Journal of Organometallic Chemistry, 179 (1979) 357—366

TRISUBSTITUTED DIAMINOCARBENE COMPLEXES OF IRON

Bryce V. Johnson* and Joyce E. Shade
Department of Chemistry, University of Louisville, Louisville, Kentucky
40208 (U.S.A.)

(Received June 21st, 1979)

SUMMARY

Neutral and cationic isocyanide complexes of the form CpFe(CO)(L)(CNR) where L = CN or CNR and R = Me or i-Pr react with dimethylamine to form trisubstituted diaminocarbenes. Secondary amines having larger alkyl groups were unreactive under the same conditions. The new complexes are characterized by their infrared, ^{13}C and ^{1}H NMR spectra. In contrast to dialkyl diaminocarbenes, these compounds exist totally in one isomeric conformation, exhibit significantly lower C-N rotational barriers, and readily revert to their isocyanide precursors.

INTRODUCTION

Primary amines react with coordinated isocyanides in a number of transition metal systems to yield coordinated diaminocarbenes.[1,2] We recently reported the identification of structural and rotational isomers of these species in a series of cyclopentadienyl iron complexes.[3] The observed dependence of isomeric populations on steric considerations of both ligand and metal environment prompted us to consider the effect of introducing a third substituent to the carbene through the use of secondary amines. Initial results indicated that the addition of this substituent had a considerable effect on isomer populations, dynamic behavior, reactivity, and overall stability of these complexes. Although secondary amines have been used to generate carbenes in a few previous studies,[4,5] comparisons of this nature have not yet been made.

RESULTS AND DISCUSSION

Diaminocarbene formation

Neutral or cationic complexes of the form η^5-$C_5H_5Fe(CO)(CNR)(L)$ where L = CN, CNR, PPh_3 and R = Me or i-Pr were treated with an excess of a given secondary amine*. Reactivity was found to be considerably reduced, relative to rates encountered with primary amines, although similar trends were evident.[3] Diaminocarbene formation was detected only in the case of dimethylamine. Amines having larger alkyl substituents were unreactive. The complex η^5-$C_5H_5Fe(CO)(PPh_3)(CNMe)^+$, which reacts very slowly with methylamine,[6] was unreactive even toward dimethylamine. Successful syntheses of carbene complexes were evident from infrared spectra where, in each case, loss of one CNR stretching band was accompanied by a decrease of about 40 cm^{-1} in the frequency of the carbonyl ligand. Infrared spectra of the new compounds are summarized in Table 1.

TABLE 1

INFRARED SPECTRA IN C≡O AND C≡N STRETCHING REGIONS[a]

Compound	ν(C≡O)	ν(C≡N)	ν(C≡NR), cm^{-1}
η^5-$C_5H_5Fe(CO)(CN)[C(NHMe)(NMe_2)]$	1952	2081	
η^5-$C_5H_5Fe(CO)(CNMe)[C(NHMe)(NMe_2)]^+$	1982		2189
η^5-$C_5H_5Fe(CO)(CNi\text{-}Pr)[C(NHMe)(NMe_2)]^+$	1983		2157
η^5-$C_5H_5Fe(CO)(CNi\text{-}Pr)[C(NHi\text{-}Pr)(NMe_2)]^+$	1983		2154

[a] Spectra recorded in $CHCl_3$

---

*Dicarbonyl compounds (L=CO) were not included since Angelici has shown that these species undergo amine attack at the carbonyl, rather than the isocyanide[6].

Unlike disubstituted diaminocarbenes, all of which were stable in refluxing dichloromethane, each of the trisubstituted complexes was found to revert to the starting isocyanide complex when left in solution at room temperature. Both steric and electronic effects appear to affect this tendency. The neutral complex η^5-$C_5H_5Fe(CO)(CN)[C(NHMe)(NMe_2)]$, presumably having the least possibility of steric interactions between carbene and other metal ligands, was nonetheless the least stable and was impossible to prepare as more than a 50-50 mixture with η^5-$C_5H_5Fe(CO)(CN)(CNMe)$, even in the presence of excess amine. Cationic derivatives were considerably more stable but showed decreasing stability as the size of the isocyanide alkyl groups increased. The complex having methyl isocyanide and methyl carbene substituents exhibited the greatest stability and could be isolated for satisfactory elemental analysis. When both methyl and isopropyl isocyanides were present reaction occurred only at the methyl isocyanide site, as it had with primary amines. The resulting complex, differing only in the size of the remaining alkyl isocyanide, was considerably less stable in solution than the methylisocyanide analog. When the carbene itself contained an isopropyl group, the half-life of the complex was reduced further and rapid reversion to η^5-$C_5H_5Fe(CO)(CNi\text{-}Pr)_2^+$ occurred. In all cases, the reverse reaction generated the starting complex and free dimethylamine. Although we have previously shown that amines can be converted to isocyanides in complexes of this type,[3] no evidence of this was found when products of the carbene dissociation were analyzed. It should be further noted, however, that we observed such conversions only when the amine substituents were bulkier than those of the starting isocyanide, which was not the case in the present system.

Rate constants for the reaction carbene → amine + isocyanide were obtained by integrating the cyclopentadienyl resonances of the isocyanide and carbene complexes as a function of time. First order plots over a period of several half lives were obtained and are summarized in Table 2.

TABLE 2

KINETIC DATA[a]

$$CpFe(CO)(L)[C(NHR)(NMe_2)] \xrightarrow{300°K} CpFe(CO)(L)(CNR) + NHMe_2{}^{+}$$

L	R	k (sec^{-1})	$t_{1/2}$ (min)
CN	Me	4.7×10^{-2}	15
CNi-Pr	i-Pr	2.7×10^{-2}	26
CNi-Pr	Me	5.3×10^{-3}	130
CNMe	Me	4.3×10^{-4}	1610

[a] Slope of ln $(a/(a-x))$ versus time plots expressed as k (sec^{-1}).

Rotational isomerism

In contrast to disubstituted carbenes, analysis of ^{13}C and ^{1}H spectra of each of the tri-substituted compounds in this study (Tables 3 and 4) indicate the presence of only one isomer. The predominant species can be

TABLE 3

CARBON-13 NUCLEAR MAGNETIC RESONANCE DATA[a]

Compound	Carbene Substituents	Carbene Carbon	Remaining Ligands
$CpFe(CO)(CNMe)[C(NMe_2)(NHMe)]^{+}$	48.1 } (NMe_2) 38.4 } 36.2 (NHMe)	207.4	31.2 CNMe 84.5 Cp 215.7 CO
$CpFe(CO)(CNi\text{-}Pr)[C(NMe_2)(NHMe)]^{+}$	48.0 } (NMe_2) 41.2 } 37.3 (NHMe)	205.2	23.4 CCH_3 50.1 NCH- 84.4 Cp 216.8 CO
$CpFe(CO)(CNi\text{-}Pr)[C(NMe_2)(NHi\text{-}Pr)]^{+}$	48.1 } (NMe_2) 40.4 } 23.0 (CCH_3) 52.3 (NCH-)	203.0	23.0 CCH_3 50.0 NCH- 84.0 Cp 215.7 CO

[a] Chemical shifts relative to TMS in $CDCl_3$ at -50°C. Values for ^{13}CNR are not included in the table but were observed as broad signals at 154-155 ppm.

TABLE 4

PROTON NUCLEAR MAGNETIC RESONANCE DATA[a]

Compound	Diaminocarbene[b]	Other Ligands
$CpFe(CO)(CN)[C(NHMe)(NMe_2)]$	3.2-3.3 m $NHCH_3$ & $N(CH_3)_2$	4.74 s Cp
$CpFe(CO)(CNMe)[C(NHMe)(NMe_2)]^+$	3.37 s $N(CH_3)_2$ 3.29 d (4.5) $NHCH_3$	5.09 s Cp 3.62 s NCH_3
$CpFe(CO)(CNi\text{-}Pr)[C(NHMe)(NMe_2)]^+$	3.38 s $N(CH_3)_2$ 3.23 d (4.7) $NHCH_3$	5.09 s Cp 4.30 m NCH- 1.44 d CCH_3
$CpFe(CO)(CNi\text{-}Pr)[C(NHi\text{-}Pr)(NMe_2)]^+$	4.40 m NCH- 3.41 s $N(CH_3)_2$ 1.35 d CCH_3	5.12 s Cp 4.30 m NCH- 1.37 d CCH_3

[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. NH protons are not included in the table but were observed for each complex as broad signals at approximately 7.7 ppm. At low temperatures (-50°C) two singlets, separated bv 0.4 ppm are observed for the $N(CH_3)_2$ group.

assigned to the structure shown in Figure 1 in which the alkyl group originating on the isocyanide (R) is exclusively *cis* to the metal. We have shown previously that alkyl substituents of the two rotational isomers of diaminocarbenes in the *amphi* configuration have consistently characteristic ^{13}C and ^1H chemical shifts.[3] Methyl groups *cis* to the metal had ^{13}C chemical shifts of 35.1 - 36.8 ppm and ^1H shifts of 3.10 - 3.25 ppm. Values for

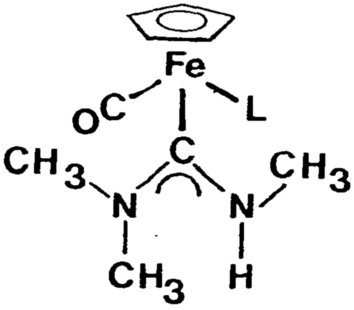

Fig. 1. Preferred Rotational Conformation of Trisubstituted Diaminocarbenes

trans groups were 31.4 - 32.6 and 2.88 - 2.96 ppm. In isopropyl groups ^{13}C chemical shifts of the nitrogen-bonded carbon were either in the 51.4 - 52.6 (*cis*) or 45.6 - 45.8 (*trans*) range. Both ^{13}C and ^{1}H chemical shifts of NHMe and NHi-Pr groups in the present compounds fall within the narrow range assigned to alkyl groups *cis* to the metal. Relative to the carbene moiety, *cis* substituents are considered to be in an exterior position. Diamonocarbenes having both NHR and NHMe groups have been found to have greater populations of isomers in which R, as a larger alkyl group, occupied exterior positions. The steric interactions of interior groups, which are known to be unfavorable, apparently preclude the possibility of having two interior methyl groups in trisubstituted derivatives. Interactions with the remaining metal ligands are therefore offset by more demanding interior steric factors. It should be noted, however, that interactions with remaining ligands do play a role in determining the stereochemistry of these compounds. This has been illustrated in the disubstituted compounds by introduction of a triphenylphosphine ligand which was found to reverse isomeric preferences.[3] Our attempt to synthesize a trisubstituted diaminocarbene having a triphenylphosphine ligand to determine which factor dominates when interactions are maximized was unsuccessful. Most likely the increased interactions of the phosphine group made the isocyanide + amine $\rightleftharpoons$ carbene equilibrium overwhelmingly favor the reactants.

As a result of the thermodynamic dominance of one rotational isomer, NMR signals of the NHR alkyl groups are insensitive to temperature variation. However rotation about the C-N bond can be observed via the exchange of the methyl groups in the $-NMe_2$ portion of the molecule. The interior and exterior methyls show up as singlets in ^{13}C and ^{1}H low temperature spectra and as averaged signals at high temperature. Line width measurements from variable temperature spectra permitted calculations of rate constants and rotational free energy barriers, using methods outlined previously[3]. Free energy values obtained in this manner are reported in Table 5. These barriers are significantly lower than found for disubstituted diaminocarbenes (17.0 - 18.0 kcal/mole) but are consistent with the observations that, unlike the latter,

TABLE 5

ESTIMATED ROTATIONAL FREE ENERGY BARRIERS

Compound	$\Delta G^* \pm 0.3$ (kcal/mol)[a]
η^5-$C_5H_5Fe(CO)(CNi\text{-}Pr)[C(NHi\text{-}Pr)(NMe_2)]^+$	13.1
η^5-$C_5H_5Fe(CO)(CNi\text{-}Pr)[C(NHMe)(NMe_2)]^+$	13.6
η^5-$C_5H_5Fe(CO)(CNMe)[C(NHMe)(NMe_2)]^+$	14.1

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

trisubstituted complexes revert to isocyanides by dissociation of the C-NMe_2 bond. Although differences in values for the three compounds in this study are only 1 kcal/mole, lower barriers do occur as observed stabilities decrease (see Table 2). The reduction in C-N bond order evident from the rotational free energy barriers may indicate enhanced multiple bond character in the Fe-C (carbene) bond.* Disubstituted complexes exhibited free rotation about this bond on the NMR time scale. However, spectra of the trisubstituted complexes run at temperatures below the point at which C-N rotation stopped showed significant broadening of the carbene substituent signals, while the cyclopentadienyl signal remained sharp. However it was impossible to stop the dynamic process accounting for this broadening due to the solubility restrictions of the ionic complexes.

Introduction of a third substituent in diaminocarbenes is thus seen to have a significant effect on their rotational characteristics and thermodynamic stabilities. Further work, centering on the reactivity differences exhibited in these complexes is currently in progress.

---

*As pointed out by one of the referees, the free energy barriers may be lower for the trisubstituted complexes due to a greater release of in-plane steric strain energy upon going to the excited state.

EXPERIMENTAL

Chromatographic separations utilized low activity alumina (Fisher A-540). All ^1H and ^{13}C spectra were obtained using a Bruker WH 90-DS spectrometer with B-ST 100/700 variable temperature accessory. Infrared spectra were recorded on a Perkin-Elmer 283 calibrated with DCl. The microanalysis was performed by the Kentucky Center for Energy Research Laboratory, Lexington, Kentucky.

With the exception of reactions involving gaseous dimethylamine, all preparations were carried out under an atmosphere of prepurified nitrogen.

The isocyanide complexes η^5-$C_5H_5Fe(CO)(CN)(CNMe)$[3], $[\eta^5$-$C_5H_5Fe(CO)(CNMe)_2]PF_6$[7], $[\eta^5$-$C_5H_5Fe(CO)(CNMe)(CNi$-$Pr)]PF_6$[8], $[\eta^5$-$C_5H_5Fe(CO)(CNi$-$Pr)_2]PF_6$[7], and $[\eta^5$-$C_5H_5Fe(CO)(PPh_3)(CNMe)]PF_6$[6] were prepared by the literature methods cited and were characterized by infrared and NMR data.

Attempted Reactions of $[\eta^5$-$C_5H_5Fe(CO)(CNMe)_2]PF_6$

In a series of experiments, the isocyanide complex was dissolved in dichloromethane and treated with excess quantities of methylisopropylamine, diethylamine, and di-isopropylamine under temperatures ranging from 0°C to reflux. After as long as five days, infrared spectra indicated no evidence of reaction.

Attempted Reaction of $[\eta^5$-$C_5H_5Fe(CO)(PPh_3)(CNMe)]PF_6$ *with dimethylamine*

The isocyanide complex was dissolved in dichloromethane and treated with excess dimethylamine at 0°C for approximately six hours. Infrared spectra indicated no evidence of reaction.

Preparation of η^5-$C_5H_5Fe(CO)(CN)[C(NHMe)(NMe_2)]$

The compound was obtained by bubbling dimethylamine through a solution of η^5-$C_5H_5Fe(CO)(CN)(CNMe)$ in dichloromethane at 0°C. After approximately three hours, infrared spectra showed the reaction to be 50% complete. Additional reaction time did not alter this ratio. Infrared and ^1H NMR spectra of the product were obtained from the mixture by subtraction of signals from the reactant.

Preparation of $[\eta^5\text{-}C_5H_5Fe(CO)(CNMe)[C(NHMe_2)]]PF_6$

The complex was prepared by bubbling dimethylamine through a solution of $[\eta^5\text{-}C_5H_5Fe(CO)(CNMe)_2]PF_6$ in methanol at 0°C. The reaction was complete after four hours. After evaporation of excess amine and methanol a yellow solid was obtained yielding the following analytical data: found: C, 34.21; H, 4.12; N, 9.90. $C_{12}H_{18}F_6FeOPN_3$ calcd.: C, 34.23; H, 4.28; N, 9.98. When kept below 0°C the compound showed only slight reversion to $[\eta^5\text{-}C_5H_5Fe(CO)(CNMe)_2]PF_6$ over a period of several weeks.

Preparation of $[\eta^5\text{-}C\ H\ Fe(CO)(CNi\text{-}Pr)[C(NHMe)(NMe)]]PF_6$ *and* $[\eta^5\text{-}C_5H_5Fe(CO)(CNi\text{-}Pr)[C(NHi\text{-}Pr)(NMe_2)]]PF_6$

Methanol solutions of the appropriate isocyanide were treated with gaseous dimethylamine at 0°C. In the case of $[\eta^5\text{-}C_5H_5Fe(CO)(CNMe)(CNi\text{-}Pr)]PF_6$ infrared spectra showed complete conversion to the product in four hours. For $[\eta^5\text{-}C_5H_5Fe(CO)(CNi\text{-}Pr)_2]PF_6$ the reaction required six hours. Following the reaction excess dimethylamine and methanol were evaporated and the products remained as amber colored oils. As a result of the ease with which the isocyanides reformed, further attempts at recrystallization were impractical and elemental analyses were not attempted.

Kinetic Measurements

Solutions for kinetic studies were prepared at a concentration of 0.2M in acetone-d_6 at 195°K in the NMR probe. Spectra were recorded at periodic intervals with relative concentrations obtained by integrating ^1H NMR cyclopentadienyl signals of the carbene and isocyanide complexes along with a reference signal of dichloromethane. The cylcopentadienyl signals in all instances were sufficiently far apart to give accurate integrations and the total integration of reactant and product remained constant. Rate constants were obtained from the slope of ln $(a/(a-x))$ versus time plots.

ACKNOWLEDGEMENTS

Acknowledgement is made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society for partial support of this research. We are also indebted to the National Science Foundation for support in obtaining the Department's Bruker WH 90-DS spectrometer which was used to obtain all NMR spectra.

REFERENCES

1 D. Doonan and A. L. Balch, Inorg. Chem., 13 (1974) 921, and references therein.

2 See reviews on carbene ligands; D. J. Cardin, M. J. Doyle, and M. F. Lappert, Chem. Soc. Rev., 2 (1973) 99; F. A. Cotton and C. M. Lukehart, Prog. Inorg. Chem., 16 (1972) 487; C. P. Casey, in H. Alper (Ed.), Transition Metal Organometallics in Organic Synthesis, Academic Press, New York, 1976, p. 189 - 233.

3 B. V. Johnson, D. P. Sturtzel, and J. E. Shade, J. Organometal. Chem., 154 (1978) 89.

4 L. Calligaro, P. Uguagliati, B. Crociani and U. Belluco, J. Organometal. Chem., 92 (1975) 399.

5 J. E. Parks and A. L. Balch, J. Organometal Chem., 71 (1974) 453.

6 R. J. Angelici, P. A. Christian, B. D. Dombek, and G. A. Pfeffer, J. Organometal. Chem., 67 (1974) 287.

7 C. E. Coffey, J. Inorg. Nucl. Chem., 25 (1963) 179.

8 B. V. Johnson, D. P. Sturtzel, and J. E. Shade, Inorg. Chim. Acta, 32 (1979) 243.