ORGANOMETALLICS
Article

*Organometallics* **2010,** *29,* 6065–6076 6065
DOI: 10.1021/om100841j

# Phosphine-Tethered Carbene Ligands: Template Synthesis and Reactivity of Cyclic and Acyclic Functionalized Carbenes

Insun Yu,[†] Christopher J. Wallis,[†] Brian O. Patrick,[†] Paula L. Diaconescu,[‡] and Parisa Mehrkhodavandi*,[†]

[†]*Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, British Columbia, Canada, and* [‡]*Department of Chemistry & Biochemistry, University of California, Los Angeles, California, United States*

*Received August 30, 2010*

Reaction of the phosphine-tethered isocyanide iron(II) complex **1**, [CpFe(CO)(PCN)]I, with primary and secondary amines forms the corresponding acyclic (diamino)carbene complexes [CpFe(CO)(PCXNH)]I; X = *n*-butylamine (**4**), 4-methylaniline (**5**), dihexylamine (**6**). Five- and six-membered cyclic (diamino)carbene complexes [CpFe(CO)(PCNHN-*n*Cy)]I (*n* = 5 (**9**), 6 (**10**)) are generated in two steps from the reaction of **1** with 2-chloroethyl and 3-chloropropylamine, first forming acyclic diaminocarbene complexes [CpFe(CO)($PC_{NX}NH$)]I (X = chloroethyl (**7**), chloropropyl (**8**)), respectively, followed by deprotonation and intramolecular cyclization. This methodology is not effective for alcohols; however, acyclic (oxy)(amino)carbene complexes are produced in two steps by the reaction of **1** with potassium methoxide, ethoxide, and isopropoxide to form the corresponding ylidene complexes CpFe(CO)($PC_{O(X)}N$) (X = Me (**11**), Et (**12**), *i*-Pr (**13**)), which, in the second step, can be protonated with an equimolar amount of $HBF_4$ to form acyclic (oxy)-(amino)carbene complexes [CpFe(CO)($PC_{O(X)}NH$)]$BF_4$ (X = Me (**14**), Et (**15**), *i*-Pr (**16**)). Five and six-membered cyclic (oxy)(amino)carbene complexes [CpFe(CO)(PCNO-*n*Cy)]Cl (*n* = 5 (**17**), 6 (**18**)) are formed by the concerted reaction of **1** with 2-chloroethoxide and 3-chloropropoxide followed by intramolecular cyclization. The reversible conversion of acyclic (silyl)(amino)carbene complex [CpFe(CO)($P_{Ph}C_{Si(Ph)3}N_H$)]$BF_4$ (**20**) to its ylidene precursor CpFe(CO)($P_{Ph}C_{Si(Ph)3}N$) (**19**) via slow deprotonation with an equivalent of $NaHB(OAc)_3$ is demonstrated, and the structure of **20** is reported. All complexes were characterized by IR and NMR spectroscopy and, where possible, by single-crystal X-ray diffraction. DFT calculations were used to support the electronic structure of complexes deduced from structural and spectroscopic data.

## Introduction

The excellent properties of stable, singlet N-heterocyclic carbenes (NHCs) as ligands for transition metals[1−3] have prompted a massive effort to modify their electronic and steric properties by varying the carbene-bound substituents and developing multidentate donor-functionalized analogues.[4−7] Although the major focus in the literature has been on ligands based on two donors to stabilize the carbene (push−push carbenes), early work on acyclic carbenes[8−11] and recent expansion to stable cyclic (alkyl)(amino)carbenes[12,13] have reinforced the importance of investigating unconventional carbene ligands.

The two main routes to metal-carbene complexes are ligand substitution using the free carbenes or their precursor imidazolium salts, and template synthesis using a modification of an existing metal-C(ligand) functionality.[14−16] While ligand substitution is the most versatile and generally applicable route to

*To whom correspondence should be addressed. E-mail: mehr@chem.ubc.ca.

(1) Scholl, M.; Ding, S.; Lee, C. W.; Grubbs, R. H. *Org. Lett.* **1999**, *1*, 953–956.
(2) Scholl, M.; Trnka, T. M.; Morgan, J. P.; Grubbs, R. H. *Tetrahedron Lett.* **1999**, *40*, 2247–2250.
(3) Huang, J. K.; Stevens, E. D.; Nolan, S. P.; Petersen, J. L. *J. Am. Chem. Soc.* **1999**, *121*, 2674–2678.
(4) de Frémont, P.; Marion, N.; Nolan, S. P. *Coord. Chem. Rev.* **2009**, *253*, 862–892.
(5) Jacobsen, H.; Correa, A.; Poater, A.; Costabile, C.; Cavallo, L. *Coord. Chem. Rev.* **2009**, *253*, 687–703.
(6) Hahn, F. E.; Jahnke, M. C. *Angew. Chem., Int. Ed.* **2008**, *47*, 3122–3172.
(7) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290–1309.
(8) Vignolle, J.; Cattoën, X.; Bourissou, D. *Chem. Rev.* **2009**, *109*, 3333–3384.
(9) Jones, N. D.; Cavell, R. G. *J. Organomet. Chem.* **2005**, *690*, 5485–5496.
(10) Canac, Y.; Soleilhavoup, M.; Conejero, S.; Bertrand, G. *J. Organomet. Chem.* **2004**, *689*, 3857–3865.
(11) Bourissou, D.; Guerret, O.; Gabbai, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39–91.
(12) Lavallo, V.; Canac, Y.; Prasang, C.; Donnadieu, B.; Bertrand, G. *Angew. Chem., Int. Ed.* **2005**, *44*, 5705–5709.
(13) Anderson, D. R.; Lavallo, V.; O'Leary, D. J.; Bertrand, G.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2007**, *46*, 7262–7265.
(14) Tamm, M.; Hahn, F. E. *Coord. Chem. Rev.* **1999**, *182*, 175–209.
(15) Michelin, R. A.; Pombeiro, A. J. L.; Fatima, M.; da Silva, C. G. *Coord. Chem. Rev.* **2001**, *218*, 75–112.
(16) Basato, M.; Michelin, R. A.; Mozzon, M.; Sgarbossa, P.; Tassan, A. *J. Organomet. Chem.* **2005**, *690*, 5414–5420.

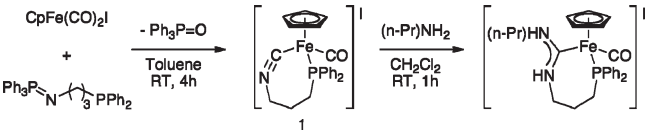

Published on Web 10/15/2010

metal carbene complexes, in the past few years there has been a resurgence of the classic template synthesis of Fischer carbenes to enable formation of unusual and difficult to obtain complexes.[17−21]

Nucleophilic attack on the coordinated carbon of a metal-bound isocyanide is an attractive and commonly used route for the formation of aminocarbene metal complexes with sufficiently electrophilic metals.[14,15] Precursor metal isocyanide complexes have long been used in the reaction with protic nucleophiles, such as primary and secondary amines or alcohols, to yield acyclic diamino- and (alkoxy)(amino)-carbene complexes.[22−24] They can also be used to afford NHC complexes (cyclic diamino-, (oxy)(amino)-, and (thio)-(amino)carbenes) by spontaneous, base-promoted, 1,3-dipolarophile- and 1,3-dipole-promoted cyclization.[25−29] Complexes with benzannulated carbenes (benzoxazolylidenes and benzimidazolinylidenes) can be formed from the use of 2-hydroxyaryl isocyanide and 2-aminoarylisocyanide as precursors by spontaneous cyclization, though they must be protected before metalation.[30−35]

In 1995, Liu and co-workers[36] reported the synthesis of an acyclic diamino carbene iron(II) complex from the reaction of phosphino-isocyanide chelated iron(II) complex **1** with *n*-propylamine. Complex **1**, a piano stool iron(II) complex bearing a chelating isocyanide-phosphine ligand, is generated by reacting a phosphinimine-phosphine compound with $CpFe(CO)_2I$ (Scheme 1). In the course of our studies of phosphinimine donor complexes of late transition metals,[37,38] we have recently communicated our methodology for the synthesis of rare, acyclic (phosphino)(amino)- and (silyl)-(amino)carbenes using complex **1** as a starting scaffold.[39] Herein, we report an expanded family of acyclic and cyclic tethered carbene complexes. Their electronic properties and reactivity have been systematically studied, and DFT calculations have been used to understand the trends observed.

**Scheme 1. Synthesis of Phosphine-Tethered Diaminocarbene Complexes from 1**[36]




**Scheme 2. Synthesis of Acyclic Diaminocarbene Complexes 3−6**


1 ($R^1$ = Ph)
2 ($R^1$ = t-Bu)

3 ($R^1$ = t-Bu, $R^2$ = H, $R^3$ = n-Bu)
4 ($R^1$ = Ph, $R^2$ = H, $R^3$ = n-Bu)
5 ($R^1$ = Ph, $R^2$ = $R^3$ = n-Hex)
6 ($R^1$ = Ph, $R^2$ = H, $R^3$ = 3-methylphenyl)

## Results and Discussion

**Acyclic Diaminocarbene Complexes.** We have repeated Liu's initial experiment as well as synthesized the *tert*-butyl analogue of the proligand $Ph_3P{=}N(CH_2)_3P(t\text{-}Bu)_2$, which formed the (*tert*-butyl)phosphine-functionalized isocyanide complex **2**.[36] The IR spectrum of **2** shows peaks corresponding to the isocyanide ($\nu_{CN}$ = 2089 $cm^{-1}$) and carbonyl ($\nu_{CO}$ = 1999 $cm^{-1}$) moieties. The $^{13}C\{^1H\}$ NMR spectrum of **2** shows signals for the isocyanide and carbonyl carbons at 183.1 and 214.2 ppm, respectively. These data confirm the formation of the isocyanide complex **2** and $Ph_3P{=}O$ and suggest a nucleophilic attack of the iminophosphorane at the carbonyl ligand. The $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture containing **2** shows a signal at 29.9 ppm for $Ph_3P{=}O$ as well as a signal at 53.8 ppm, which indicates the formation of a phosphino moiety coordinated to the metal center (87.7 ppm for **1**).

Reactions of the iron isocyanide complexes **1** and **2** with excess *n*-butyl-, dihexyl-, or 3-methylphenylamine at room temperature in $CH_2Cl_2$ yield the acyclic, diaminocarbene complexes **3**−**6** in greater than 70% yield (Scheme 2). The characteristic features of **3** are two singlets in the $^1H$ NMR spectrum at 5.96 and 7.97 ppm, corresponding to the N-*H* protons, an upfield-shifted $^{31}P\{^1H\}$ NMR signal at 77.9 ppm, and a significant downfield shift of the $^{13}C\{^1H\}$ NMR signal to 221 ppm. The NMR spectral features of carbene complexes **4**−**6** are similar to those of **3**; complex **5**, which was formed from a secondary amine, shows only one singlet for the N-*H* proton, at 7.75 ppm. The average $\nu_{CO}$ and $\nu_{CN}$ stretching frequencies for **3**−**6** are 1950 and 1541 $cm^{-1}$, respectively, indicating minimal electronic changes with ligand substitution. Although it is possible to form orthometalated aminocarbene complexes of electron-poor metals substituted with a

(17) Ruiz, J.; Garcia, G.; Mosquera, M. E. G.; Perandones, B. F.; Gonzalo, M. P.; Vivanco, M. *J. Am. Chem. Soc.* **2005**, *127*, 8584–8585.
(18) Ruiz, J.; Perandones, B. F.; Garcia, G.; Mosquera, M. E. G. *Organometallics* **2007**, *26*, 5687–5695.
(19) Hahn, F. E.; Langenhahn, V.; Pape, T. *Chem. Commun.* **2005**, 5390–5392.
(20) Hahn, F. E.; Langenhahn, V.; Lugger, T.; Pape, T.; Le Van, D. *Angew. Chem., Int. Ed.* **2005**, *44*, 3759–3763.
(21) Kaufhold, O.; Stasch, A.; Pape, T.; Hepp, A.; Edwards, P. G.; Newman, P. D.; Hahn, E. *J. Am. Chem. Soc.* **2009**, *131*, 306–317.
(22) Miller, J.; Balch, A. L.; Enemark, J. H. *J. Am. Chem. Soc.* **1971**, *93*, 4613–4614.
(23) Bonati, F.; Minghetti, G. *J. Organomet. Chem.* **1970**, *24*, 251–256.
(24) Minghetti, G.; Bonati, F. *J. Organomet. Chem.* **1973**, *54*, C62–C63.
(25) Michelin, R. A.; Zanotto, L.; Braga, D.; Sabatino, P.; Angelici, R. J. *Inorg. Chem.* **1988**, *27*, 85–92.
(26) Michelin, R. A.; Zanotto, L.; Braga, D.; Sabatino, P.; Angelici, R. J. *Inorg. Chem.* **1988**, *27*, 93–99.
(27) Liu, C. Y.; Chen, D. Y.; Lee, G. H.; Peng, S. M.; Liu, S. T. *Organometallics* **1996**, *15*, 1055–1061.
(28) Wehlan, M.; Thiel, R.; Fuchs, J.; Beck, W.; Fehlhammer, W. P. *J. Organomet. Chem.* **2000**, *613*, 159–169.
(29) Langenhahn, V.; Beck, G.; Zinner, G.; Lentz, D.; Herrschaft, B.; Fehlhammer, W. P. *J. Organomet. Chem.* **2007**, *692*, 2936–2948.
(30) Hahn, F. E.; Plumed, C. G.; Munder, M.; Lugger, T. *Chem.—Eur. J.* **2004**, *10*, 6285–6293.
(31) Hahn, F. E.; Langenhahn, V.; Meier, N.; Lugger, T.; Fehlhammer, W. P. *Chem.—Eur. J.* **2003**, *9*, 704–712.
(32) Hahn, F. E.; Tamm, M. *J. Organomet. Chem.* **1993**, *456*, C11–C14.
(33) Hahn, F. E.; Tamm, M. *J. Chem. Soc., Chem. Commun.* **1993**, 842–844.
(34) Hahn, F. E.; Tamm, M. *Organometallics* **1995**, *14*, 2597–2600.
(35) Hahn, F. E.; Tamm, M. *J. Chem. Soc., Chem. Commun.* **1995**, 569–570.
(36) Liu, C. Y.; Chen, D. Y.; Cheng, M. C.; Peng, S. M.; Liu, S. T. *Organometallics* **1995**, *14*, 1983–1991.
(37) Wallis, C. J.; Kraft, I. L.; Patrick, B. O.; Mehrkhodavandi, P. *Dalton Trans.* **2010**, *39*, 541–547.
(38) Wallis, C. J.; Kraft, I. L.; Murphy, J. N.; Patrick, B. O.; Mehrkhodavandi, P. *Organometallics* **2009**, *28*, 3889–3895.
(39) Yu, I. S.; Wallis, C. J.; Patrick, B. O.; Mehrkhodavandi, P. *Organometallics* **2009**, *28*, 6370–6373.

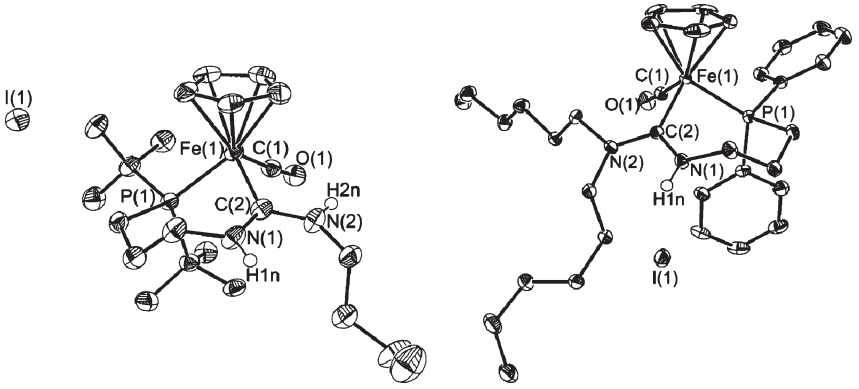


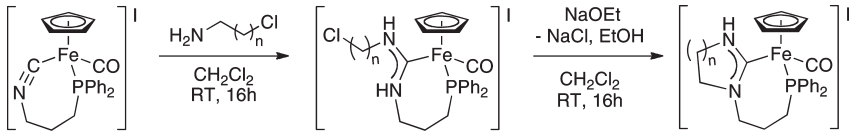

**Figure 1.** Molecular structures of complexes **3** (left) and **5** (right) (depicted with thermal ellipsoids at 50% probability and most H atoms omitted for clarity). Selected distances (Å) and angles (deg) for **3**: C1−Fe1 1.742(3), C2−Fe1 1.958(3), P1−Fe1 2.287(9), C1−O1 1.152(3), C2−N1 1.332(4), C2−N2 1.342(4), N1−C2−N2 115.1(3), N1−C2−Fe1 126.7(2), N2−C2−Fe1 117.9(2), Fe1−C1−O1 175.8(2), Cl−Fe1−C2 95.93(12), C1−Fe1−P1 89.58(10), C2−Fe1−P1 94.55(9). For **5**: C1−Fe1 1.749(3), C2−Fe1 1.992(3), P1−Fe1 2.2029(8), C1−O1 1.151(3), C2−N1 1.345(3), C2−N2 1.356(3), N1−C2−N2 113.6(2), N1−C2−Fe1 122.7(2), N2−C2−Fe1 123.6(2), Fe1−C1−O1 175.6(3), C2−N1−C10 128.1, C2−N2−C23 124.1(2), C2−N2−C29 122.7(2), C1−Fe1−C2 95.23(12), C1−Fe1−P1 89.00(10), C2−Fe1−P1 95.03(8).

**Table 1. Comparison of Electronic Parameters for the Cations of 3, 4, and 5[a]**

| complex | Fe−$C_{carbene}$ NM[b] bond order (Mayer) | $N_P$−$C_{carbene}$ NM[b,c] bond order (Mayer) | N−$C_{carbene}$ NM[b] bond order (Mayer) | Hirshfeld charge of Fe (Mulliken) | Hirshfeld charge of $C_{carbene}$ (Mulliken) |
|---|---|---|---|---|---|
| **3** | 0.85 (0.88) | 1.44 (1.21) | 1.46 (1.20) | 0.02 (−0.08) | 0.06 (0.25) |
| **4** | 0.83 (0.90) | 1.45 (1.22) | 1.46 (1.20) | 0.00 (−0.16) | 0.05 (0.26) |
| **5** | 0.79 (0.90) | 1.44 (1.20) | 1.45 (1.30) | 0.02 (−0.11) | 0.05 (0.24) |

[a] Numbers in parentheses represent a different value for the same parameter, as indicated at the top of each column. [b] NM is Nalewajski−Mrozek bond order calculated from two-electron valence indices (three-index set). [c] $N_P$ is the nitrogen part of the same cycle as the phosphine.

**Scheme 3. Synthesis of Cyclic Diaminocarbene Complexes 9 and 10**




1 7 (n = 2) 8 (n = 3) 9 (n = 1) 10 (n = 2)

phenyl group,[40] orthometalation is not observed with complex **6** due to the electronically saturated iron center.

The molecular structures of **3** and **5** were determined by single-crystal X-ray diffraction and show piano-stool iron centers with a distorted octahedral geometry coordinated to planar carbenes (Figure 1). The Fe−$C_{carbene}$ (**3**, 1.958 Å; **5**, 1.992 Å), $C_{carbene}$−N1 (**3**, 1.332 Å; **5**, 1.345 Å), and $C_{carbene}$−N2 (**3**, 1.342 Å; **5**, 1.356 Å) distances are longer than those of the parent isocyanide complex **1** (Fe−$C_{isocyanide}$, 1.77 Å and $C_{isocyanide}$−N, 1.20 Å).[36] The Fe−$C_{carbene}$−N1 angles (∼120°) are more acute than the Fe−C−N angle in **1** (169°). The N1−$C_{carbene}$−N2 angles (**3**, 115.1°; **5**, 113.6°) are intermediate between free acyclic diaminocarbenes (121°)[41,42] and NHCs (104.7° and 102.2°),[43,44] but larger than reported for half-sandwich iron(II) NHC complexes likely due to their acyclic nature.[45] These results indicate that there are no significant differences between primary and secondary amino substituents on the carbene carbon.

The above electronic interpretation, which is based on structural characteristics, is supported by the results of DFT calculations performed on the cations of **3**, **4**, and **5**. The comparison between the two primary amine complexes (**3** and **4**) and between the primary (**4**) and secondary (**5**) amine complexes indicates that all the electronic parameters investigated are similar for the three complexes (Table 1).

**Cyclic Diaminocarbene Complexes.** Analogous tethered N-heterocyclic carbene complexes are generated via a two-step route (Scheme 3). Reactions of **1** with 4 equiv of 2-chloroethylamine or 3-chloropropylamine afford the corresponding acyclic diaminocarbene complexes **7** and **8** in greater than 90% yield. Subsequent dehydrohalogenations of **7** and **8** by excess NaOEt yield the air-stable, five- and six-membered, cyclic diaminocarbene complexes **9** and **10** in

(40) Yam, V. W. W.; Chu, B. W. K.; Cheung, K. K. *Chem. Commun.* **1998**, 2261–2262.
(41) Alder, R. W.; Allen, P. R.; Murray, M.; Orpen, A. G. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1121–1123.
(42) Alder, R.; Blake, M. E. *Chem. Commun.* **1997**, 1513–1514.
(43) Arduengo, A. J.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361–363.
(44) Arduengo, A. J.; Goerlich, J. R.; Marshall, W. J. *J. Am. Chem. Soc.* **1995**, *117*, 11027–11028.
(45) Ohki, Y.; Hatanaka, T.; Tatsumi, K. *J. Am. Chem. Soc.* **2008**, *130*, 17174–17186.

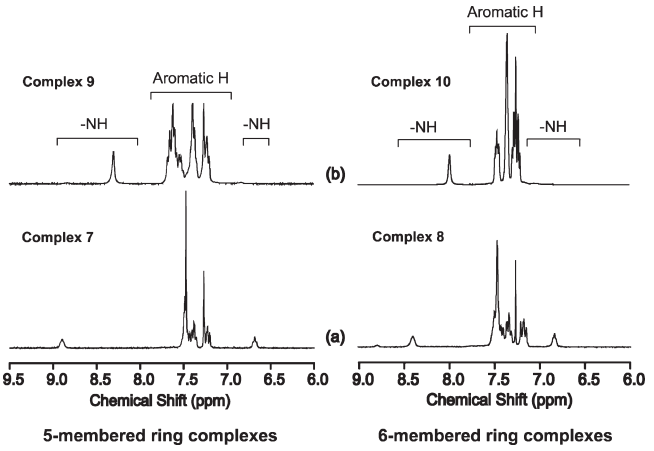



**Figure 2.** $^1$H NMR spectra of (a) the acyclic diaminocarbene complexes, **7** (left) and **8** (right), and (b) the five- and six-membered cyclic diaminocarbene complexes, **9** (left) and **10** (right).

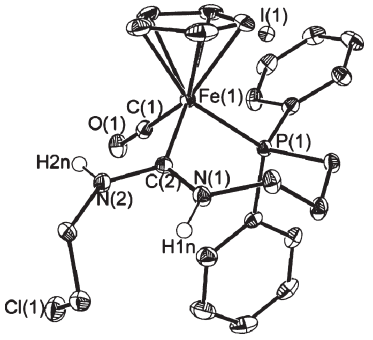



**Figure 3.** Molecular structure of complex **7** (depicted with thermal ellipsoids at 50% probability and most H atoms omitted for clarity). Selected distances (Å) and angles (deg): C1−Fe1 1.744(3), C2−Fe1 1.949(3), P1−Fe1 2.192(8), C1−O1 1.147(4), C2−N1 1.330(4), C2−N2 1.344(4), N1−C2−N2 115.7(3), N1−C2−Fe1 127.2(2), N2−C2−Fe1 117.1(2), Fe1−C1−O1 177.5(3), C2−N1−C10 127.2(2), C1−Fe1−C2 93.38(13), C1−Fe1−P1 89.66(10), C2−Fe1−P1 95.23(9).

greater than 80% yield. Transformation of the acyclic diaminocarbene **7** to the five-membered cyclic diaminocarbene **9** is readily monitored by $^1$H NMR spectroscopy: the two broad singlets for the N-*H* protons at 6.69 and 8.84 ppm of **7** are replaced by one broad resonance at 8.31 ppm for **9** (Figure 2a). Similar results are observed for the transformation of **8** to **10** (Figure 2b).

The molecular structures of **7** and **10** were determined by single-crystal X-ray diffraction and show similar octahedral piano-stool iron centers, consistent with those of the acyclic diaminocarbene complexes **3** and **5** (Figures 3 and 4). The carbonyl stretching frequencies of the acyclic ($\nu_{CO}$ = 1948−1959 cm$^{-1}$) and cyclic ($\nu_{CO}$ = 1949−1952 cm$^{-1}$) diaminocarbene fragments are also similar, indicating very little electronic difference between the two species. More pronounced differences in CO frequencies are reported between acyclic ($\nu_{CO}$ av of 2021 cm$^{-1}$) and saturated cyclic ($\nu_{CO}$ av of 2038 cm$^{-1}$) square-planar carbene complexes such as *cis*-$(CO)_2$Rh(carbene)Cl.[46]

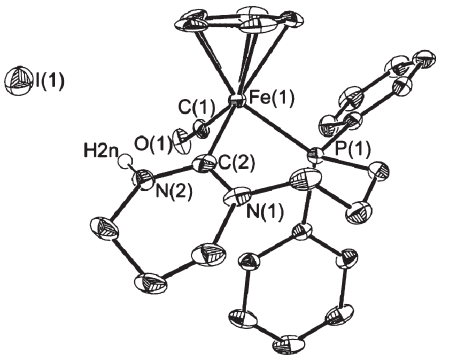



**Figure 4.** Molecular structure of complex **10** (depicted with thermal ellipsoids at 50% probability and most H atoms as well as solvent molecules omitted for clarity). Selected distances (Å) and angles (deg): C1−Fe1 1.751(7), C2−Fe1 1.972(7), P1−Fe1 2.1958(19), C1−O1 1.137(9), C2−N1 1.336(9), C2−N2 1.336(10), N1−C2−N2 116.7(6), N1−C2−Fe1 127.2(6), N2−C2−Fe1 116.1(5), Fe1−C1−O1 172.9(6), C2−N1−C5 123.7(6), C1−Fe1−C2 96.5(3), C1−Fe1−P1 88.5(2), C2−Fe1−P1 93.4(2).

The electronic similarity between **7** and **9** and between **9** and **10** deduced from structural characteristics is supported by the results of DFT calculations performed on the cations for the three complexes. The comparison between the three complexes indicates that all the electronic parameters investigated are similar to each other and to those for complexes **3**−**5** (Table 2).

Formation of the intermediate species **7** and **8** suggests a mechanism different from that proposed for the reaction of haloamines with isocyanide complexes.[15] In one case, the formation of the cyclic diaminocarbene palladium complexes is proposed to occur by initial nucleophilic attack of the bromoethylamine on the palladium-bound isocyanide carbon to yield an imino intermediate (**I**) with subsequent deprotonation and ring closure in the presence of a further molecule of 2-chloroethylamine (Scheme 4). However, intermediate **I** was neither observed nor proposed in this and other similar systems.[47−49]

We propose a similar first step; however, in our system this is followed by proton transfer in intermediate **I** from the amine to the imido to give the acyclic diaminocarbene complex **7**, which is not observed nor proposed in the case of the palladium complexes.[15] The NOE spectrum of **7**, in which we selectively saturated the N2-*H* signal, shows that N1-*H* (6.69 ppm) and N2-*H* (8.84 ppm) are not close enough to show dipole−dipole coupling. In addition, the four methylene protons of the chloroethyl functionality are close enough to have a through-space interaction with the saturated N2-*H* resonance (Figure 5). Deprotonation of **7** by the addition of NaOEt results in a spontaneous intramolecular cyclization to yield complex **9**.

**(Oxy)(amino)carbene Complexes.** The chemistry of the diamino carbenes can be expanded to (oxy)(amino)carbenes. Literature reports show that the reaction of some metal-activated isocyanide ligands with alcohols can form cyclic and acyclic (oxy)(amino)carbenes in one step.[15] However, Hahn et al. have reported that the enhanced back-bonding

(46) Herrmann, W. A.; Ofele, K.; von Preysing, D.; Herdtweck, E. *J. Organomet. Chem.* **2003**, *684*, 235–248.

(47) Motschi, H.; Angelici, R. J. *Organometallics* **1982**, *1*, 343–349.

(48) Belluco, U.; Crociani, B.; Michelin, R.; Uguagliati, P. *Pure Appl. Chem.* **1983**, *55*, 47–54.

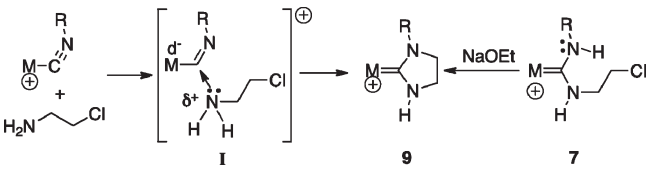
(49) Belluco, U.; Michelin, R. A.; Uguagliati, P. *J. Organomet. Chem.* **1983**, *250*, 565–587.

**Table 2. Comparison of Electronic Parameters for the Cations of 7, 9, and 10[a]**

| complex | Fe−$C_{carbene}$ NM[b] bond order (Mayer) | $N_P$−$C_{carbene}$[c] NM[b] bond order (Mayer) | N−$C_{carbene}$ NM[b] bond order (Mayer) | Hirshfeld charge of Fe (Mulliken) | Hirshfeld charge of $C_{carbene}$ (Mulliken) |
|---|---|---|---|---|---|
| **7** | 0.83 (0.90) | 1.46 (1.22) | 1.44 (1.17) | 0.00 (−0.18) | 0.05 (0.26) |
| **9** | 0.84 (0.91) | 1.43 (1.25) | 1.43 (1.17) | 0.01 (−0.16) | 0.04 (0.28) |
| **10** | 0.81 (0.88) | 1.45 (1.28) | 1.44 (1.17) | 0.00 (−0.16) | 0.05 (0.27) |

[a] Numbers in parentheses represent a different value for the same parameter, as indicated at the top of each column. [b] NM is Nalewajski−Mrozek bond order calculated from two-electron valence indices (three-index set). [c] $N_P$ is the nitrogen part of the same cycle as the phosphine.

**Scheme 4. The Two Proposed Mechanisms for the Formation of 9**




from the electron-rich CpFe fragments can deactivate a coordinated isocyanide carbon toward nucleophilic attack from an alcohol.[34,35] The lack of a reaction between the coordinated isocyanide in **1** and protic alcohols prompted us to use a two-step route comprised of the direct nucleophilic attack on the isocyanide by an alkoxide (a more nucleophilic fragment than alcohol), followed by protonation of the resulting ylidene to form carbene complexes (Scheme 5).[39]

Reactions of complex **1** with KOR (R = Me, Et, *i*-Pr) form ylidene complexes **11**−**13** in quantitative yield. These complexes lead to the acyclic (oxy)(amino)carbene complexes **14**−**16** in 90% isolated yield upon subsequent protonations of the imido nitrogen with $HBF_4$ (Scheme 5). The carbonyl stretching frequencies of the ylidene complexes are approximately 20 $cm^{-1}$ lower than those of the carbene complexes, indicating a more electron-rich iron center with a formally anionic carbon ligand in the case of the ylidene complexes. The respective average C═N stretching frequencies of complexes **11**−**13** (∼1560 $cm^{-1}$) and **14**−**16** (1550 $cm^{-1}$) suggest a greater electronic communication through the carbene carbon and the lone pair on the neighboring oxygen.

DFT calculations performed on the full molecule of **11** and the cation of **14** also indicate that there are larger electronic differences between these two complexes than between any other pair/series considered (Table 3). As expected, the N−$C_{carbene}$ bond order is higher for **11** than for **14**, while the opposite is true for the O−$C_{carbene}$ bond order. In addition, although the iron and $C_{carbene}$ charges are similar for the two complexes, the Fe−$C_{carbene}$ bond order is higher for **14** than for **11**, in agreement with a larger electron delocalization in **14**.

The $^1$H NMR spectra of the ylidene complexes **11**−**13** show characteristic resonances for the methyl and methine groups of the alkoxide substituents at high fields. The spectra of the corresponding carbene complexes **14**−**16** show one additional broad singlet for the N-*H* resonance at ∼8.7 ppm. The $^{13}C\{^1H\}$ NMR spectra of **14**−**16** show signals that are ∼40 ppm downfield of **11**−**13**, signifying a slight difference of electron density between the carbene and ylidene carbons. The molecular structure of **11** was determined by X-ray crystallography (Figure 6). The $C_{ylidene}$−Fe distance in **11** (1.965 Å) is similar to that of **3** (1.958 Å) and about 0.19 Å greater than that of isocyanide complex **1** (1.77 Å).[36]

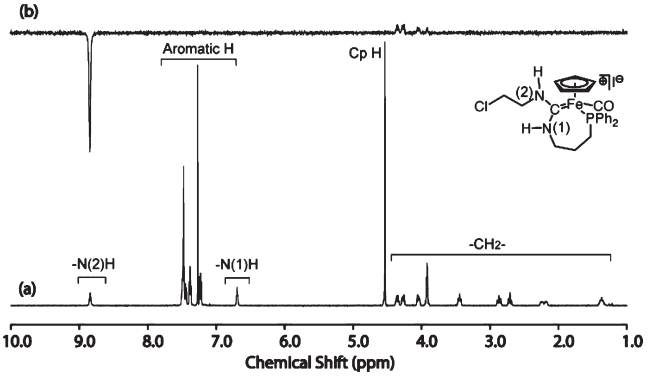
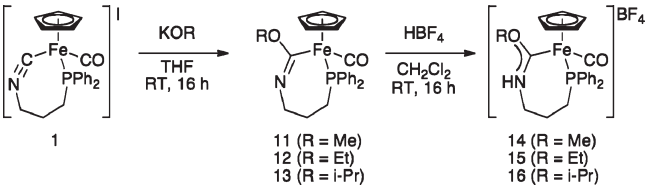



**Figure 5.** (a) $^1$H NMR spectrum and (b) the nuclear Overhauser effect (NOE) spectrum of complex **7** saturating the N2-*H* signal at 8.84 ppm.

**Scheme 5. Synthesis of Acyclic (Oxy)(amino)carbanion and Carbene Complexes 11−13 and 14−16, Respectively**




Five- and six-membered cyclic (oxy)(amino)carbene complexes **17** and **18** were synthesized by the reaction of lithium 2-chloroethoxide or 3-chloropropanoxide with complex **1** in $CH_2Cl_2$ at room temperature (Scheme 6). The $^1$H NMR spectrum of each complex shows new methine resonances, while the $^{13}C\{^1H\}$ NMR spectra show downfield-shifted carbene carbon signals at 229.0 and 231.3 ppm for **17** and **18**, respectively. The IR spectra of **17** and **18** show C═N absorptions at 1529 $cm^{-1}$ for both complexes, a ∼34 $cm^{-1}$ decrease in $\nu_{CO}$ compared to **1**. The carbonyl stretch in **18** (1966 $cm^{-1}$) is similar to that in the acyclic analogues **14**−**16** and higher than in the ylidene complex **11** (1937 $cm^{-1}$), suggesting a more electron-rich iron center in the latter compounds. These results also suggest that, as with the cyclic diaminocarbene complexes, the change in ring size does not have a significant effect on the electronic properties of the complexes.

The molecular structure of **18** was determined by X-ray crystallography (Figure 7). The Fe−$C_{carbene}$ distance (1.976 Å) is slightly longer than the analogous distance in the ylidene complex **11** (1.965 Å), but the difference is within experimental error. As with previously discussed complexes, the $C_{carbene}$−N1 distance of **18** (1.322 Å) is longer than that of the acyclic (oxy)(amino) ylidene complex **11** (1.260 Å) and that of the isocyanide complex **1** (1.20 Å). The $C_{carbene}$−O2 distance of **18** (1.330 Å) is shorter than that of complex **11**

**Table 3. Comparison of Electronic Parameters for Complex 11 and the Cations of 14 and 18[a]**

| complex | Fe−$C_{carbene}$ NM[b] bond order (Mayer) | N−$C_{carbene}$ NM[b] bond order (Mayer) | O−$C_{carbene}$ NM[b] bond order (Mayer) | Hirshfeld charge of Fe (Mulliken) | Hirshfeld charge of $C_{carbene}$ (Mulliken) |
|---|---|---|---|---|---|
| **11** | 0.79 (0.85) | 1.90 (1.78) | 1.18 (0.90) | 0.00 (−0.20) | 0.04 (0.38) |
| **14** | 0.91 (0.95) | 1.50 (1.25) | 1.33 (1.01) | 0.01 (−0.21) | 0.08 (0.44) |
| **18** | 0.87 (0.92) | 1.48 (1.30) | 1.33 (1.01) | 0.00 (−0.21) | 0.08 (0.44) |

[a] Numbers in parentheses represent a different value for the same parameter, as indicated at the top of each column. [b] NM is Nalewajski−Mrozek bond order calculated from two-electron valence indices (three-index set).

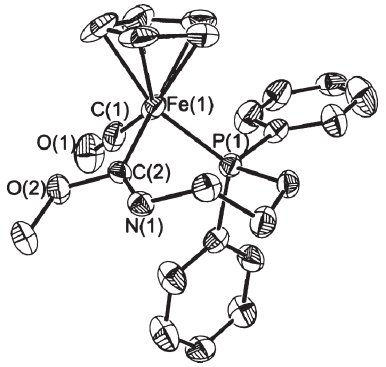



**Figure 6.** Molecular structure of complex **11** (depicted with thermal ellipsoids at 50% probability and all H atoms as well as solvent molecules omitted for clarity). Selected distances (Å) and angles (deg): C1−Fe1 1.744(6), C1−O1 1.160(7), C2−Fe1 1.965(6), P1−Fe1 2.263(5), C2−N1 1.260(6), C2−O2 1.403(6), O2−C2−N1 114.9(5), O2−C2−Fe1 174.41(1), N1−C2−Fe1 134.8(4), C2−O−C11 116.09(7), C2−N1−C8 120.2(4), Cl−Fe1−C2 92.4(2), C1−Fe1−P1 90.96(18), C2−Fe1−P1 90.48(16).

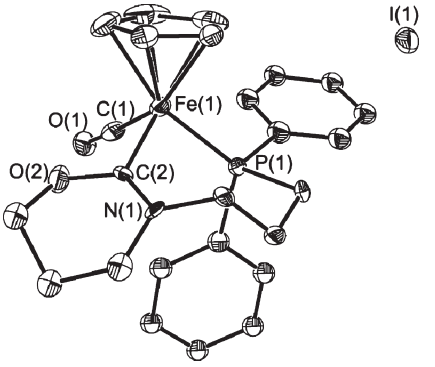
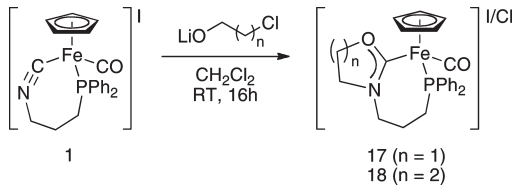


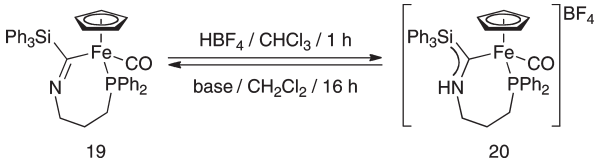

**Figure 7.** Molecular structure of **18** (depicted with thermal ellipsoids at 50% probability and all H atoms omitted for clarity). Selected distances (Å) and angles (deg): C1−Fe1 1.742(4), C1−O1 1.146(5), C2−Fe1 1.976(5), P1−Fe1 2.185(7), C2−N1 1.322(9), C2−O2 1.330(11), N1−C2−O2 122.8(7), N1−C2−Fe1 127.6(5), O2−C2−Fe1 109.5(5), Fe1−C1−O1 176.9(3), C2−N1−C10 123.6(8), C2−N1−C23 122.5(9), C10−N1−C23 113.8(9), C1−Fe1−C2 92.0(2), C1−Fe1−P1 93.27(19), C2−Fe1−P1 93.5(3).

**Scheme 6. Synthesis of Five- and Six-Membered Cyclic (Oxy)(amino)carbene Complexes 17 and 18**




1 — 17 (n = 1), 18 (n = 2)

**Scheme 7. Reversible Reaction of Acyclic (Silyl)(amino) Ylidene (19) and Carbene (20) Complexes**




19 — 20

(1.403 Å). Interestingly, the $C_{carbene}$−N1 (1.332 Å) and $C_{carbene}$−O2 (1.330 Å) distances are similar. DFT calculations on the full cation of **18** agree with the crystallographic observations: similar distances were found for Fe−$C_{carbene}$ in **11** (1.99 Å) and **18** (1.95 Å) and for $C_{carbene}$−N1 (1.34 Å) and $C_{carbene}$−O2 (1.35 Å). A comparison between the electronic parameters for **14** (acyclic carbene) and **18** (cyclic carbene) shows that the two complexes are similar (Table 3).

**Acyclic (Silyl)(amino)carbene Complexes.** We have communicated the first examples of donor-functionalized acyclic (phosphino)- and (silyl)(amino)carbenes, which were generated via a two-step template synthesis on a piano-stool iron(II) complex.[39] Spectroscopic analysis of these complexes indicates that, although they are both "push-spectator" carbenes, they are, nevertheless, electronically distinct. We showed that reacting complex **1** with $KSiPh_3$ yielded the ylidene complex **19**, which upon protonation formed the carbene complex **20** (Scheme 7).

The molecular structure of **20** has since been elucidated by X-ray crystallography and shows a distorted-octahedral iron center similar to that of **19** (Figure 8). The Fe−$C_{carbene}$ distance (1.943 Å) of **20** is shorter than that of **19** (2.005 Å), in agreement with the ionic nature of **20**. The $C_{carbene}$−N1 distance (1.302 Å) of the (silyl)(amino)carbene complex **20** is longer than that of the ylidene complex **19** (1.289 Å). The $C_{carbene}$−Si distance (1.933 Å) in **20** is shorter than that of complex **19** (1.913 Å). The distances and angles of **20** are consistent with those in the only other reported (silyl)(amino)carbene complex, (COD)(Cl)Rh=C($NMe_2$)($SiMePh_2$) (C−N 1.316 Å, C−Si 1.927 Å, C−Rh 1.993 Å).[50] The structural data support the fact that the silyl substituent acts as a spectator, as observed previously.

The above interpretation is supported by the results of DFT calculations performed on the full molecule of **19** and the cation of **20** (Table 4). These results are also compared to those obtained from a geometry optimization on the full molecule (COD)(Cl)Rh=C($NMe_2$)($SiMePh_2$).[50] The comparison between the three complexes indicates that all the electronic parameters investigated are similar to each other and to those for the complexes discussed herein. The most noticeable difference is the Hirshfeld and Mulliken charges,

(50) Canac, Y.; Conejero, S.; Donnadieu, B.; Schoeller, W. W.; Bertrand, G. *J. Am. Chem. Soc.* **2005**, *127*, 7312–7313.

which have negative values for the carbene carbon of the three silyl complexes, while these parameters have a positive value for all the other compounds investigated.

The (silyl)(amino)carbene complex **20** can be converted back to the ylidene complex **19** via reaction with 6 equiv of sodium triacetoxyborohydride ($NaHB(OAc)_3$) in $CH_2Cl_2$, at room temperature under static vacuum overnight. The conversion was monitored by $^{31}P\{^1H\}$ NMR spectroscopy. The reaction is slow; about 30% of complex **20** is converted to **19** in one day without any further decomposition. The full conversion of **20** to **19** requires four evacuations of the reaction mixture in four days. A more reactive hydride source such as $LiAlH_4$ reacts rapidly (1 h) at room temperature and even at −35 °C; however, many byproducts are observed along with the desired product **19**.

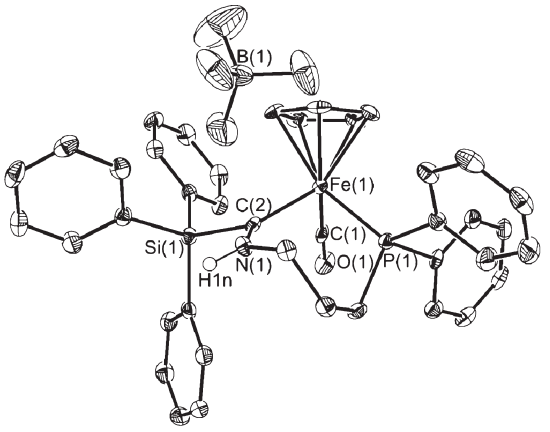



**Figure 8.** Molecular structure of complex **20** (depicted with thermal ellipsoids at 50% probability and most H atoms omitted for clarity). Selected distances (Å) and angles (deg): C1−Fe1 1.750(3), C1−O1 1.149(4), C2−Fe1 1.943(3), P1−Fe1 2.2094(9), C2−N1 1.302(4), C2−Si(1) 1.933(3), Si1−C2−N1 110.6(2), Si1−C2−Fe1 121.90(16), N1−C2−Fe1 127.5(2), C2−N1−C10 127.7(3), Fe1−C1−O1 178.1(3).

## Conclusions

Herein we describe the synthesis and characterization of a family of phosphine-tethered ylidene and carbene complexes of iron(II) via template synthesis from a half-sandwich complex bearing a chelating isocyanide-phosphine ligand.

The acyclic diamino carbene complexes are prepared by the reaction of the isocyanide iron(II) complex with primary and secondary amines, while the five- and six-membered cyclic analogues are synthesized using routes reported in the literature, via spontaneous cyclization and base-promoted cyclization, respectively. A new mechanism for the formation of cyclic diaminocarbene complexes is proposed on the basis of in situ observation and crystallographic identification of intermediates.

The direct reaction of alcohols, phosphines,[39] and silanes with the isocyanide iron(II) complex does not form XCN carbene complexes (X = O, P, or Si). These complexes may be generated, however, via a two-step procedure involving the synthesis of ylidene complexes via nucleophilic attack on the iron-bound isocyanide carbon followed by protonation of the resulting cyclic imine to form the carbene complexes.

Diagnostic $^{13}C\{^1H\}$ NMR data for the resulting carbenes show a distinct trend with the nature of the substituent: $C_{carbene}$−N (∼219 ppm) < $C_{carbene}$−O (∼230 ppm) < $C_{carbene}$−P (∼276 ppm)[39] < $C_{carbene}$−Si (∼299 ppm). The shifts correlate well with the donor−acceptor properties of

**Table 4. Comparison of Electronic Parameters for 19, the Cation of 20, and (COD)(Cl)Rh=C(NMe$_2$)(SiMePh$_2$)[a]**

| complex | M−$C_{carbene}$ NM[b] bond order (Mayer) | N−$C_{carbene}$ NM[b] bond order (Mayer) | Si−$C_{carbene}$ NM[b] bond order (Mayer) | Hirshfeld charge of M (Mulliken) | Hirshfeld charge of $C_{carbene}$ (Mulliken) |
|---|---|---|---|---|---|
| **19** | 0.84 (0.91) | 1.96 (1.72) | 0.86 (0.75) | 0.00 (−0.09) | −0.08 (−0.29) |
| **20** | 1.00 (1.03) | 1.64 (1.33) | 0.83 (0.77) | 0.01 (−0.10) | −0.05 (−0.30) |
| **[Rh]**[c] | 0.99 (0.54) | 1.61 (1.42) | 0.87 (0.87) | 0.27 (0.63) | −0.07 (−0.46) |

[a] Numbers in parentheses represent a different value for the same parameter, as indicated at the top of each column. [b] NM is Nalewajski−Mrozek bond order calculated from two-electron valence indices (three-index set). [c] **[Rh]** is (COD)(Cl)Rh=C(NMe$_2$)(SiMePh$_2$).[50]

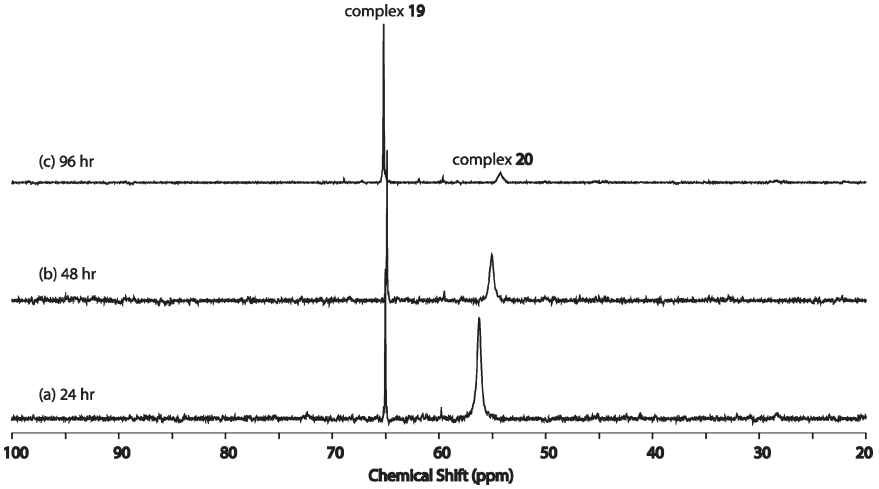



**Figure 9.** $^{31}P\{^1H\}$ NMR ($CH_2Cl_2$) spectra for conversion of complex **20** to complex **19** by reacting with (a) 6 (at 24 h), (b) 12 (at 48 h), and (c) 24 (at 96 h) equiv of $NaHB(OAc)_3$.

**Table 5. Summary of IR and NMR Spectroscopic Data for Complexes 1−20**

| | | IR ($cm^{-1}$) | | | | $^{13}C\{^1H\}$ (ppm) | | |
|---|---|---|---|---|---|---|---|---|
| | complex | $\nu_{max}$(CO) | $\nu_{max}$(CN) | $\nu_{max}$(C=N) | $^{31}P\{^1H\}$ (ppm) | $^{13}C_{carbonyl}$ | $^{13}C_{carbanion}$ | $^{13}C_{carbene}$ |
| **1**[a] | $[CpFe(CO)(P_{Ph}CN)]^+I^-$ | 1998 | 2089 | | 54.0 | 213.0 (d, $^2J_{C-P}$ = 22.3 Hz) | | |
| **2** | $[CpFe(CO)(P_{t\text{-butyl}}CN)]^+I^-$ | 2001 | 2090 | | 87.7 | 214.2 (d, $^2J_{C-P}$ = 19.5 Hz) | | |
| **3** | $[CpFe(CO)(P_{t\text{-butyl}}C_{N(n\text{-butyl})}N_H)]^+I^-$ | 1950 | | 1546 | 77.9 | 210.7 (d, $^2J_{C-P}$ = 27.3 Hz) | | 221.0 (d, $^2J_{C-P}$ = 33.2 Hz) |
| **4** | $[CpFe(CO)(P_{Ph}C_{NH(n\text{butyl})}N_H)]^+I^-$ | 1949 | | 1546 | 56.7 | 209.61 (d, $J$ = 24.91 Hz) | | 218.05 (d, $J$ = 31.83 Hz) |
| **5** | $[CpFe(CO)(P_{Ph}C_{N(n\text{hexyl})2}N_H)]^+I^-$ | 1948 | | 1535 | 55.9 | 210.00 (d, $J$ = 20.96 Hz) | | 219.16 (d, $J$ = 36.99 Hz) |
| **6** | $[CpFe(CO)(P_{Ph}C_{NH(3\text{-methylphenyl})}N_H)]^+I^-$ | 1954 | | 1536 | 57.9 | 216.43 (d, $J$ = 24.54 Hz) | | 217.58 (d, $J$ = 32.20 Hz) |
| **7** | $[CpFe(CO)(PC_{N(chloroethyl)}N_H)]^+I^-$ | 1959 | | 1551 | 56.4 | 211.35 (d, $J$ = 28.36 Hz) | | 218.11 (d, $J$ = 32.06 Hz) |
| **8** | $[CpFe(CO)(PC_{N(chloropropyl)}N_H)]^+I^-$ | 1952 | | 1551 | 56.4 | 211.04 (d, $J$ = 24.66 Hz) | | 218.16 (d, $J$ = 32.06 Hz) |
| **9** | $[CpFe(CO)(PC_{NH}N\text{-}5Cy)]^+I^-$ | 1949 | | 1487 | 57.0 | 211.54 (d, $J$ = 27.60 Hz) | | 218.81 (d, $J$ = 29.14 Hz) |
| **10** | $[CpFe(CO)(PC_{NH}N\text{-}6Cy)]^+I^-$ | 1952 | | 1548 | 56.2 | 205.75 (d, $J$ = 24.91 Hz) | | 218.25 (d, $J$ = 33.22 Hz) |
| **11** | $CpFe(CO)(PC_{O(Me)}N)$ | 1937 | | 1566 | 60.6 | 221.08 (d, $J$ = 31.83 Hz) | 198.03 (d, $J$ = 33.22 Hz) | |
| **12** | $CpFe(CO)(PC_{O(Et)}N)$ | 1937 | | 1561 | 61.1 | 221.22 (d, $J$ = 32.06 Hz) | 197.64 (d, $J$ = 30.83 Hz) | |
| **13** | $CpFe(CO)(PC_{O(iPr)}N)$ | 1936 | | 1561 | 61.3 | 221.37 (d, $J$ = 33.31 Hz) | 196.27 (d, $J$ = 33.31 Hz) | |
| **14** | $[CpFe(CO)(PC_{O(Me)}N_H)]^+BF_4^-$ | 1960 | | 1552 | 55.6 | 218.25 (d, $J$ = 27.60 Hz) | | 237.08 (d, $J$ = 27.60 Hz) |
| **15** | $[CpFe(CO)(PC_{O(Et)}N_H)]^+BF_4^-$ | 1958 | | 1551 | 55.6 | 218.09 (d, $J$ = 27.13 Hz) | | 236.34 (d, $J$ = 29.59 Hz) |
| **16** | $[CpFe(CO)(PC_{O(iPr)}N_H)]^+BF_4^-$ | 1959 | | 1544 | 56.0 | 217.92 (d, $J$ = 28.36 Hz) | | 234.63 (d, $J$ = 25.89 Hz) |
| **17** | $[CpFe(CO)(PC_{NO}\text{-}5Cy)]^+Cl^-$ | 1964 | | 1523 | 55.8 | 217.62 (d, $J$ = 26.66 Hz) | | 229.00 (d, $J$ = 28.50 Hz) |
| **18** | $[CpFe(CO)(PC_{NO}\text{-}6Cy)]^+Cl^-$ | 1966 | | 1534 | 56.3 | 217.97 (d, $J$ = 29.06 Hz) | | 231.32 (d, $J$ = 29.06 Hz) |
| **19** | $CpFe(CO)(P_{Ph}C_{Si(Ph)3}N)$ | 1915 | | 1569 | 57.8 | 223.2 (br s) | 218.3 (d, $^2J_{C-P}$ = 26.4 Hz) | |
| **20** | $[CpFe(CO)(P_{Ph}C_{Si(Ph)3}N_H)]^+BF_4^-$ | 1959 | | 1518 | 55.4 | 216.4 (d, $^2J_{C-P}$ = 32.3 Hz) | | 299.4 (br s) |

[a] Ref [36].

the substituent X in XCN carbene complexes. The greater degree of $C_{carbene}$−X interaction, where X = N rather than X = O, P,[39] and Si, is reflected in the greater shielding of $C_{carbene}$ in aminocarbene complexes. IR spectroscopic data on these octahedral iron complexes are not as diagnostic for determining the different electronic properties of the carbene complexes. DFT calculations were used to support the electronic interpretations based on crystallographic and NMR spectroscopic data. For a series of complexes with different $C_{carbene}$ substituents, the Fe−$C_{carbene}$ Mayer bond order increases from **4** (0.90) to **14** (0.95) and to **20** (1.03). This systematic study of the template synthesis of acyclic and cyclic carbenes on a model system has enabled us to directly compare a diverse family of functionalized carbene ligands.

## Experimental Section

**General Methods.** Unless otherwise specified, all procedures were carried out using standard Schlenk techniques or in an MBraun glovebox. A Bruker Avance 300 MHz spectrometer and Bruker Avance 400dir MHz spectrometer were used to record the $^1H$ NMR, $^{13}C\{^1H\}$ NMR, and $^{31}P\{^1H\}$ NMR spectra. $^1H$ NMR chemical shifts are given in ppm versus residual protons in deuterated solvents as follows: $\delta$ 5.32 for $CD_2Cl_2$ and $\delta$ 7.27 for $CDCl_3$. $^{13}C\{^1H\}$ NMR chemical shifts are given in ppm versus residual $^{13}C$ in solvents as follows: $\delta$ 54.00 for $CD_2Cl_2$ and $\delta$ 77.23 for $CDCl_3$. $^{31}P\{^1H\}$ NMR chemical shifts are given in ppm versus 85% $H_3PO_4$ set at 0.00 ppm. A Waters/Micromass LCT mass spectrometer equipped with an electrospray (ESI) ion source and a Kratos-50 mass spectrometer equipped with an electron impact ionization (EI) source were used to record low-resolution and high-resolution spectra. IR spectra were obtained on a Thermo Scientific FT-IR spectrometer (Nicolet 4700). Diffraction measurements for X-ray crystallography were made on a Bruker X8 APEX II diffraction with graphite-monochromated Mo K$\alpha$ radiation. The structure was solved by direct methods and refined by full-matrix least-squares using the SHELXTL crystallographic software of Bruker-AXS (Table 6). Unless specified, all non-hydrogen atoms were refined with anisotropic displacement parameters, and all hydrogen atoms were constrained to geometrically calculated positions but were not refined. ESI mass spectra were obtained on a Waters/Micromass LCT time-of-flight (TOF) mass spectrometer equipped with an electrospray ion source. CHN analysis was performed using a Carlo Erba EA1108 elemental analyzer. The elemental composition of an unknown sample is determined by using a calibration factor. The calibration factor is determined by analyzing a suitable certified organic standard (OAS) of a known elemental composition.

All solvents were degassed and dried using 3 Å molecular sieves in an MBraun solvent purification system. THF, $Et_2O$, and $C_6H_6$ ($C_6D_6$) were further dried over Na/benzophenone and distilled under $N_2$. $CH_3CN$ ($CD_3CN$), $CH_2Cl_2$ ($CD_2Cl_2$), and $CHCl_3$ ($CDCl_3$) were dried over $CaH_2$ and vacuum-transferred to a Strauss flask and then degassed through a series of freeze−pump−thaw cycles. Deuterium-labeled NMR solvents were purchased from Cambridge Isotope Laboratory. Other chemicals and solvents were purchased from Aldrich, Fisher, Alfa Aesar, or Strem and were used without further purification. 1-Azido-3-chloropropane,[51] *N*-(3-chloroprophyl)triphenylphosphinimine,[36] *N*-(3-(diphenylphosphino)propyl)triphenylphosphinimine,[36] $CpFe(CO)_2I$, and complexes **19** and **20**[39] were prepared according to literature procedures.

**Synthesis of Complex 1.** The preparation of complex **1** is a modification of a literature procedure.[36] A solution of

(51) Yao, L.; Smith, B. T.; Aube, J. *J. Org. Chem.* **2004**, *69*, 1720–1722.

**Table 6. Selected Crystallographic Data for Compounds 3, 5, 7, 10, 11, 18, and 20**

| | 3 | 5 | 7 | 10 | 11 | 18 | 20 |
|---|---|---|---|---|---|---|---|
| empirical formula | $C_{23}H_{40}N_2OPFeI\cdot 2CHCl_3$ | $C_{34}H_{48}FeIN_2OP$ | $C_{24}H_{27}ClFeIN_2OP$ | $C_{25}H_{28}N_2OPFeI\cdot CH_2Cl_2$ | $C_{23}H_{24}NO_3FeP$ | $C_{25}H_{27}NO_2PFeI$ | $C_{40}H_{37}BF_4FeNOPSi$ |
| fw | 801.02 | 741.46 | 608.65 | 671.14 | 433.25 | 587.2 | 749.43 |
| $T$ (K) | 173 | 173 | 173 | 173 | 173 | 173 | 173 |
| $a$ (Å) | 15.1631(5) | 12.9690(4) | 20.2320(3) | 8.6746(2) | 7.4296(2) | 8.6529(4) | 8.9075(3) |
| $b$ (Å) | 14.9065(5) | 16.5713(6) | 20.232 | 22.2743(8) | 15.3027(5) | 20.7218(8) | 13.6417(4) |
| $c$ (Å) | 16.0890(6) | 15.7782(5) | 10.5999(2) | 14.2245(5) | 17.9529(6) | 13.1388(6) | 15.2165(4) |
| $\alpha$ (deg) | 90 | 90 | 90 | 90 | 90 | 90 | 97.466(2) |
| $\beta$ (deg) | 111.237(1) | 104.923(2) | 90 | 100.8600(10) | 90 | 99.379(2) | 98.451(2) |
| $\gamma$ (deg) | 90 | 90 | 120 | 90 | 90 | 90 | 107.810(2) |
| volume (Å$^3$) | 3389.6(2) | 3276.58(19) | 3757.59(9) | 2699.24(15) | 2041.12(11) | 2324.34(18) | 1710.99(9) |
| $Z$ | 4 | 4 | 6 | 4 | 4 | 4 | 2 |
| cryst syst | monoclinic | monoclinic | trigonal | monoclinic | orthorhombic | monoclinic | triclinic |
| space group | $P2_1/c$ | $P2_1/n$ | $P6_5$ | $P2_1/c$ | $P2_12_12_1$ | $Cc$ | $P\bar{1}$ |
| $d_{calc}$ (g/cm$^3$) | 1.570 | 1.448 | 1.614 | 1.652 | 1.410 | 1.678 | 1.455 |
| $\mu$(Mo K$\alpha$) (cm$^{-1}$) | 18.97 | 14.80 | 20.24 | 19.82 | 8.36 | 20.68 | 5.80 |
| $2\theta_{max}$ (deg) | 55.9 | 55.9 | 56.2 | 56.2 | 50.1 | 55.1 | 51.1 |
| absorp corr ($T_{min}$, $T_{max}$) | 0.584, 0.738 | 0.541, 0.800 | 0.512, 0.641 | 0.573, 0.820 | 0.656, 0.882 | 0.502, 0.733 | 0.877, 0.955 |
| total no. of reflns | 65 575 | 74 450 | 69 259 | 22 180 | 12 288 | 46 854 | 21 956 |
| no. of indep reflns ($R_{int}$) | 8102 (0.038) | 40 387 (0.050) | 6085 (0.035) | 6535 (0.056) | 3619 (0.040) | 30439 (0.076) | 6306 (0.046) |
| residuals (refined on $F^2$, all data): $R_1$; $wR_2$ | 0.048; 0.082 | 0.0492; 0.0834 | 0.0225; 0.0611 | 0.103; 0.236 | 0.054; 0.098 | 0.040; 0.073 | 0.0726; 0.1166 |
| GOF | 1.05 | 1.035 | 1.176 | 1.041 | 1.15 | 1.049 | 1.025 |
| no. obsrvns [$I > 2\sigma(I)$] | 6513 | 6669 | 5874 | 4650 | 3193 | 4806 | 4741 |
| residuals (refined on $F^2$): $R_1{}^a$, $wR_2{}^b$ | 0.032; 0.072 | 0.0353; 0.0765 | 0.0207; 0.0603 | 0.0720; 0.216 | 0.045; 0.095 | 0.032; 0.071 | 0.048; 0.105 |

$^aR_1 = \sum||F_o| - |F_d||/\sum|F_o|$. $^bwR_2 = [\sum(w(F_o^2 - F_c^2)^2)/\sum w(F_o^2)^2]^{1/2}$.

*N*-(3-(diphenylphosphino)propyl)triphenylphosphinimine (2.52 g, 5.01 mmol) and $CpFe(CO)_2I$ (1.52 g, 5.01 mmol) in toluene (200 mL) was stirred at room temperature overnight. A yellow precipitate was collected on a fine frit. The yellow solid was washed with toluene and THF to remove triphenylphosphine oxide completely and then dried under vacuum to yield **1** as a yellow solid (2.44 g, 92% yield). IR ($CDCl_3$): 2089 cm$^{-1}$ ($\nu_{CN}$) and 1999 cm$^{-1}$ ($\nu_{CO}$). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 1.90−2.18 (m, −C$H_2$, 1H), 2.18−2.47 (m, −C$H_2$, 1H), 2.73 (td, $J$ = 13.42, 9.25 Hz, −C$H_2$, 1H), 3.39 (ddd, $J$ = 14.50, 4.45, 4.34 Hz, −C$H_2$, 1H), 3.78−3.98 (m, −C$H_2$, 1H), 4.80 (ddd, $J$ = 14.90, 8.74, 4.23 Hz, −C$H_2$, 1H), 5.02 (d, $J$ = 1.14 Hz, *Cp H*, 5H), 7.42−7.79 (m, *aryl H*, 10H). $^{13}$C{$^1$H} NMR (75.44 MHz, $CDCl_3$): $\delta$ 28.45 (d, $J$ = 6.13 Hz, −C$H_2$, 1C), 31.66 (d, $J$ = 32.20 Hz, −C$H_2$, 1C), 48.76 (s, −C$H_2$, 1C), 85.90 (s, *Cp C*, 5C), 123.44, 134.95 (m, *aryl C*, 12C), 183.58 (d, $J$ = 35.27 Hz, $C_{isocyanide}$), 212.51 (d, $J$ = 23.00 Hz, $C_{carbonyl}$). $^{31}$P{$^1$H} NMR (121.44 MHz, $CDCl_3$): $\delta$ 53.8.

**Synthesis of Complex 2.** The preparation of complex **2** followed the same procedure as complex **1** with the corresponding proligand *N*-(3-(di(*tert*-butyl)phosphino)propyl)triphenylphosphinimine (0.92 g, 1.98 mmol). Complex **2** was obtained as a yellow solid (0.56 g, 73%). IR ($CDCl_3$): 2090 cm$^{-1}$ ($\nu_{CN}$) and 2001 cm$^{-1}$ ($\nu_{CO}$). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 1.28 (d, $J$ = 13.9 Hz, −C$H_3$, 9H), 1.49 (d, $J$ = 13.7 Hz, −C$H_3$, 9H), 1.69−1.83 (m, −C$H_2$, 1H), 2.60−2.86 (m, −C$H_3$, 3H), 3.51 (dd, $J$ = 15.1, 4.6 Hz, −C$H_2$, 1H), 4.04−4.14 (m, −C$H_2$, 1H), 5.16 (s, *Cp H*, 5H). $^{13}$C{$^1$H} NMR (75.44 MHz, $CDCl_3$): $\delta$ 26.50 (d, $J$ = 22.41 Hz, −C$H_2$, 1C), 29.54 (d, $J$ = 5.17 Hz, −C$H_2$, 1C), 29.69 (d, $J$ = 2.30 Hz, −C$H_3$, 3C), 31.02 (br s, −C$H_3$, 3C), 39.06 (d, $J$ = 10.92 Hz, −C$H_2$, 1C), 40.57 (d, $J$ = 12.64 Hz, −C$(CH_3)_3$, 1C), 48.78 (s, −C$(CH_3)_3$, 1C), 84.03 (s, *Cp C*, 5C), 183.14 (d, $J$ = 29.88 Hz, $C_{isocyanide}$), 214.18 (d, $J$ = 19.54 Hz, $C_{carbonyl}$). $^{31}$P{$^1$H} NMR (121.44 MHz, $CDCl_3$): $\delta$ 87.74. Anal. Calcd for **2** ($C_{18}H_{29}FeINOP$): N, 2.86; C, 44.20; H, 5.98. Obtained: N, 3.13; C, 44.37; H, 5.86.

**Synthesis of Complex 3.** An excess amount of *n*-butylamine (5 mL, 50.6 mmol) was added to a solution of complex **2** (500 mg, 0.945 mmol) in $CH_2Cl_2$ (20 mL) at room temperature. The reaction mixture was stirred overnight, and it was concentrated *in vacuo*. $Et_2O$ (10 mL) was added to precipitate the yellow solid, complex **3**. Complex **3** was collected on a fine frit and dried *in vacuo* (0.423 g, 89%). Complex **3**: IR ($CDCl_3$) 19450 cm$^{-1}$ ($\nu_{CO}$). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 1.17 (d, $J$ = 12.46 Hz, −C$H_3$, 9H), 1.24 (d, $J$ = 12.12 Hz, −C$H_3$, 9H), 1.29−1.49 (m, −C$H_3$, 3H), 1.54 (br s, −C$H_2$, 2H), 1.79 (br s, −C$H_2$, 3H), 1.97 (br s, −C$H_2$, 1H), 2.10−2.31 (m, −C$H_2$, 1H), 2.48−2.65 (m, −C$H_2$, 1H), 3.22 (br s, −C$H_2$, 1H), 3.27−3.48 (m, −C$H_2$, 2H), 3.98−4.13 (m, −C$H_2$, 1H), 4.75 (s, *Cp C*, 5H), 5.96 (br s, −N*H*, 1H), 7.97 (br s, −N*H*, 1H). $^{13}$C{$^1$H} NMR (100.58 MHz, $CDCl_3$): $\delta$ 13.48 (s, −C$H_3$, 1C), 19.84 (s, −C$H_2$, 1C), 25.67 (s, −C$H_2$, 1C), 28.90 (d, $J$ = 9.69 Hz, −C$H_2$, 1C), 29.60 (br s, −C$H_3$, 3C), 29.81 (br s, −C$H_3$, 3C), 30.25 (s, −C$H_2$, 1C), 37.52 (d, $J$ = 17.99 Hz, −C$H_2$, 1C), 38.40 (d, $J$ = 17.99 Hz, −C$H_2$, 1C), 45.94 (s, −C$(CH_3)_3$, 1C), 46.78 (s, −C$(CH_3)_3$, 1C), 84.30 (s, *Cp C*, 5C), 210.71 (d, $C_{carbonyl}$, 1C), 221.00 (d, $J$ = 31.83 Hz, $C_{carbene}$, 1C). $^{31}$P{$^1$H} NMR (121.44 MHz, $CDCl_3$): $\delta$ 77.88. Anal. Calcd for **3** ($C_{22}H_{41}FeIN_2OP$): N, 4.97; C, 46.91; H, 7.34. Obtained: N, 5.48; C, 46.54; H, 7.19.

**Synthesis of Complex 4.** An excess amount of *n*-butylamine (5 mL, 50.6 mmol) was added to a solution of complex **1** (500 mg, 0.945 mmol) in $CH_2Cl_2$ (20 mL) at room temperature. The reaction mixture was stirred overnight, and the solution was concentrated *in vacuo*. $Et_2O$ (10 mL) was added to precipitate the yellow solid and dried *in vacuo* to obtain complex **4** (0.524 g, 92%). IR ($CDCl_3$): 1948.91 cm$^{-1}$ ($\nu_{CO}$). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 0.98 (t, $J$ = 7.31 Hz, −C$H_3$, 3H), 1.16−1.39 (m, −C$H_2$, 2H), 1.42−1.64 (m, −C$H_2$, 2H), 1.64−1.85 (m, −C$H_2$, 2H), 2.09−2.31 (m, −C$H_2$, 1H), 2.68−2.85 (m, −C$H_2$, 1H), 3.45−3.72 (m, −C$H_2$, 3H), 4.13−4.36 (m, −C$H_2$, 1H), 4.54 (s, *Cp H*, 5H), 6.50 (br s, −N*H*, 1H), 7.10 − 7.58 (m, *aryl H*, 10H),

8.15 (br s, −N*H*, 1H). $^{13}C\{^1H\}$ NMR (100.58 MHz, $CDCl_3$): δ 13.54 (d, *J* = 8.30 Hz, −*C*H$_3$, 1C), 19.91 (s, −*C*H$_2$, 1C), 24.68 (s, −*C*H$_2$, 1C), 30.44 (s, −*C*H$_2$, 1C), 35.35 (m, *J* = 22.14 Hz, −*C*H$_2$, 1C), 41.80 (s, −*C*H$_2$, 1 C), 45.68 (s, −*C*H$_2$, 1C), 46.07 (s, −*C*H$_2$, 1C), 84.76 (s, *Cp C*, 5C), 128.07 (d, *J* = 9.69 Hz, *aryl C*, 2C), 128.61 (d, *J* = 9.69 Hz, *aryl C*, 2C), 129.68 (d, *J* = 8.30 Hz, *aryl C*, 2C), 131.82 (d, *J* = 11.07 Hz, *aryl C*, 2C) 132.43 (d, *J* = 8.30 Hz, *aryl C*, 2C) 132.83 (s, *aryl C*, 1 C), 138.75 (m, *J* = 48.44 Hz, *aryl C*, 1C), 209.61 (d, *J* = 24.91 Hz, $C_{carbonyl}$, 1C), 218.05 (d, *J* = 31.83 Hz, $C_{carbene}$, 1C). $^{31}P\{^1H\}$ NMR (121.44 MHz, $CDCl_3$): δ 56.70. Anal. Calcd for **4** ($C_{26}H_{32}FeIN_2OP$): N, 4.65; C, 51.85; H, 5.36. Obtained: N, 5.38; C, 51.64; H, 5.80.

**Synthesis of Complex 5.** The preparation of complex **5** followed the same procedure as complex **4** with the corresponding amine (5 mL, 21.3 mmol). Complex **5** was obtained as a yellow solid (0.628 g, 93%). IR ($CDCl_3$): 1947.76 $cm^{-1}$ ($\nu_{CO}$). $^1H$ NMR (400 MHz, $CDCl_3$): δ 0.82−0.91 (m, −C*H*$_3$, 6H), 1.30 (d, *J* = 3.58 Hz, −C*H*$_2$, 9H), 1.43−1.60 (m, −C*H*$_2$, 2H), 1.60−1.86 (m, −C*H*$_2$, 3H), 1.93 (br s, −C*H*$_2$, 1H), 2.11−2.33 (m, −C*H*$_2$, 1H), 2.60−2.72 (m, −C*H*$_2$, 1H), 2.82−2.91 (m, −C*H*$_2$, 1H), 3.08−3.20 (m, −C*H*$_2$, 1H), 3.43 (dt, *J* = 13.61, 6.76 Hz, −C*H*$_2$, 1H), 3.64−3.81 (m, −C*H*$_2$, 2H), 3.95−4.06 (m, −C*H*$_2$, 1H), 4.29−4.43 (m, −C*H*$_2$, 2H), 4.50 (s, *Cp H,* 5H), 4.78 (br s, *aryl H*, 2H), 7.03−7.11 (m, *aryl H*, 2H), 7.18−7.25 (m, *aryl H*, 2H), 7.32−7.44 (m, *aryl H*, 2H), 7.47−7.56 (m, *aryl H*, 2H), 7.75 (br s, −N*H*, 1H). $^{13}C\{^1H\}$ NMR (100.58 MHz, $CDCl_3$): δ 13.82 (d, *J* = 13.56 Hz, −*C*H$_3$, 2C), 22.24 (s, −*C*H$_2$, 1C), 22.35 (s, −*C*H$_2$, 2C), 24.51 (s, −*C*H$_2$, 1C), 26.41 (s, −*C*H$_2$, 1C), 26.70 (s, −*C*H$_2$, 1C), 26.94 (s, −*C*H$_2$, 1C), 28.97 (s, −*C*H$_2$, 1C), 31.41 (d, *J* = 3.70 Hz, −*C*H$_2$, 2C), 35.11 (d, −*C*H$_2$, 1C), 49.90 (s, −*C*H$_2$, 1C), 59.78 (s, −*C*H$_2$, 1C), 85.21 (s, *Cp C*, 5C), 128.00 (d, *J* = 9.86 Hz, *aryl C*, 2C), 128.80 (d, *J* = 9.86 Hz, *aryl C*, 2C), 129.72 (d, *J* = 8.63 Hz, *aryl C*, 2C), 129.95 (s, *aryl C*, 1C), 130.82 (s, *aryl C*, 1C), 132.47 (d, *J* = 46.86 Hz, *aryl C*, 1C), 133.29 (d, *J* = 9.86 Hz, *aryl C*, 2C), 139.28 (d, *J* = 51.79 Hz, *aryl C*, 1C), 210.00 (d, *J* = 20.96 Hz, $C_{carbonyl}$, 1C), 219.16 (d, *J* = 36.99 Hz, $C_{carbene}$, 1C). $^{31}P\{^1H\}$ NMR (121.44 MHz, $CDCl_3$): δ 55.87. Anal. Calcd for **5** ($C_{34}H_{48}FeIN_2OP$): N, 3.92; C, 57.16; H, 6.77. Obtained: N, 4.12; C, 57.72; H, 7.33.

**Synthesis of Complex 6.** The preparation of complex **6** followed the same procedure as complex **4** with the corresponding amine (0.409 g, 3.82 mmol) and complex **1** (0.505 g, 0.96 mmol). Complex **6** was obtained as a yellow solid (0.550 g, 90%). IR ($CDCl_3$): 1954.00 $cm^{-1}$ ($\nu_{CO}$). $^1H$ NMR (400 MHz, $CDCl_3$): δ 1.01 (br s, −C*H*$_2$, 1H), 1.95−2.19 (m, −C*H*$_2$, 1H), 2.23 (s, −C*H*$_3$, 3H), 2.70 (t, *J* = 15.19 Hz, −C*H*$_2$, 1H), 3.04 (br s, −C*H*$_2$, 1H), 3.38 (dd, *J* = 13.83, 6.83 Hz, −C*H*$_2$, 1H), 3.59−3.77 (m, −C*H*$_2$, 1H), 4.43 (br s, −C*H*$_2$, 1H), 4.64 (br s, *Cp H*, 5H), 7.11 (br s, −N*H*, 1H), 7.19−7.26 (m, *aryl H*, 6H), 7.33 (br s, *aryl H*, 6H), 7.45 (br s, *aryl H*, 2H), 9.38 (br s, −N*H*, 1H). $^{13}C\{^1H\}$ NMR (100.58 MHz, $CDCl_3$): δ 21.77 (br s, −*C*H$_3$, 1C), 24.15 (br s, −*C*H$_2$, 1C), 34.55 (d, *J* = 25.89 Hz, −*C*H$_2$, 1C), 45.17 (br s, −*C*H$_2$, 1C), 73.52 (br s, *aryl H*, 2C), 85.60 (br s, *Cp C*, 5C), 127.63−135.68 (m, *aryl H*, 16C), 217.92 (d, *J* = 28.36 Hz, $C_{carbonyl}$, 1C), 234.63 (d, *J* = 25.89 Hz, $C_{carbene}$, 1C). $^{31}P\{^1H\}$ NMR (121.44 MHz, $CDCl_3$): δ 57.90. Anal. Calcd for **6** ($C_{29}H_{30}FeIN_2OP$): N, 4.40; C, 54.74; H, 4.75. Obtained: N, 4.26; C, 54.99; H, 4.84.

**Synthesis of Complex 7.** A solution of 2-chloroethylamine hydrochloride (0.70 g, 6.05 mmol) was treated with a solution of an equimolar amount of NaOEt (0.41 g, 6.03 mmol) in EtOH (2 mL) at room temperature. The reaction mixture was continuously stirred for 10 min to complete the formation of 2-chloroethylamine as well as a NaCl salt. The amine solution was filtered through a glass fiber filter and added dropwise to a solution of complex **1** (0.80 g, 1.51 mmol) in $CH_2Cl_2$ (10 mL) at room temperature. The mixture was stirred overnight. A yellow precipitate was collected, washed with $Et_2O$ (2 × 10 mL), and dried under vacuum. Complex **7** was obtained as a yellow solid (0.85 g, 93%). IR ($CDCl_3$): 1958.83 $cm^{-1}$ ($\nu_{CO}$). $^1H$ NMR (600 MHz, $CDCl_3$): δ 11.32−1.42 (m, −C*H*$_2$, 1H), 2.14−2.29 (m, −C*H*$_2$, 1H), 2.67−2.75 (m, −C*H*$_2$, 1H), 2.82−2.92 (m, −C*H*$_2$, 1H), 3.44 (ddd, *J* = 14.63, 9.76, 5.06 Hz, −C*H*$_2$, 1H), 3.88−3.96 (m, −C*H*$_2$, 2H), 4.01−4.09 (m, −C*H*$_2$, 1H), 4.24−4.31 (m, −C*H*$_2$, 1H), 4.35 (ddd, *J* = 14.59, 7.23, 7.10 Hz, −C*H*$_2$, 1H), 4.50−4.57 (m, *Cp H*, 5H), 6.69 (t, *J* = 5.57 Hz, −N*H*, 1H), 7.23 (dd, *J* = 10.63, 7.68 Hz, *aryl H*, 2H), 7.38 (td, *J* = 7.68, 1.92 Hz, *aryl H*, 2H), 7.42−7.53 (m, *aryl H*, 6H), 8.84 (br s, −N*H*, 1H). $^{13}C\{^1H\}$ NMR (100.58 MHz, $CDCl_3$): δ 24.71 (s, −*C*H$_2$, 1C), 35.56 (d, *J* = 22.19 Hz, −*C*H$_2$, 1C), 43.99 (s, −*C*H$_2$, 1C), 45.50 (br s, −*C*H$_2$, 1C), 47.52 (s, −*C*H$_2$, 1C), 84.67 (s, *Cp C*, 5C), 128.92 (d, *J* = 9.86 Hz, *aryl C*, 2C), 129.16 (d, *J* = 8.63 Hz, *aryl C*, 2C), 129.93 (d, *J* = 8.63 Hz, *aryl C*, 2C), 130.39 (d, *J* = 2.46 Hz, *aryl C*, 1C), 131.33 (d, *J* = 2.47 Hz, *aryl C*, 1C), 132.59 (s, *aryl C*, 1C), 132.91 (d, *J* = 9.87 Hz, *aryl C*, 1C), 138.33 (d, *J* = 49.31 Hz, *aryl C*, 1C), 211.35 (d, *J* = 28.36 Hz, $C_{carbonyl}$, 1C), 218.11 (d, *J* = 32.06 Hz, $C_{carbene}$, 1C). $^{31}P\{^1H\}$ NMR (121.44 MHz, $CDCl_3$): δ 56.44. Anal. Calcd for **7** ($C_{24}H_{27}ClFeIN_2OP$): N, 4.60; C, 47.36; H, 4.47. Obtained: N, 4.66; C, 47.58; H, 4.52.

**Synthesis of Complex 8.** A solution of 3-chloropropylamine hydrochloride (0.79 g, 6.05 mmol, $[Cl(CH_2)_2NH_3]Cl$) was treated with a solution of an equimolar amount of NaOEt (0.41 g, 6.03 mmol) in EtOH (2 mL) at room temperature. The reaction mixture was continuously stirred for 10 min to complete the formation of 2-chloroethylamine as well as a NaCl salt. The amine solution was filtered through a glass fiber membrane filter and added dropwise to a solution of complex **1** (0.80 mg, 1.51 mmol) in $CH_2Cl_2$ (10 mL) at room temperature, and then the mixture was stirred overnight. The reaction mixture was then concentrated under vacuum. $Et_2O$ (10 mL) was added to the residue, and a yellow solid precipitated and was collected on a frit, washed with pentane (2 × 5 mL), and taken to dryness under vacuum to yield complex **8** as a yellow solid (0.89 g, 95%). IR ($CDCl_3$): 1952.12 $cm^{-1}$ ($\nu_{CO}$). $^1H$ NMR (300 MHz, $CDCl_3$): δ 1.27−1.51 (m, −C*H*$_2$, 1H), 2.08−2.47 (m, −C*H*$_2$, 3H) 2.64−2.96 (m, −C*H*$_2$, 2H) 3.38−3.59 (m, −C*H*$_2$, 1H), 3.66−4.05 (m, −C*H*$_2$, 4H), 4.14−4.39 (m, −C*H*$_2$, 1H), 4.56 (d, *J* = 1.37 Hz, *Cp H*, 5H), 6.84 (br s, −N*H*, 1H), 7.18 (dd, *J* = 10.62, 7.42 Hz, *aryl H*, 2H), 7.30−7.38 (m, *aryl H*, 2H), 7.39−7.56 (m, *aryl H*, 6H), 8.41 (br s, −N*H*, 1H). $^{13}C\{^1H\}$ NMR (100.58 MHz, $CDCl_3$): δ 24.74 (s, −*C*H$_2$, 1C), 31.17 (s, −*C*H$_2$, 1C), 35.34 (d, *J* = 22.20 Hz, −*C*H$_2$, 1C), 43.11 (s, −*C*H$_2$, 2C), 45.56 (d, *J* = 2.47 Hz, −*C*H$_2$, 1C), 84.83 (s, *Cp C*, 5C), 128.44 (d, *J* = 9.86 Hz, *aryl C*, 2C), 128.87 (d, *J* = 8.63 Hz, *aryl C*, 2C), 129.80−130.15 (m, *aryl C*, 3C), 130.77 (s, *aryl C*, 1C), 132.73 (d, *J* = 9.86 Hz, *aryl C*, 2C), 133.15 (s, *aryl C*, 1C), 138.99 (d, *J* = 49.32 Hz, *aryl C*, 1C), 211.04 (d, *J* = 24.66 Hz, $C_{carbonyl}$, 1C), 218.16 (d, *J* = 32.06 Hz, $C_{carbene}$, 1C). $^{31}P\{^1H\}$ NMR (121.44 MHz, $CDCl_3$): δ 56.45. Anal. Calcd for **8** ($C_{25}H_{29}ClFeIN_2OP$): N, 4.50; C, 48.22; H, 4.69. Obtained: N, 4.43; C, 48.14; H, 4.67.

**Synthesis of Complex 9.** A suspension of complex **7** (200 mg, 0.328 mmol) in $CH_2Cl_2$ (10 mL) was reacted with a 5 mL EtOH solution of four equimolar amount of NaOEt (89.3 mg, 1.312 mmol) at room temperature. After stirring overnight, the solution mixture was taken to dryness and the residue was dissolved in the minimum amount of $CH_2Cl_2$ (3 mL). The solution was filtered through Celite for removal of a NaCl salt and excess NaOEt. The filtrate was concentrated, and $Et_2O$ (10 mL) was added to filter the solution and obtain a yellow precipitate, **9** (0.156 g, 83%). IR ($CDCl_3$): 1948.77 $cm^{-1}$ ($\nu_{CO}$). $^1H$ NMR (400 MHz, $CDCl_3$): δ 1.51 (br s, −C*H*$_2$, 1H), 1.79 (br s, −C*H*$_2$, 1H), 2.64−2.80 (m, −C*H*$_2$, 1H), 2.87−3.04 (m, −C*H*$_2$, 1H), 3.37−3.57 (m, −C*H*$_2$, 2H), 3.57−3.73 (m, −C*H*$_2$, 4H), 4.75 (s, *Cp H*, 5H), 7.13−7.23 (m, *aryl H*, 2H), 7.28−7.41 (m, *aryl H*, 3H), 7.42−7.48 (m, *aryl H*, 1H), 7.51 (t, *J* = 6.49 Hz, *aryl H*, 2H), 7.55−7.63 (m, *aryl H*, 2H), 8.31 (br s, −N*H*, 1H). $^{13}C\{^1H\}$ NMR (100.58 MHz, $CDCl_3$): δ 23.04 (s, −*C*H$_2$, 1C), 34.24 (d, *J* = 24.54 Hz, −*C*H$_2$, 1C), 44.75 (s, −*C*H$_2$, 1C), 48.39 (s, −*C*H$_2$, 1C), 52.31 (s, −*C*H$_2$, 1C), 85.47 (s, *Cp C*, 5C), 128.61 (d, *J* = 10.73 Hz, *aryl C*, 2C), 129.23 (d, *J* = 9.20 Hz, *aryl C*, 2C), 130.43 (s, *aryl C*, 1C), 130.74 (s, *aryl C*, 1C), 131.22 (d, *J* = 9.20 Hz, *aryl C*,

2C), 131.54 (d, $J$ = 9.20 Hz, *aryl C*, 2C), 211.54 (d, $J$ = 27.60 Hz, $C_{carbonyl}$, 1C), 218.81 (d, $J$ = 29.14 Hz, $C_{carbene}$, 1C). $^{31}P\{^1H\}$ NMR (121.44 MHz, $CDCl_3$): $\delta$ 56.95. Anal. Calcd for **9** ($C_{24}H_{26}FeIN_2OP$): N, 4.90; C, 50.38; H, 4.58. Obtained: N, 5.38; C, 50.08; H, 4.91.

**Synthesis of Complex 10.** A suspension of complex **8** (200 mg, 0.321 mmol) in $CH_2Cl_2$ (10 mL) was reacted with a 5 mL EtOH solution of four equimolar amount of NaOEt (87.4 mg, 1.284 mmol) at room temperature. After stirring overnight, the solution mixture was taken to dryness and the residue was dissolved in the minimum amount of $CH_2Cl_2$ (3 mL). The solution was filtered through Celite for removal of NaCl and excess NaOEt. The filtrate was concentrated and $Et_2O$ (10 mL) was added to filter the solution and obtain a yellow precipitate, **10** (0.152 g, 81%). IR ($CDCl_3$): 1952.24 $cm^{-1}$ ($\nu_{CO}$). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 1.02−1.20 (m, $-CH_2$, 1H), 1.78−1.94 (m, $-CH_2$, 1H), 1.96−2.09 (m, $-CH_2$, 1H), 2.09−2.32 (m, $-CH_2$, 1H), 2.61−2.77 (m, $-CH_2$, 1H), 2.94−3.06 (m, $-CH_2$, 1H), 3.11 (d, $J$ = 12.63 Hz, $-CH_2$, 1H), 3.26−3.53 (m, $-CH_2$, 4H), 4.26 (dd, $J$ = 14.59, 9.47 Hz, $-CH_2$, 1H), 4.67 (s, *Cp H*, 5H), 7.20−7.33 (m, *aryl H*, 4H), 7.36 (br s, *aryl H*, 4H), 7.43−7.53 (m, *aryl H*, 2H), 8.00 (br s, $-NH$, 1H). $^{13}C\{^1H\}$ NMR (100.58 MHz, $CDCl_3$): $\delta$ 20.87 (s, $-CH_2$, 1C), 22.02 (s, $-CH_2$, 1C), 34.26 (d, $J$ = 22.14 Hz, $-CH_2$, 1C), 41.17 (s, $-CH_2$, 1 C), 49.42 (s, $-CH_2$, 1C), 56.29 (br s, $-CH_2$, 1C) 84.84 (s, *Cp C*, 5C), 128.32 (d, $J$ = 11.07 Hz, *aryl C*, 2C), 128.80 (d, $J$ = 8.30 Hz, *aryl C*, 2C), 129.87 (d, $J$ = 8.30 Hz, *aryl C*, 2C), 130.74 (s, *aryl C*, 2C), 132.87 (d, $J$ = 8.30 Hz, *aryl C*, 2C), 133.38 (s, *aryl C*, 1C), 139.22 (d, $J$ = 47.06 Hz, *aryl C*, 1C), 205.75 (d, $J$ = 24.91 Hz, $C_{carbonyl}$, 1C), 218.25 (d, $J$ = 33.22 Hz, $C_{carbene}$, 1C). $^{31}P\{^1H\}$ NMR (121.44 MHz, $CDCl_3$): $\delta$ 56.21. Anal. Calcd for **10** ($C_{25}H_{28}FeIN_2OP\cdot CH_2Cl_2$): N, 4.46; C, 48.72; H, 4.65. Obtained: N, 4.38; C, 48.38; H, 4.74.

**Synthesis of Complex 11.** A solution of potassium *tert*-butoxide, $KO^tBu$ (0.22 g, 1.96 mmol), in methanol (MeOH) (5 mL) was added to a solution of complex **1** (1.01 g, 1.91 mmol) in THF (10 mL) at room temperature. The solution mixture was stirred overnight, after which the solvent was removed completely *in vacuo* and the remaining residue dissolved in benzene. The solution was filtered through Celite to remove KI. The filtrate was evaporated *in vacuo* to obtain the desired product **11** as a yellow solid (0.745 g, 90%). IR ($CDCl_3$): 1936.99 $cm^{-1}$ ($\nu_{CO}$). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 1.33−1.49 (m, $-CH_2$, 1H), 1.83−2.01 (m, $-CH_2$, 1H), 2.52−2.64 (m, $-CH_2$, 1H), 2.73−2.85 (m, $-CH_2$, 1H), 3.54 (dd, $J$ = 12.46, 9.73 Hz, $-CH_2$, 1H), 3.72 (s, $-CH_3$, 3H), 3.81 (dd, $J$ = 12.29, 7.17 Hz, $-CH_2$, 1H), 4.46 (d, $J$ = 1.37 Hz, *Cp H*, 5H), 7.26−7.34 (m, *aryl H*, 3H), 7.36−7.44 (m, *aryl H*, 5H), 7.51−7.58 (m, *aryl H*, 2H). $^{13}C\{^1H\}$ NMR (100.58 MHz, $CDCl_3$): $\delta$ 24.75 (s, $-CH_2$, 1C), 35.71 (d, $J$ = 22.14 Hz, $-CH_2$, 1C), 49.99 (d, $J$ = 4.15 Hz, $-CH_2$, 1C), 53.76 (s, $-CH_3$, 1C), 83.27 (s, *Cp C*, 5C), 127.91 (d, $J$ = 9.69 Hz, *aryl C*, 2C), 128.30 (d, $J$ = 8.30 Hz, *aryl C*, 2C), 129.26 (s, *aryl C*, 1C), 129.66 (s, *aryl C*, 1C), 130.63 (d, $J$ = 9.69 Hz, *aryl C*, 2C), 132.90 (d, $J$ = 9.69 Hz, *aryl C*, 2C), 136.04 (d, $J$ = 45.67 Hz, *aryl C*, 1C), 140.36 (d, $J$ = 41.52 Hz, *aryl C*, 1C), 198.03 (d, $J$ = 33.22 Hz, $C_{ylidene}$, 1C), 221.08 (d, $J$ = 31.83 Hz, $C_{carbonyl}$, 1C). $^{31}P\{^1H\}$ NMR (121.44, $CDCl_3$): $\delta$ 60.55. Anal. Calcd for **11** ($C_{23}H_{24}FeNO_2P$): N, 3.23; C, 63.76; H, 5.58. Obtained: N, 3.32; C, 64.11; H, 5.67.

**Synthesis of Complex 12.** The preparation of complex **12** followed the same procedure as complex **11** with $KO^tBu$ (0.22 g, 1.96 mmol) in ethanol (EtOH) (5 mL) and complex **1** (1.01 g, 1.91 mmol) in THF (10 mL). Complex **12** was obtained as a yellow solid (0.760 g, 89%). IR ($CDCl_3$): 1937.11 $cm^{-1}$ ($\nu_{CO}$). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 1.30 (t, $-CH_3$, $J$ = 7.08 Hz, 3H), 1.34−1.52 (m, $-CH_2$, 1H), 1.73−1.96 (m, $-CH_2$, 1H), 2.48−2.64 (m, $-CH_2$, 1H), 2.74 (m, $J$ = 13.46, 13.46, 6.36, 3.41 Hz, $-CH_2$, 1H), 3.43−3.59 (m, $-CH_2$, 1H), 3.74 (dd, $J$ = 12.37, 7.77 Hz, $-CH_2$, 1H), 4.02 (dq, $J$ = 10.37, 7.01 Hz, $-CH_2$, 1H), 4.17 (dq, $J$ = 10.39, 7.06 Hz, $-CH_2$, 1H), 4.43 (d, $J$ = 1.02 Hz, *Cp H*, 5H), 7.22−7.33 (m, *aryl H*, 2H), 7.33−7.43 (m, *aryl H*, 5H), 7.48−7.61 (m, *aryl H*, 3H). $^{13}C\{^1H\}$ NMR (100.58 MHz, $CDCl_3$): $\delta$ 14.99 (s, $-CH_3$, 1C), 24.78 (s, $-CH_2$, 1C), 35.38 (d, $J$ = 22.19 Hz, $-CH_2$, 1C), 49.94 (br s, $-CH_2$, 1C), 61.14 (s, $-CH_2$, 1 C), 83.46 (s, *Cp C*, 5C), 127.76 (d, $J$ = 9.86 Hz, *aryl C*, 2C), 128.19 (d, $J$ = 8.63 Hz, *aryl C*, 2C), 129.26 (s, *aryl C*, 1C), 129.49 (s, *aryl C*, 1C), 130.84 (d, $J$ = 8.63 Hz, 2C), 132.61 (d, $J$ = 8.63 Hz, 2C), 133.56, (d, $J$ = 17.26 Hz, 1 C), 136.67 (d, 1C), 197.64 (d, $J$ = 30.83 Hz, 1C, $C_{ylidene}$), 221.22 (d, $J$ = 32.06 Hz, 1C, $C_{carbonyl}$). $^{31}P\{^1H\}$ NMR (121.44 MHz, $CDCl_3$): $\delta$ 61.09. Anal. Calcd for **12** ($C_{24}H_{26}FeNO_2P$): N, 3.13; C, 64.44; H, 5.86. Obtained: N, 3.12; C, 64.47; H, 5.90.

**Synthesis of Complex 13.** The preparation of complex **13** followed the same procedure as complex **11** with $KO^tBu$ (0.22 g, 1.96 mmol) in 2-propanol ($^i$PrOH) (5 mL) and complex **1** (1.01 g, 1.91 mmol) in THF (10 mL). Complex **13** was obtained as a yellow solid (0.819 g, 93%). IR ($CDCl_3$): 1935.67 $cm^{-1}$ ($\nu_{CO}$). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 1.20 (d, $J$ = 6.14 Hz, $-CH_3$, 3H), 1.30 (d, $J$ = 6.14 Hz, $-CH_3$, 3H), 1.35−1.52 (m, $-CH_2$, 1H), 1.75−1.93 (m, $-CH_2$, 1H), 2.48−2.61 (m, $-CH_2$, 1H), 2.72 (m, $J$ = 13.48, 13.48, 6.32, 3.41 Hz, $-CH_2$, 1H), 3.52 (dd, $J$ = 12.37, 9.47 Hz, $-CH_2$, 1H), 3.69−3.81 (m, $-CH_2$, 1H), 4.40 (s, *Cp H*, 5H), 5.24 (spt, $J$ = 6.17 Hz, $-CH$, 1H), 7.27−7.33 (m, *aryl H*, 3H) 7.39−7.47 (m, *aryl H*, 5H), 7.52−7.65 (m, *aryl H*, 2H). $^{13}C\{^1H\}$ NMR (100.58 MHz, $CDCl_3$): $\delta$ 22.49 (s, $-CH_3$, 1C), 22.80 (s, $-CH_3$, 1C), 24.77 (s, $-CH_2$, 1C), 35.45 (d, $J$ = 22.57 Hz, $-CH_2$, 1C), 50.19 (d, $J$ = 5.37 Hz, $-CH_2$, 1C), 65.27 (s, $-CH$, 1C), 83.52 (s, *Cp C*, 5C), 127.71 (d, $J$ = 9.67 Hz, *aryl C*, 2C), 128.22 (d, $J$ = 9.67 Hz, *aryl C*, 2C), 129.24 (s, *aryl C*, 1 C), 129.47 (s, *aryl C*, 1C), 130.95 (d, $J$ = 8.60 Hz, *aryl C*, 2C), 132.86 (d, $J$ = 9.67 Hz, *aryl C*, 2C), 136.79 (d, $J$ = 45.13 Hz, *aryl C*, 1C), 140.00 (d, $J$ = 39.76 Hz, *aryl C*, 1C), 196.27 (d, $J$ = 33.31 Hz, $C_{ylidene}$, 1C) 221.37 (d, $J$ = 33.31 Hz, $C_{carbonyl}$, 1C). $^{31}P\{^1H\}$ NMR (121.44 MHz, $CDCl_3$): $\delta$ 61.28. Anal. Calcd for **13** ($C_{25}H_{28}FeNO_2P$): N, 3.04; C, 65.09; H, 6.12. Obtained: N, 3.00; C, 64.91; H, 6.07.

**Synthesis of Complex 14.** An equivalent amount of 6.2 M $HBF_4$ (0.12 mL, 0.744 mmol) in $Et_2O$ was added dropwise to a solution of complex **11** (0.304 g, 0.702 mmol) in $CH_2Cl_2$ (10 mL) at room temperature. The reaction solution was stirred overnight. The solution was concentrated *in vacuo*, and a yellow solid of complex **14** was precipitated by addition of diethyl ether to the residue. The yellow precipitate, complex **14** (0.340 g, 93%), was collected on a fine frit. IR ($CDCl_3$): 1960.15 $cm^{-1}$ ($\nu_{CO}$). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 1.67 (br s, $-CH_2$, 1H), 1.89 (br s, $-CH_2$, 1H), 2.88 (br s, $-CH_2$, 2H), 3.87 (br s, $-CH_2$, 2H), 4.02 (br s, $-CH_3$, 3H), 4.59 (br s, *Cp H*, 5H), 7.10−7.26 (m, *aryl H*, 2H), 7.32−7.47 (m, *aryl H*, 3H), 7.52 (br s, *aryl H*, 5H), 8.81 (br s, $-NH$, 1H). $^{13}C\{^1H\}$ NMR (100.58 MHz, $CDCl_3$): $\delta$ 24.28 (s, $-CH_3$, 1C), 34.63 (d, $J$ = 27.60 Hz, $-CH_2$, 1C), 45.10 (s, $-CH_2$, 1C), 57.50 (s, $-CH_2$, 1C), 85.56 (s, *Cp C*, 5C), 128.17−130.00 (m, *aryl C*, 5C), 130.30−132.20 (m, *aryl C*, 7C), 218.25 (d, $J$ = 27.60 Hz, $C_{carbonyl}$, 1C) 237.08 (d, $J$ = 27.60 Hz, $C_{carbene}$, 1C). $^{31}P\{^1H\}$ NMR (121.44 MHz, $CDCl_3$): $\delta$ 55.59. Anal. Calcd for **14** ($C_{23}H_{25}BF_4FeNO_2P$): N, 2.69; C, 53.01; H, 4.84. Obtained: N, 2.63; C, 52.74; H, 4.98.

**Synthesis of Complex 15.** The preparation of complex **15** followed the same procedure as complex **14** with 6.2 M $HBF_4$ (0.11 mL, 0.682 mmol) in $Et_2O$ and complex **12** (0.298 g, 0.666 mmol) in $CH_2Cl_2$ (10 mL). Complex **15** was obtained as a yellow solid (0.324 g, 91%). IR ($CDCl_3$): 1958.49 $cm^{-1}$ ($\nu_{CO}$). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 1.51 (br s, $-CH_3$, 3H), 1.71 (br s, $-CH_2$, 1H), 1.90 (br s, $-CH_2$, 1H), 2.87 (br s, $-CH_2$, 2H), 3.86 (br s, $-CH_2$, 2H), 4.25 (br s, $-CH_2$, 2H), 4.58 (br s, *Cp H*, 5H), 7.16−7.26 (m, *aryl H*, 1H), 7.33−7.47 (m, *aryl H*, 3H), 7.53 (br s, *aryl H*, 6H), 8.73 (br s, $-NH$, 1H). $^{13}C\{^1H\}$ NMR (100.58 MHz, $CDCl_3$): $\delta$ 13.88 (br s, $-CH_3$, 1C), 24.15 (br s, $-CH_2$, 1C), 34.22 (d, $J$ = 24.66 Hz, $-CH_2$, 1C), 44.83 (br s, $-CH_2$, 1C), 66.22 (br s, $-CH_2$, 1C), 85.43 (br s, *Cp C*, 5C), 127.98−129.44 (m, *aryl C*, 4 C), 130.17−132.12 (m, *aryl C*, 5C), 132.25−135.96 (m, *aryl C*, 3C), 218.09 (d, $J$ = 27.13 Hz, $C_{carbonyl}$, 1C), 236.34 (d, $J$ = 29.59 Hz,

$C_{carbene}$, 1C). $^{31}P\{^1H\}$ NMR (121.44 MHz, $CDCl_3$): $\delta$ 55.60. Anal. Calcd for **15** ($C_{24}H_{27}BF_4FeNO_2P$): N, 2.62; C, 53.87; H, 5.09. Obtained: N, 2.49; C, 54.14; H, 5.22.

**Synthesis of Complex 16.** The preparation of complex **16** followed the same procedure as complex **14** with 6.2 M $HBF_4$ (0.11 mL, 0.682 mmol) in $Et_2O$ and complex **13** (0.299 g, 0.648 mmol) in $CH_2Cl_2$ (10 mL). Complex **16** (0.310 g, 87%) as a yellow solid was obtained. IR ($CDCl_3$): 1958.91 $cm^{-1}$ ($\nu_{CO}$). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 1.46 (d, $J$ = 25.13 Hz, $-CH_3$, 6H), 1.67 (br s, $-CH_2$, 1H), 1.97 (br s, 1H), 2.86 (br s, $-CH_2$, 2H), 3.89 (br s, $-CH_2$, 2H), 4.54 (br s, *Cp H*, 5H), 5.02 (br s, $-CH$, 1H), 7.24 (br s, *aryl H*, 1H), 7.31−7.47 (m, *aryl H*, 3H), 7.52 (br s, *aryl H*, 6 H), 8.55 (br s, $-NH$, 1H). $^{13}C\{^1H\}$ NMR (100.58 MHz, $CDCl_3$): $\delta$ 21.77 (br s, $-CH_3$, 1C) 21.97 (br s, $-CH_3$, 1C) 24.15 (br s, $-CH_2$, 1C) 34.55 (d, $J$ = 25.89 Hz, $-CH_2$, 1C) 45.17 (br s, $-CH_2$, 1C) 73.52 (br s, $-CH$, 1C) 85.60 (br s, *Cp C*, 5C) 127.63−135.68 (m, *aryl C*, 12C) 217.92 (d, $J$ = 28.36 Hz, $C_{carbonyl}$, 1C) 234.63 (d, $J$ = 25.89 Hz, $C_{carbene}$, 1C). $^{31}P\{^1H\}$ NMR (121.44 MHz, $CDCl_3$): $\delta$ 56.02. Anal. Calcd for **16** ($C_{25}H_{29}BF_4FeNO_2P$): N, 2.55; C, 54.68; H, 5.32. Obtained: N, 2.49; C, 54.20; H, 5.27.

**Synthesis of Complex 17.** To a solution of 2-chloroethanol (0.3 mL, 4.46 mmol) in THF (3 mL) at room temperature was added 1.6 M *n*-BuLi in *n*-hexane (1 mL, 1.6 mmol), followed by the complex **1** (800 mg, 1.51 mmol) in $CH_2Cl_2$ (10 mL), and the reaction mixture was stirred overnight. The mixture was dried *in vacuo*, and the resulting yellow solid was dissolved in the minimum amount of $CH_2Cl_2$ (3 mL). The solution was then filtered through Celite to remove salt, and then the solvent was removed *in vacuo*. $Et_2O$ (10 mL) was added to the residue, and a yellow solid was precipitated and collected on a fine frit, washed with pentane (5 mL), and dried *in vacuo* to yield complex **17** (0.788 g, 91%). IR ($CDCl_3$): 1963.60 $cm^{-1}$ ($\nu_{CO}$). $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ 1.78 (br s, $-CH_2$, 1H) 1.85 (br s, $-CH_2$, 1H) 2.78−2.94 (m, $-CH_2$, 1H) 3.03−3.23 (m, $-CH_2$, 1H) 3.83−4.14 (m, $-CH_2$, 4H), 4.66 (t, $-CH_2$, $J$ = 9.71 Hz, 2H), 4.73 (d, $J$ = 1.14 Hz, *Cp H*, 5H) 7.22−7.33 (m, *aryl H*, 2H) 7.38−7.50 (m, *aryl H*, 3H) 7.57 (d, $J$ = 5.48 Hz, *aryl H*, 5H). $^{13}C\{^1H\}$ NMR (100.58 MHz, $CDCl_3$): $\delta$ 22.35 (s, $-CH_2$, 1C), 33.75 (d, $J$ = 27.58 Hz, $-CH_2$, 1C), 47.15 (s, $-CH_2$, 1C), 52.27 (s, $-CH_2$, 1C), 70.04 (s, $-CH_2$, 1C), 85.78 (s, *Cp C*, 5C), 128.56 (d, $J$ = 10.11 Hz, *aryl C*, 2C), 128.94 (d, $J$ = 10.11 Hz, *aryl C*, 2C), 130.07 (d, $J$ = 9.19 Hz, *aryl C*, 2C), 130.34 (s, *aryl C*, 1C), 131.12 (s, *aryl C*, 1C), 131.67 (d, $J$ = 10.11 Hz, *aryl C*, 2C), 135.35 (d, $J$ = 46.88 Hz, *aryl C*, 2C), 217.62 (d, $J$ = 26.66 Hz, $C_{carbonyl}$, 1C), 229.00 (d, $J$ = 28.50 Hz, $C_{carbene}$, 1C). $^{31}P\{^1H\}$ NMR (121.44 MHz, $CDCl_3$): $\delta$ 55.79. Anal. Calcd for **17** ($C_{24}H_{25}FeINO_2P$): N, 2.44; C, 50.29; H, 4.40. Obtained: N, 2.58; C, 50.56; H, 4.92.

**Synthesis of Complex 18.** To a solution of 3-chloroethanol (0.3 mL, 3.59 mmol) in THF (3 mL) at room temperature was added 1.6 M *n*-BuLi in *n*-hexane (1 mL, 1.6 mmol), followed by complex **1** (800 mg, 1.51 mmol) in $CH_2Cl_2$ (10 mL), and the reaction mixture was stirred overnight. The mixture was dried *in vacuo*, and the resulting yellow solid was dissolved in the minimum amount of $CH_2Cl_2$ (3 mL). The solution was then filtered through Celite to remove salt, and then the solvent was removed *in vacuo*. $Et_2O$ (10 mL) was added to the residue, and a yellow solid was precipitated and collected on a fine frit, washed with pentane (5 mL), and dried *in vacuo* to yield complex **18** as a yellow powder (0.798 g, 90%). IR ($CDCl_3$): 1966.33 $cm^{-1}$ ($\nu_{CO}$). $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ 1.33 (br s, $-CH_2$, 1H), 1.95−2.15 (m, $-CH_2$, 1H), 2.15−2.30 (m, $-CH_2$, 2H), 2.73−2.93 (m, $-CH_2$, 1H), 3.07−3.31 (m, $-CH_2$, 2H), 3.73−3.97 (m, $-CH_2$, 2H), 4.32−4.50 (m, $-CH_2$, 2H), 4.50−4.62 (m, $-CH_2$, 1H), 4.76 (s, *Cp H*, 5H), 7.24−7.58 (m, *aryl H*, 10H). $^{13}C\{^1H\}$ NMR (100.58 MHz, $CDCl_3$): $\delta$ 20.93 (s, $-CH_2$, 1C), 21.31 (s, $-CH_2$, 1C), 33.77 (d, $J$ = 24.91 Hz, $-CH_2$, 1C), 48.50 (s, $-CH_2$, 1C), 66.99 (s, $-CH_2$, 1C), 84.78 (br s, *Cp C*, 5C), 128.28 (d, $J$ = 9.69 Hz, *aryl C*, 2C), 128.65 (d, $J$ = 9.69 Hz, *aryl C*, 2C), 129.92 (br s, *aryl C*, 3C), 130.60 (s, *aryl C*, 1C), 131.91 (d, $J$ = 8.30 Hz, *aryl C*, 2C), 133.02 (d, $J$ = 48.44 Hz, *aryl C*, 1C), 137.19 (s, *aryl C*, 1C), 217.97 (d, $J$ = 29.06 Hz, $C_{carbonyl}$, 1C), 231.32 (d, $J$ = 29.06 Hz, $C_{carbene}$, 1C). $^{31}P\{^1H\}$ NMR (121.44 MHz, $CDCl_3$): $\delta$ 56.30. Anal. Calcd for **18** ($C_{25}H_{27}FeINO_2P$): N, 2.39; C, 51.13; H, 4.63. Obtained: N, 2.50; C, 51.66; H, 4.69.

**Reversible Reaction of Acyclic (Silyl)(amino) Carbene (20) to Ylidene (19) Complexes.** A suspension of $NaHB(OAc)_3$ (15.2 mg, 0.40 mmol) in $CH_2Cl_2$ (2 mL) was added to a solution of complex **20** (50.1 mg, 0.07 mmol) in $CH_2Cl_2$ (5 mL) at room temperature and was kept *under static vacuum* overnight. This step was repeated four days to complete the conversion from complex **20** to complex **19** while adding more equivalents of the reducing reagent each day. The solution was concentrated *in vacuo* for an NMR sample.

**DFT Calculations.**[52] The Amsterdam Density Functional (ADF) package (version ADF2009.01)[53,54] was used to do geometry optimizations on Cartesian coordinates as specified in the text. All structures were optimized in the gas phase starting with geometries obtained from the X-ray crystal structures. For all atoms, standard triple-$\zeta$ STA basis sets from the ZORA ADF database TZP with frozen cores were employed. The local density approximation (LDA) by Becke−Perdew was used together with the exchange and correlation corrections that are employed by default by the ADF2009.01 program suite. Calculations for all complexes were carried out using the scalar spin−orbit relativistic formalism.

**Acknowledgment.** The authors thank UBC, NSERC, CFI, and BCKDF for funding. P.L.D. thanks UCLA and the Sloan Foundation for support.

**Supporting Information Available:** Computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

(52) *ADF2009.01*; SCM; http://www.scm.com: Theoretical Chemistry, Vrije Universiteit: Amsterdam, The Netherlands.

(53) Velde, G. T.; Bickelhaupt, F. M.; Baerends, E. J.; Guerra, C. F.; Van Gisbergen, S. J. A.; Snijders, J. G.; Ziegler, T. *J. Comput. Chem.* **2001**, *22*, 931–967.

(54) Guerra, C. F.; Snijders, J. G.; te Velde, G.; Baerends, E. J. *Theor. Chem. Acc.* **1998**, *99*, 391–403.