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Reactions of the Thiocarbene Complex $Cp(CO)_2Fe[CH(SMe)]^+$ with Amines

Yeung S. Yu and Robert J. Angelici*

Department of Chemistry and Ames Laboratory—U.S. DOE,[1] Iowa State University, Ames, Iowa 50011

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Pyridine (py) reacts with $Cp(CO)_2Fe[CH(SMe)]^+$, **1**, to form the carbene adduct $Cp(CO)_2Fe[CH(SMe)(py)]^+$, **2**. With primary ($NH_2Me$, NH_2Cy, NH_2-*i*-Pr, and NH_2-*t*-Bu) and secondary ($HNMe_2$, $HNEt_2$) amines and NH_3, **1** and **2** react to form the air-stable secondary aminocarbene complexes $Cp(CO)_2Fe[CH(NR_2)]^+$. The phosphite-substituted complex $Cp(CO)(P(OPh)_3)Fe[CH(NEt_2)]^+$ was prepared similarly from $Cp(CO)(P(OPh)_3)Fe[CH(SMe)]^+$ and $HNEt_2$. Nonequivalence of the alkyl groups in ^1H NMR spectra of the complexes containing $[CH(NMe_2)]$ and $[CH(NEt_2)]$ carbene groups indicates a high barrier to rotation around the C(carbene)–N bond. The $Cp(CO)_2Fe[CH(NHR)]^+$ complexes are deprotonated by the bases NaOH–EtOH and NaH to yield the formimidoyl complexes $Cp(CO)_2Fe[CH({=}NR)]$ which their ^1H NMR spectra indicate exist in anti and syn forms. The anti:syn ratio decreases with the R group in the order *t*-Bu > *i*-Pr > Cy. Methylation of $Cp(CO)_2Fe[CH({=}NR)]$ with $MeOSO_2F$ gives a mixture of *E* and *Z* isomers of $Cp(CO)_2Fe[CH(NMe\text{-}i\text{-}Pr)]^+$. Reactions of the $Cp(CO)_2Fe[CH(NR_2)]^+$ (NR_2 = NHMe, NHCy, NH-*t*-Bu, and NMe_2) complexes with amine (HNR_2) lead to removal of the aminocarbene ligand from the metal, thereby giving the formamidinium ion $HC(NR_2)_2^+$ together with $Cp(CO)_2FeH$. A mechanism involving β-hydrogen transfer from an N atom to the Fe is proposed. The reaction of $Cp(CO)_2Fe[CH(NHCy)]^+$ with Me_3NO in MeCN, instead of giving products resulting from amine oxide attack at the carbene carbon, gives the stable CO-substituted product $Cp(CO)(MeCN)Fe[CH(NHCy)]^+$, which can also be prepared by photolysis of $Cp(CO)_2Fe[CH(NHCy)]^+$ in MeCN. New complexes are characterized by their IR and ^1H and ^{13}C NMR spectra.

Introduction

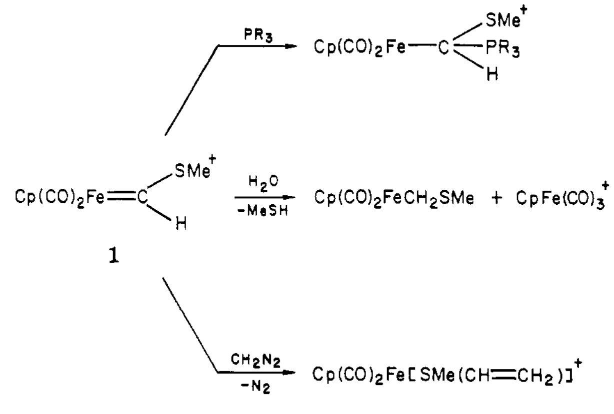
In a recent paper,[2] we reported methods of preparing the thiocarbene complex $Cp(CO)_2Fe[CH(SMe)]^+$, **1**, and its reactions with nucleophiles. With a range of phosphorus donor ligands PR_3 (PPh_2Me, PPh_3, PPh_2Cl, PCl_3, $P(OPh)_3$, $P(OCH_2)_3CMe$, PPh_2H, PCy_2H, $PPhH_2$, and $PCyH_2$), **1** gave carbene adducts of the type $Cp(CO)_2Fe[CH(SMe)PR_3]^+$ (Scheme I). Thermolysis of $Cp(CO)_2Fe[CH(SMe)(PPh_3)]^+$ gave the phosphine complex $Cp(CO)_2Fe(PPh_3)^+$, and the carbene group was liberated as the olefin *cis*/*trans*-(MeS)CH=CH(SMe). Thermolysis of the secondary phosphine adducts $Cp(CO)_2Fe[CH(SMe)(PR_2H)]^+$, R = Ph or Cy, led to rearrangement of the ylide ligand to give the phosphine complex $Cp(CO)_2Fe[PR_2(CH_2SMe)]^+$.

Reaction of **1** with H_2O gave the two organometallic products shown in Scheme I; this reaction was proposed to proceed through a formyl $Cp(CO)_2Fe[CH({=}O)]$ intermediate. Diazomethane reacted to form the methyl vinyl sulfide complex in which the olefin ligand was coordinated through the S atom. All of the reactions in Scheme I are presumed to proceed by initial nucleophilic attack at the carbene carbon atom. In the present report, we describe reactions of **1** with N-donor nucleophiles which lead to products that are quite different than those obtained from analogous P donors.

Results and Discussion

Reaction of $Cp(CO)_2Fe[CH(SMe)]^+$, 1, with Pyridine. While several carbene adducts with P-donor molecules have been described,[2,3] analogous reactions with tertiary amines are relatively rate. The DABCO (1,4-diazabicyclo[2.2.2]octane) adduct of $(CO)_5Cr[C(OMe)Ph]$ is known,[4] as is the quinuclidine adduct of $(CO)_5W[C(OMe)Ph]$.[5] Recently, the adduct $Cp(NO)(PPh_3)Re[CH_2(py)]^+$ was reported as resulting from the reaction of $Cp(NO)(PPh_3)ReCH_2^+$ and pyridine.[6] In contrast to these adduct-forming reactions, $Cp(CO)_2Fe[C(SMe)_2]^+$ reacts at room temperature with tertiary amines such as Me_3N to give $Cp(CO)_2Fe[C(SMe)_3]$ (34%) as the major product, which presumably results from initial formation of the adduct $Cp(CO)_2Fe[C(SMe)_2(NMe_3)]^+$ followed by transfer of one of the MeS^- groups to another carbene ligand.[7] Transfer of the MeS^- is presumably related to its demonstrated good leaving-group ability in other thiocarbene reactions.[8]

Scheme I



Although $\{Cp(CO)_2Fe[CH(SMe)]\}CF_3SO_3$, **1**, does not react at room temperature with DABCO, it combines rapidly with pyridine to afford the bright yellow solid adduct $\{Cp(CO)_2Fe[CH(SMe)(py)]\}CF_3SO_3$, **2**, in 38% isolated yield. In contact with moisture, **2** hydrolyzes to $Cp(CO)_2FeCH_2SMe$ and $CpFe(CO)_3^+$; this reaction presumably proceeds through **1**, which is known[2] to hydrolyze to the same products. At −20 °C under an N_2 atmosphere,

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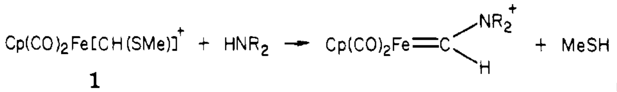
$$\underset{\mathbf{1}}{\mathrm{Cp(CO)_2Fe[CH(SMe)]^+}} + \mathrm{py} \rightarrow \underset{\mathbf{2}}{\mathrm{Cp(CO)_2Fe[CH(SMe)(py)]^+}} \quad (1)$$

2 may be stored indefinitely. While it can be stored much more readily than **1**, it is much less stable toward moisture than are the P-donor adducts $Cp(CO)_2Fe[CH(SMe)(L)]^+$, L = PPh_3 or $P(OCH_2)_3CMe$.[2] The IR spectrum (Table I) of **2** shows two strong $\nu(CO)$ absorptions (2022, 1974 cm^{-1}) similar in position to those observed for the PR_3 adducts (e.g., $Cp(CO)_2Fe[CH(SMe)(PPh_2Me)]^+$; 2021, 1971 cm^{-1}). However, the methine FeCH proton resonance (Table I) at δ 6.42 is considerably more deshielded than the corresponding signal in the PR_3 adducts (e.g., $Cp(CO)_2Fe[CH(SMe)(PPh_2Me)]^+$; δ 3.75). This suggests that the pyridine N atom is a weaker electron donor toward the carbene carbon than are the PR_3 groups. In the ^{13}C NMR spectrum (Table II), the methine FeCH carbon is observed at δ 64.5, which is more than 50 ppm downfield from the corresponding carbon of any of the PR_3 adducts.[2] The chirality of the methine carbon in **2** makes the two CO ligands diastereotopic; they are therefore observed as separate resonances (Table II), as was the case for the phosphorus-donor adducts.[2]

Reactions of $Cp(CO)_2Fe[CH(SMe)]^+$ with Amines. Secondary amines (HNR_2) are known[8,9] to replace a thioalkoxyl group in $Cp(CO)_2Fe[C(SMe)_2]^+$ to give aminothiocarbenes $Cp(CO)_2Fe[C(SMe)(NR_2)]^+$ and MeSH. Similar reactions of a few other thiocarbene complexes have also been reported.[10,11] The secondary thiocarbene ligand in $Cp(CO)_2Fe[CH(SMe)]^+$ reacts with secondary and primary amines and ammonia to give the corresponding aminocarbene products **4–11** according to eq 2.



$$\underset{\mathbf{1}}{\mathrm{Cp(CO)_2Fe[CH(SMe)]^+}} + \mathrm{HNR_2} \rightarrow \underset{\mathbf{4-11}}{\mathrm{Cp(CO)_2Fe{=}C(NR_2)(H)^+}} + \mathrm{MeSH} \quad (2)$$

NR_2 = NMe_2 (**4**), NEt_2 (**5**), NHMe (**6**), NHCy (**7**),
NH-*i*-Pr (**9**), NH-*t*-Bu (**10**), NH_2 (**11**)

The reactions occur rapidly at room temperature in CH_2Cl_2 solvent. In addition to the isolation of complexes **4–11** in yields ranging from 28 to 38%, the yellow air-sensitive $Cp(CO)_2Fe[CH(SMe)_2]$, **3**, is obtained in yields of 20–35% which depend upon the initial concentration of **1**. The formation of **3** probably occurs in a secondary reaction between the product MeSH and yet unreacted **1** (eq 3).

$$\mathrm{Cp(CO)_2Fe[CH(SMe)]^+} + \mathrm{MeSH} + \mathrm{HNR_2} \rightarrow \underset{\mathbf{3}}{\mathrm{Cp(CO)_2Fe[CH(SMe)_2]}} + \mathrm{H_2NR_2^+} \quad (3)$$

Complex **3** was identified by its previously reported IR and NMR spectra.[12] When an excess of amine is used in the reactions with **1**, yields of the aminocarbene products are drastically reduced. For example, when a 5:1 ratio of $HNMe_2$/**1** is used, the predominate products are $[CpFe(CO)_2]_2$ and $HC(NMe_2)_2^+$; the latter product was identified by its IR ($\nu(CN)$ = 1700 cm^{-1}) and NMR spectra.[13] This reaction is discussed in detail below.

The aminocarbene complexes **4–11** are air stable and, in contrast to **1**, do not hydrolyze in moist air. An attempt to form a phosphine adduct $Cp(CO)_2Fe[CH(NHCy)(PPh_3)]^+$ by reacting **7** with PPh_3 gave no reaction, unlike **1** which forms the stable $Cp(CO)_2Fe[CH(SMe)(PPh_3)]^+$.[2] These observations indicate that the $=CH(NR_2)$ ligand is less susceptible to nucleophilic attack than is $=CH(SMe)$. The better π-donor ability of N as compared with S is important in making the carbene C less electrophilic in the aminocarbene complexes. The substituted thiocarbene $Cp(CO)(P(OPh)_3)Fe[CH(SMe)]^+$ also reacts readily with $HNEt_2$ to give the pale yellow, air-stable $Cp(CO)(P(OPh)_3)Fe[CH(NEt_2)]CF_3SO_3$, **13**, in 56% yield.

Although a large number of carbene complexes in which an NHR or NR_2 group is attached to the carbene carbon are known,[3] examples with an NH_2 group are relatively rare.[14-16] When NH_3 is reacted with **1** in either CH_3CN or CH_2Cl_2, an oil, presumed to be $Cp(CO)_2Fe[CH(NH_2)]CF_3SO_3$, **11**, with $\nu(CO)$ absorptions at 2056 and 2010 cm^{-1} is obtained. Pale yellow, air-stable **11** may however be isolated (20% yield) as a solid from the reaction of $Cp(CO)_2Fe[CH(SMe)(py)]CF_3SO_3$, **2**, with NH_3. The complex was characterized by its IR and ^1H NMR spectrum that shows unresolvable and complex patterns in the NH and CH regions (Table I). The complexity of these regions is presumed to be due to coupling among the three nonequivalent protons resulting from restricted rotation around the C–NH_2 bond. A substantial rotational barrier around the C–NH_2 bond was previously observed in $(CO)_5Cr[C(Me)NH_2]$.[17]

Not only is **2** useful in preparing **11**, but also it gives higher yields of other aminocarbenes. For example, $Cp(CO)_2Fe[CH(SMe)(py)]CF_3SO_3$, **2**, reacts with $HNEt_2$ and H_2N-*t*-Bu to afford complexes **5** and **10** in yields (42 and 47%, respectively) somewhat higher than those (31 and 38%, respectively) obtained from **1** (eq 2). The amounts of **3** formed in these reactions are significantly less than obtained in reaction 2. Although extensive reactivity studies of **2** have not been undertaken, these amine reactions suggest that **2** may be a stable equivalent of **1** for other synthetic applications.

Spectroscopic Properties of the Aminocarbene Complexes. In their infrared spectra (Table I), the aminocarbene complexes **4–11** show two $\nu(CO)$ absorptions in the regions 2048–2056 and 2004–2010 cm^{-1}, which are about 20 cm^{-1} lower than for the thiocarbene **1**. This $\nu(CO)$ difference suggests that the aminocarbene ligand is a better electron-donor ligand. The higher field position of the carbene hydrogen in ^1H NMR spectra (Table I) of the aminocarbene complexes as compared with that of **1** also suggests that the NR_2 group is a stronger electron donor than the SMe group. The resonance assigned to the NH proton in complexes **6–10** disappears when D_2O is added to the NMR solutions; this indicates that the NH proton exchanges rapidly with D_2O.

The carbene carbon resonance (239.0 ppm) in the ^{13}C NMR spectrum (Table II) of **13** is 80 ppm further upfield than that (320.6 ppm) in $Cp(CO)(P(OPh)_3)Fe[CH(SMe)]^+$. The upfield position of the carbene carbon in aminocarbenes relative to thiocarbenes has been noted previously.[8,12,18]

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Table I. Infrared and ^1H NMR (δ) Spectra of the Complexes

complex	IR,[a] ν(CO), cm^{-1}	Cp	CH	NH	other
$\{Cp(CO)_2Fe[CH(SMe)]\}CF_3SO_3$ (1)	2067 (s), 2026 (s)	5.11[b]	14.86		3.00 (s, SMe)
$\{Cp(CO)_2Fe[CH(SMe)(C_5H_5N)]\}CF_3SO_3$ (2)	2022 (s), 1974 (s)	5.10[c]	6.42		[9.31 (d, J_{HH} = 5.49 Hz), 8.30 (t, J_{HH} = 6.96 Hz), 7.92 (t, J_{HH} = 6.60 Hz) (Py)], 1.92 (s, SMe)
$\{Cp(CO)_2Fe[CH(NMe_2)]\}PF_6$ (4)	2049 (s), 2005 (s)	5.30[d]	10.79		[1.94 (d, J_{HH} = 2.6 Hz), 1.89 (d, J_{HH} = 2.2 Hz) NMe]
$\{Cp(CO)_2Fe[CH(NEt_2)]\}CF_3SO_3$ (5)	2048 (s), 2004 (s)	5.59[e]	11.30		[3.99 (q, J_{HH} = 7.3 Hz), 3.96 (q, J_{HH} = 7.3 Hz) (NCH_2)], [1.47 (t, J_{HH} = 7.3 Hz), 1.36 (t, J_{HH} = 7.3) (NCH_2*Me*)]
$\{Cp(CO)_2Fe[CH(NHMe)]\}PF_6$ (6)	2055 (s), 2007 (s)	5.29[d]	10.69	10.90	3.33 (d, J_{HH} = 3.3 Hz, NMe)
$\{Cp(CO)_2Fe[CH(NHCy)]\}CF_3SO_3$ (7)	2054 (s), 2004 (s)	5.25[b]	10.76	10.55	[3.52 (br), 1.56 (m) (Cy)]
$\{Cp(CO)_2Fe[CD(NHCy)]\}CF_3SO_3$ (8)	2053 (s), 2007 (s)	5.25[b]		11.63 (br)	[3.49 (br), 1.56 (m) (Cy)]
$\{Cp(CO)_2Fe[CH(NH\text{-}i\text{-}Pr)]\}PF_6$ (9)	2053 (s), 2005 (s)	5.28[c]	10.85	10.64	3.89 (h, J_{HH} = 6.6, NC*H*Me_2), 1.38 (d, J_{HH} = 6.6, NCHMe_2)
$\{Cp(CO)_2Fe[CH(NH\text{-}t\text{-}Bu)]\}CF_3SO_3$ (10)	2055 (s), 2007 (s)	5.27[c]	10.83	10.63	1.42 (s, *t*-Bu)
$\{Cp(CO)_2Fe[CH(NH_2)]\}CF_3SO_3$ (11)	2056 (s), 2010 (s)	5.33[d]	11.30 (m)	11.51 (m)	
$\{Cp(CO)(MeCN)Fe[CH(NHCy)]\}CF_3SO_3$ (12)	1994	4.76[c]	11.62	11.84	[3.56 (m), 1.88–1.26 (m) (Cy)], 2.35 (s, MeCN)
$\{Cp(CO)(P(OPh)_3)Fe[CH(NEt_2)]\}CF_3SO_3$ (13)	1981	4.82[f]	11.36[g]		7.41 (m, Ph), [4.11, 3.89 (q, J_{HH} = 7.33 Hz, NCH_2)], [1.44, 1.30 (t, J_{HH} = 7.33 Hz NCH_2*Me*)]
$Cp(CO)_2Fe(CHNCy)$ (14)	2030 (s) , 2021 (s), 2013 (s), 1982 (sh), 1971 (vs), 1963 (s)[h]	4.85[c,i] 4.90[c,j]	10.15[i] 10.18[j,k]		2.91 (m, Cy), 1.58 (m, Cy)[i] 2.91 (m, Cy), 1.58 (m, Cy)[j]
$Cp(CO)_2Fe(CHN\text{-}i\text{-}Pr)$ (15)	2028 (sh), 2014 (s), 1980 (sh), 1971 (s), 1963 (s)[h]	4.94[c,i] 4.91[c,j]	10.21[i] 10.16[j,l]		3.20 (m, C*H*Me_2), 1.17 (d, J_{HH} = 6.23 Hz, Me)[i] 3.20 (m, C*H*Me_2), 1.22 (d, J_{HH} = 6.23 Hz, Me)[j]
$Cp(CO)_2Fe(CHN\text{-}t\text{-}Bu)$ (16)	2019 (s), 1972 (vs)[h]	4.84[c,j]	10.22[j]		1.10 (s, Me)[j]
$\{Cp(CO)_2Fe[CH(NMe\text{-}i\text{-}Pr)]\}SO_3F$ (17)	2044 (s), 2000 (s)	5.30[d]	10.83		3.90 (h, NC*H*Me),[m] 3.42 (d, NMe),[n] 1.36 (d, NCHMe_2)[p]
		5.32[d]	11.04		4.20 (h, NC*H*Me),[m] 3.45 (d, NMe),[o] 1.32 (d, NCHMe_2)[p]

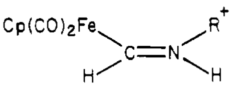
[a] CH_2Cl_2 solvent. [b] CD_2Cl_2. [c] $CDCl_3$. [d] CD_3CN. [e] $(CD_3)_2C{=}O$. [f] d, J_{PH} = 1.10 Hz. [g] d, J_{PH} = 5.13 Hz. [h] Hexane solvent. [i] Syn isomer. [j] Anti isomer. [k] d, $^4J_{HH}$ = 1.79 Hz. [l] d, $^4J_{HH}$ = 2.20 Hz. [m] J_{HH} = 6.60 Hz. [n] J_{HH} = 0.74 Hz. [o] J_{HH} = 0.73 Hz. [p] J_{HH} = 6.60 Hz.

Table II. ^{13}C NMR Spectra (ppm) of the Complexes in CD_3CN Solvent

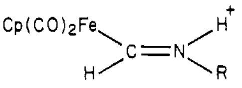
complex	carbene	CO	Cp	others
2[a]		213.6 213.2	87.2	19.8 (SMe), [143.0, 141.9, 128.2 (Py)] 64.5 (CH)
4	234.9	211.8	88.8	[55.9, 47.7 (NMe)]
5	232.4	211.7	88.9	[58.8, 53.2 (NCH_2)], [14.4, 13.2 (NCH_2*Me*)]
6	238.6	211.2	88.6	45.8 (NMe)
7	235.1	211.3	88.8	[69.9, 32.5, 25.3, 25.1 (Cy)]
8	234.5[b]	211.3	88.8	[69.8, 32.5, 25.3, 25.1 (Cy)]
9	234.5	211.5	88.8	63.3 (N*C*HMe_2), 21.8 (NCHMe_2)
10	231.2	212.5	89.7	66.5 (N*C*Me_3), 29.0 (NCMe_3)
12[a]	243.9	216.1	83.7	133.7 (CN), [69.1, 32.1, 24.8, 24.6 (Cy)], 5.1 (Me)
13	239.0[c]	216.6[d]	86.6	[151.5 (d, J_{PC} = 9.77), 131.4, 127.1, 121.9 (d, 3.82) (Ph)], [60.1, 52.1 (NCH_2)], [14.8, 13.9 (NCH_2*Me*)]

[a] $CDCl_3$ solvent. [b] t, J_{CD} = 23.44 Hz. [c] d, J_{PC} = 39.07 Hz. [d] d, J_{PC} = 41.02 Hz.

As for other secondary aminocarbene complexes,[19-21] ^{1}H NMR and ^{13}C NMR spectra of the dialkyl carbene complexes (=CH(NR$_2$)) **4**, **5**, and **13** at ambient temperature show inequivalent R groups, which indicates restricted rotation around the C(carbene)–N bond. (In the case of $Cl_3(PEt_3)_2Rh[CH(NMe_2)]$, the separate methyl resonances do not coalesce even up to 150 °C.[19a]) For the monoalkyl carbene complexes **6–10** and **12**, this means that two isomers (syn and anti) are possible:



syn



anti

However, both the ^{1}H and ^{13}C NMR spectra of these complexes indicate that only one isomer is present, even for the sterically undemanding methyl group in **6**. The CH_3 protons are observed as a doublet due to coupling with the NH proton; when D_2O is added to the solution, the doublet collapses to a singlet. While only one isomer is observed in this system, both were detected in *trans*-$Cl(PEt_3)_2Pt[CH(NHR)]^+$ (R = tolyl)[20] and syn/anti structural assignments were made based on $^3J_{NHCH}$ coupling constants. Such coupling was not resolved in **6**. However, since the anti isomer predominates in other systems where assignments could be made, it is likely that **6–10** and **12** exist as the anti isomers. Although there is no direct evidence for slow rotation around the C(carbene)–N bond, the observation and separation of anti/syn isomers of the related $Cp(CO)_2Fe[C(Ph)(NHR)]^+$[19b] suggests that such isomerization is also slow for **6–10** and **12**.

Deprotonation of $Cp(CO)_2Fe[CH(NHR)]^+$ to the Formimidoyl Complexes $Cp(CO)_2Fe[CH{=}NR]$. The amino proton of the secondary aminocarbene complexes $\{Cl(PEt_3)_2Pt[CH(NHR)]\}^+$[20] and $\{(CO)_2(PPh_3)_2(Cl)Os[CH(NHMe)]\}^+$[10] have been reported to undergo rapid exchange with D_2O and deprotonation with bases such as amines and OH^- to give the corresponding formimidoyl complexes M—CH=NR.

When **7** reacts with a saturated NaOH-EtOH solution in CH_2Cl_2, deprotonation occurs immediately to produce $Cp(CO)_2Fe(CHNCy)$, **14**, in 78% yield. The reaction of **7** with NaH also gives **14** in nearly as good yield. Compounds **9** and **10** are also deprotonated by NaOH to give $Cp(CO)_2Fe(CHN$-*i*-Pr), **15** (68%), and $Cp(CO)_2Fe(CHN$-*t*-Bu), **16** (76%), respectively. These formimidoyl complexes are very sensitive to air and even decompose thermally in a few hours at room temperature. Upon reaction with acid (CF_3SO_3H) in Et_2O, they immediately protonate to give the parent carbene complex.

Due to the instability of **14**, **15**, and **16**, elemental analyses were not performed; however, the complexes were fully characterized by their IR and NMR spectra. The IR spectrum of **16** in hexane exhibits two ν(CO) absorptions (2019, 1972 cm^{-1}), and its ^{1}H NMR spectrum in $CDCl_3$ shows the CH proton at a position upfield from that of **10**, a shift that would be expected for the removal of H^+ from the ligand (Table I). These IR and NMR data are consistent with the presence of only one isomer of this *t*-Bu complex **16**.

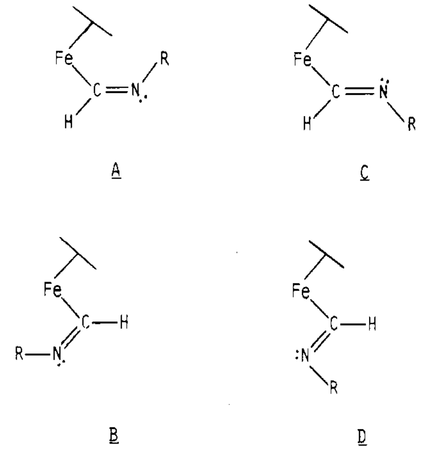


Figure 1. Four possible isomers of $Cp(CO)_2Fe(CH{=}NR)$ (CO groups omitted for clarity).

In contrast, the cyclohexyl and isopropyl derivatives **14** and **15** show more complex spectra. The IR spectra of **14** and **15** display six and five ν(CO) bands, respectively. In their ^{1}H NMR spectra, both compounds show two Cp resonances, while the formyl CH proton occurs as three lines, a doublet and singlet (Table I). The CH doublet in **15** collapses to a singlet when the methine hydrogen of the isopropyl group is irradiated in a homonuclear gated decoupled experiment; this shows that the CH doublet is caused by coupling to the *i*-Pr methine proton.

The observation of two sets of formyl CH and Cp resonances indicates that at least two isomers of **14** and **15** are in solution. However, the large number of ν(CO) bands suggests that more isomers (probably three) are present, some of which are rapidly interconverting on the ^{1}H NMR time scale. If one assumes that the most favorable orientation of the formimidoyl ligand is perpendicular to the Cp plane, as has been calculated for carbene ligands,[24-26] there are four possible isomers of the $Cp(CO)_2Fe(CH{=}NR)$ complexes (Figure 1). . If only three isomers are present as suggested by the IR spectra, the most sterically crowded A isomer (Figure 1) is most likely to be the missing isomer.

It is likely that the rate of rotation around the Fe—C bond is fast on the ^{1}H NMR time scale, whereas the rate of rotation around the C=N bond is slow. Thus, the separate signals for the Cp and formyl CH protons are most logically assigned to the syn B isomer and an average of the anti C and D isomers.

Anti/syn structural assignments to the isomers of $Cl(PEt_3)_2Pt(CH{=}NR)$, where R = *p*-tolyl, were made on the basis of ^{1}H NMR studies.[22d] Other anti/syn assignments to formimidoyl complexes are more difficult to find in the literature. However, it seemed that coupling constants between the carbene (CH) proton and protons on the R group may be useful. Despite numerous ^{1}H NMR studies of organic formimidoyl compounds, long-range coupling constants $^4J_{CHNCH_2R'}$ across the C=N bond for the syn and anti isomers are few in number because most iminoyl formyls exist predominately in the anti form.[27] The ^{1}H NMR spectrum[28] of $H_2C{=}NCH_3$ exhibits an ABX_3 pattern

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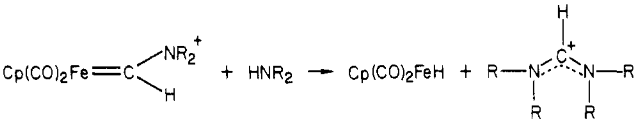
with $^4J_{cis}$ identical with $^4J_{trans}$, indicating that ^4J coupling constants may not be helpful in assigning syn or anti structures to the isomers of **14** and **15**. In the related vinyl system $H_2C{=}C(CH_3)X$, however, it has been suggested[29] that ^4J cis is larger than $^4J_{trans}$. Assuming that $^4J_{cis} > {^4J_{trans}}$ in **14** and **15**, we tentatively assign the CH doublet to the anti isomers (C and D) and the singlet to the syn isomer (B). Using this assignment, the anti/syn isomer ratio is 52:48 for **15** and 58:42 for **15** in $CDCl_3$ solvent. Including the *t*-Bu complex which exists as only one isomer, presumably the anti, the anti/syn ratio decreases in the expected order *t*-Bu > *i*-Pr > Cy.

Since the anti/syn isomeric mixtures of **14** and **15** are generated by deprotonating one isomer, presumably the anti, of **7** and **9**, anti/syn isomerization must be occurring after the removal of the amine proton, i.e., the formimidoyl complexes must isomerize quite rapidly. This rapid isomerization of a formimidoyl group was observed in $Cl(PEt_3)_2Pt(CH{=}NR)$ using variable-temperature ^1H NMR.[22d]

Evidence that suggests the formimidoyl groups in **14** and **15** also isomerize fast is the rapid reaction of the anti/syn mixtures of **14** and **15** with CF_3SO_3H to give exclusively the anti isomers of **7** and **9**. Further evidence comes from reactions of **15** with varying amounts of $MeOSO_2F$ in Et_2O solution at room temperature. When 6 equiv of $MeOSO_2F$ is added to **15**, a precipitate of $\{Cp(CO)_2Fe[CH(NMe\text{-}i\text{-}Pr)]\}SO_3F$, **17**, characterized by its IR and ^1H NMR spectra, forms rapidly. The ^1H NMR spectrum (Table I) of **17** shows the presence of two isomers, presumably the *E* and *Z* isomers resulting from restricted rotation around the C(carbene)–N bond, in relative amounts of 62:38. When only 3 equiv of $MeOSO_2F$ is used under the same conditions, the relative amounts of the isomers changes to 95:5. The change in isomer distribution with varying amounts of $MeOSO_2F$ suggests that the syn and anti isomers of **15** are methylated at different rates and syn/anti isomerization in **15** is occurring during the rapid methylation reaction. It also suggests that methylation occurs more rapidly, or by a different mechanism, than protonation by CF_3SO_3H which only gives the anti isomer. Although further study of this reaction is necessary, it is clear that the different isomer distributions are not caused by isomerization of the product **17**.

Reaction of $Cp(CO)_2Fe[CH(NR_2)]^+$ with Amines. As noted previously $Cp(CO)_2Fe[CH(SMe)]^+$, **1**, reacts with excess NH_2Cy to give $[Cp(CO)_2Fe]_2$ and $HC(NHCy)_2^+$. It seemed likely that this reaction proceeded through $Cp(CO)_2Fe[CH(NHCy)]^+$, **7**, as an intermediate which reacted with additional amine to give the observed products. Thus, the reaction of **7** with NH_2Cy was examined more closely.

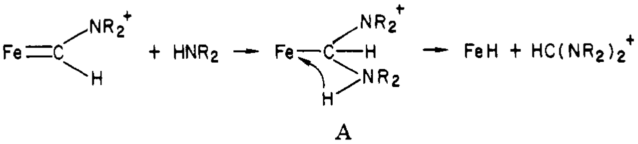
When 5 equiv of NH_2Cy reacts with **7** in CH_2Cl_2 at room temperature, 75% of **7** is consumed in 30 min and new bands corresponding to the formamidinium ion $HC(NHCy)_2^+$ ($\nu(CN)$ = 1712 cm^{-1}) and $Cp(CO)_2FeH$ ($\nu(CO)$ = 2010 (s), 1958 (vs) cm^{-1}) appear in IR spectra of the reaction solution. When the solution is vacuum distilled, $Cp(CO)_2FeH$ is collected together with the solvent. The spectrum of $Cp(CO)_2FeH$ is identical with that of a sample synthesized from $Cp(CO)_2FeCl$ and $NaBH_1$.[30] When the reaction is allowed to stand for longer times, the $Cp(CO)_2FeH$ decomposes to $[Cp(CO)_2Fe]_2$ as has been noted previously.[30,31] The formamidinium product $[HC(NHCy)_2]CF_3SO_3$ is isolated as a white solid whose IR and ^1H NMR spectra are the same as those of an authentic sample prepared from $CyN{\equiv}C$ and H_2NCy followed by protonation with CF_3SO_3H.[32] The identity of the formamidinium ion was confirmed by its mass spectrum[33,34] which showed a peak at *m/e* 209 for the parent $HC(NHCy)_2^+$. Thus the overall reaction proceeds as follows with no other side products:



NR_2 = NHMe, NHCy, NH-*t*-Bu, NMe_2

(4)

Scheme II



A

Fe = $Cp(CO)_2Fe$

Since no other reactions of secondary aminocarbene complexes in which the carbene ligand is removed from the metal have been reported, it was of interest to examine the mechanism of reaction 4. In order to determine whether the carbene CH proton remained attached to the carbon in the formamidinium product or was transferred to the $Cp(CO)_2FeH$ product, the deuterated complex $\{Cp(CO)_2Fe[CD(NHCy)]\}CF_3SO_3$ was reacted with 5 equiv of H_2NCy. The mass spectrum of the organic product showed a peak for the parent ion $DC(NHCy)_2^+$ at *m/e* 210. The ^1H NMR spectrum of the formamidine DC(NHCy)(NCy) generated by adding *n*-BuLi to the organic reaction product showed no methine proton resonance. Thus, the carbene CH proton is not transferred to the iron during the reaction but remains attached to the carbon in the formamidinium product.

One mechanism for reaction 4 would involve initial rapid deprotonation of the carbene $Cp(CO)_2Fe[CH(NHR)]^+$ by the amine to give the formimidoyl $Cp(CO)_2Fe(CH{=}NR)$ which would react with additional amine to give the observed products. This mechanism may be discounted because there is no reaction between **14** and 5 equiv of NH_2Cy at room temperature in CH_2Cl_2 solvent during a 30-min period, a time during which **7** would have reacted to a major extent with NH_2Cy. When 5 equiv of CF_3SO_3H is added to the reaction solution, an IR spectrum of the solution shows that **7** forms immediately and bands for $Cp(CO)_2FeH$ and the formamidinium ion grow in more slowly. Thus, the protonated form of the complex, i.e., $Cp(CO)_2Fe[CH(NHR)]^+$, is necessary for reaction 4 to proceed.

The most likely mechanism for reaction 4 then appears to involve initial amine attack at the carbene carbon to form intermediate A (Scheme II), which undergoes β-hydrogen transfer from the N to the Fe with liberation of the

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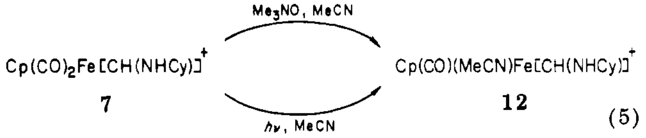
formamidinium product. Instead of this β-hydrogen transfer mechanism, it is possible that the N atom of intermediate A is deprotonated by excess amine to give the neutral $Cp(CO)_2Fe[CH(NR_2)_2]$, B. If one of the R groups were a hydrogen in this intermediate (B), as in the reaction of NH_2Cy, β-hydrogen transfer in B would lead to $Cp(CO)_2FeH$ and the formamidine. That β-hydrogen transfer in intermediate B is not involved is established from the reaction of $Cp(CO)_2Fe[CH(NMe_2)]^+$, 4, with $HNMe_2$. Although slower than the NH_2Cy reaction, this reaction also produces $Cp(CO)_2FeH$, $[Cp(CO)_2Fe]_2$, and $HC(NMe_2)_2^+$ (identified by its IR and ^1H NMR spectra).[13] Since a type B intermediate in this reaction would have no β-hydrogen atoms, a β-hydrogen transfer would not be possible. Thus, the most probable mechanism for reaction 4 using primary and secondary amines is that summarized in Scheme II.

Reaction 4 also occurs between 6 and NH_2Me and between 10 and *t*-$BuNH_2$. Steric factors are important as the qualitative rates of these reactions decrease in the order $MeNH_2 > CyNH_2 > t\text{-}BuNH_2$. When 7 is reacted with $MeNH_2$, $Cp(CO)_2FeH$ and a mixture of the three possible formamidinium products $HC(NHR)(NHR')^+$, where R and/or R′ are Me or Cy, are obtained. The different formamidinium products were identified by their mass spectra. This mixture could arise from exchange reactions of the initial formamidinium product with free amines. Indeed, $HC(NHCy)_2^+$ reacts readily with $MeNH_2$ in CH_2Cl_2 at room temperature for 30 min to give all three possible $HC(NHR)(NHR')^+$ products.

Decarbonylation of $Cp(CO)_2Fe[CH(NHCy)]^+$, 7. Although Me_3NO is known[35-37] to attack CO ligands and convert them to free CO_2, it seemed that in carbene complexes such as 7, Me_3NO may attack the carbene center converting it into the formamide HC(=O)(NHCy). When 1.2 equiv of Me_3NO is added to a MeCN solution of 7, only the CO-substituted product $Cp(CO)(MeCN)Fe[CH(NHCy)]CF_3SO_3$, 12, is obtained in 93% yield (eq 5). The same yellow, air-stable, crystalline product (85% yield) is obtained when a MeCN solution of 7 is irradiated with 254-nm light for 2 h.



(5)

Experimental Section

General Methods. Methods and instrumentation were the same as described in the previous paper.[2] All amines, except very volatile ones, Me_2NH, $MeNH_2$, and NH_3, were stored over KOH overnight and distilled from BaO. The $Me_3NO\cdot 2H_2O$ was dried by azeotropic distillation of the water with benzene. Syntheses of the complexes $Cp(CO)_2Fe[CH(SMe)]CF_3SO_3$, 1,[2] and $Cp(CO)(P(OPh)_3)Fe[CH(SMe)]CF_3SO_3$[2] were described previously.

Reaction of $\{Cp(CO)_2Fe[CH(SMe)]\}CF_3SO_3$, 1, with Pyridine. A sample of 0.5 mL of pyridine was added to a 10 mL CH_2Cl_2 solution of 1 (0.24 g, 0.62 mmol); a golden solution was obtained. This solution was evaporated to dryness, and the residue was washed a few times with Et_2O to remove a trace amount of 3, leaving an oily substance. That material was allowed to recrystallize from CH_2Cl_2–Et_2O at -20 °C for 24 h to yield $\{Cp(CO)_2Fe[CH(SMe)(py)]\}CF_3SO_3$, 2 (0.11 g, 38%), and traces of 3, $Cp(CO)_2FeCH_2SMe$, and $CpFe(CO)_3^+$. The remaining mother liquor was then diluted with Et_2O and placed in a -20 °C freezer for recrystallization. After a few days, golden platelike crystals of 2 (0.078 g, 27%) were obtained. They are very sensitive to moisture and decompose upon prolonged exposure to light. They may be kept indefinitely at -20 °C under an inert atmosphere. Anal. Calcd for $C_{15}H_{14}O_5S_2F_3NFe$: C, 38.71; N, 3.01, H, 3.01. Found: C, 39.47; N, 2.97; H, 3.13.

Synthesis of $\{Cp(CO)_2Fe[CH(NMe_2)]\}PF_6$, 4. A sample of 1 (0.24 g, 0.62 mmol) was suspended in 10 mL of CH_2Cl_2; 15 mL of gaseous Me_2NH was bubbled into the mixture by using a syringe. The golden solution turned yellow-brown. The solution was diluted with 10 mL of heptane; its volume was reduced to half under vacuum, and the remaining solvent was decanted affording a brown residue. The product was obtained by metathesis with $(NH_4)PF_6$ in acetone and recrystallization from CH_2Cl_2–Et_2O at -20 °C to furnish 4 (0.070 g, 30%). Anal. Calcd for $C_{10}H_{12}O_2NPF_6Fe$: C, 31.68; H, 3.17; N, 3.70. Found: C, 31.68; H, 3.16; N, 3.49.

Synthesis of $\{Cp(CO)_2Fe[CH(NEt_2)]\}CF_3SO_3$, 5. Diethylamine (65 μL, 0.62 mmol) was added to a rapidly stirred CH_2Cl_2 suspension of 1 (0.24 g, 0.62 mmol) and allowed to react for 2 min. The solution volume was reduced, giving a precipitate which was recrystallized from CH_2Cl_2–Et_2O at -20 °C. The product 5 (0.079 g, 31%) was characterized by its spectra (Tables I and II).

Reaction of $\{Cp(CO)_2Fe[CH(SMe)(py)]\}CF_3SO_3$, 2, with Et_2NH. Diethylamine (14 μL, 0.12 mmol) was injected into a 5 mL CH_2Cl_2 solution containing 2 (0.03 g, 0.06 mmol). Subsequently, 10 mL of heptane was added. The resulting solution was slowly evaporated under vacuum until the bulk of the CH_2Cl_2 was removed; precipitation was apparent. The rest of the heptane was decanted, leaving a pale yellow precipitate, which was recrystallized from CH_2Cl_2–Et_2O at -20 °C to afford 5 (0.010 g, 42%).

Synthesis of $\{Cp(CO)_2Fe[CH(NHMe)]\}PF_6$, 6. Ten milliliters of gaseous methylamine was bubbled into a 10 mL CH_2Cl_2 solution containing 1 (0.24 g, 0.62 mmol). The resulting solution was stirred for 2 min and was then evaporated to dryness under reduced pressure; the remaining residue was washed with Et_2O to remove 3, metathesized with $(NH_4)PF_6$ in acetone, and recrystallized from CH_2Cl_2–Et_2O at -20 °C to give 6 (0.063 g, 28%). Anal. Calcd for $C_9H_{10}O_2NPF_6Fe$: C, 29.50; N, 3.84; H, 2.74. Found: C, 29.72; N, 3.58; H, 2.75.

Preparation of $\{Cp(CO)_2Fe[CH(NHCy)]\}CF_3SO_3$, 7. To a 10 mL CH_2Cl_2 solution of 1 (0.24 g, 0.62 mmol) was added cyclohexylamine (80 μL, 0.62 mmol). The mixture was stirred for 2 min and then diluted with 10 mL of heptane. After the solution volume was reduced to half under reduced pressure, a yellow solution containing 3 and a pale yellow precipitate were evident. The solution was decanted, and the resulting residue was washed with Et_2O and then recrystallized from CH_2Cl_2–Et_2O at -20 °C affording pale yellow analytically pure crystals of 7 (0.094 g, 35%). This substance is stable in air and may be stored indefinitely in the dark at -20 °C under N_2. Anal. Calcd for $C_{15}H_{18}O_5NF_3SFe$: C, 41.20; H, 4.12; N, 3.20. Found: C, 41.23; H, 4.25; N, 3.16.

Synthesis of $\{Cp(CO)_2Fe[CD(NHCy)]\}CF_3SO_3$, 8. A freshly prepared sample of $\{Cp(CO)_2Fe[CD(SMe)]\}CF_3SO_3$[2] (0.10 g, 0.26 mmol) was allowed to react with 32 μL (0.26 mmol) of cyclohexylamine in 10 mL of CH_2Cl_2. Purification as in the preceding procedure afforded 8 (0.036 g, 32%).

Synthesis of $\{Cp(CO)_2Fe[CH(NH\text{-}i\text{-}Pr)]\}PF_6$, 9. As in the preparation of 6, the reaction of isopropylamine (0.036 g, 0.62 mmol) and 1 (0.24 g, 0.62 mmol) in 10 mL of CH_2Cl_2 afforded 9 (0.074 g, 30%), which was characterized by its IR and NMR spectra.

Preparation of $\{Cp(CO)(P(OPh)_3)Fe[CH(NEt_2)]\}CF_3SO_3$, 13. A freshly prepared sample of $\{Cp(CO)(P(OPh)_3)Fe[CH(SMe)]\}CF_3SO_3$ (0.094 g, 0.14 mmol) was taken up in 10 mL of CH_2Cl_2; Et_2NH (27 μL, 0.28 mmol) was added. Then 5 mL of heptane was added to the solution, and the solution volume was slowly reduced to one-third its original size; a pale yellow precipitate formed. The remaining solvent was carefully decanted, and the precipitate was recrystallized from CH_2Cl_2–Et_2O at -20 °C to afford bright yellow crystals of 13 (0.054 g, 56%). Anal. Calcd for $C_{30}H_{31}NO_7F_3PSFe$: C, 51.95; H, 4.47; N, 2.02. Found: C, 51.61; H, 4.41; N, 1.87.

Synthesis of $\{Cp(CO)_2Fe[CH(NH\text{-}t\text{-}Bu)]\}CF_3SO_3$, 10. Analogous to the preparation of 7, the reaction of *tert*-butylamine (0.045 g, 0.62 mmol) and 1 (0.24 g, 0.62 mmol) in CH_2Cl_2 produced a 0.15-g mixture of 10 and $(NH_3\text{-}t\text{-}Bu)CF_3SO_3$ upon recrystallization from CH_2Cl_2–Et_2O at -20 °C. The mixture was dissolved in 5 mL of CH_2Cl_2, and 100 μL of NaOH-saturated EtOH was added. The solution was allowed to react for 2 min and was then pumped to dryness. The resulting residue was extracted with hexane to give a golden solution after it had been filtered through a Celite-padded frit under N_2. The hexane was evaporated under vacuum, and the residue was dissolved in Et_2O. The ether solution was treated with CF_3SO_3H until precipitation was completed (ca. 35 μL). The precipitate was recrystallized from CH_2Cl_2–Et_2O at −20 °C affording analytically pure crystals of **10** (0.097 g, 38%). Anal. Calcd for $C_{13}H_{16}O_5F_3SNFe$: C, 37.96; N, 3.41; H, 3.89. Found: C, 37.55; N, 3.44; H, 4.00.

Reaction of {Cp(CO)$_2$Fe[CH(SMe)(py)]}CF$_3$SO$_3$, 2, with *t*-BuNH$_2$. A sample of *t*-BuNH$_2$ (12 μL, 0.12 mmol) was added to **2** (0.030 g, 0.064 mmol) in 5 mL of CH_2Cl_2; the resulting solution was stirred for 10 min. The solvent was then removed under reduced pressure, and the residue was recrystallized from CH_2Cl_2–Et_2O at −20 °C to provide **10** (0.012 g, 47%).

Reaction of {Cp(CO)$_2$Fe[CH(SMe)(py)]}CF$_3$SO$_3$, 2, with NH$_3$. A 5-mL gas sample of NH_3 was bubbled slowly (ca. 30 s) into a rapidly stirred 10-mL CH_2Cl_2 solution of **2** (0.030 g, 0.064 mmol); as soon as the addition of ammonia was completed, the solution was diluted with 10 mL of heptane. The solution volume was reduced to half by fast evaporation under reduced pressure. The remaining solvent was decanted, yielding a pale yellow precipitate. It was recrystallized from CH_2Cl_2–Et_2O at −20 °C to give {Cp(CO)$_2$Fe[CH(NH$_2$)]}CF$_3$SO$_3$, **11** (4 mg, 20%). It is quite stable to air and only soluble in very polar organic solvents, e.g., CH_2Cl_2 and MeCN. It was characterized by its spectra (Table I).

Preparation of Cp(CO)$_2$Fe[CH(NCy)], 14. To a 2 mL CH_2Cl_2 solution of **7** (0.030 g, 0.069 mmol) was added 100 μL of NaOH-saturated EtOH; the light yellow solution turned gold at once. The solution was evaporated to dryness under reduced pressure; the remaining residue was extracted with hexane. The extract was then filtered through a Celite-padded frit under N_2 and pumped dry under vacuum, leaving a thin yellow film of **14** (0.015 g, 78%). Compound **14** is very sensitive to air and decomposes at room temperature under N_2 when allowed to stand for a few hours to give [Cp(CO)$_2$Fe]$_2$ and cyclohexyl isocyanide, which was identified by its characteristic odor.

Like the NaOH–EtOH reaction, the reaction of **7** with 50% NaH–mineral oil also produced a 75% yield of **14** under similar conditions.

Preparation of Cp(CO)$_2$Fe[CH(N-*i*-Pr)], 15. Analogous to the preparation of **14**, the reaction of **9** (0.030 g, 0.076 mmol) and 100 μL of NaOH-saturated EtOH in 2 mL of CH_2Cl_2 produced **15** (0.013 g, 68%).

Synthesis of Cp(CO)$_2$Fe[CH(N-*t*-Bu)], 16. Following the preparation of **14**, **10** (0.030 g, 0.73 mmol) reacted with 100 μL of NaOH–EtOH to yield **16** (0.014 g, 76%).

Reaction of Cp(CO)$_2$Fe[CH(N-*i*-Pr)] with MeOSO$_2$F. Freshly prepared **15** (0.013 g, 0.053 mmol) in 2 mL of Et_2O was stirred vigorously, and 25 μL (0.30 mmol) of MeOSO$_2$F was injected; a pale yellow precipitate formed. The solution was carefully decanted, leaving the precipitate which was then washed with Et_2O a few times and pumped to dryness in vacuo to give an isomeric mixture of {Cp(CO)$_2$Fe[CH(N(Me)(*i*-Pr)]}SO$_3$F, **17** (0.013 g, 77%). Likewise, **17** was isolated in 74% yield when 3 equiv of MeOSO$_2$F was employed in the reaction. The product was characterized by its IR and NMR spectra.

Reaction of {Cp(CO)$_2$Fe[CH(NHCy)]}CF$_3$SO$_3$, 7, with H$_2$NR. A 5-mg (0.01-mmol) sample of **7** was dissolved in 1 mL of CH_2Cl_2; 5 μL (0.05 mmol) of CyNH$_2$ was injected. The mixture was stirred for 30 min. After that time, the IR spectrum of the solution showed that ~75% of **7** had been consumed, and Cp(CO)$_2$FeH (2010 (s), 1958 (vs) cm^{-1}) and *N,N'*-dicyclohexylformamidinium (1712 (vs) cm^{-1}) had formed. The solvent was evaporated, and the remaining solid was found to contain [Cp(CO)$_2$Fe]$_2$ and the organic product; this solid was extracted with Et_2O, and its mass spectrum was obtained. It showed peaks at *m/e* 209 (HC(NHCy)$_2$$^+$ M), 208 (M − H), and 110 (M − CyNH$_2$).

Under the same conditions, 5 equiv of NH$_2$Me also converted 75% of **7** to Cp(CO)$_2$FeH and a mixture of [HC(NHR)(NHR')]CF$_3$SO$_3$ (R and/or R' = Cy or Me) in 20 min. The [HC(NHCy)(NHMe)]CF$_3$SO$_3$ compound was the major product on the basis of the mass spectrum, which gave peaks at the following *m/e* values: 141, HC(NHCy)(NHMe)$^+$, M; 140 (M − H); 110 (M − MeNH$_2$).

The reaction of *t*-BuNH$_2$ with **7** was noticeably slower, and 20 equiv of the amine were needed to observe appreciable reaction.

Reaction of {Cp(CO)$_2$Fe[CD(NHCy)]}CF$_3$SO$_3$, 8, with NH$_2$Cy. A 30-mg (0.068-mmol) sample of **8** reacted with 60 μL (0.30 mmol) of CyNH$_2$ in 5 mL of CH_2Cl_2. After 30 min of reaction, the solution was evaporated, and the residue was analyzed by MS; the spectrum showed peaks at *m/e* values of 210 (DC(NHCy)$_2$$^+$, M), 209 (M − H), and 111 (M − CyNH$_2$), which demonstrated that the deuterium was incorporated into the formamidinium product. After MS study, the sample was allowed to react with *n*-BuLi in THF to afford DC(NHCy)(NCy), whose ^{1}H NMR spectrum in CD$_3$CN showed no δ 7.31 resonance for the CHN$_2$ proton which was observed in the hydrogen analogue.

Decarbonylation of {Cp(CO)$_2$Fe[CH(NHCy)]}CF$_3$SO$_3$, 7. Into a 5 mL CH_2Cl_2 solution of **7** (0.030 g, 0.068 mmol) was injected 670 μL of a 0.123 M acetonitrile solution of Me$_3$NO; the pale yellow solution turned yellow-red instantly. The solution was allowed to stir for an additional 10 min and was evaporated to dryness in vacuo. Extraction with CH_2Cl_2 and evaporation of the solvent gave {Cp(CO)(MeCN)Fe[CH(NHCy)]}CF$_3$SO$_3$, **12** (0.028, 93%).

A 0.10-g sample of **7** was added to a quartz tube equipped with a magnetic stir bar and a water-cooled probe; then 35 mL of acetonitrile was added. The solution was irradiated with UV light at 254 nm for 2 h at ambient temperature which was maintained by running water through the cold finger; a brown solution was obtained. Evaporation and recrystallization from CH_2Cl_2–Et_2O–hexane at −20 °C afforded golden crystals of **12** (0.086 g, 85%). Anal. Calcd for $C_{16}H_{21}O_4SF_3Fe$: C, 42.67; H, 4.67; N, 6.22. Found: C, 43.28; H, 4.70; N, 6.08.

Registry No. **1**, 76136-46-4; **2**, 87249-67-0; **3**, 76136-44-2; **4**, 87249-69-2; **5**, 87249-71-6; **6**, 87249-73-8; **7**, 87249-75-0; **8**, 87249-77-2; **9**, 87249-79-4; **10**, 87249-81-8; **11**, 87249-83-0; **12**, 87249-85-2; **13**, 87249-87-4; **14** (syn), 87304-50-5; **14** (anti), 87249-74-9; **15** (syn), 87304-51-6; **15** (anti), 87249-78-3; **16**, 87249-80-7; (*E*)-**17**, 87249-89-6; (*Z*)-**17**, 87304-53-8; Cp(CO)$_2$FeCH$_2$SMe, 12108-33-7; CpFe(CO)$_3$$^+$, 32660-74-5; {Cp(CO)$_2$Fe[CD(SMe)]}CF$_3SO_3$, 87249-91-0; {Cp(CO)P(OPh)$_3$)Fe[CH(SMe)]}CF$_3$SO$_3$, 85629-31-8; [Cp(CO)$_2$Fe]$_2$, 38117-54-3; Cp(CO)$_2$FeH, 35913-82-7; NHMe$_2$, 124-40-3; HNEt$_2$, 109-89-7; NH$_2$Me, 74-89-5; NH$_2$Cy, 108-91-8; NH$_2$-*i*-Pr, 75-31-0; NH$_2$-*t*-Bu, 75-64-9; NH$_3$, 7664-41-7; MeOSO$_2$F, 421-20-5; CyN≡C, 931-53-3; [HC(NHCy)$_2$]CF$_3$SO$_3$, 87249-63-6; [HC(HHCy)(NHMe)CF$_3$SO$_3$, 87249-64-7.