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STRUCTURAL AND ROTATIONAL ISOMERISM IN DIAMINOCARBENE COMPLEXES OF IRON

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Summary

Primary amines react with a variety of cationic and neutral iron isocyanide complexes to yield structural and rotational diaminocarbene isomers characterized by variable temperature ^1H and ^{13}C NMR spectra. Structural isomers result from the conversion of amines to isocyanide ligands via the base-catalyzed nucleophilic attack of initially formed diaminocarbenes on cis isocyanides. Although rotational barriers are insensitive to variation of metal and carbene substituents, the effect on isomer populations is often marked. Factors influencing structural and rotational isomeric preferences are discussed.

INTRODUCTION

The nucleophilic reaction of primary amines with coordinated isocyanides to yield diaminocarbenes has been reported for a variety of transition metal systems.[1,2] Carbene complexes of this type are often characterized by restricted rotation about carbon-nitrogen bonds, resulting in rotational isomerism when nitrogen substituents are nonequivalent.[3,4,5] Little is known, however, of the factors influencing rotational barriers or preferred rotamer configurations.

In the present study we have investigated the reaction of primary amines with isocyanide complexes of the form η^5-$C_5H_5Fe(CO)(X)(CNR)$ where

$X = CN$, CNR, or PR_3. This system appeared to us to offer a wide variety of steric, electronic, and potentially stereoselective environments in which to study diaminocarbene formation and its rotational characteristics. Also, the presence of cis isocyanides in complexes where $X = CNR$ presented the possibility of amine addition to both ligands to form chelated species. This phenomenon has been observed in a number of octahedral metal complexes[1,6,7] containing cis isocyanides and was also shown to result in the conversion of primary amines to coordinated isocyanides when reversible ring opening and closing occurred.[8]

The only previous work with this system was the report by Angelici that methylamine reacts with the cationic species $\eta^5\text{-}C_5H_5Fe(CO)(CNMe)_2^+$ and $\eta^5\text{-}C_5H_5Fe(CO)(PPh_3)(CNMe)^+$ to form monodentate dimethylaminocarbenes.[5] Despite the presence of cis isocyanides in the former complex, chelated products were not observed.

RESULTS AND DISCUSSION

Diaminocarbene formation and amine to isocyanide conversion in bis-isocyanide complexes

Primary amines reacted with cyclopentadienyl and indenyl iron complexes containing equivalent cis isocyanide ligands to yield species having a single diaminocarbene moiety:

$$CpFe(CO)(CNR)_2^+ \xrightarrow{R'NH_2} CpFe(CO)(CNR)[C(NHR)(NHR')]^+$$

Reaction rates depended primarily on the identity of the amine and decreased markedly in the sequence $MeNH_2 > EtNH_2 \gg i\text{-}PrNH_2 \gg t\text{-}BuNH_2$. Using an excess of amine at room temperature, reactions of bisisocyanides were 90% complete in one to four hours for methylamine and ethylamine addition while isopropylamine required nearly two hundred hours and tertbutylamine necessitated refluxing reaction mixtures for more than five hundred hours. Reactions were monitored by infrared spectra which showed a decrease in the carbonyl stretching frequency of nearly 50 cm^{-1}, relative to bisisocyanide complexes, and the loss

TABLE 1

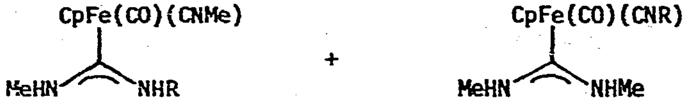
INFRARED SPECTRA IN C≡O AND C≡N STRETCHING REGIONS

Compound	$\nu(C\equiv O)$[a]	$\nu(C\equiv N)$[a]	$\nu(C\equiv NR)$[a]
η^5-C_5H_5Fe(CO)(CN)[C(NHMe)$_2$]	1957	2082	
η^5-C_5H_5Fe(CO)(CN)[C(NHMe)(NHEt)]	1957	2081	
η^5-C_5H_5Fe(CO)(CN)[C(NHMe)(NHn-Pr)]	1957	2082	
η^5-C_5H_5Fe(CO)(CN)[C(NHMe)(NHi-Pr)]	1958	2082	
η^5-C_5H_5Fe(CO)(PMe_3)[C(NHMe)$_2$]$^+$	1943		
η^5-C_5H_5Fe(CO)(PMe_3)[C(NHMe)(NHEt)]$^+$	1942		
η^5-C_5H_5Fe(CO)(PPh_3)[C(NHMe)$_2$]$^+$	1958		
η^5-C_5H_5Fe(CO)(PPh_3)[C(NHMe)(NHEt)]$^+$	1958		
η^5-C_5H_5Fe(CO)(PPh_3)[C(NHMe)(NHi-Pr)]$^+$	1959		
η^5-C_5H_5Fe(CO)(CNMe)[C(NHMe)$_2$]$^+$	1978		2197
η^5-C_5H_5Fe(CO)(CNMe)[C(NHMe)(NHEt)]$^+$	1978		2195
η^5-C_5H_5Fe(CO)(CNMe)[C(NHMe)(NHi-Pr)]$^+$	1976		2195
η^5-C_5H_5Fe(CO)(CNEt)[C(NHMe)(NHEt)]$^+$	1976		2183
η^5-C_5H_5Fe(CO)(CNEt)[C(NHEt)$_2$]$^+$	1976		2182
η^5-C_5H_5Fe(CO)(CNi-Pr)[C(NHMe)$_2$]$^+$	1976		2173
η^5-C_5H_5Fe(CO)(CNi-Pr)[C(NHMe)(NHi-Pr)]$^+$	1976		2171
η^5-C_5H_5Fe(CO)(CNi-Pr)[C(NHi-Pr)$_2$]$^+$	1977		2172
η^5-C_5H_5Fe(CO)(CNt-Bu)[C(NHMe)$_2$]$^+$	1976		2164
η^5-C_9H_7Fe(CO)(CNMe)[C(NHMe)$_2$]$^+$	1974		2191
η^5-C_9H_7Fe(CO)(CNMe)[C(NHMe)(NHEt)]$^+$	1976		2190
η^5-C_9H_7Fe(CO)(CNMe)[C(NHMe)(NHi-Pr)]$^+$	1976		2194
η^5-C_9H_7Fe(CO)(CNEt)[C(NHMe)(NHEt)]$^+$	1975		2180
η^5-C_9H_7Fe(CO)(CNi-Pr)[C(NHMe)$_2$]$^+$	1976		2172
η^5-C_9H_7Fe(CO)(CNt-Bu)[C(NHMe)$_2$]$^+$	1976		2158

[a] Spectra recorded in $CHCl_3$.

of one of the isocyanide stretching bands (Table 1). Reaction products were identified by ^1H and ^{13}C NMR spectra which, when accompanied by decoupling experiments and temperature variation, permitted characterization of specific isomers. Chemical shifts and splittings for all of the diaminocarbene complexes are reported in Tables 2 and 3.

In addition to inclusion in a diaminocarbene, we found that primary amines were converted to isocyanides in this system when reacted with cis methyl isocyanide complexes. The resulting compounds are structural isomers of the initially formed diaminocarbenes, in that a dimethylaminocarbene is also formed:



Evidence for the additional carbene complex can be found in both ^1H and ^{13}C NMR spectra. In particular, ^{13}C spectra of reaction mixtures show additional

(Continued on p. 97)

TABLE 2

PROTON NUCLEAR MAGNETIC RESONANCE DATA[a]

Compound	Diaminocarbene[b]			Other Ligands	
CpFe(CO)(CN)[C(NHMe)$_2$]	3.16 d (4.4)	NCH_3		4.60 s	Cp
	2.90 d (4.9)	NCH_3			
CpFe(CO)(CN)[C(NHMe)(NHEt)]	3.70 m	NCH_2-	B	4.60 s	Cp
	3.25 m	NCH_2-	A		
	3.13 d (4.6)	NCH_3	A		
	2.90 d (4.9)	NCH_3	B		
	1.22 t (7.3)	CCH_3	A,B		
CpFe(CO)(CN)[C(NHMe)(NHn-Pr)]	3.56 m	NCH_2-	B	4.61 s	Cp
	3.18 m	NCH_2-	A	4.59 s	Cp
	3.12 d (4.5)	NCH_3	A		
	2.91 d (4.9)	NCH_3	B		
	1.59 m	CCH_2	A,B		
	0.97 t (6.7)	CCH_3	A,B		
	0.95 t (6.7)	CCH_3			
CpFe(CO)(CN)[C(NHMe)(NHi-Pr)]	4.25 m	NCH-	A,B	4.61 s	Cp
	3.13 d (4.5)	NCH_3	A		
	2.88 d (4.9)	NCH_3	B*		
	1.28 d (6.8)	CCH_3	A,B		
	1.24 d (6.8)	CCH_3			

TABLE 2 (cont.)

$CpFe(CO)(PMe_3)[C(NHMe)_2]^+$	3.25 d (4.4)	NCH_3		5.04 d^c	Cp
	2.92 d (4.9)	NCH_3		1.58 d^c	PMe_3
$CpFe(CO)(PMe_3)[C(NHMe)(NHEt)]^+$	3.80 m	NCH_2-	B*	5.02 d^c	Cp
	3.45 m	NCH_2-	A	1.62 d^c	PMe_3
	3.26 d (4.5)	NCH_3	A		
	2.96 d (4.9)	NCH_3	B*		
	1.22 m	CCH_3	A,B		
$CpFe(CO)(PPh_3)[C(NHMe)_2]^+$	3.25 d (4.5)	NCH_3		5.01 d^c	Cp
	2.62 d (4.8)	NCH_3		7.2-7.6 m	PPh_3
$CpFe(CO)(PPh_3)[C(NHMe)(NHEt)]^+$	3.82 m	NCH_2-	B	5.02 d^c	Cp
	3.30 d (4.4)	NCH_3	A*	7.2-7.6 m	PPh_3
	3.17 m	NCH_2-	A*		
	2.69 d (5.1)	NCH_3	B		
	1.26 t (7.2)	CCH_3	B		
	0.58 t (7.2)	CCH_3	A*		
$CpFe(CO)(PPh_3)[C(NHMe)(NHi\text{-}Pr)]^+$	4.01 m	NCH-	A,B	5.00 d^c	Cp
	3.34 d (4.4)	NCH_3	A*	7.2-7.6 m	PPh_3
	2.67 d (4.9)	NCH_3	B		
	0.80 d (6.4)	CCH_3	A,B		
	0.65 d (6.4)	CCH_3			
$CpFe(CO)(CNMe)[C(NHMe)_2]^+$	3.20 d (4.6)	NCH_3		5.07 s	Cp
	2.95 d (4.9)	NCH_3		3.63 s	NCH_3
$CpFe(CO)(CNMe)[C(NHMe)(NHEt)]^+$	3.62 m	NCH_2-	B*	5.00 s	Cp
	3.42 m	NCH_2-	A	3.59 s	NCH_3
	3.18 d (4.5)	NCH_3	A		
	2.96 d (4.9)	NCH_3	B*		
	1.27 t (7.3)	CCH_3	B*		
	1.18 t (7.3)	CCH_3	A		
$CpFe(CO)(CNMe)[C(NHMe)(NHi\text{-}Pr)]^+$	4.40 m	NCH-	A,B	5.07 s	Cp
	3.19 d (4.5)	NCH_3	A	3.63 s	NCH_3
	2.90 d (4.9)	NCH_3	B*		
	1.32 m	CCH_3	A,B		
$CpFe(CO)(CNEt)[C(NHMe)(NHEt)]^+$	3.66 m	NCH_2-	B*	5.08 s	Cp
	3.41 m	NCH_2-	A	3.93 q	NCH_2-
	3.17 d (4.4)	NCH_3	A	1.37 t	CCH_3
	2.91 d (4.9)	NCH_3	B*		
	1.24 t (7.3)	CCH_3	B*		
	1.16 t (7.3)	CCH_3	A		
$CpFe(CO)(CNEt)[C(NHEt)_2]^+$	3.71 m	NCH_2-		5.07 s	Cp
	3.49 m	NCH_2-		3.96 q	NCH_2-
	1.28 t (7.3)	CCH_3		1.40 t	CCH_3
	1.19 t (7.3)	CCH_3			
$CpFe(CO)(CNi\text{-}Pr)[C(NHMe)_2]^+$	3.18 d (4.5)	NCH_3		5.09 s	Cp
	2.90 d (4.9)	NCH_3		4.36 m	NCH-
				1.41 d	CCH_3
$CpFe(CO)(CNi\text{-}Pr)[C(NHMe)(NHi\text{-}Pr)]^+$	4.40 m	NCH-	A,B	5.09 s	Cp
	3.20 d (4.5)	NCH_3	A	4.40 m	NCH-
	2.96 d (4.9)	NCH_3	B*	1.40 m	CCH_3
	1.40 m	CCH_3	A,B		

TABLE 2 (cont.)

$\mathrm{CpFe(CO)(CNi\text{-}Pr)[C(NHi\text{-}Pr)_2]^+}$	4.40 m	NCH-		5.09 s	Cp
	1.35 d (6.3)	$\mathrm{CCH_3}$		4.40 m	NCH-
	1.27 d (6.3)	$\mathrm{CCH_3}$		1.47 d	$\mathrm{CCH_3}$
$\mathrm{CpFe(CO)(CNt\text{-}Bu)[C(NHMe)_2]^+}$	3.19 d (4.5)	$\mathrm{NCH_3}$		5.08 s	Cp
	2.92 d (4.9)	$\mathrm{NCH_3}$		1.53 s	$\mathrm{CCH_3}$
$\mathrm{InFe(CO)(CNMe)[C(NHMe)_2]^+}$	2.96 d (4.4)	$\mathrm{NCH_3}$		7.3-7.6 m	In
	2.92 d (4.9)	$\mathrm{NCH_3}$		5.90 m	In
				5.70 m	In
				5.25 t	In
				3.60 s	$\mathrm{NCH_3}$
$\mathrm{InFe(CO)(CNMe)[C(NHMe)(NHEt)]^+}$	3.36 m	$\mathrm{NCH_2}$-	A,B	7.3-7.6 m	In
	2.92 m	$\mathrm{NCH_3}$	A,B	5.85 m	In
	1.19 t (7.3)	$\mathrm{CCH_3}$	B*	5.70 m	In
	1.10 t (7.3)	$\mathrm{CCH_3}$	A	5.25 t	In
				3.60 s	$\mathrm{NCH_3}$
$\mathrm{InFe(CO)(CNMe)[C(NHMe)(NHi\text{-}Pr)]^+}$	4.40 m	NCH-	A,B	7.3-7.6 m	In
	2.92 m	$\mathrm{NCH_3}$	A,B	5.93 m	In
	1.30 m	$\mathrm{CCH_3}$	A,B	5.72 m	In
				5.25 m	In
				3.62 s	$\mathrm{NCH_3}$
$\mathrm{InFe(CO)(CNEt)[C(NHMe)(NHEt)]^+}$	3.44 m	$\mathrm{NCH_2}$-	A,B	7.3-7.6 m	In
	2.91 m	$\mathrm{NCH_3}$	A,B	5.89 m	In
	1.16 t (7.3)	$\mathrm{CCH_3}$	B*	5.70 m	In
	0.99 t (7.3)	$\mathrm{CCH_3}$	A	5.24 t	In
				3.89 m	$\mathrm{NCH_2}$-
				1.36 m	$\mathrm{CCH_3}$
$\mathrm{InFe(CO)(CNi\text{-}Pr)[C(NHMe)_2]^+}$	2.94 d (4.4)	$\mathrm{NCH_3}$		7.4-7.7 m	In
	2.92 d (4.8)	$\mathrm{NCH_3}$		6.00 m	In
				5.70 m	In
				5.30 m	In
				4.35 m	NCH-
				1.40 d	$\mathrm{CCH_3}$
				1.35 d	$\mathrm{CCH_3}$
$\mathrm{InFe(CO)(CNt\text{-}Bu)[C(NHMe)_2]^+}$	2.97 m	$\mathrm{NCH_3}$		7.2-7.7 m	In
				5.96 m	In
				5.72 m	In
				5.22 m	In
				1.50 s	$\mathrm{CCH_3}$

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[a] Chemical shifts (δ) relative to TMS in acetone-d_6 at room temperature.

[b] Splittings are given in Hz as s, singlet; d, doublet; t, triplet; m, multiplet. A and B refer to rotational isomers in Figure 2 with predominant isomers denoted by an asterisk (*). NH protons are not included in the table but were observed for each complex as broad signals in the region 8.5 - 7.0 ppm.

[c] J(PFeCp) 1.4 Hz; $J(PCH_3)$ 10.3 Hz.

TABLE 3

CARBON-13 NUCLEAR MAGNETIC RESONANCE DATA[a]

Compound	Carbene Substituents[b]	Carbene Carbon	Carbonyl Carbon	Other Ligands
CpFe(CO)(CN)[C(NHMe)$_2$]	35.9 NCH_3 30.4 NCH_3	214.4	220.3	82.5 Cp
CpFe(CO)(CN)[C(NHMe)(NHEt)]	44.3 NCH_2- B 38.4 NCH_2- A 36.2 NCH_3 A 30.3 NCH_3 B 16.1 CCH_3 B 14.0 CCH_3 A	214.2	220.5	82.7 Cp
CpFe(CO)(CN)[C(NHMe)(NHn-Pr)]	51.2 NCH_2- B 45.2 NCH_2- A 35.7 NCH_3 A 30.0 NCH_3 B 23.9 CCH_2- }A,B 21.8 CCH_2- 11.5 CCH_3 A,B	215.8	220.8	82.8 Cp
CpFe(CO)(CN)[C(NHMe)(NHi-Pr)]	52.0 NCH- B* 43.9 NCH- A 36.0 NCH_3 A 30.5 NCH_3 B* 24.7 CCH_3 } A,B 23.0 CCH_3	215.6	220.6	82.9 Cp
CpFe(CO)(PMe$_3$)[C(NHMe)$_2$]$^+$	36.6 NCH_3 32.4 NCH_3	208.9	217.9	84.1 Cp 20.5 PMe_3
CpFe(CO)(PMe$_3$)[C(NHMe)(NHEt)]$^+$	44.6 NCH_2- B* 39.9 NCH_2- A 36.8 NCH_3 A 32.0 NCH_3 B* 16.7 CCH_3 B* 13.7 CCH_3 A	206.8	218.4	84.1 Cp 20.5 PMe_3
CpFe(CO)(PPh$_3$)[C(NHMe)$_2$]$^+$	35.8 NCH_3 34.1 NCH_3	209.4	218.9	133.3 PPh_3 132.6 PPh_3 131.3 PPh_3 129.4 PPh_3 84.4 Cp
CpFe(CO)(PPh$_3$)[C(NHMe)(NHEt)]$^+$	44.2 NCH_2- B 41.5 NCH_2- A* 36.0 NCH_3 A* 33.8 NCH_3 B 16.4 CCH_3 B 12.7 CCH_3 A*	207.2	219.6	133.1 PPh_3 132.7 PPh_3 131.4 PPh_3 129.6 PPh_3 84.5 Cp
CpFe(CO)(PPh$_3$)[C(NHMe)(NHi-Pr)]$^+$	46.4 NCH- A* 36.3 NCH_3 A* 22.7 CCH_3 A* 21.7 CCH_3 A*	206.3	219.2	133.1 PPh_3 132.7 PPh_3 131.8 PPh_3 129.8 PPh_3 84.9 Cp

TABLE 3 (cont.)

CpFe(CO)(CNMe)[C(NHMe)$_2$]$^+$	35.9	NCH$_3$		206.4	216.9	84.2	Cp
	32.4	NCH$_3$				32.9	NCH$_3$
CpFe(CO)(CNMe)[C(NHMe)(NHEt)]$^+$	43.6	NCH$_2$-	B*	204.9	216.4	83.7	Cp
	39.3	NCH$_2$-	A	204.0		32.5	NCH$_3$
	35.1	NCH$_3$	A				
	31.4	NCH$_3$	B*				
	16.1	CCH$_3$	B*				
	14.2	CCH$_3$	A				
CpFe(CO)(CNMe)[C(NHMe)(NHi-Pr)]$^+$	51.4	NCH-	B*	204.5	216.3	84.1	Cp
	45.6	NCH-	A	203.3		32.7	NCH$_3$
	35.9	NCH$_3$	A				
	32.5	NCH$_3$	B*				
	23.6	CCH$_3$	} A,B				
	23.4	CCH$_3$					
CpFe(CO)(CNEt)[C(NHMe)(NHEt)]$^+$	44.2	NCH$_2$-	B*	205.3	216.6	84.0	Cp
	39.7	NCH$_2$-	A	204.5		41.6	NCH$_2$-
	35.7	NCH$_3$	A			15.1	CCH$_3$
	31.9	NCH$_3$	B*				
	16.3	CCH$_3$	B*				
	14.3	CCH$_3$	A				
CpFe(CO)(CNEt)[C(NHEt)$_2$]$^+$	44.2	NCH$_2$-		203.9	216.7	84.2	Cp
	41.7	NCH$_2$-				41.7	NCH$_2$-
	16.4	CCH$_3$				15.2	CCH$_3$
	14.3	CCH$_3$					
CpFe(CO)(CNi-Pr)[C(NHMe)$_2$]$^+$	35.9	NCH$_3$		206.4	217.1	84.3	Cp
	32.6	NCH$_3$				50.7	NCH-
						23.5	CCH$_3$
CpFe(CO)(CNi-Pr)[C(NHMe)(NHi-Pr)]$^+$	51.7	NCH-	B*	204.3	216.2	83.9	Cp
	45.8	NCH-	A	202.5		83.7	Cp
	35.6	NCH$_3$	A			50.1	NCH-
	31.7	NCH$_3$	B*			23.4	CCH$_3$
	23.6	CCH$_3$	} A,B				
	22.9	CCH$_3$					
CpFe(CO)(CNi-Pr)[C(NHi-Pr)$_2$]$^+$	52.6	NCH-		201.6	216.4	84.3	Cp
	45.8	NCH-				50.5	NCH-
	23.4	CCH$_3$				23.4	CCH$_3$
	22.3	CCH$_3$					
InFe(CO)(CNMe)[C(NHMe)$_2$]$^+$	35.3	NCH$_3$		206.3	217.1	128.3}	In C(4),
	32.7	NCH$_3$				125.5}	In C(5),
						104.0}	In C(8)
						102.7}	In C(9)
						92.0	In C(2)
						71.9}	In C(1)
						70.8}	In C(3)
						32.9	NCH$_3$
InFe(CO)(CNMe)[C(NHMe)(NHEt)]$^+$	43.5	NCH$_2$-	B*	205.1	216.9	128.1}	In C(4),
	40.0	NCH$_2$-	A	204.3		125.3}	In C(5),
	35.1	NCH$_3$	A			104.0}	In C(8)
	32.4	NCH$_3$	B*			102.9}	In C(9)
	16.3	CCH$_3$	B*			91.7	In C(2)
	15.2	CCH$_3$	A			71.8}	In C(1)
						71.4}	In C(3)
						32.7	NCH$_3$

TABLE 3 (cont.)

$\mathrm{InFe(CO)(CNEt)[C(NHMe)(NHEt)]^+}$	43.7 $\mathrm{NCH_2}$- B* 40.2 $\mathrm{NCH_2}$- A 35.6 $\mathrm{NCH_3}$ A 32.3 $\mathrm{NCH_3}$ B* 16.5 $\mathrm{CCH_3}$ B* 15.4 $\mathrm{CCH_3}$ A	205.5 204.8	217.0	128.2} In C(4),C(7) 125.4 In C(5),C(6) 103.9} In C(8) 102.8 In C(9) 91.9 In C(2) 71.8 In C(1),C(3) 41.8 $\mathrm{NCH_2}$- 15.3 $\mathrm{CCH_3}$
$\mathrm{InFe(CO)(CNi\text{-}Pr)[C(NHMe)_2]^+}$	35.5 $\mathrm{NCH_3}$ 33.2 $\mathrm{NCH_3}$	206.5	217.5	128.2} In C(4),C(7) 125.7 In C(5),C(6) 104.6 In C(8),C(9) 92.2 In C(2) 72.4} In C(1) 71.9 In C(3) 50.7 NCH- 23.7 $\mathrm{CCH_3}$
$\mathrm{InFe(CO)(CNt\text{-}Bu)[C(NHMe)_2]^+}$	35.6 $\mathrm{NCH_3}$ 33.3 $\mathrm{NCH_3}$	206.4	217.4	128.4} In C(4),C(7) 125.9 In C(5),C(6) 104.6} In C(8) 102.8 In C(9) 92.3 In C(2) 72.6} In C(1) 71.8 In C(3) 59.1 NC- 31.0 $\mathrm{CCH_3}$

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[a] Chemical shifts relative to TMS in $\mathrm{CDCl_3}$ at room temperature.

[b] A and B refer to rotational isomers in Figure 2 with major isomer resonances, where observed, denoted by an asterisk (*). Signals for ^{13}CN and ^{13}CNR are not included in the table but were observed as broad signals at 145-155 ppm.

signals in the carbene region (≈208 ppm) in addition to those characteristic of the newly formed CNR group (see Tables 2 and 3). Identification of the resonances in reaction mixtures was verified by off-resonance decoupling and analysis of high temperature spectra. At elevated temperatures rotational isomer signals broadened and coalesced while those of the structural isomer remained sharp. Structural isomers were also distinguishable by infrared spectra as C≡N stretching frequencies decreased by approximately 10 cm^{-1} for each isocyanide in the series CNMe>CNEt>CNi-Pr>CNt-Bu (Table 1).

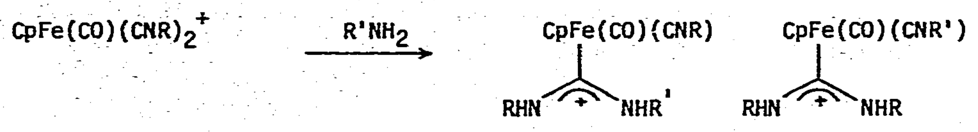
The distribution of isomeric products depended considerably on the identity of the amine and the specific reaction conditions. Reaction with equimolar quantities of ethyl and isopropylamine appeared to yield primarily $CpFe(CO)(CNMe)[C(NHMe)(NHR)]^+$. In an excess of amine this product was converted to $CpFe(CO)(CNR)[C(NHMe)_2]^+$. The addition of heat significantly increased the rate of conversion. Reaction conditions necessary for tert-butylamine addition resulted in the observation of only $CpFe(CO)(CNt\text{-}Bu)[C(NHMe)_2]^+$ Indenyl derivatives showed similar patterns of reaction.

The reaction of methylamine with <u>cis</u> ethyl or isopropyl isocyanides did not result in products containing methyl isocyanide ligands, nor were these products obtained by the addition of heat or excess amine to the diaminocarbenes.

A comparison of the relative ratios of structural isomers is seen in Table 4. The ratios represent the distribution of products upon complete

TABLE 4

RELATIVE STRUCTURAL ISOMER DISTRIBUTIONS[a]



Ring	R	R'	%	%
Cp	Me	Et	85	15
In	Me	Et	70	30
Cp	Me	i-Pr	80	20
In	Me	i-Pr	65	35
Cp	Me	t-Bu[b]	< 1	>99
In	Me	t-Bu[b]	< 1	>99
Cp	Et	Me	>99	< 1
In	Et	Me	>99	< 1
Cp	i-Pr	Me	>99	< 1

[a] Upon completion of bisisocyanide reaction at room temperature in CH_2Cl_2 with excess amine. [b] Required reflux.

reaction of the bisisocyanide complex in excess amine. These values are not equilibrium values, since continued reaction eventually converted all bismethyl isocyanide complexes to CpFe(CO)(CNR)[C(NHMe)$_2$]$^+$.

The conversion of the primary amine to an isocyanide most likely occurs in the series of steps outlined in Figure 1. Initial nucleophilic attack by the amine on methyl isocyanide results in the diaminocarbene II, which can be isolated as a stable species. When solutions of II are treated with excess amine, complete conversion to VIII occurs in less than 24 hours.*

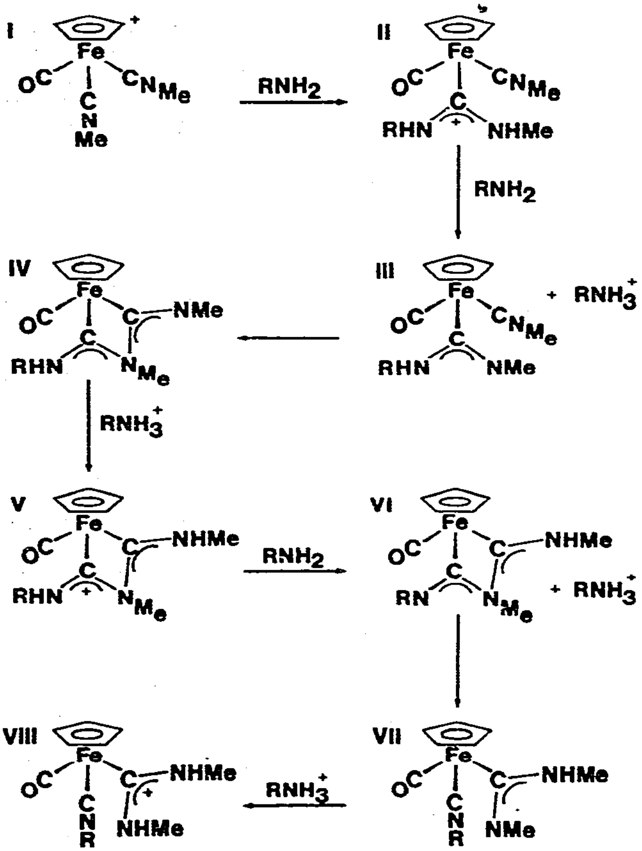


Fig. 1. Proposed pathway for conversion of η^5-C_5H_5Fe(CO)(CNMe)[C(NHMe)(NHR)]$^+$ to η^5-C_5H_5Fe(CO)(CNR)[C(NHMe)$_2$]$^+$.

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*Some conversion to VIII in the absence of amine did occur in refluxing CH_2Cl_2 over a period of 10 days, although catalytic amounts of base may have been present.

The role of the amine in deprotonating II to give the amidine III has been proposed by Angelici for $Mn(CO)_4(CNR)[C(NHMe)_2]^+$ complexes.[7] The existence of chelated species similar to VI, V, and IV was demonstrated in the same study and similar species have been observed by Balch in the migration of carbene and isocyanide substituents on FeC_6 and RuC_6 cores.[8] Unlike the octahedral iron complexes, these reactions do not appear to be reversible in this system and do not result in a statistical randomization of isomer distributions. Rather, the conversion of the amine to the isocyanide appears irreversible and isolation of the chelated intermediate was not possible.

The possiblity of a dissociative mechanism, in which a molecule of methylamine leaves II and attacks the methylisocyanide was also considered. However, it was observed that an isolated solution of CpFe(CO)(CNMe)[C(NHMe)(NHi-Pr)] in the presence of excess ethylamine resulted in conversion to CpFe(CO)(CNi-Pr)-$[C(NHMe)_2]^+$, without the inclusion of ethylamine in the final complex. A dissociative mechanism in the presence of excess ethylamine would most likely result in ethyl-substituted carbene products.

Steric factors appear to be important in accounting for the irreversibility of the isomer conversion and the failure to observe chelated intermediates. The presence of bulky groups on the isocyanide may prevent the dimethylaminocarbene from approaching the isocyanide favorably for the reverse reaction to occur. The failure to observe rearrangement products when methylamine reacts with cis isopropyl or ethyl isocyanides is consistent with this argument. Here also the larger alkyl substituent may prevent carbene attack. Additionally, conversion to terminal methyl isocyanides would require a chelated intermediate with the larger alkyl group bonded to the central nitrogen and thus in an interior position with respect to each carbene. As will be seen, our analysis of rotational isomerism in these complexes indicates this to be an unfavorable position for a bulkier alkyl group.

Diaminocarbene formation and amine to isocyanide conversion in monoisocyanide complexes

Although susceptibility to nucleophilic attack is enhanced by positive charge on a complex, we have observed that diaminocarbene formation also occurs with the uncharged isocyanide complexes, CpFe(CO)(CN)(CNR). Reaction rates are considerably slower than the bisisocyanide complexes however; CpFe(CO)(CN)(CNMe) reacts with isopropylamine only under reflux conditions and tertbutylamine shows no evidence of reaction. Where amine addition occurred, diaminocarbenes could again be identified by their IR and NMR spectra (Tables 1-3). Where long periods of reflux in excess amine were necessary, as in the reaction of CpFe(CO)(CN)(CNMe) with isopropylamine, conversion to the isocyanide complex CpFe(CO)(CN)(CNi-Pr) was observed. Evidence of further reaction to form the diaminocarbene $\mathrm{CpFe(CO)(CN)[C(NHi\text{-}Pr)_2]}$ was also seen but the product was not isolated. The formation of these additional products was eliminated by preparation of CpFe(CO)(CN)(CNR) where R = Et, n-Pr, i-Pr followed by room temperature reaction with methylamine. Formation of the diaminocarbene was complete over a period of several hours without evidence of the formation of CpFe(CO)(CN)(CNMe) or $\mathrm{CpFe(CO)(CN)[C(NHMe)_2]}$. Although further studies of the amine to isocyanide conversion in the neutral complexes were not pursued, it was noted that solutions of CpFe(CO)(CN)[C(NHMe)(NHR)] were stable in refluxing methylene chloride but converted to CpFe(CO)(CN)(CNR) in the presence of excess amine.

Our study of rotational isomerism in diaminocarbenes also involved the synthesis of several tertiary phosphine complexes in a manner analogous to that described for the bis isocyanide and cyano complexes. Although these complexes are cationic, their reactions with amines, as noted by Angelici[5], are significantly slower than those of the bis isocyanide complexes. Eventual amine to isocyanide conversion occurred in the same manner as described for the neutral cyano complexes when ethyl and isopropylamine were reacted with the methylisocyanide complexes. Again, diaminocarbenes of the form $\mathrm{CpFe(CO)(PR_3)[C(NHR)(NHMe)]^+}$ were most conveniently prepared by the reaction of $\mathrm{CpFe(CO)(PR_3)(CNR)^+}$ with methylamine.

Rotational isomerism in diaminocarbenes

The averaging of nonequivalent carbene ^1H methyl signals in η^5-C_5H_5Fe(CO)(CNMe)[C(NHMe)$_2$]$^+$ at elevated temperatures has been attributed to restricted rotation about the carbon-nitrogen bond.[5] As expected, each of the cationic and neutral complexes in the present study exhibited restricted rotation of the same nature. To determine the effect of varying carbene substituents and other ligands bound to the metal on the barrier to rotation, variable temperature ^1H NMR spectra of a number of the complexes were analyzed. Using the slow-exchange limiting equation, $k = \pi(\Delta\nu'_{1/2} - \Delta\nu_{1/2})$, which depends only on the increase in half-width of the signal due to averaging, first order rate constants were calculated from line broadening measurements of averaging carbene substituents. Rotational free energy barriers were then determined using the equation, $\Delta G = 2.3\ RT(10.3 + \log T - \log k)$. Free energy values obtained in this manner are reported for a number of complexes in Table 5. Values were found to lie in a narrow range between 16.7 and 17.9 kcal/mole. Rotational barriers were thus quite insensitive to changes in carbene substituents or other metal ligands. Barriers in the neutral complexes were in the same range as those of the cationic compounds, indicating that the partial double bond character of the carbon-nitrogen bond was unaffected by the overall charge difference in the molecules.

Although rotational barriers varied only slightly, complexes existing as rotational isomers often exhibited significant differences in isomer populations. Carbene groups in both neutral and cationic complexes were found to exist exclusively in the _amphi_ configuration (as depicted in Figure 2) since ^1H and ^{13}C spectra of [C(NHR)$_2$] derivatives revealed nonequivalent resonances for R groups in the absence of rotation about the carbon-nitrogen bond. As a result, when the alkyl group of the amine differed from that of the isocyanide, the resulting diaminocarbene existed as a mixture of rotamers (Figure 2).

Methyl substituents in each of the rotamers were found to yield consistent ^1H chemical shift and coupling patterns as seen in Table 2. Cyclopentadienyl complexes, with the exception of triphenylphosphine

TABLE 5

ESTIMATED ROTATIONAL FREE ENERGY BARRIERS

Compound	$\Delta G^* \pm 0.3$ (kcal/mol)[a]
η^5-$C_5H_5Fe(CO)(CN)[C(NHMe)_2]$	17.3
η^5-$C_5H_5Fe(CO)(CN)[C(NHMe)(NHEt)]$	16.9
η^5-$C_5H_5Fe(CO)(CN)[C(NHMe)(NHi\text{-}Pr)]$	16.9
η^5-$C_5H_5Fe(CO)(PMe_3)[C(NHMe)_2]^+$	16.7
η^5-$C_5H_5Fe(CO)(PPh_3)[C(NHMe)(NHEt)]^+$	17.1
η^5-$C_5H_5Fe(CO)(CNMe)[C(NHMe)_2]^+$	17.8
η^5-$C_5H_5Fe(CO)(CNEt)[C(NHMe)(NHEt)]^+$	16.9
η^5-$C_5H_5Fe(CO)(CNi\text{-}Pr)[C(NHMe)(NHi\text{-}Pr)]^+$	17.3
η^5-$C_5H_5Fe(CO)(CNi\text{-}Pr)[C(NHMe)_2]^+$	17.3
η^5-$C_9H_7Fe(CO)(CNMe)[C(NHMe)_2]^+$	17.9

[a] Calculated from 90 MHz ^1H spectra in acetone-d_6.

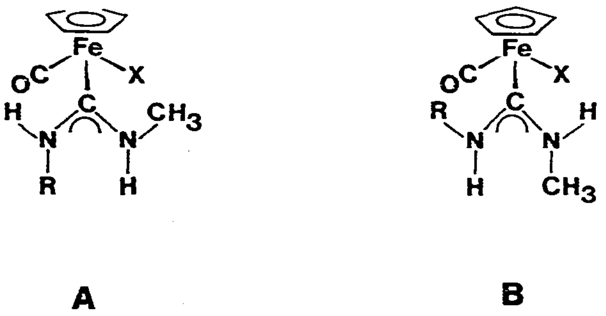

Fig. 2. Rotational isomers in diaminocarbene complexes.

derivatives, exhibited high field methyl signals at 2.88 - 2.96 ppm and lower field signals at 3.10 - 3.25 ppm. Methyl substituents on triphenylphosphine derivatives had chemical shifts slightly outside of these ranges (2.65 and 3.30 ppm). High field methyl signals also exhibited slightly higher splittings as a result of coupling to N-H protons than did those at lower fields (4.4-4.6 vs 4.8-5.1 Hz). In similar metal complexes[3,9] and in amidinium ions themselves,[10] the higher field methyl resonances have been assigned to interior positions trans to the carbon-metal bond. This results in the assignment of the resonances in Table 2 to structures A and B as denoted in Figure 2. Further evidence for assigning the lower field methyl resonances to exterior positions was obtained from the η^5-indenyl derivatives of several of the complexes. The ^1H NMR spectra of these derivatives showed an upfield shift of the low field methyl resonance of nearly 0.4 ppm with no change observed in the high field chemical shift. Inspection of molecular models indicates that a methyl cis to the metal would come close enough to the plane of the six-membered indene ring to be affected by ring currents while a trans methyl would not. This effect, resulting in upfield shifts, has been observed for coordinated olefin and allyl groups in similar complexes and has been used to assign orientational preferences.[11,12]

Rotational isomers could also be characterized by ^{13}C spectra as diaminocarbene substituents of A and B had consistent chemical shifts. With

TABLE 6

DISTRIBUTION OF ROTATIONAL ISOMERS IN η^5-$C_5H_5Fe(CO)(X)[C(NHMe)(NHR)]$ COMPLEXES[a]

X	R	A	B
CN	Et	50	50
CN	n-Pr	50	50
CN	i-Pr	25	75
CNMe	Et	35	65
CNMe	i-Pr	30	70
CNEt	Et	35	65
CNi-Pr	i-Pr	20	80
PMe_3	Et	30	70
PPh_3	Et	75	25
PPh_3	i-Pr	>95	< 5

[a] Based on integration of ambient temperature ^1H spectra in $CDCl_3$. A and B refer to Figure 2.

the aid of ^1H spectra, assignment of the ^{13}C resonances (Table 3) to structures A and B were made. As a result, methyl groups with higher-field ^1H resonances attributed to structure B were also found to have slightly higher field ^{13}C chemical shifts, in the region 30.0 - 34.1 ppm. Methyl groups with lower field ^1H resonances assigned to A had ^{13}C chemical shifts in the region 36.8 - 35.1 ppm.

The relative isomer populations based on the assignments of Figure 2 are seen in Table 6. Ratios are reported in $CDCl_3$ solutions at room temperature. Although rotamer populations are known to be sensitive to solvent in some carbene complexes,[3] measurements of the ratios in acetone, acetonitrile, and dimethyl sulphoxide did not result in a drastic change in the relative populations of the complexes in this study and in no case was a reversal in preferred configuration noted in changing solvent. Table 6 is interesting in that it shows a strong preference for a specific configuration in a number of cases. In all compounds except those containing triphenylphosphine, any deviation from equal populations results in a preference for configuration B in which the larger group is in an exterior or cis to metal position. This is particularly evident for isopropyl substituents. Steric arguments may account for the rotational preferences observed in these complexes. The major interaction of the carbene substituents appears to be with the cyclopentadienyl ring. Although rotation about the metal-carbon bond is rapid on the NMR time scale, the carbene would likely prefer conformations in which the bulkier R group was directed away from the ring. Interaction of the methyl group with the ring would thus become the dominant factor and this interaction is significantly reduced when the methyl is in a trans or interior position. Within the ligand itself, steric interactions of interior groups are known to be unfavorable. This could be an additional factor accounting for the preference of methyl rather than larger alkyl groups for interior positions. Introduction of a triphenylphosphine results in a complete reversal of isomeric preferences. Interaction of the phosphine ligand with the exterior carbene substituents is most likely the dominant factor. As a result ethyl substituents yield a 75% preference of A and the bulkier isopropyl group effects virtually complete predominance of A. Steric factors arising from other metal ligands can thus be a dominating factor in determining preferred carbene configurations.

Studies of isocyanide-amine reactions are continuing, with particular emphasis on the reaction of optically active amines with chiral and prochiral isocyanide complexes.

EXPERIMENTAL

Chromatographic separations utilized low activity alumina (Fisher A-540). All ^1H and ^{13}C NMR spectra were obtained using a Bruker WH 90-DS spectrometer. Infrared spectra were recorded on a Perkin-Elmer 283 calibrated with DCl. Microanalyses were performed by the Kentucky Center for Energy Research Laboratory, Lexington, Kentucky.

With the exception of reactions involving gaseous methylamine, all preparations were carried out under an atmosphere of prepurified nitrogen. Both $K[\eta^5\text{-}C_5H_5Fe(CO)(CN)_2]$ and $K[\eta^5\text{-}C_9H_7Fe(CO)(CN)_2]$, used as starting materials in many of the syntheses, were prepared according the the method originally outlined by Coffey.[13]

Complete IR and NMR characterization of the products has been provided in Tables 1-3. Melting points and analytical data are reported in Table 7.

TABLE 7

MELTING POINTS AND ANALYTICAL DATA

Compound	Mp,°C	Exptl (calcd) analyses, %		
		C	H	N
$\eta^5\text{-}C_5H_5Fe(CO)(CN)[C(NHMe)_2]$	186	48.55 (48.61)	5.20 (5.30)	16.78 (17.01)
$\eta^5\text{-}C_5H_5Fe(CO)(CN)[C(NHMe)(NHEt)]$	97	50.36 (50.60)	5.50 (5.79)	16.22 (16.10)
$\eta^5\text{-}C_5H_5Fe(CO)(CN)[C(NHMe)(NHn\text{-}Pr)]$	26-28	52.32 (52.38)	6.44 (6.23)	14.82 (15.28)
$\eta^5\text{-}C_5H_5Fe(CO)(CN)[C(NHMe)(NHi\text{-}Pr)]$	26-28	53.28 (52.38)	6.01 (6.23)	15.26 (15.28)

TABLE 7 (cont.)

$\{\eta^5\text{-}C_5H_5Fe(CO)(PMe_3)[C(NHMe)_2]\}I$	218 d	34.08 (33.99)	5.22 (5.23)	6.31 (6.61)
$\{\eta^5\text{-}C_5H_5Fe(CO)(PMe_3)[C(NHMe)(NHEt)]\}I$	214 d	35.95 (35.64)	5.51 (5.52)	5.96 (6.40)
$\{\eta^5\text{-}C_5H_5Fe(CO)(PPh_3)[C(NHMe)_2]\}I$			see ref. 5	
$\{\eta^5\text{-}C_5H_5Fe(CO)(PPh_3)[C(NHMe)(NHEt)]\}I$	195	54.15 (53.87)	4.88 (4.84)	4.37 (4.49)
$\{\eta^5\text{-}C_5H_5Fe(CO)(PPh_3)[C(NHMe)(NHi\text{-}Pr)]\}I$	205 d	54.63 (54.57)	5.13 (5.05)	4.29 (4.39)
$\{\eta^5\text{-}C_5H_5Fe(CO)(CNMe)[C(NHMe)_2]\}I$			see ref. 5	
$\{\eta^5\text{-}C_5H_5Fe(CO)(CNMe)[C(NHMe)(NHEt)]\}I$	58 d[a]	35.70 (35.77)	4.57 (4.50)	10.07 (10.43)
$\{\eta^5\text{-}C_5H_5Fe(CO)(CNEt)[C(NHMe)(NHEt)]\}I$	129	37.44 (37.45)	4.83 (4.84)	10.01 (10.08)
$\{\eta^5\text{-}C_5H_5Fe(CO)(CNEt)[C(NHEt)_2]\}I$	146	38.88 (39.02)	5.18 (5.15)	9.81 (9.75)
$\{\eta^5\text{-}C_5H_5Fe(CO)(CNi\text{-}Pr)[C(NHMe)_2]\}I$	182	37.34 (37.45)	4.86 (4.84)	10.14 (10.08)
$\{\eta^5\text{-}C_5H_5Fe(CO)(CNi\text{-}Pr)[C(NHMe)(NHi\text{-}Pr)]\}I$	68-70	40.77 (40.49)	5.39 (5.44)	9.09 (9.44)
$\{\eta^5\text{-}C_5H_5Fe(CO)(CNi\text{-}Pr)[C(NHi\text{-}Pr)_2]\}I$	179	43.26 (43.17)	6.02 (5.97)	8.88 (8.88)
$\{\eta^5\text{-}C_9H_7Fe(CO)(CNMe)[C(NHMe)_2]\}I$	< 25	40.97 (41.05)	3.93 (4.13)	9.68 (9.57)
$\{\eta^5\text{-}C_9H_7Fe(CO)(CNMe)[C(NHMe)(NHEt)]\}I$	< 25	42.53 (42.43)	4.26 (4.45)	9.37 (9.28)
$\{\eta^5\text{-}C_9H_7Fe(CO)(CNEt)[C(NHMe)(NHEt)]\}I$	< 25	43.69 (43.73)	5.15 (4.75)	8.54 (9.00)
$\{\eta^5\text{-}C_9H_7Fe(CO)(CNi\text{-}Pr)[C(NHMe)_2]\}I$	< 25	43.59 (43.73)	4.55 (4.75)	8.92 (9.00)
$\{\eta^5\text{-}C_9H_7Fe(CO)(CNt\text{-}Bu)[C(NHMe)_2]\}I$	40 d	45.25 (44.95)	4.60 (5.03)	8.30 (8.74)

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[a] Product included 15% isomeric $\{\eta^5\text{-}C_5H_5Fe(CO)(CNEt)[C(NHMe)_2]\}I$

Preparation of η^5-$C_5H_5Fe(CO)(CN)[C(NHCH_3)(NHR)]$ Complexes

The neutral species η^5-$C_5H_5Fe(CO)(CN)(CNR)$ where R = $-CH_3$, $-CH_2CH_3$, $-CH_2CH_2CH_3$ and $-CH(CH_3)_2$ were prepared by refluxing equimolar quantities of $K[\eta^5$-$C_5H_5Fe(CO)(CN)_2]$ and RI in acetonitrile. Reactions were monitored by infrared spectra which showed the following characteristic stretching frequencies for each of the isocyanide complexes: $\nu(CO) = 2000$ cm^{-1}, $\nu(CN) = 2103$ cm^{-1}, $\nu(CNR) = 2188$ cm^{-1}. After approximately twelve hours the solvents were removed and reaction mixtures were chromatographed. Products were eluted with dichloromethane and were obtained in yields of 70-80%. In addition to the mono-substituted products, small amounts of $K[\eta^5$-$C_5H_5Fe(CO)(CNR)_2]$ were also formed but eluted at a much slower rate.

The neutral diaminocarbene complexes were prepared by bubbling methylamine through solutions of η^5-$C_5H_5Fe(CO)(CN)(CNR)$ in CH_2Cl_2 at 0°C for several hours until reactions were complete. In each case the solvent was then reduced to approximately 10 ml., the mixture was filtered and the filtrate chromatographed on alumina. Products were eluted with CH_2Cl_2. Concentration of the CH_2Cl_2 and addition of $O(C_2H_5)_2$ resulted in precipitation of the desired product. Although not optimized, estimated yields were at least 80%.

Preparation of $\{\eta^5$-$C_5H_5Fe(CO)(PR_3)[C(NHCH_3)(NHR')]\}I$ Complexes

The complexes η^5-$C_5H_5Fe(CO)(PMe_3)(CN)$ and η^5-$C_5H_5Fe(CO)(PPh_3)(CN)$, prepared by literature methods,[14] were reacted with RI (R = Me, Et, i-Pr) to yield $[\eta^5$-$C_5H_5Fe(CO)(PR_3)(CNR)]I$[5]. The diaminocarbene complexes were obtained by bubblying methylamine through CH_2Cl_2 solutions of the isocyanide complex as outlined by Angelici.[5]

Preparation of $\{\eta^5$-$C_5H_5Fe(CO)(CNR)[C(NHR)_2]\}I$ Complexes

The bisisocyanide complexes $[\eta^5$-$C_5H_5Fe(CO)(CNMe)_2]I$, $[\eta^5$-$C_5H_5Fe(CO)(CNEt)_2]I$, and $[\eta^5$-$C_5H_5Fe(CO)(CNi$-$Pr)_2]I$ were prepared by refluxing $K[\eta^5$-$C_5H_5Fe(CO)(CN)_2]$ and an excess of the desired alkyl iodide in acetonitrile as described by Coffey.[13]

{η^5-C_5H_5Fe(CO)(CNMe)[C(NHMe)$_2$]}I was prepared by bubbling methylamine through a solution of [η^5-C_5H_5Fe(CO)(CNMe)$_2$]I in CH_2Cl_2.[5] The reaction was complete after one hour and the product was purified by chromatography on alumina, with a 10/1 CH_2Cl_2/CH_3OH mixture used to elute it. After evaporation of the solvents, crystalline products were obtained using CH_2Cl_2/O(C_2H_5).

Syntheses of the ethyl and isopropyl analogs proceded in the same manner except that in the latter case reflux conditions were necessary to obtain sufficient reaction. Based on the starting bisisocyanides, the non-optimized yields were approximately 60% in each case.

Preparation of {η^5-C_5H_5Fe(CO)(CNR)[C(NHMe)(NHR)]}I Complexes

The compounds {η^5-C_5H_5Fe(CO)(CNEt)[C(NHMe)(NHEt)]}I and {η^5-C_5H_5Fe(CO)-(CNi-Pr)[C(NHMe)(NHi-Pr)]}I were obtained by bubbling methylamine through CH_2Cl_2 solutions of [η^5-C_5H_5Fe(CO)(CNEt)$_2$]I or [η^5-C_5H_5Fe(CO)(CNi-Pr)$_2$]I for several hours followed by chromatography and crystallization as described for {η^5-C_5H_5Fe(CO)(CNMe)[C(NHMe)$_2$]}I.

Reactions of [η^5-C_5H_5Fe(CO)(CNMe)$_2$]I with Ethylamine

The reaction of the bismethylisocyanide complex with an equimolar quantity of $EtNH_2$ in CH_2Cl_2 at 0°C for approximately four hours resulted in 85% {η^5-C_5H_5Fe(CO)(CNMe)[C(NHMe)(NHEt)]}I and 15% {η^5-C_5H_5Fe(CO)(CNEt)[C(NHMe)$_2$]}I, as determined by NMR spectra of the reaction mixtures. Chromatography and crystallization with CH_2Cl_2/O(C_2H_5) resulted in recovery of the product as a mixture of the two isomers. Further attempts to separate these isomers were not made. When excess ethylamine was used and reaction times were lengthened, an increased proportion of {η^5-C_5H_5Fe(CO)(CNEt)[C(NHMe)$_2$]}I was formed.

Reactions of [η^5-C_5H_5Fe(CO)(CNMe)$_2$]I with Isopropylamine

The reaction of the bismethylisocyanide complex with an equimolar quantity of i-$PrNH_2$ in CH_2Cl_2 at room temperature resulted in approximately 80% {η^5-C_5H_5Fe(CO)(CNMe)[C(NHMe)(NHi-Pr)]}I after nearly 200 hours. When the reaction was stopped after 24 hours and unreacted [η^5-C_5H_5Fe(CO)(CNMe)$_2$]I removed by chromatography the proportion of $\{\eta^5\text{-}C_5H_5Fe(CO)(CNMe)[C(NHMe)(NHi\text{-}Pr)]\}I$ was nearly 100%. On the other hand, complete conversion to the isopropyl isocyanide isomer was achieved when an excess of isopropylamine and $[\eta^5\text{-}C_5H_5Fe(CO)(CNMe)_2]I$ were refluxed for approximately 48 hours.

Reaction of $[\eta^5\text{-}C_5H_5Fe(CO)(CNMe)_2]I$ with Tertbutylamine

The reaction of $t\text{-}BuNH_2$ with the bismethylisocyanide required an excess of amine and refluxing in CH_2Cl_2 for reaction to occur. Complete reaction of the starting complex required more than 10 days and the severity of the reaction conditions resulted in formation of only $\{\eta^5\text{-}C_5H_5Fe(CO)(CNt\text{-}Bu)[C(NHMe)_2]\}I$. After chromatography on alumina the yield of the product was about 35%.

Indenyl Complexes

A number of indenyl complexes were prepared in the same manner as described for the cyclopentadienyl analogs except that $K[\eta^5\text{-}C_9H_7Fe(CO)(CN)_2]$ was used to prepare the starting isocyanide complexes.

In general, reactions of the indenyl isocyanide compounds with amines occurred at a slightly faster rate than did those of the cyclopentadienyl species. Final product yields were similar but most of the complexes were recovered as liquids at room temperature (see Table 7).

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