crystals of **3**, **8**, and **11** were obtained by recrystallization at reduced temperature as described above. The crystal data for all three compounds were measured on an Enraf-Nonius CAD-4 diffractometer using monochromated Mo Kα radiation (λ = 0.71069 Å). The data were corrected for Lorentz and polarization effects. No absorption corrections was applied since it was judged to be insignificant in all three cases. The atomic scattering factors were taken from the International Tables for X-ray Crystallography, and the structures were solved and refined anisotropically by the full-matrix least-squares method (SHELX-76). For **3**, four of the six fluorine atoms of the PF_6^- ion were disordered and each of them was refined with 60% and 40% occupancy at two sites. A summary of the crystal and data collection parameters is provided in Table I, positional parameters are given in Tables II–IV, and bond distances and angles are given in Table V.

Acknowledgment. We are grateful for support provided by the U.S. Department of Energy, Basic Energy Sciences, Chemistry Division (89ER 13997). K.M.N. also acknowledges an AWU Faculty Fellowship supporting a sabbatical stay at the National Renewable Energy Laboratory where (in part) this paper was written.

Supplementary Material Available: Tables of thermal parameters and complete listings of interatomic distances and angles for **3**, **8**, and **11** (14 pages). Ordering information is given on any current masthead page.

OM9200159

Formation of Substituted Ferracyclopentadiene Complexes by the Reaction of Alkynes with Protonated Diferra-μ-azaallylidene Complexes

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Received December 23, 1991

The dinuclear complexes $[Fe_2\{\mu\text{-}C(H)(CH{=}NHR')\}(CO)_8][BF_4]$ (R′ = Bu^t, Ph), which possess protonated μ_2,η^1-azaallylidene ligands and are derivatives of the parent methylene complex $Fe_2(\mu\text{-}CH_2)(CO)_8$, react with alkynes ($R^1C{\equiv}CR^2$) to give isomeric hydroxy-imino-ferracyclopentadiene complexes, $Fe_2(\mu\text{-}CR^1CR^2C(OH)C\{C(H){=}NR'\})(CO)_6$, and amino-ferracyclopentadiene complexes, $Fe_2(\mu\text{-}CR^1CR^2CHC\{N(H)R'\})(CO)_6$, with the distribution of products dependent on the alkyne employed. The former were also isolated as their BF_3 adducts $Fe_2(\mu\text{-}CR^1CR^2C(O\text{-}BF_3)C\{C(H){=}NHR'\})(CO)_6$, and two of these latter complexes have been crystallographically characterized. They have a typical ferracyclopentadiene (ferrole) ring with an iminium substituent (C(H)=NHR′) on the α-carbon of the ring, which is hydrogen-bonded though the nitrogen atom to the oxygen substituent on the β-carbon of the ferracyclopentadiene ring, which is in turn coordinated by the BF_3 group. The BF_3 group can be removed by reaction with aqueous base to give the free hydroxy-imino-ferracyclopentadiene complexes. The amino-ferracyclopentadiene complex with R′ = Bu^t and $R^1 = R^2$ = Ph has also been crystallographically characterized. It is a typical ferracyclopentadiene complex with an amino group on the α-carbon. The amino-ferracyclopentadiene complexes are also formed in near quantitative yield by an acid-catalyzed ring contraction of the 2-ferrapyridine complexes $Fe_2(\mu\text{-}CR^1CR^2CHCHNR')(CO)_6$.

Introduction

We recently reported that the protonated azaallylidene complexes **2a,b** result from the addition of $HBF_4{\cdot}Et_2O$ and CO to the 2-ferrapyrrolinone complexes **1a,b**, eq 1.[1] These compounds are derivatives of the well-known complex $Fe_2(\mu\text{-}CH_2)(CO)_8$ (**3**).[2] This latter compound has been

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[†] Present address: Department of Chemistry, Northwestern University, Evanston, IL 60208-3113.

(1) (a) Mirkin, C. A.; Lu, K.-L.; Geoffroy, G. L.; Rheingold, A. L.; Staley, D. *J. Am. Chem. Soc.* 1989, *111*, 7279. (b) Mirkin, C. A.; Lu, K.-L.; Snead, T. E.; Young, B. A.; Geoffroy, G. L.; Rheingold, A. L.; Haggerty, B. S. *J. Am. Chem. Soc.* 1991, *113*, 3800.

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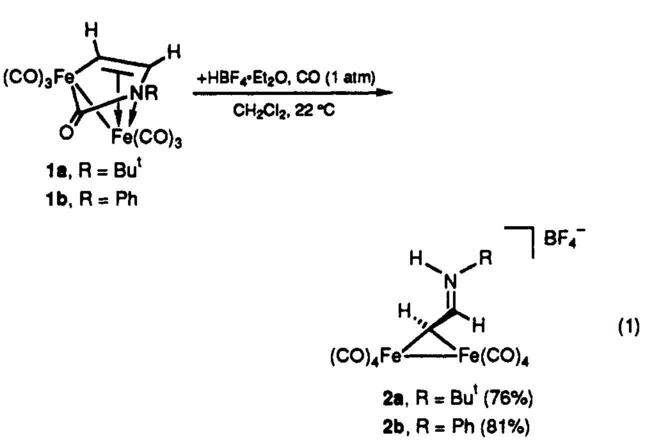
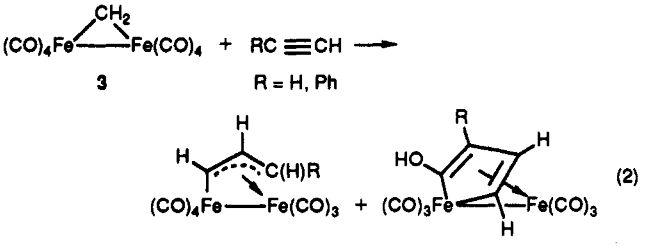


1a, R = Bu^t
1b, R = Ph

(1)

2a, R = Bu^t (76%)
2b, R = Ph (81%)

shown to undergo a number of transformations, and particularly interesting are its reactions with alkynes to form mixtures of binuclear allyl complexes and hydroxy-ferracyclopentadiene complexes, eq 2.[2b] The former com-



(2)

pounds result from alkyne insertion into an Fe–CH$_2$ bond followed by hydrogen migration from the methylene group to the alkyne carbon. The hydroxy-ferracyclopentadiene complexes result from a combination of CO and alkyne insertion and migration of one of the methylene hydrogens to the carbonyl oxygen.

The reactions of Fe$_2$(μ-CH$_2$)(CO)$_8$ with alkynes prompted us to examine the corresponding reactions of **2a,b**. As reported herein, these complexes do react with alkynes, but instead of giving products like those of eq 2, they form isomeric hydroxy-imino-ferracyclopentadiene complexes and amino-ferracyclopentadiene complexes. Details of these reactions are described herein along with crystal structures of three of the ferracyclopentadiene complexes and an analysis of the factors controlling the course of the reaction.[3]

Results

Reaction of Azaallylidene Complexes with Alkynes To Form Imino- and Amino-Substituted Ferracyclopentadiene Complexes. Complex **2a** has been most extensively studied and has been found to react with alkynes under mild conditions to give the hydroxylated imino-ferracyclopentadiene complexes **4**–**6** and the amino-ferracyclopentadiene complexes **7**, Scheme I, with the relative yields dependent upon the alkyne employed. The single reaction of **2b** with PhC≡CH was also examined, and **2b** behaves similarly to **2a** (see entry e in Scheme I). The products of these reactions were isolated as microcrystalline solids in the yields indicated in Scheme I and have been spectroscopically characterized. Complexes **4c**, **4e**, and **7d** have been further defined by X-ray diffraction studies, and ORTEP drawings are shown in Figures 1–3.

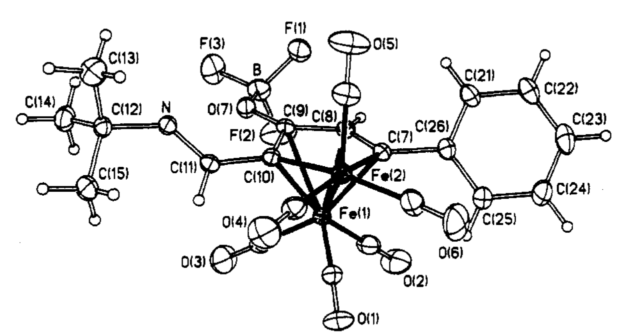


Figure 1. Molecular view and labeling scheme for Fe$_2$(μ-C{Ph}CHCO{BF$_3$}C{CH=NHBu^t})(CO)$_6$ (**4c**). Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 40% probability.

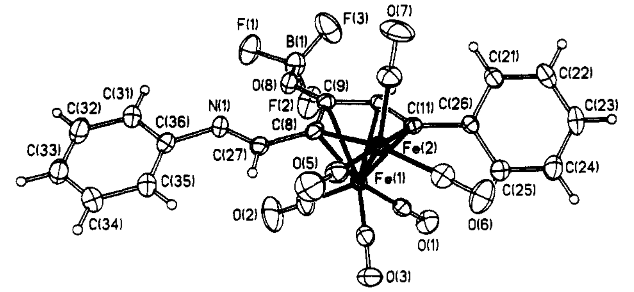
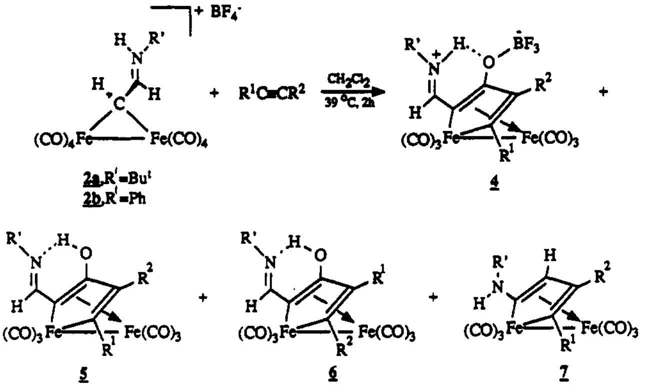


Figure 2. Molecular view and labeling scheme for Fe$_2$(μ-C{Ph}CHCO{BF$_3$}C{CH=NHPh})(CO)$_6$ (**4e**). Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 40% probability.

Scheme I



Cpd	R'	R^1	R^2	4	5	6	7
a	Bu^t	Me	H	31%	7%	22%	-
b	Bu^t	Bu^t	H	-	-	-	67%
c	Bu^t	Ph	H	53%	7%	13%	14%
d	Bu^t	Ph	Ph	-	-	-	45%
e	Ph	Ph	H	42%	-	-	4%

All of these new complexes are derivatives of the large class of ferracyclopentadiene (ferrole) complexes that often form upon addition of alkynes to iron carbonyl compounds.[4] Complexes **4**–**6** differ from previously described

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(2) (a) Sumner, C. E., Jr.; Riley, P. E.; Davis, R. E.; Pettit, R. *J. Am. Chem. Soc.* **1980**, *102*, 1752. (b) Sumner, C. E., Jr.; Collier, J. A.; Pettit, R. *Organometallics* **1982**, *1*, 1350. (c) Meyer, B. B.; Riley, P. E.; Davis, R. E. *Inorg. Chem.* **1981**, *20*, 3024. (d) Xiang, S. F.; Chen, H. W.; Eyermann, C. J.; Jolly, W. L.; Smit, S. P.; Theopold, K. H.; Bergman, R. G.; Herrmann, W. A.; Pettit, R. *Organometallics* **1982**, *1*, 1200.

(3) Aspects of these results were communicated in: Mirkin, C. A.; Lu, K.-L.; Geoffroy, G. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 461. However, this communication claimed the formation of a fluorine-substituted ferracyclopentadiene complex, but that conclusion was subsequently shown to be in error and was corrected in: Mirkin, C. A.; Lu, K.-L.; Geoffroy, G. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 6155.

(4) (a) For reviews, see: Fehlhammer, W. P.; Stolzenberg, H. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Eds.; Pergamon: Oxford, 1982; p 548. (b) *Gmelins Handbuch der Anorganischen Chemie*; Pergamon: Oxford, 1980; Vol. 4, p 24.

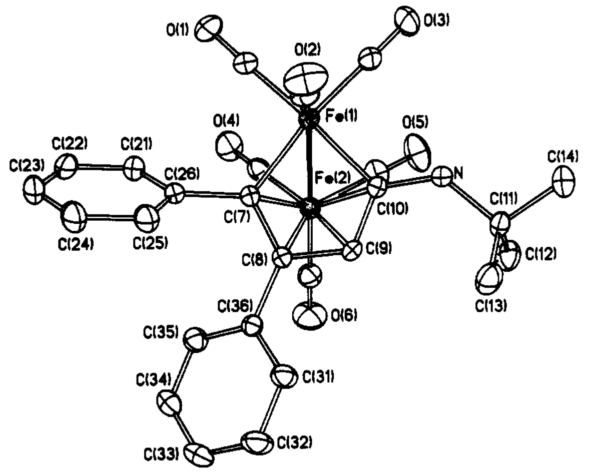
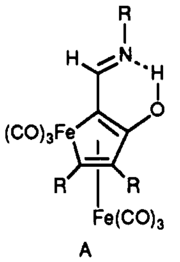
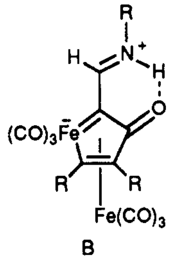
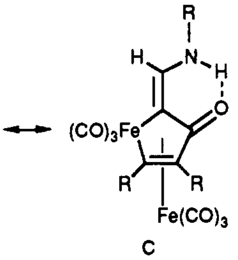


Figure 3. Molecular view and labeling scheme for $Fe_2(\mu\text{-}C\{Ph\}C\{Ph\}CHCNHBu^t)(CO)_6$ (**7d**). Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 35% probability.

ferracyclopentadiene complexes by having an imine (or iminium) substituent in the α-position and a hydroxy (or OBF_3) substituent in the β-position, while complex **7** has an amino group in the α-position. The crystal structures of **4c** and **4e** show that a BF_3 group formed from the BF_4^- counterion is bound to the oxygen atom of these derivatives (see Figures 1 and 2 and below). Spectroscopic data summarized below indicate that the imine nitrogen in **5** and **6** is hydrogen-bonded to the hydroxy group. On the basis of the similarity of **5** and **6** to the many characterized ferracyclopentadiene derivatives,[4] including the large number of such complexes having a hydroxy substituent on the α-carbon (see eq 2),[4] we have chosen to represent these compounds as hydroxy-substituted ferracyclopentadiene complexes (A) rather than its tautomeric carbonyl form depicted by resonance structures B and C.

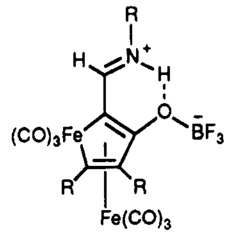

A


B


C

The available spectroscopic data are insufficient to distinguish between these structures, and we have been unable to grow crystals of **5** and **6** suitable for X-ray diffraction studies. We note that each complex shows an IR band in the 1603–1616-cm^{-1} region that we have attributed to the ν(C=N) stretch of A. Although this band could be assigned to the ν(C=O) stretch of B and C, it appears at a lower frequency than typically observed for divinyl ketones (~1660 cm^{-1}).[5] Although these complexes are drawn herein as structure A, it is likely that B and C are important contributing forms. In contrast to the ambiguity for **5** and **6**, the crystallographic data for **4c** and **4e** (see below) indicate that, at least in the solid state, the iminium structure D is the best formulation for these compounds.

The spectroscopic data for all these new complexes are consistent with their proposed and determined structures. Complexes **5**–**7** showed parent ions in their mass spectra, and the IR spectra of all the complexes are similar to other $Fe_2(CO)_6(\mu\text{-}L)$ complexes. The NMR data of **4c** is typical, and, for example, its ^{13}C NMR spectrum showed four resonances assigned to the ferracyclopentadiene ring carbons at δ 184.6 (FeCPh), 161.9 (COH), 102.3 (d, $^1J_{CH}$ = 173.9 Hz, CH), and 99.0 (FeC(CH=N) along with resonances due to the imine carbon [175.3 (d, $^1J_{CH}$ = 173.9 Hz)], the metal carbonyls, the *tert*-butyl group, and the phenyl group. When **4c** was prepared from **2a** that had been enriched with ^{13}CO, its ^{13}C NMR spectrum showed a significant intensity enhancement of the metal carbonyl resonances as well as the δ 161.9 resonance, which is attributed to the ring carbon bearing the hydroxy substituent, which derives from a CO ligand of **2a** (see Scheme I in the Discussion section). In addition to typical phenyl and *tert*-butyl resonances, the ^1H NMR spectrum of **4c** showed a broad resonance at δ 11.58 assigned to the N–H··O hydrogen, a doublet at δ 7.94 (J_{HH} = 15.8 Hz) attributed to the hydrogen on the exocyclic imine carbon (FeC{C*H*=NHBu^t}), and a quartet at δ 6.62 ($^4J_{H-F}$ = 1.2 Hz) assigned to the hydrogen atom in the R^2 position on the ferracyclopentadiene ring. We attribute the weak H–F coupling to a strong dipole–dipole interaction between this hydrogen and the three fluorine atoms on the BF_3 group. Similar interactions have been reported for several organic systems.[6a] The 15.8-Hz coupling constant for the hydrogen atom on the exocyclic imine carbon is a typical value for trans hydrogen atoms in an unsaturated system and implies the presence of a hydrogen atom on the imine nitrogen (or strong hydrogen bonding of the hydroxy hydrogen to this nitrogen atom if **4** existed in the tautomeric form A with a coordinated BF_3 group). The ^{11}B NMR spectrum of **4c** showed a broad resonance at δ −0.99, which is within the range reported for other BF_3–oxygen atom donor groups.[6b] The ^{19}F NMR spectrum of **4c** showed resonances at δ 152.29 (F on ^{10}B) and 152.35 (F on ^{11}B) in a 1:4 ratio (^{10}B, 18.83%, and ^{11}B, 81.17%). Such dependence of the ^{19}F NMR chemical shift on the boron isotope has been previously reported for $BF_3 \cdot H_2O$.[7] The IR spectrum of **4c** showed a vibration at 1612 cm^{-1} assigned to the imine stretch in addition to ν_{CO} bands at 2078, 2049, 2017, and 1997 cm^{-1}. The ^1H NMR spectrum of each of the compounds **5a**,**c** and **6a**,**c** shows a broad resonance in the δ 13.3–14.0 region attributed to the hydroxy proton and a doublet (J_{HH} = 9–13 Hz) in the δ 7.9–8.2 region assigned to the proton on the iminium carbon (FeC{C*H*=NBu^t}). The observed proton–proton coupling indicates that the iminium nitrogen is hydrogen-bonded to the hydroxy proton as represented in the proposed structures for these compounds (A).


D

Complexes **5a** and **5c** result from **4a** and **4c** by loss of the BF_3 group, a reaction that can be induced by treatment with aqueous Et_3N (see below), and their spectroscopic data listed in the Experimental Section are similar to those given above for **4c**, except for the absence of H–F coupling. Complexes **6a**, **6c**, and **6e** are isomers of **5** and differ in the

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[5] Pasto, D. J.; Johnson, C. R. *Laboratory Text for Organic Chemistry*; Prentice-Hall: Englewood Cliffs, NJ, 1979; p 145.

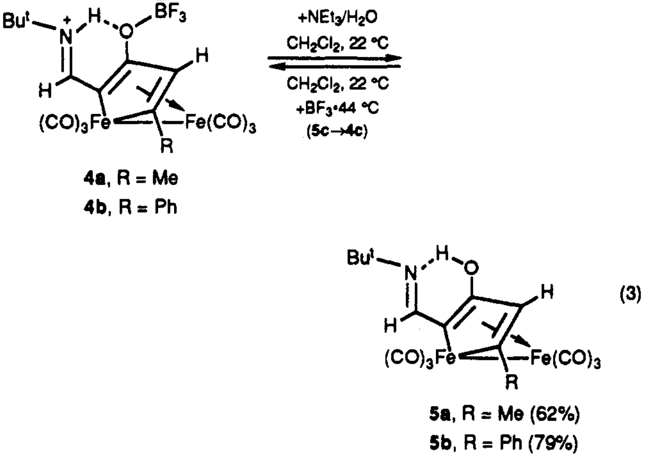
[6] (a) Jameson, C. J. In *Multinuclear NMR*; Mason, J., Ed.; Plenum Press: New York, 1987; Chapter 16, p 443. (b) Nöth, H.; Wrackmeyer, B. *Nuclear Magnetic Resonance Spectroscopy of Boron Compounds*; Springer: Berlin, 1978.

[7] Gillespie, R. J.; Hartman, J. S. *Can. J. Chem.* **1967**, *45*, 859.

regiochemistry of the alkyne insertion. This is indicated by their ^{13}C NMR spectra, which show a different ferracyclopentadiene ring carbon resonance pattern [**6c**, δ 185.1 (*C*OH), 159.0 (d, $^1J_{CH}$ = 158.7 Hz, *C*H), 117.1 (*C*Ph), and 94.1 (Fe*C*(CH=N)); compare to **5c**, δ 186.1 (*C*OH), 184.8 (*C*Ph), 99.2 (d, $^1J_{CH}$ = 166.0 Hz, *C*H), 93.0 (Fe*C*(CH=N))], and especially by the position of the phenyl-ipso carbon resonance, which appears at 136.2, within the δ 136–138 region, which has been shown to be typical for a phenyl substituent on the β-carbon of a ferracyclopentadiene ring.[8] In contrast, the phenyl-ipso carbon resonance of phenyl groups attached to ferracyclopentadiene α-carbons typically appears in the δ 148–150 range,[8] as they do for complexes **4a**, **4c**, and **4e**.

Complexes **7b**, **7c** and **7d** have been prepared in near-quantitative yield by an alternate route involving protonation of 2-ferrapyridine complexes, and those reactions and the characterization of the products will be discussed below.

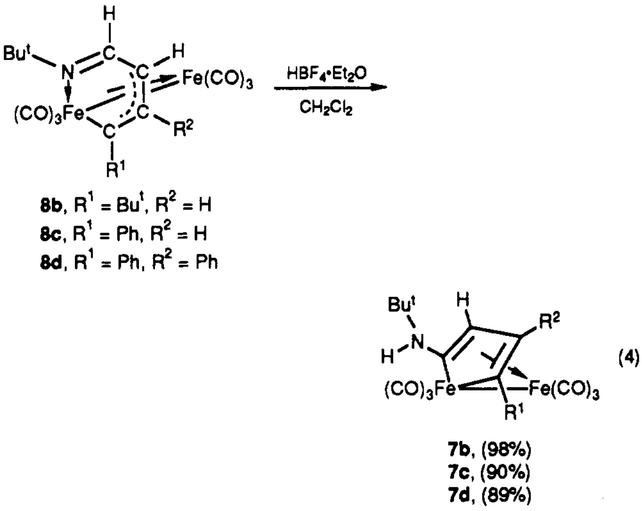
Displacement of BF_3 from 4c and 4e by Treatment with Base. Addition of aqueous Et_3N to a CH_2Cl_2 solution of complex **4c** gave immediate formation of the hydroxy-ferracyclopentadiene complex **5c** by loss of the BF_3 group, apparently as $[Et_3NH][BF_3OH]$, eq 3. It is interesting that this reaction occurs only when wet Et_3N is used and no reaction was obtained with use of anhydrous NEt_3. Complex **4c** can be reformed in good yield (83%) by treating **5c** with $BF_3{\cdot}Et_2O$, eq 3.



4a, R = Me
4b, R = Ph

5a, R = Me (62%)
5b, R = Ph (79%)

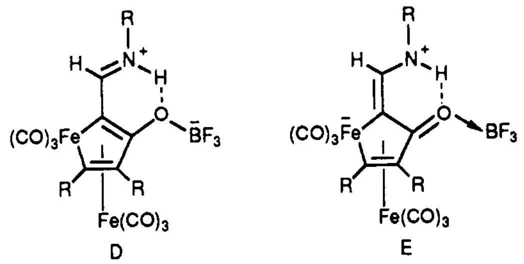
Formation of 2-Amino-ferracyclopentadiene Complexes by Protonation-Induced Ring Contraction of 2-Ferrapyridine Complexes. We have also found that addition of $HBF_4{\cdot}Et_2O$ to the 2-ferrapyridine complexes **8b–d**[9] generates the 2-amino-ferracyclopentadiene complexes **7b–d** in high yield, eq 4. Note that this is an acid-catalyzed rearrangement involving the formal transfer of a hydrogen atom from the β-carbon of the 2-ferrapyridine ring to the nitrogen atom. IR analysis indicated that the reaction occurred immediately following addition of $HBF_4{\cdot}Et_2O$ without the observation of cationic intermediates at room temperature. Complexes **7b–d** were isolated as microcrystalline solids and have been spectroscopically characterized, with complex **7d** fully defined by a crystallographic study (see Figure 3). Each complex showed a molecular ion in its mass spectrum, and the ^1H NMR, ^{13}C NMR, and IR spectra (see Experimental Section) are fully consistent with their indicated formations and with the structure determined for **7d**. For example, the ^{13}C NMR spectrum of **7c** showed four resonances assigned to the ferracyclopentadiene ring carbons at δ 213.3 (d, J_{CH} = 13.4 Hz, Fe*C*(NHBu^t)), 174.2 (Fe*C*Ph), 104.3 (dd, $^1J_{CH}$ = 167.2 Hz, $^2J_{CH}$ = 3.7 Hz, FeCPh*C*H), and 69.0 (dd, $^1J_{CH}$ = 163.6 Hz, $^2J_{CH}$ = 8.5 Hz, FeC(NHBu^t)*C*H) along with resonances due to the metal carbonyls, the *tert*-butyl group, and the phenyl group. In addition to methyl and *tert*-butyl resonances, the ^1H NMR spectrum of **7c** showed doublets at δ 5.83 (J_{HH} = 3.1 Hz) and 4.80 (J_{HH} = 5.6 Hz) assigned to the ring hydrogen atoms.



8b, R^1 = Bu^t, R^2 = H
8c, R^1 = Ph, R^2 = H
8d, R^1 = Ph, R^2 = Ph

7b, (98%)
7c, (90%)
7d, (89%)

Crystal and Molecular Structures of 4c, 4e, and 7d. ORTEP drawings of **4c**, **4e**, and **7d** are shown in Figures 1–3, and important crystallographic data are given in Tables I–VII. Complex **4c** differs from **4e** only in having a *tert*-butyl group on the nitrogen atom in contrast to the phenyl group of **4e**, and in both cases the crystallographic data imply a dominant contribution from the iminium structure D rather than its enamine resonance form E. The Fe–Fe bond distances in the two compounds are similar [**4c**, 2.498 (1) Å; **4e**, 2.505 (1) Å] and are in the typical range for Fe–Fe single bonds.[10a] In complex **4c**, the metallacyclic ring is bound to Fe(2) via σ-bonds to C(7) and C(10) and to Fe(1) via π-coordination of C(7), C(8), C(9), and C(10), while in complex **4e** the metallacyclic ring is bound to Fe(2) via σ-bonds to C(8) and C(11) and to Fe(1) via π-coordination of C(8), C(9), C(10), and C(11). In each complex the iron atoms have a pseudooctahedral coordination geometry with the octahedra in a staggered conformation and with the carbonyl ligands occupying facial coordination sites. There is one slightly semibridging carbonyl ligand in each complex [**4c**, Fe(1)–C(1)–O(1) = 167.5 (3)°; **4e**, Fe(1)–C(3)–O(3) = 169.8 (5)°] as has been seen in other crystallographically characterized ferracyclopentadiene complexes.[4a]



D E

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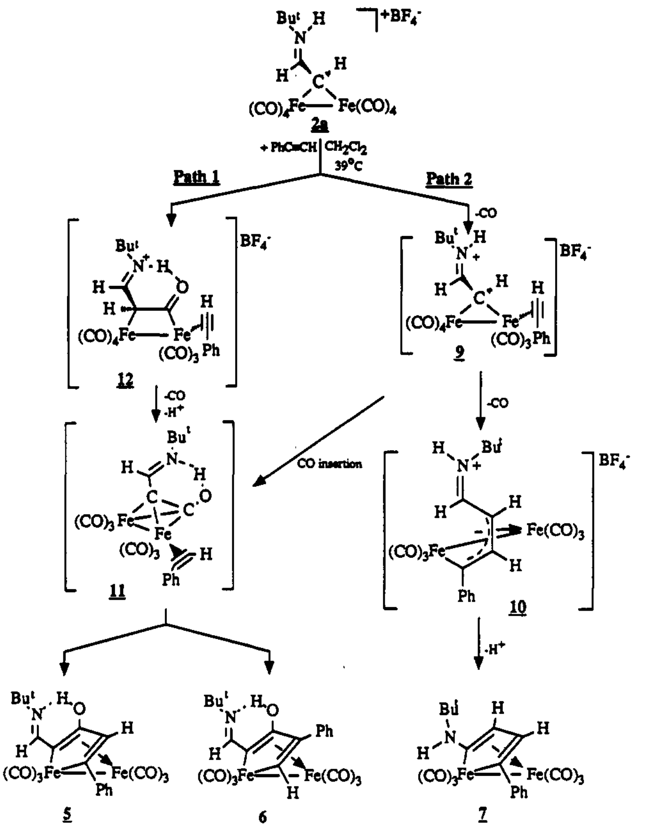
[9] (a) Mirkin, C. A.; Lu, K.-L.; Snead, T. E.; Geoffroy, G. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 2809. (b) Snead, T. E.; Mirkin, C. A.; Lu, K.-L.; Beckman, H. L.; Geoffroy, G. L.; Rheingold, A. L.; Haggerty, B. S. *Organometallics* **1992**, *11*, 942.

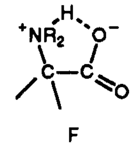
[10] (a) Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Oxford University Press: Oxford 1984. (b) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1–S19.

Scheme II



In each case, the oxygen atom on the ferracyclopentadiene ring is bound to both the ring carbon and the boron atom with typical C_{sp^2}–O single bond distances [**4c**, 1.316 (3) Å; **4e**, 1.329 (5) Å; 1.324–1.342 Å is typical for enols[10b]]. The boron–oxygen bond distances [**4c**, 1.499 (5) Å; **4e**, 1.528 (8) Å] are between characteristic values for Lewis acid–base adducts (1.581 Å)[11] and covalent compounds (1.468 Å),[10b] and the C(9)–O–B(1) bond angles approximate 120° in each complex [**4c**, C(9)–O–B(1) = 123.1 (2)°; **4e**, C(9)–O–B(1) = 126.4 (4)°]. The carbon–nitrogen bond distances [**4c**, 1.285 (3) Å; **4e**, 1.294 (6) Å] in the imine substituent are toward the long end of values typical for carbon–nitrogen double bonds (1.279 Å for imines[10b]) but are substantially shorter than C_{sp^2}–N single bond values (1.336 Å in enamines[10b]), consistent with the iminium formulation D rather than E. Similarly, the imine carbon–ring carbon distances [**4c**, 1.442 (4) Å; **4e**, 1.464 (7) Å] are typical C_{sp^2}–C_{sp^2} single bond values (1.455 Å in dienes[10b]) and further argue against the importance of E.

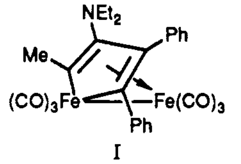
The final difference Fourier map of **4e** shows a peak between N(1) and O(8) that can be attributed to the hydrogen atom. It is located on N(1) [N(1)–H = 1.16 Å; O(8)–H = 1.80 Å] and forms a planar sp^2 nitrogen atom [sum of the angles around N(1) = 359.7°], consistent with structure D. These values compare well to the N–H (1.01–1.06 Å) and O··H (1.7–1.9 Å) distances commonly observed by neutron diffraction studies for amino acids where similar hydrogen bonding is invoked (F).[12]



F

It should be noted that in the original communication[3] of these compounds the ring carbonyl oxygen atom was incorrectly assigned as a fluorine atom, due in part to the difficulty in crystallographically distinguishing fluorine and oxygen atoms.

Complex **7d** is a typical ferracyclopentadiene complex and differs from previously reported examples only in having an amino substituent on the α-carbon. The organic ligand is bound to Fe(1) via σ-bonds to C(7) and C(10) and to Fe(2) via π-coordination of C(7), C(8), C(9), and C(10); the C–C distances within the ring compare well to those found in other ferracyclopentadiene complexes.[4a] The Fe–Fe bond distance, 2.568 (1) Å, is in the range typical of Fe–Fe single bonds.[10a] The iron atoms are pseudooctahedral, with the carbonyl ligands occupying facial coordination sites. Unlike most ferracyclopentadiene complexes,[4a] there are no semibridging carbonyl ligands, and the carbonyl ligands on the $Fe(CO)_3$ groups are eclipsed rather than staggered as indicated by the dihedral angles for C(1)Fe(1)Fe(2)C(4), 8.8°, and C(3)Fe(1)Fe(2)C(5), 8.2°. An interesting feature of this structure is the near planarity of the nitrogen atom and its substituents as indicated by the 360.0 (3)° sum of the bond angles about N (including the found H(9)). The N–C(10) bond distance of 1.339 (4) Å is in the range expected for nitrogen–carbon single bond distances in aromatic amines[10b] and along with the planarity of the nitrogen atom indicates delocalization of the nitrogen lone pair electrons into the ferracyclopentadiene ring. The low basicity of **7b–d** compared to other secondary amines, as evidenced by the spontaneous deprotonation of each complex during their formation from **8b–d** and HBF_4·Et_2O, may also be attributed to the delocalization of the nitrogen lone pair electrons into the ferracyclopentadiene ring. A related amino-ferracyclopentadiene complex (I), which has the amino group on the β-carbon of the ferrole ring, has been prepared by Daran and co-workers.[13] Like **7d**, it has a nearly planar geometry about the nitrogen atom, and its N–C(β) distance of 1.385 (4) Å compares well to the N–C(α) distance of 1.339 (4) Å in **7d**.



I

Discussion

The results presented herein show that the protonated azaallylidene complexes **2a** and **2b** react with alkynes to give ferracyclopentadiene complexes having imine (or iminium) and hydroxy (or O-BF_3) substituents (**4–6**) or amino substituents (**7**). This work is related to Pettit's earlier studies of the insertion of alkynes into the iron–methylene bond of $Fe_2(\mu\text{-}CH_2)(CO)_8$ (eq 2)[2b] and to Vrieze's several studies of the reactions of alkynes with binuclear 1-aza 1,3-diene and 1,4-diaza 1,3-diene complexes.[14] While we

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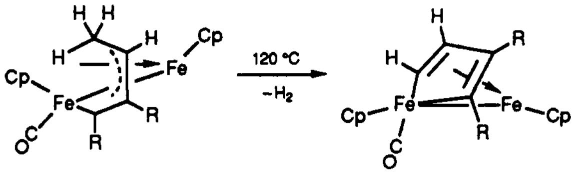
[11] Shambayati, S.; Crowe, W. E.; Schreiber, S. L. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 256.

[12] (a) Olovsson, I.; Jönsson, P. G. In *The Hydrogen Bond*; Schuster, P., Zundel, G., Sandorfy, C., Eds.; North-Holland: Amsterdam, 1976, Vol. 2, Chapter 8. (b) Hamilton, W. C.; Ibers, J. A. *Hydrogen Bonding in Solids*; W. A. Benjamin: San Francisco, 1968.

[13] Cabrera, E.; Daran, J.-C.; Jeannin, Y. *Organometallics* **1988**, *7*, 2010.

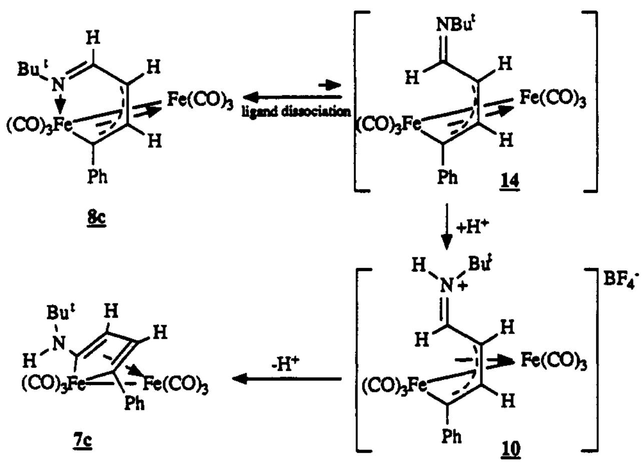
have not conducted a detailed study of the mechanism by which these products form, they can be rationalized by transformations like those shown in Scheme II for the reaction of **2a** with $PhC\equiv CH$. Complexes **7b–e** do not incorporate a CO ligand into the ferracyclopentadiene ring and thus result from direct insertion of the added alkyne into the Fe–C bond of **2**. This reaction is similar to the reported insertion of alkynes into the Fe–C bond of $Fe_2(\mu\text{-}CH_2)(CO)_8$ to give allyl products as well as ferracyclopentadiene complexes having a hydroxy group on the α-carbon (see eq 2).[2b] Logical intermediates for **7** are complexes **9**, formed by initial substitution of the alkyne for a CO ligand in **2**, and **10**, which would result from coupling of the alkyne and μ-azaallylidene ligands. Complex **10** could decay into **7** by β-hydrogen elimination from the exocyclic imine carbon and then loss of the proton from the resulting FeH group. A somewhat related transformation has been observed by Knox and co-workers, eq 5.[15]

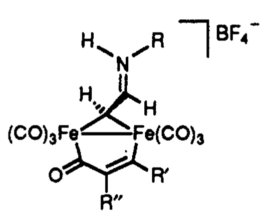


(5)

Complexes **4–6** incorporate a CO ligand into the metallacycle between the alkyne fragment and the bridging (μ-CH(CH=NHR)) carbon, and thus CO insertion must occur before the alkyne couples with the azaallylidene ligand. That insertion could be enhanced by hydrogen bonding between the carbonyl oxygen and the iminium group since Lewis acids in general[16] and intramolecular hydrogen bonding in particular[17] are well-known to accelerate CO insertion reactions. A possible intermediate in the formation of **4–6** is species **11**, which could form from **9** by CO insertion and concomitant proton loss from the bridging azaallylidene carbon. Alternatively, complex **11** could form via an associative process involving coordination of the added alkyne to induce CO insertion to form the ketene intermediate **12**, similar to the nucleophile- and ligand-induced insertion of CO into the Fe–carbon bond of $Fe_2(\mu\text{-}CH_2)(CO)_8$[18] and the alkyne-induced insertion of CO into the metal–carbon bond of $CpM(CO)_2R$ (M = Mo, W) and $(CO)_5MnR$ complexes.[19] Complex **11** can be viewed as having a bridging $HOC\equiv CCH=NR$ alkyne ligand, and complexes **5** and **6** could then form by coupling of this alkyne with the added alkyne as in the typical formation of ferracyclopentadiene complexes from coupling of alkynes on iron carbonyl compounds.[4,13] An alternative route to **5** and **6** could involve initial coupling of the added alkyne with a CO ligand to give a species like **13**, which could then collapse to the observed products by coupling of the two bridging ligands. Alkyne–CO coupling like that illustrated in **13** has been shown to occur in other diiron complexes studied by Knox and co-workers.[20]

Scheme III





13

The distribution of the products from the reaction of **2** with alkynes is dependent upon the alkyne employed (see Scheme I), and although the data set is small these observations suggest that there is a correlation with the size of the alkyne. For example, reaction of **2a** with the small alkyne $MeC\equiv CH$ gave exclusive formation of the carbonylated products **4a**, **5a**, and **6a**, while the larger alkynes $Bu^tC\equiv CH$ and $PhC\equiv CPh$ gave only the amino-substituted complexes **7**. Reaction of **2a** with $PhC\equiv CH$, an alkyne of intermediate size, gave a mixture of the carbonylated products **4–6** as well as the amino-substituted ferracyclopentadiene **7**.

The formation of the amino-substituted ferracyclopentadiene complexes **7** from the 2-ferrapyridine complexes is proposed to occur by the pathway outlined in Scheme III. We suggest that the imine group can dissociate from the iron atom to which it is bound to produce intermediate **14**. Protonation at the nitrogen atom would give **10**, which would in turn form **7c** by β-hydrogen elimination from the exocyclic imine carbon and then loss of the proton from the resulting FeH group. Note that the

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(14) (a) Muller, F.; Van Koten, G.; Vrieze, K.; Heijdenrijk, D. *Inorg. Chim. Acta* **1989**, *158*, 69. (b) Elsevier, C. J.; Muller, F.; Vrieze, K.; Zoet, R. *New J. Chem.* **1988**, *12*, 571. (c) Muller, F.; Van Koten, G.; Polm, L. H.; Vrieze, K.; Zoutberg, M. C.; Heijdenrijk, D.; Kragten, E.; Stam, C. H. *Organometallics* **1989**, *8*, 1340. (d) Muller, F.; Dijkhuis, D. I. P.; Van Koten, G.; Vrieze, K.; Heijdenrijk, D.; Rotteveel, M. A.; Stam, C. H.; Zoutberg, M. C. *Organometallics* **1989**, *8*, 992. (e) Muller, F.; Van Koten, G.; Kraakman, M. J. A.; Vrieze, K.; Heijdenrijk, D.; Zoutberg, M. C. *Organometallics* **1989**, *8*, 1331. (f) Muller, F.; Van Koten, G.; Kraakman, M. J. A.; Vrieze, K.; Zoet, R.; Duineveld, K. A. A.; Heijdenrijk, D.; Stam, C. H.; Zoutberg, M. C. *Organometallics* **1989**, *8*, 982. (g) Staal, L. H.; Van Koten, G.; Vrieze, K.; Van Santen, B.; Stam, C. H. *Inorg. Chem.* **1981**, *20*, 3598. (h) De Lange, P. P. M.; Frühauf, H. W.; Van Wijnkoop, M.; Vrieze, K.; Wang, Y.; Heijdenrijk, D.; Stam, C. H. *Organometallics* **1990**, *9*, 1691. (i) Muller, F.; Han, I. M.; Van Koten, G.; Vrieze, K.; Heijdenrijk, D.; Van Mechelen, J.; Stam, C. H. *Inorg. Chim. Acta* **1989**, *158*, 99. (j) Muller, F.; Han, I. M.; Van Koten, G.; Vrieze, K.; Heijdenrijk, D.; De Jong, R. L.; Zoutberg, M. C. *Inorg. Chim. Acta* **1989**, *158*, 81. (k) Muller, F.; Van Koten, G.; Vrieze, K.; Heijdenrijk, D. *Organometallics* **1989**, *8*, 33. (l) Muller, F.; Van Koten, G.; Vrieze, K.; Heijdenrijk, D.; Krijnen, B. B.; Stam, C. H. *Organometallics* **1989**, *8*, 41. (m) Muller, F.; Van Koten, G.; Vrieze, K.; Krijnen, B.; Stam, C. H. *J. Chem. Soc., Chem. Commun.* **1986**, 150.

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(16) See, for example: *Principles and Applications of Organotransition Metal Chemistry*; Collman, J. P., Hegedus, L. S., Norton, J. R., Finke, R. G. Eds.; University Science Books: Mill Valley, CA, 1987; p 372.

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(18) (a) Denise, B.; Navarre, D.; Rudler, H. *J. Organomet. Chem.* **1987**, *326*, C83. (b) Navarre, D.; Rudler, H.; Daran, J.-C. *J. Organomet. Chem.* **1986**, *314*, C34. (c) Röper, M.; Strutz, H.; Keim, W. *J. Organomet. Chem.* **1981**, *219*, C5.

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Table I. Crystal, Data Collection, and Refinement Parameters for $Fe_2(\mu\text{-}PhCCHCO\{BF_3\}C\{CH{=}NR\})(CO)_6$ (4c, R = Bu^t; 4e, R = Ph) and $Fe_2(\mu\text{-}PhCCHCHC\{CN(H)Bu^t\})(CO)_6$ (7d)

	4c	4e	7d
	Crystal Parameters		
formula	$C_{21}H_{17}BF_3NO_7Fe_2$	$C_{23}H_{13}BF_3NO_7Fe_2$	$C_{26}H_{21}NO_6Fe_2$
fw	573.86	593.85	555.15
cryst system	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a, Å	9.365 (3)	21.188 (6)	9.645 (2)
b, Å	10.772 (4)	8.552 (2)	10.325 (2)
c, Å	13.933 (6)	13.429 (4)	13.163 (3)
α, deg	84.95 (3)		103.29 (2)
β, deg	73.80 (3)	94.13 (2)	91.201 (2)
γ, deg	65.45 (3)		99.812 (2)
V, Å^3	1227.2 (8)	2427.0 (11)	1254.6 (5)
Z	2	4	2
μ (Mo Kα), cm^{-1}	12.45	12.7	11.94
D_{calc}, g cm^{-3}	1.553	1.625	1.469
color	red	red	orange
size, mm	0.32 × 0.40 × 0.46	0.25 × 0.25 × 0.37	0.26 × 0.32 × 0.47
temp, K	296	296	296
	Data Collection		
diffractometer	Nicolet R3m		
monochromator	graphite		
scan method	Wyckoff		
wavelength	Mo Kα (λ = 0.71073 Å)		
data collected	±13,±15,+20	±24,+10,+15	±13,±14,+18
scan limits, deg	4–58	4–46	4–55
rflns collected	6772	3830	5958
indep rflns	6516	3376	5718
R_{int}, %	2.33	2.97	1.55
indep rflns, $F_o \geq 5\sigma(F_o)$	4800	2360	3867
	Refinement[a]		
$R(F)$, %	3.93	4.13	4.23
$R(wF)$, %	4.31	4.27	4.46
$\Delta(\rho)_{max}$, e Å^{-3}	0.650	0.497	0.580
Δ/σ_{max}	0.033	0.059	0.005
GOF	1.156	1.1094	1.102
N_o/N_v	15.8	7.6	12.9

[a] $R(F) = \sum(|F_o| - |F_c|)/\sum|F_o|$; $R(wF) = \sum(w^{1/2}(|F_o| - |F_c|))/(w^{1/2}|F_o|)$; GOF $= [\sum w||F_o| - |F_c||/N_o - N_v]^{1/2}$.

Table II. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for $Fe_2(\mu\text{-}PhCCHCO\{BF_3\}C\{CH{=}NBu^t\})(CO)_6$ (4c)

	x	y	z	U[a]
Fe(1)	6524 (1)	1741 (1)	3424 (1)	31 (1)
Fe(2)	4365 (1)	1676 (1)	2732 (1)	32 (1)
O(7)	9387 (2)	222 (2)	1403 (1)	55 (1)
F(1)	10144 (2)	1799 (2)	326 (1)	61 (1)
F(2)	10782 (3)	1386 (3)	1798 (2)	88 (1)
F(3)	12053 (2)	−261 (2)	542 (2)	77 (1)
B	10638 (4)	800 (4)	1013 (3)	48 (1)
O(1)	3958 (3)	1633 (3)	5149 (2)	61 (1)
O(2)	6793 (4)	3961 (3)	4341 (2)	80 (2)
O(3)	9254 (4)	−321 (3)	4101 (2)	91 (1)
O(4)	3138 (3)	−424 (3)	3593 (2)	70 (1)
O(5)	4142 (4)	1696 (4)	676 (2)	82 (2)
O(6)	1016 (3)	3665 (3)	3607 (3)	86 (1)
N	8256 (3)	−1941 (2)	1741 (2)	33 (1)
C(1)	4866 (4)	1664 (3)	4405 (2)	40 (1)
C(2)	6678 (4)	3100 (3)	3981 (2)	49 (1)
C(3)	8209 (4)	483 (3)	3841 (2)	51 (1)
C(4)	3632 (3)	363 (3)	3252 (2)	43 (1)
C(5)	4200 (4)	1673 (4)	1474 (2)	49 (1)
C(6)	2320 (4)	2945 (3)	3266 (3)	31 (1)
C(7)	5391 (3)	3001 (2)	2379 (2)	33 (1)
C(8)	7084 (3)	2442 (3)	1917 (2)	31 (1)
C(9)	7843 (3)	980 (3)	1821 (2)	31 (1)
C(10)	6729 (3)	406 (2)	2366 (2)	21 (1)
C(11)	7208 (3)	−1050 (3)	2425 (2)	32 (1)
C(12)	8627 (3)	−3448 (3)	1734 (2)	35 (1)
C(13)	8016 (4)	−3695 (4)	893 (3)	55 (2)
C(14)	10473 (4)	−4194 (3)	1499 (3)	51 (1)
C(15)	7800 (5)	−3860 (3)	2734 (3)	62 (2)
C(21)	4641 (2)	5183 (2)	1475 (1)	41 (1)
C(22)	3798	6594	1446	51 (1)
C(23)	2789	7350	2325	60 (2)
C(24)	2624	6694	3233	60 (2)
C(25)	3498	5283	3261	48 (1)
C(26)	4475	4527	2382	35 (1)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

proposed intermediate 10 is common to both Schemes II and III and connects these two independent routes to 7c.

Experimental Section

The compounds $[Fe_2(\mu\text{-}CHCH{=}NHR)(CO)_8][BF_4]$ (R = Bu^t, Ph)[1] and $[Fe_2(\mu\text{-}(CR^1)(CR^2)CHCH{=}NHR)(CO)_6]$[9] were prepared by literature methods, and Et_3N, PhC≡CH, PhC≡CPh, Bu^{t}C≡CH, $MeO_2CC{\equiv}CH$, and $HBF_4{\cdot}Et_2O$ were purchased from Aldrich Chemical Co. and were used as received. The alkyne MeC≡CH was purchased from Matheson Gas Products, Inc. Solvents were dried by stirring over Na/benzophenone (THF and Et_2O) or CaH_2 (CH_2Cl_2, pentane, and hexane) and were freshly distilled prior to use. The silica gel chromatography support (Baker 3405, 60–200 mesh) was purchased from Thomas Scientific. Complex **2a** (350 mg, 1.0 mmol) was enriched in ^{13}CO by stirring it in 40 mL of CH_2Cl_2 in a 50-mL Schlenk flask under 1 atm of ^{13}CO (99%) for 5 days. All manipulations were performed by using standard Schlenk techniques unless otherwise specified. IR spectra were recorded on an IBM FTIR-32 spectrometer operated in the absorption mode, NMR spectra were obtained on a Bruker AM 300 FT NMR spectrometer, and electron impact (EI) and fast bombardment (FAB) mass spectra were recorded on an AEI-MS9 and AFAB-MS9 mass spectrometers. Elemental analyses were obtained from Schwarzkopf Microanalytical Laboratories, Woodside, NY, or Galbraith Microanalytical Laboratories, Inc., Knoxville, TN.

Reaction of 2a with MeC≡CH. Complex **2a** (200 mg, 0.38 mmol) was placed in a 200-mL Schlenk flask and dissolved in 60 mL of CH_2Cl_2, and MeC≡CH was bubbled through the resulting orange solution for 5 min. The flask was then sealed, and the solution was stirred at 25 °C for 3 days during which time the color changed from light red to dark red. Diethyl ether (20 mL) was added to form a cloudy solution, which was filtered, and the supernatant was evaporated to dryness leaving a dark red solid. Repeated recrystallizations from CH_2Cl_2/pentane yielded complex **4a** as a microcrystalline red solid. The filtrate from the recrystallizations contained the imino-ferracyclopentadiene complexes **5a** and **6a**, which were separated by column chromatography on silica gel. Complex **6a** eluted first, using CH_2Cl_2 as the eluent, and was isolated as a red microcrystalline solid. Complex **5a** eluted when the eluent was changed to 20:1 CH_2Cl_2/Et_2O and was isolated as a red microcrystalline solid. The yields and analytical data for each complex are given below.

4a. Yield = 31% (59.4 mg, 0.11 mmol). Anal. Calcd for $C_{16}H_{15}BF_3NOFe_2$ (%): C, 37.48; H, 2.95. Found: C, 36.94; H, 2.90. IR (CH_2Cl_2): ν_{CO} 2077 (m), 2049 (vs), 2014 (m), 1994 (s) cm^{-1}; ν_{CN} 1616 (w) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 11.42 (br, 1 H, O*H*), 7.86 (d, 1 H, J_{HH} = 15.9 Hz, C*H*), 6.38 (s, 1 H, C*H*), 2.59 (s, 1 H, CH_3), 1.47 (s, 9 H, Bu^t). ^{13}C NMR (CD_2Cl_2): δ 210.2, 209.8, 209.0, 206.7 (*C*O), 188.0 (Fe*C*Me), 175.1 (d, $^1J_{CH}$ = 174.6 Hz, N═*C*H), 162.6 (*C*OH), 103.1 (d, $^1J_{CH}$ = 172.1 Hz, *C*H), 98.6 (Fe*C*(CH═N)), 60.1 (*C*Me$_3$), 34.6 (q, J_{CH} = 128.2 Hz, *C*H$_3$), 28.5 (C(*C*H$_3$)$_3$).

5a. Yield = 7% (11.0 mg, 0.025 mmol). Anal. Calcd for $C_{16}H_{15}NOFe_2$ (%): C, 43.19; H, 3.40. Found: C, 43.08; H, 3.55. MS: m/z 445 and fragment ions corresponding to the loss of six carbonyls. IR (CH_2Cl_2): ν_{CO} 2060 (m), 2025 (vs), 1978 (s) cm^{-1}; ν_{CN} 1605 (w) cm^{-1}. ^1H NMR (DMSO-d_6): δ 13.31 (br, 1 H, O*H*), 8.00 (d, 1 H, J_{HH} = 9.2 Hz, C*H*), 5.54 (s, 1 H), C*H*), 2.46 (s, 1 H, CH_3), 1.35 (s, 9 H, Bu^t). ^{13}C NMR (CD_2Cl_2): δ 212.6, 210.7, 209.3, 208.5 (*C*O), 186.7 (Fe*C*Me), 176.2 (d, $^1J_{CH}$ = 170.9 Hz, N═*C*H), 160.1 (*C*OH), 101.1 (d, $^1J_{CH}$ = 172.1 Hz, *C*H), 94.4 (Fe*C*(CH═N)), 56.8 (*C*Me$_3$), 34.6 (q, J_{CH} = 125.7 Hz, *C*H$_3$), 28.8 (C(*C*H$_3$)$_3$).

6a. Yield = 22% (38.0 mg, 0.085 mmol). Anal. Calcd for $C_{16}H_{15}NOFe_2$ (%): C, 43.19; H, 3.40. Found: C, 42.87; H, 3.46. MS: m/z 445 and fragment ions corresponding to the loss of six carbonyls. IR (CH_2Cl_2): ν_{CO} 2060 (m), 2025 (vs), 1978 (s) cm^{-1}; ν_{CN} 1605 (w) cm^{-1}. ^1H NMR (DMSO-d_6): δ 13.4 (br, 1 H, O*H*), 8.01 (d, 1 H, J_{HH} = 12.9 Hz, C*H*), 7.77 (s, 1 H, C*H*), 1.95 (s, 1 H,

Table III. Selected Bond Distances and Angles for $Fe_2(\mu\text{-}PhCCHCO\{BF_3\}C\{CH{=}NBu^t\})(CO)_6$ (4c)

Bond Distances, Å			
Fe(1)–Fe(2)	2.498 (1)	Fe(1)–C(1)	1.787 (3)
Fe(1)–C(2)	1.790 (4)	Fe(1)–C(3)	1.806 (3)
Fe(1)–C(7)	2.098 (3)	Fe(1)–C(8)	2.165 (2)
Fe(1)–C(9)	2.264 (2)	Fe(1)–C(10)	2.064 (3)
Fe(2)–C(4)	1.829 (4)	Fe(2)–C(5)	1.801 (4)
Fe(2)–C(6)	1.816 (3)	Fe(2)–C(7)	1.988 (3)
Fe(2)–C(10)	2.002 (2)	O(7)–B	1.499 (5)
O(7)–C(9)	1.316 (3)	F(1)–B	1.392 (4)
F(2)–B	1.374 (6)	F(3)–B	1.372 (3)
N–C(11)	1.283 (3)	N–C(12)	1.512 (4)
C(7)–C(8)	1.413 (3)	C(7)–C(26)	1.505 (3)
C(8)–C(9)	1.434 (3)	C(9)–C(10)	1.435 (4)
Bond Angles, deg			
Fe(2)–Fe(1)–C(7)	50.4 (1)	Fe(2)–Fe(1)–C(8)	76.6 (1)
C(7)–Fe(1)–C(8)	38.7 (1)	Fe(2)–Fe(1)–C(9)	75.9 (1)
C(7)–Fe(1)–C(9)	66.6 (1)	C(8)–Fe(1)–C(9)	37.7 (1)
Fe(2)–Fe(1)–C(10)	51.0 (1)	C(7)–Fe(1)–C(10)	75.3 (1)
C(8)–Fe(1)–C(10)	67.7 (1)	C(9)–Fe(1)–C(10)	38.4 (1)
Fe(1)–Fe(2)–C(7)	54.3 (1)	Fe(1)–Fe(2)–C(10)	53.2 (1)
C(7)–Fe(2)–C(10)	79.1 (1)	B–O(7)–C(9)	123.1 (2)
F(1)–B–O(7)	109.8 (3)	O(7)–B–F(2)	108.9 (3)
F(1)–B–F(2)	108.9 (3)	O(7)–B–F(3)	106.6 (3)
F(1)–B–F(3)	109.5 (3)	F(2)–B–F(3)	113.2 (3)
C(11)–N–C(12)	126.3 (2)	Fe(1)–C(1)–O(1)	167.5 (3)
Fe(1)–C(2)–O(2)	179.2 (3)	Fe(1)–C(3)–O(3)	178.8 (4)
Fe(2)–C(4)–O(4)	178.0 (2)	Fe(2)–C(5)–O(5)	177.1 (4)
Fe(2)–C(6)–O(6)	175.5 (4)	Fe(1)–C(7)–Fe(2)	75.3 (1)
Fe(1)–C(7)–C(8)	73.2 (1)	Fe(2)–C(7)–C(8)	116.1 (2)
Fe(1)–C(7)–C(26)	130.8 (2)	Fe(2)–C(7)–C(26)	125.0 (2)
C(8)–C(7)–C(26)	117.8 (2)	Fe(1)–C(8)–C(7)	68.1 (1)
Fe(1)–C(8)–C(9)	74.9 (1)	C(7)–C(8)–C(9)	115.0 (3)
Fe(1)–C(9)–F(1)	130.8 (2)	Fe(1)–C(9)–C(8)	67.4 (1)
F(1)–C(9)–C(8)	126.6 (3)	Fe(1)–C(9)–C(10)	63.2 (1)
F(1)–C(9)–C(10)	122.4 (2)	C(8)–C(9)–C(10)	110.5 (2)
Fe(1)–C(10)–Fe(2)	75.8 (1)	Fe(1)–C(10)–C(9)	78.4 (2)
Fe(2)–C(10)–C(9)	116.3 (2)	Fe(1)–C(10)–C(11)	128.2 (2)
Fe(2)–C(10)–C(11)	120.1 (2)	C(9)–C(10)–C(11)	121.8 (2)
N–C(11)–C(10)	125.6 (2)		

Table IV. Atomic Coordinates (×10⁴) and Isotropic Thermal Parameters (Å² × 10³) for $Fe_2(\mu\text{-}PhCCHCO\{BF_3\}C\{CH{=}NPh\})(CO)_6$ (4e)

	x	*y*	*z*	*U*[a]
Fe(1)	7194.9 (3)	−1758.0 (8)	2704.4 (5)	33.0 (2)
Fe(2)	6947.6 (3)	579.4 (8)	1622.1 (5)	34.9 (2)
C(1)	6652 (2)	3021 (6)	3308 (4)	41 (2)
C(2)	7838 (3)	−3108 (7)	2990 (5)	56 (2)
C(3)	6944 (2)	−2395 (6)	1466 (4)	42 (2)
C(5)	7293 (3)	637 (6)	411 (4)	46 (2)
C(6)	6147 (3)	504 (6)	1003 (4)	47 (2)
C(7)	6958 (3)	2626 (6)	1873 (4)	52 (2)
C(8)	7772 (2)	80 (6)	2356 (4)	37 (2)
C(9)	7776 (2)	183 (6)	3425 (4)	35 (2)
C(10)	7156 (2)	156 (5)	3761 (4)	33 (2)
C(11)	6663 (2)	216 (5)	2985 (4)	34 (2)
C(21)	5822 (2)	1493 (4)	3911 (3)	47 (2)
C(22)	5195	1637	4152	58 (2)
C(23)	4734	626	3728	62 (2)
C(24)	4900	−531	3063	58 (2)
C(25)	5527	−676	2822	47 (2)
C(26)	5988	336	3245	34 (2)
C(27)	8360 (2)	−304 (6)	1898 (4)	41 (2)
N(1)	8916 (2)	−299 (5)	2363 (3)	45 (2)
C(31)	10040 (2)	−671 (5)	2616 (2)	60 (2)
C(32)	10620	−1138	2288	71 (3)
C(33)	10653	−1727	1324	70 (3)
C(34)	10104	−1848	688	75 (3)
C(35)	9524	−1380	1017	63 (2)
C(36)	9491	−792	1980	47 (2)
O(1)	6319 (2)	−3802 (5)	3701 (3)	63 (2)
O(2)	8257 (2)	−3899 (6)	3165	105 (2)
O(3)	6780 (2)	−3021 (4)	735 (3)	54 (1)
O(5)	7497 (2)	778 (5)	−335 (3)	77 (2)
O(6)	5669 (2)	433 (6)	585 (3)	80 (2)
O(7)	6959 (2)	3902 (5)	2092 (4)	89 (2)
B(1)	8384 (3)	−90 (10)	5129 (5)	58 (3)
O(8)	8313 (2)	157 (4)	3999 (2)	69 (1)
F(1)	9027 (2)	11 (5)	5350 (3)	84 (2)
F(2)	8164 (2)	−1560 (5)	5330 (3)	91 (2)
F(3)	8059 (2)	1034 (5)	5580 (3)	103 (2)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

CH_3), 1.36 (s, 9 H, Bu^t). ^{13}C NMR (CD_2Cl_2): δ 213–209 (*C*O), 186.2 (*C*OH), 176.4 (d, $^1J_{CH}$ = 170.9 Hz, N=*C*H), 160.2 (dq, $^1J_{CH}$ = 156.3 Hz, $^3J_{CH}$ = 3.7 Hz, *C*H), 115.7 (q, $^2J_{CH}$ = 4.9 Hz, *C*Me), 94.3 (q, $^2J_{CH}$ = 7.3 Hz, Fe*C*(CH=N)), 56.8 (*C*Me_3), 28.8 (C(*C*H_3)$_3$), 17.8 (qd, $^1J_{CH}$ = 128.2 Hz, $^3J_{CH}$ = 3.7 Hz, *C*H_3).

Reaction of 2a and 2b with Phenylacetylene. Complex **2a** (500 mg, 0.96 mmol) was placed in a 500-mL Schlenk flask and dissolved in 150 mL of CH_2Cl_2. To the resulting orange solution was added phenylacetylene (1.00 mmol). The solution was then heated at reflux in an oil bath at 40 °C for 7 h during which time the color changed from light red to dark red. Diethyl ether (50 mL) was added to form a cloudy solution. The mixture was filtered, and the supernatant was evaporated to dryness, leaving a dark red solid. Repeated recrystallizations from CH_2Cl_2/pentane yielded complex **4c** as a microcrystalline red solid. The filtrate from the recrystallizations contained the neutral ferracyclopentadiene complexes **5c**, **6c**, and **7c**, which were separated by column chromatography on silica gel. The amino-ferracyclopentadiene complex **7c** was eluted first with 3:1 pentane/CH_2Cl_2 and was isolated as a yellow microcrystalline solid. The imino-ferracyclopentadiene complex **6c** eluted next with CH_2Cl_2 as eluent and was isolated as a red microcrystalline solid. Finally the imino-ferracyclopentadiene complex **5c** was eluted with 20:1 CH_2Cl_2/Et_2O and isolated as a red microcrystalline solid. The reaction of **2b** (520 mg, 0.96 mmol) with PhC≡CH was similarly conducted to yield **4e** and **7e**. Yields and analytical data for each complex are given below.

4c. Yield = 53% (290.9 mg, 0.51 mmol). Anal. Calcd for $C_{21}H_{17}BF_3NO_7Fe_2$ (%): C, 43.87; H, 2.99; F, 9.91. Found: C, 43.32; H, 3.13; F, 9.71. IR (CH_2Cl_2): ν_{CO} 2078 (m), 2049 (vs), 2017 (m), 1997 (m) cm^{-1}; ν_{CN} 1612 (w) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 11.58 (br, 1 H, O*H*), 7.94 (d, 1 H, J_{HH} = 15.8 Hz, C*H*), 7.32–7.21 (m, 5 H, Ph), 6.62 (q, 1 H, $^4J_{H-F}$ = 1.2 Hz, C*H*), 1.50 (s, 9 H, Bu^t). ^{13}C NMR (CD_2Cl_2): δ 210.1, 209.0, 206.4, 205.6 (*C*O), 184.6 (Fe*C*Ph), 175.3 (d, $^1J_{CH}$ = 173.9 Hz, N=*C*H), 161.9 (*C*OH), 149.8, 128.9, 128.5, 127.9 (Ph), 102.3 (d, $^1J_{CH}$ = 173.9 Hz, *C*H), 99.0 (Fe*C*(CH=N)), 60.3 (*C*Me_3), 28.6 (C(*C*H_3)$_3$). ^{11}B NMR (CD_2Cl_2): δ −0.99 (br, *B*F_3). ^{19}F NMR (CD_2Cl_2): δ −152.29 (^{10}B*F*$_3$), 152.35 (^{11}B*F*$_3$).

5c. Yield = 7% (34.6 mg, 0.07 mmol). Anal. Calcd for $C_{21}H_{17}NO_7Fe_2$ (%): C, 49.74; H, 3.38. Found: C, 49.20; H, 3.50. MS: *m*/*z* 507 and fragment ions corresponding to the loss of six carbonyls. IR (CH_2Cl_2): ν_{CO} 2061 (m), 2027 (vs), 1984 (s) cm^{-1}; ν_{CN} 1606 (w) cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 13.47 (br, 1 H, O*H*), 8.18 (d, 1 H, J_{HH} = 10.7 Hz, C*H*), 7.33–7.13 (m, 5 H, Ph), 5.66 (s, 1 H, C*H*), 1.38 (s, 9 H, Bu^t). ^{13}C NMR ($CDCl_3$): δ 213.0, 210.5, 208.8, 206.9 (*C*O), 186.1 (*C*OH), 184.8 (Fe*C*Ph), 176.5 (d, $^1J_{CH}$ = 170.9 Hz, N=*C*H), 150.6 (ipso Ph), 127.9, 127.6 (Ph), 99.2 (d, J_{CH} = 166.0 Hz, *C*H), 93.0 (Fe*C*(CH=N)), 57.1 (*C*Me_3), 28.8 (C(*C*H_3)$_3$).

6c. Yield = 13% (65.0 mg, 0.13 mmol). Anal. Calcd for $C_{21}H_{17}NO_7Fe_2$ (%): C, 49.74; H, 3.38. Found: C, 50.30; H, 3.70. MS: *m*/*z* 507 and fragment ions corresponding to the loss of six carbonyls. IR (CH_2Cl_2): ν_{CO} 2060 (m), 2025 (s), 1983 (s) cm^{-1}; ν_{CN} 1606 (w) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 13.95 (br, 1 H, O*H*), 8.34 (s, 1 H, C*H*), 7.89 (d, 1 H, J_{HH} = 12.8 Hz, C*H*NBu^t), 7.76 (dd, 2 H, J_{HH} = 7.0, 1.5 Hz, Ph), 7.39–7.26 (m, 3 H, Ph), 1.43 (s, 9 H, Bu^t). ^{13}C NMR ($CDCl_3$): δ 211.9, 210.0, 209.5, 208.3 (*C*O), 185.1 (*C*OH), 176.6 (d, $^1J_{CH}$ = 172.1 Hz, N=*C*H), 159.0 (d, $^1J_{CH}$ = 158.7 Hz, *C*H), 136.2 (ipso Ph), 128.3, 128.1, 127.9 (Ph), 117.1 (*C*Ph), 94.1 (Fe*C*(CH=N)), 57.0 (*C*Me_3), 28.8 (C(*C*H_3)$_3$).

7c. Yield = 14% (64.4 mg, 0.13 mmol). Anal. Calcd for $C_{20}H_{17}NO_6Fe_2$ (%): C, 50.14; H, 3.55. Found: C, 50.40; H, 3.78. IR (Pentane): ν_{CO} 2062 (m), 2022 (vs), 1993 (s), 1979 (s), 1954 (w) cm^{-1}. MS: *m*/*z* 479 (M^+) and fragment ions corresponding to the loss of six carbonyls. ^{1}H NMR ($CDCl_3$): δ 7.31–7.18 (m, 5 H, Ph), 5.83 (d, 1 H, *J* = 3.1 Hz, FeC*H*), 5.78 (b, 1 H, N*H*), 4.80 (d, 1 H, *J* = 5.5 Hz, FeC(NHBu^t)C*H*), 1.40 (s, 9 H, NC(C*H*$_3$)$_3$). ^{13}C NMR ($CDCl_3$): δ 213.3 (d, 13.4 Hz, Fe*C*(NHBu^t)), 212.4, 212.0,

Table V. Selected Bond Distances and Angles for $Fe_2(\mu\text{-}PhCCHCO\{BF_3\}C\{CH{=}NPh\})(CO)_6$ (4e)

	Bond Distances, Å		
Fe(1)–Fe(2)	2.505 (1)	Fe(1)–C(1)	1.811 (5)
Fe(1)–C(2)	1.806 (5)	Fe(1)–C(3)	1.793 (5)
Fe(1)–C(8)	2.066 (5)	Fe(1)–C(9)	2.244 (5)
Fe(1)–C(10)	2.171 (5)	Fe(1)–C(11)	2.079 (5)
Fe(2)–C(5)	1.831 (5)	Fe(2)–C(6)	1.836 (5)
Fe(2)–C(7)	1.782 (5)	Fe(2)–C(8)	1.989 (5)
Fe(2)–C(11)	1.993 (5)	C(8)–C(9)	1.438 (7)
C(8)–C(27)	1.464 (7)	C(9)–C(10)	1.419 (7)
C(9)–O(8)	1.329 (5)	C(10)–C(11)	1.422 (6)
C(11)–C(26)	1.501 (6)	C(27)–N(1)	1.294 (6)
N(1)–C(36)	1.420 (6)	B(1)–O(8)	1.528 (8)
B(1)–F(1)	1.375 (8)	B(1)–F(2)	1.374 (9)
B(1)–F(3)	1.354 (9)		
	Bond Angles, deg		
Fe(2)–Fe(1)–C(8)	50.5 (1)	Fe(2)–Fe(1)–C(9)	75.2 (1)
C(8)–Fe(1)–C(9)	38.7 (2)	Fe(2)–Fe(1)–C(10)	76.2 (1)
C(8)–Fe(1)–C(10)	68.0 (2)	C(9)–Fe(1)–C(10)	37.4 (2)
Fe(2)–Fe(1)–C(11)	50.5 (1)	C(8)–Fe(1)–C(11)	76.2 (2)
C(9)–Fe(1)–C(11)	67.0 (2)	C(10)–Fe(1)–C(11)	39.0 (2)
Fe(1)–Fe(2)–C(8)	53.2 (1)	Fe(1)–Fe(2)–C(11)	53.6 (1)
C(8)–Fe(2)–C(11)	79.9 (2)	Fe(1)–C(1)–O(1)	178.7 (5)
Fe(1)–C(2)–O(2)	177.0 (5)	Fe(1)–C(3)–O(3)	169.8 (5)
Fe(3)–C(5)–O(5)	175.3 (5)	Fe(2)–C(6)–O(6)	176.7 (5)
Fe(2)–C(7)–O(7)	175.8 (5)	Fe(1)–C(8)–Fe(2)	76.3 (2)
Fe(1)–C(8)–C(9)	77.4 (3)	Fe(2)–C(8)–C(9)	115.0 (3)
Fe(1)–C(8)–C(27)	117.4 (3)	Fe(2)–C(8)–C(27)	125.7 (4)
C(9)–C(8)–C(27)	119.2 (4)	Fe(1)–C(9)–C(8)	63.9 (3)
Fe(1)–C(9)–C(10)	68.5 (3)	C(8)–C(9)–C(10)	112.2 (4)
Fe(1)–C(9)–O(8)	131.2 (3)	C(8)–C(9)–O(8)	121.4 (4)
C(10)–C(9)–O(8)	126.1 (4)	Fe(1)–C(10)–C(9)	74.1 (3)
Fe(1)–C(10)–C(11)	67.0 (3)	C(9)–C(10)–C(11)	114.5 (4)
Fe(1)–C(11)–Fe(2)	75.9 (2)	Fe(1)–C(11)–C(10)	74.0 (3)
Fe(2)–C(11)–C(10)	115.1 (3)	Fe(1)–C(11)–C(26)	129.5 (3)
Fe(2)–C(11)–C(26)	124.0 (3)	C(10)–C(11)–C(26)	119.7 (4)
C(8)–C(27)–N(1)	124.8 (5)	C(27)–N(1)–C(36)	126.9 (4)
O(8)–B(1)–F(1)	103.3 (5)	O(8)–B(1)–F(2)	108.1 (5)
F(1)–B(1)–F(2)	111.1 (6)	O(8)–B(1)–F(3)	109.6 (5)
F(1)–B(1)–F(3)	112.5 (6)	F(2)–B(1)–F(3)	111.7 (6)
C(9)–O(8)–B(1)	126.6 (4)		

Table VI. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for $Fe_2(\mu\text{-}C\{Ph\}C\{Ph\}CHCNHBu^t)(CO)_6$ (7d)

	x	*y*	*z*	*U*[a]
Fe(1)	7655.7 (5)	3504.1 (5)	6218.9 (3)	31.9 (2)
Fe(2)	5951.2 (5)	4778.8 (5)	7351.5 (4)	33.0 (2)
O(1)	8134 (4)	4882 (3)	4495 (2)	70 (1)
O(2)	10272 (3)	2461 (4)	6216 (2)	74 (1)
O(3)	5970 (3)	1184 (3)	4739 (2)	72 (1)
O(4)	5426 (3)	6378 (3)	5863 (2)	67 (1)
O(5)	3627 (3)	2557 (3)	6421 (3)	82 (1)
O(6)	4394 (4)	6250 (4)	8976 (3)	83 (1)
N	6602 (3)	1482 (3)	7406 (2)	37 (1)
C(1)	7973 (4)	4377 (4)	5172 (3)	45 (1)
C(2)	9270 (4)	2899 (4)	6207 (3)	44 (1)
C(3)	6616 (4)	2084 (4)	5318 (3)	45 (1)
C(4)	5662 (4)	5760 (4)	6448 (3)	44 (1)
C(5)	4524 (4)	3417 (4)	6781 (3)	49 (1)
C(6)	5005 (4)	5677 (4)	8355 (3)	50 (1)
C(7)	8171 (3)	5219 (3)	7312 (2)	32 (1)
C(8)	7790 (3)	5124 (3)	8327 (2)	29 (1)
C(9)	6975 (3)	3823 (3)	8326 (2)	32 (1)
C(10)	7036 (3)	2789 (3)	7420 (2)	31 (1)
C(11)	6096 (4)	814 (3)	8254 (3)	39 (1)
C(12)	4688 (4)	1188 (4)	8602 (3)	54 (2)
C(13)	7204 (4)	1179 (4)	9169 (3)	56 (2)
C(14)	5896 (5)	−697 (4)	7767 (3)	60 (2)
C(21)	8961 (2)	7308 (2)	6575 (2)	49 (1)
C(22)	10007	8385	6489	61 (2)
C(23)	11325	8584	7015	65 (2)
C(24)	11597	7706	7627	63 (2)
C(25)	10551	6629	7712	49 (1)
C(26)	9233	6430	7186	36 (1)
C(31)	8466 (3)	5703 (2)	10224 (2)	46 (1)
C(32)	8844	6625	11185	61 (2)
C(33)	8923	8006	11262	53 (1)
C(34)	8624	8465	10379	46 (1)
C(35)	8246	7544	9419	42 (1)
C(36)	8167	6163	9341	32 (1)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

211.6, 210.3 (*C*O), 174.2 (s, Fe*C*Ph), 149.3 (s, Ph ipso), 128.6, 127.9, 127.0 (s, Ph), 104.3 (dd, FeCPh*C*H, $^1J_{CH}$ = 167.2 Hz, $^2J_{CH}$ = 3.7 Hz), 69.0 (dd, FeC(NHBu^t)*C*H, $^1J_{CH}$ = 163.6 Hz, $^2J_{CH}$ = 8.5 Hz), 56.2 (s, *C*Me$_3$), 29.3 (m, NC(*C*H$_3$)$_3$).

4e. Yield = 39% (224.0 mg, 0.39 mmol). Anal. Calcd for $C_{23}H_{13}BF_3NO_7Fe_2$ (%): C, 46.44; H, 2.20. Found: C, 46.40; H, 2.37. IR (CH_2Cl_2): ν_{CO} 2079 (m), 2039 (vs), 2018 (m), 2000 (m) cm^{-1}; ν_{CN} 1603 (w) cm^{-1}. ^{1}H NMR (acetone-d_6): δ 7.94 (d, 1 H, J_{H-H} = 15.9 Hz, C*H*), 6.61 (m, 1 H, J_{HF} = 1.2 Hz, C*H*). ^{13}C NMR (CD_2Cl_2): δ 209.6, 206.8, 206.0, 205.3 (*C*O), 184.4 (Fe*C*Ph), 174.2 (N=*C*H), 159.8 (*C*OH), 150.9, 148.9, 134.7, 134.6, 133.4, 133.2, 129.2, 129.5 (Ph), 102.4 (FeCPh*C*H), 88.3 (Fe*C*(CH=N)).

7e. Yield = 4% (18.1 mg, 0.036 mmol). HRMS Calcd for $C_{22}H_{13}NO_6Fe_2$: *m/z* = 498.9441. Found: *m/z* = 498.9440. IR (CH_2Cl_2): ν_{CO} 2062 (m), 2021 (vs), 1989 (s), 1955 (sh) cm^{-1}; ν_{CC} 1601 (w) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.44–7.14 (m, 10 H, Ph), 6.86 (b, 1 H, N*H*), 5.79 (d, 1 H, *J* = 2.8 Hz, FeCPhC*H*), 5.24 (d, 1 H, *J* = 2.8 Hz, FeC(NHPh)C*H*).

Reaction of 2a with *tert*-Butylacetylene and Diphenylacetylene. Complex **2a** (50 mg, 0.09 mmol) was placed in a 50-mL Schlenk flask and dissolved in 20 mL of CH_2Cl_2. To the resulting orange solution was added Bu^{t}C≡CH (12.0 μL, 0.10 mmol). The solution was then stirred at 25 °C for 5 days, during which time the color changed from light red to dark red. Diethyl ether (5 mL) was added to form a cloudy solution. The mixture was filtered, and the supernatant was evaporated to dryness leaving **7b** as an orange solid, which was purified by column chromatography on silica gel using 3:1 pentane/CH_2Cl_2 as the eluent. Complex **7d** was also similarly prepared by using PhC≡CPh instead of Bu^{t}C≡CH, except that the solution was heated at reflux for 10 h. Yields and analytical data for each complex are given below.

7b. Yield = 65% (28.6 mg, 0.06 mmol). Anal. Calcd for $C_{18}H_{21}NO_6Fe_2$ (%): C, 47.06; H, 4.58. Found: C, 46.91; H, 4.79. IR ($CDCl_3$): ν_{CO} 2053 (m), 2013 (s), 1977 (s) cm^{-1}. MS: *m/z* 459 and fragment ions corresponding to the loss of six carbonyls. ^{1}H NMR ($CDCl_3$): δ 5.85 (d, 1 H, *J* = 3.4 Hz, FeCBu^{t}C*H*), 5.73 (br, 1 H, N*H*), 4.87 (d, 1 H, *J* = 5.5 Hz, FeC(NHBu^t)C*H*), 1.39 (s, 9 H, NC(C*H*$_3$)$_3$), 1.31 (s, 9 H, FeC{C(C*H*$_3$)$_3$}). ^{13}C NMR (C_6D_6): δ 213.7 (d, J_{CH} = 12.0 Hz, Fe*C*NHBu^t), 214.0, 212.3, 211.6, 210.3 (*C*O), 189.3 (d, Fe*C*Bu^t), 102.5 (dd, FeCBu^t*C*H, $^1J_{CH}$ = 162.9 Hz, $^2J_{CH}$ = 4.9 Hz), 70.5 (dd, FeC(NHBu^t)*C*H, $^1J_{CH}$ = 163.6 Hz, $^2J_{CH}$ = 8.5 Hz), 55.7 (n, $^2J_{CH}$ = 3.7 Hz, N*C*Me$_3$), 43.2 (n, $^2J_{CH}$ = 3.5 Hz, *C*Me$_3$), 34.6 (m, C(*C*H$_3$)$_3$), 28.8 (m, C(C*C*H$_3$)$_3$).

7d. Yield = 40% (21.0 mg, 0.04 mmol). Anal. Calcd for $C_{26}H_{21}NO_6Fe_2$ (%): C, 56.25; H, 3.81. Found: C, 56.50; H, 3.91. IR (CH_2Cl_2): ν_{CO} 2055 (m), 2016 (vs), 1982 (s), 1950 (w) cm^{-1}. MS: *m/z* 527 (M$^+$-CO) and fragment ions corresponding to the loss of five carbonyls. ^{1}H NMR ($CDCl_3$): δ 7.13–6.95 (m, 10 H, Ph), 5.61 (b, 1 H, N*H*), 5.39 (d, 1 H, *J* = 5.5 Hz, FeC(NHBu^t)C*H*), 1.48 (s, 9 H, NC(C*H*$_3$)$_3$). ^{13}C NMR ($CDCl_3$): δ 214.1, 211.6, 211.0, 208.6, 208.2 (s, *C*O and Fe*C*(NHBu^t)), 165.5 (d, $^3J_{CH}$ = 11.0 Hz, Fe*C*PhCPhCH), 149.0 (Ph ipso), 135.8 (Ph ipso), 129.9, 128.3, 128.0, 127.6, 125.5 (Ph), 89.4 (d, FeCPh*C*PhCH, $^2J_{CH}$ = 3.7 Hz), 75.2 (dd, FeC(NHBu^t)*C*H, $^1J_{CH}$ = 163.6 Hz, $^3J_{CH}$ = 8.0 Hz), 56.1 (s, *C*Me$_3$)$_3$), 29.5 (m, NC(*C*H$_3$)$_3$).

Displacement of BF$_3$ from 4c and 4a with Et$_3$N. Complex **4c** (50 mg, 0.087 mmol) was placed in a 50-mL Schlenk flask and dissolved in CH_2Cl_2 (15 mL). To the resulting red solution was added NEt$_3$ (14 μL, 0.10 mmol) and H_2O (3 μL, 0.17 mmol). IR monitoring indicated an immediate reaction to form **5c**. The solution was evaporated to dryness leaving a red solid, which was purified by chromatography on silica gel using CH_2Cl_2 as eluent to give a single orange fraction of **5c** in 79% yield (44.1 mg, 0.087 mmol). A similar experiment with **4a** (71 mg, 0.14 mmol) gave **5a** in 62% yield (38.1 mg, 0.089 mmol).

Addition of BF$_3$ to 5c. Complex **5c** (20 mg, 0.039 mmol) was placed in a 50-mL Schlenk flask and dissolved in CH_2Cl_2 (10 mL). To the resulting red solution was added BF$_3$·Et$_2$O (6 μL, 0.05

Table VII. Selected Bond Distances and Angles for $\mathrm{Fe_2}(\mu\text{-C}\{\mathrm{Ph}\}\mathrm{C}\{\mathrm{Ph}\}\mathrm{CHCNHBu^t})(\mathrm{CO})_6$ (7d)

Bond Distances, Å			
Fe(1)–Fe(2)	2.568 (1)	C(11)–C(14)	1.522 (5)
Fe(1)–C(7)	1.988 (3)	Fe(1)–C(10)	1.957 (3)
Fe(2)–C(8)	2.098 (3)	Fe(2)C(7)	2.115 (3)
Fe(2)–C(10)	2.477 (3)	Fe(2)–C(9)	2.111 (4)
N–C(11)	1.491 (5)	N–C(10)	1.339 (4)
C(7)–C(8)	1.412 (5)	C(7)–C(26)	1.520 (4)
C(8)–C(9)	1.437 (4)	C(8)–C(36)	1.501 (3)
C(9)–C(10)	1.415 (4)	C(11)–C(12)	1.525 (5)
Bond Angles, deg			
Fe(2)–Fe(1)–C(7)	53.5 (1)	N–C(11)–C(12)	110.4 (3)
Fe(2)–Fe(1)–C(10)	64.7 (1)	Fe(1)–Fe(2)–C(7)	49.1 (1)
Fe(1)–Fe(2)–C(9)	73.4 (1)	Fe(1)–Fe(2)–C(8)	75.4 (1)
C(7)–Fe(2)–C(9)	67.9 (1)	C(8)–Fe(2)–C(9)	39.9 (1)
Fe(1)–Fe(2)–C(10)	45.6 (1)	C(8)–Fe(2)–C(10)	62.9 (1)
C(7)–Fe(2)–C(10)	68.3 (1)	C(10)–N–C(11)	130.8 (2)
C(9)–Fe(2)–C(10)	34.8 (1)	C(11)–N–Hn	116.8 (21)
C(10)–N–Hn	112.3 (21)	Fe(1)–C(2)–O(2)	176.7 (4)
Fe(1)–C(1)–O(1)	177.4 (3)	Fe(2)–C(4)–O(4)	177.7 (3)
Fe(1)–C(3)–O(3)	179.2 (3)	Fe(2)–C(6)–O(6)	178.8 (4)
Fe(2)–C(5)–O(5)	180.0 (6)	Fe(1)–C(7)–C(8)	114.7 (2)
Fe(1)–C(7)–Fe(2)	77.4 (1)	C(8)–C(7)–C(26)	119.1 (2)
Fe(2)–C(7)–C(8)	69.8 (2)	Fe(2)–C(8)–C(9)	70.5 (2)
Fe(2)–C(7)–C(26)	135.1 (2)	C(9)–C(8)–C(36)	119.6 (3)
Fe(2)–C(8)–C(7)	71.1 (2)	Fe(2)–C(9)–C(10)	86.9 (2)
C(7)–C(8)–C(9)	111.9 (2)	Fe(1)–C(10)–N	125.6 (2)
C(7)–C(8)–C(36)	128.5 (3)	Fe(1)–C(10)–C(9)	112.6 (2)
Fe(2)–C(9)–C(8)	69.5 (2)	N–C(10)–C(9)	121.5 (3)
C(8)–C(9)–C(10)	115.4 (3)	N–C(11)–C(13)	110.6 (3)
Fe(1)–C(10)–Fe(2)	69.7 (1)	N–C(11)–C(14)	105.3 (3)
Fe(2)–C(10)–N	137.6 (2)	C(13)–C(11)–C(14)	109.2 (3)
Fe(2)–C(10)–C(9)	58.3 (2)		

mmol). IR monitoring indicated an immediate reaction to form **4c**. The solution was evaporated to dryness leaving a red solid, which was purified by recrystallization from $\mathrm{CH_2Cl_2}$/pentane to give **4c** in 83% yield (18.7 mg, 0.033 mmol) as a red microcrystalline solid.

Reaction of 8b–d with $\mathrm{HBF_4 \cdot Et_2O}$ To Form the Ferracyclopentadiene Complexes 7b–d. 2-Ferrapyridine complex **8b** (41.0 mg, 0.1 mmol) was placed in a 100-mL Schlenk flask and dissolved in $\mathrm{CH_2Cl_2}$ (50 mL). To the resulting solution was added $\mathrm{HBF_4 \cdot Et_2O}$ (25 μL, 0.18 mmol) under an N_2 atmosphere. The solution instantly turned from dark red to orange and to this solution was added $\mathrm{Et_3N}$ (28 μL, 0.20 mmol). Chromatography on silica gel using 3:1 pentane/$\mathrm{CH_2Cl_2}$ as eluent gave an orange band of complex **7b**, which was isolated as a yellow solid in 98% yield (40.5 mg, 0.09 mmol). Complexes **7c** [90% (37.0 mg, 0.077 mmol)] and **7d** [89% (44.6 mg, 0.084 mmol)] were similarly prepared from complexes **8c** (41.0 mg, 0.086 mmol) and **8d** (50.0 mg, 0.095 mmol), respectively.

Crystal and Molecular Structures of $\mathrm{Fe_2}(\mu\text{-C}\{\mathrm{Ph}\}\mathrm{=CHC}\{\mathrm{OBF_3}\}\mathrm{=C}\{\mathrm{C{=}N(H)Bu^t}\})(\mathrm{CO})_6$ (4c), $\mathrm{Fe_2}(\mu\text{-C}\{\mathrm{Ph}\}\mathrm{=CHC}\{\mathrm{OBF_3}\}\mathrm{=C}\{\mathrm{C{=}N(H)Ph}\})(\mathrm{CO})_6$ (4e), and $\mathrm{Fe_2}(\mu\text{-C}\{\mathrm{Ph}\}\mathrm{=C}\{\mathrm{Ph}\}\mathrm{CH{=}C}\{\mathrm{N(H)Bu^t}\})(\mathrm{CO})_6$ (7d). Crystal, data collection, and refinement parameters are collected in Table I. A red crystal of **4c**, a red crystal of **4e**, and an orange crystal of **7d** were each mounted on fine glass fibers with epoxy cement. The unit cell parameters were each obtained from the least-squares fit of 25 reflections (20° ≤ 2θ ≤ 25°). Preliminary photographic characterizations of **4c** and **7d** showed $\bar{1}$ Laue symmetry. The E-statistics suggested the centrosymmetric alternative $P\bar{1}$ for both, and the chemically sensible results of refinement proved these choices correct. A preliminary photographic characterization of **4e** showed $2/m$ Laue symmetry, and the systematic absences in the diffraction data uniquely established the space group as $P2_1/c$. No absorption corrections were applied to the data sets.

The structures were each solved by direct methods, which located the Fe atoms. The remaining non-hydrogen atoms were located through subsequent least-squares and difference Fourier syntheses. The hydrogen atoms were included as idealized isotropic contributions (d_{CH} = 0.960 Å, $U = 1.2U$ for the attached C), except for H(N) and H(9) in **7d**, which were located and refined. The phenyl rings of each structure were all constrained as rigid planar hexagons (d_{CC} = 1.396 Å). All non-hydrogen atoms were refined with isotropic thermal parameters. It was impossible from the crystallographic data to determine the elemental identity of O(7) in **4c** and O(8) in **4e**; the assignment to oxygen (and not fluorine) was made from chemical evidence discussed in the text.

All computer programs and the sources of the scattering factors are contained in the SHELXTL program library (5.1; G. Sheldrick; Nicolet (Siemens); Madison, WI).

Acknowledgment. We thank the Office of Basic Energy Sciences, Department of Energy, for support of this research and the National Science Foundation for providing funds for the purchase of the X-ray diffractometer at the University of Delaware (CHE9007852).

Supplementary Material Available: Tables of anisotropic thermal parameters, bond lengths and angles, and calculated hydrogen atom positions for **4c**, **4e**, and **7d** (10 pages). Ordering information is given on any current masthead page.

OM9107956