University. (d) Università di Trieste.

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Studies on the Interaction of Isocyanide with Transition-Metal Complexes. 15.[1] New Type of Insertion Reactions of Isocyanide into Alkyliron Complexes

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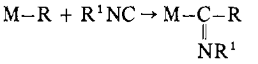
Received March 3, 1977 AIC70166Y

Reactions of η-$C_5H_5Fe(CO)(CNC_6H_{11})CH_2R$ (R = H, Ph, or p-ClC_6H_4) with $C_6H_{11}NC$ in THF or benzene at reflux produced the cyclic carbene complexes η-$C_5H_5Fe(CO)[-C(=NC_6H_{11})C(NHC_6H_{11})=C(R)C(NHC_6H_{11})-]$. The complexes having two different N substituents such as η-$C_5H_5Fe(CO)[-C(=NR^1)C(NHR^2)=C(R)C(NHR^1)-]$ (R = H or Ph; $R^1 = C_6H_{11}$; $R^2 = (CH_3)_3C$ or $PhCH_2$) and η-$C_5H_5Fe(CO)[-C(=NR^1)C(NHR^1)=C(R)C(NHR^2)-]$ (R = H; $R^1 = C_6H_{11}$; $R^2 = (CH_3)_3C$) were obtained from the reactions between η-$C_5H_5Fe(CO)(CNR^2)R$ and R^1NC or between η-$C_5H_5Fe(CO)[-C(=NR^1)C(R)=NR^1]$ and R^2NC, respectively. Reaction of η-$C_5H_5Fe(CO)[CNC(CH_3)_3]CH_3$ with *tert*-butyl isocyanide gave η-$C_5H_5Fe(CO)[CNC(CH_3)_3][C(CH_3)=NC(CH_3)_3]$. η-$C_5H_5Fe(CO)(CNR)C_6H_4X$-p ($R = C_6H_{11}$ or $(CH_3)_3C$; X = H or Cl) reacted with $C_6H_{11}NC$ to give the trisimino complex η-$C_5H_5Fe(CO)(CNC_6H_{11})[-C(=NC_6H_{11})C(=NC_6H_{11})C(C_6H_4X$-$p)=NR]$. This compound catalyzed polymerization of cyclohexyl isocyanide. The mechanism for the formation of cyclic carbene and trisimino complexes was discussed.

Introduction

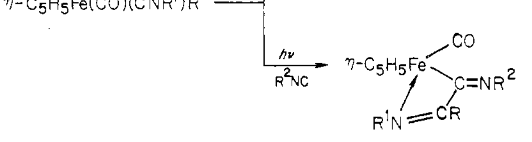
It is well known that isocyanide coordinates to a variety of transition metals.[2] One of the current interests in the coordination chemistry of isocyanide has been focused on the insertion reaction.[3,4] The reactions between isocyanides and transition metal alkyl complexes proceed with formation of the imino complexes (eq 1). Palladium[5] and nickel[6] alkyl



$$M{-}R + R^1NC \rightarrow M{-}\underset{\underset{\displaystyle NR^1}{\|}}{C}{-}R \qquad (1)$$

complexes underwent successive insertion of isocyanides to give the polyimino complexes. These multiple insertions are considered as an intermediate process of the coordinated polymerization of isocyanides catalyzed by transition metal complexes.[7]

Recently we have reported that η-$C_5H_5Fe(CO)(CNR^1)R$ reacted with carbon monoxide to give an iminoacyl complex.[8] When irradiated with a mercury lamp in the presence of isocyanide, this complex led to an insertion of two isocyanide molecules into an iron–carbon σ bond (eq 2). During our extensive studies on these subjects we found that the thermal reactions of η-$C_5H_5Fe(CO)(CNR^1)CH_2R$ with isocyanide gave the new bidentate carbene complexes which resulted from an insertion of two isocyanide molecules into a metal–carbon σ bond and from an unexpected insertion of the third isocyanide molecule into the C–H bond of an alkyl group rather than into the iron–carbon σ bond. These reactions proceed with activation of the C–H bond induced by an insertion of isocyanide.



(2)

We wish to report the new type of insertion reactions of isocyanides. A preliminary account has appeared previously.[10]

Experimental Section

The preparation and handling of organoiron complexes were carried out in an atmosphere of nitrogen. Melting points were taken on a Mitamura melting point apparatus and are uncorrected. Infrared spectra were recorded on a Shimazu IR-27G spectrometer. Proton NMR spectra were obtained on Varian HA-100B or JEOL C-60HL spectrometers, using tetramethylsilane as an internal reference. The mass spectra were measured on Nippondenshi Type JPS-1S mass spectrometer with a direct inlet system.

Materials. Isocyanides[11] were prepared by procedures described in the literature. The organoiron complexes η-$C_5H_5Fe(CO)(CNR)CH_2C_6H_4X$-$p$ ($R = C_6H_{11}$ or $PhCH_2$; X = H or Cl),[8] η-$C_5H_5Fe(CO)[CNC(CH_3)_3]R$ ($R = CH_3$[9] or Ph[12]), η-$C_5H_5Fe(CO)(CNC_6H_{11})C_6H_4Cl$-$p$,[12] η-$C_5H_5Fe(CO)(PPh_3)CH_3$,[13] η-$C_5H_5Fe(CO)[-C(=NC_6H_{11})C(CH_3)=NC_6H_{11}]$,[9] and η-$C_5H_5Fe(CO)[-C(=NC_6H_{11})C(CH_3)=NC(CH_3)_3]$[9] were prepared according to the literature methods.

Preparation of Cyclic Carbene Complexes. The representative examples are described below. Analytical data and physical properties of the carbene complexes are given in Tables I and II.

(a) η-$C_5H_5Fe(CO)[-C(=NC_6H_{11})C(NHC_6H_{11})=C(Ph)C(NHC_6H_{11})-]$ (1). A solution of η-$C_5H_5Fe(CO)(CNC_6H_{11})CH_2Ph$ (0.35 g, 1.0 mmol) and $C_6H_{11}NC$ (0.44 g, 4 mmol) in benzene (30 mL) was refluxed for 25 h and the solvent was removed under reduced pressure. The residue was purified by chromatography on alumina. Elution with n-hexane gave a pale yellow solution. Workup of the solution gave the unreacted starting material (trace). Elution with CH_2Cl_2–THF (10:1) gave a brown solution. Removal of the solvent and crystallization of the residue from CH_2Cl_2–n-hexane at −30 °C gave the title complex **1** (0.34 g, 60%).

(b) η-$C_5H_5Fe[-C(=NC_6H_{11})C(NHC_6H_{11})=C(H)C(NHC_6H_{11})-]$ (3). From η-$C_5H_5Fe(CO)(PPh_3)CH_3$. A mixture of η-C_5H_5Fe-

Table I. Analytical Data and Physical Properties of Cyclic Carbene Complexes

				Anal., %					
				C		H		N	
Compd	Mp,[a] °C	Mol wt[b]	Base peak[b]	Calcd	Found	Calcd	Found	Calcd	Found
1	142–144	567	430	71.95	71.73	7.99	7.68	7.40	7.44
2	184–187	601	464	67.83	68.30	7.37	7.46	6.98	6.93
3	146	491	463	68.42	68.50	8.41	8.49	8.55	8.49
4	133–139	541	404	70.97	71.19	8.00	8.01	7.76	7.58
5	169–171	465	328	67.09	67.29	8.45	8.24	9.03	8.93
6	89–93	575	547	73.03	73.32	7.18	7.29	7.30	7.19
7	138–141	465	328	67.09	67.17	8.45	8.31	9.03	9.00

[a] Decomposed with melting. [b] From the mass spectrum, measured by a Nippondenshi Type JPS-IS mass spectrometer with a direct-inlet system.

Table II. Infrared and Proton Magnetic Resonance Spectra of Cyclic Carbene Complexes

	IR,[a] cm^{-1}				NMR (τ)[b]	
Compd	ν(NH)	ν(C≡O)	ν(C=N)	ν(C–N)	C_5H_5	Other signals
1	3288 s 3246 b	1893 1880	1605	1562 1503	5.50 s	7.9–9.5 (b, C_6H_{10}), 7.2–7.58 (b, C_6H), 6.46–6.8 (b, C_6H), 5.6–5.9 (b, C_6H), 3.34 (b, NH), 3.24 (b, NH), 2.5–2.97 (c, C_6H_5)
2	3278 s 3179 b	1899	1605	1574 1506	5.64 s	7.85–9.45 (b, C_6H_{10}), 7.1–7.65 (b, C_6H), 6.35–6.85 (b, C_6H), 5.6–5.9 (b, C_6H), 3.43 (b, NH), 3.33 (b, NH), 2.78 (q, C_6H_4)[c]
3	3375 s 3283 b	1903 1885	1588	1563	5.62 s	7.8–9.0 (b, C_6H_{10}), 6.52 (b, C_6H), 6.18–6.5 (b, C_6H), 4.29 (s, CH), 3.1–3.28 (b, NH)
4	3288 s 3186 b	1907	1605	1599 1515	5.59 s	9.04 (s, $(CH_3)_3$) 7.9–9.2 (b, C_6H_{10}), 7.40–7.0 (b, C_6H), 5.54–5.9 (b, C_6H), 3.26 (b, NH), 3.38 (b, NH), 2.5–3.0 (c, C_6H_5)
5	3395 s 3289 b	1900	1598	1554 1559	5.63 s	8.56 (s, $(CH_3)_3$), 7.7–9.0 (b, C_6H_{10}), 7.5–7.78 (b, C_6H), 7.18–7.46 (b, C_6H), 4.10 (s, CH), 3.0–3.3 (b, NH)
6	3271 s 3223 b	1908 1901	1599	1562 1502	5.58 s	7.94–9.26 (b, C_6H_{10}), 7.42–7.62 (b, C_6H), 5.48–5.8 (b, C_6H), 6.10 (s, CH_2), 3.05 (b, NH), 3.09 (b, NH), 2.46–2.94 (c, Ph)
7	3389 s 3271 b	1933 1899	1672	1633 1578	5.67 s	8.57 (s, $(CH_3)_3$), 7.6–9.2 (c, C_6H_{10}), 6.4–7.2 (b, C_6H), 4.15 (s, CH), 3.07 (b, NH)

[a] KBr disk. [b] Measured in $CDCl_3$. Key: s = singlet, b = broad, c = complex. [c] AB type, *J*(AB) = 8 Hz, δ(AB) = 29.7 Hz.

$(CO)(PPh_3)CH_3$ (0.67 g, 1.57 mmol), $C_6H_{11}NC$ (0.65 g, 6.0 mmol), and benzene (15 mL) was charged in a sealed tube and kept at 70 °C for 30 h. The solvent was removed under reduced pressure and the residue was purified by chromatography on silica gel. Elution with *n*-hexane–benzene (20:1) gave unreacted cyclohexyl isocyanide and triphenylphosphine. Elution with CH_2Cl_2–THF (10:1) gave a brown-orange band. Removal of the solvent and crystallization of the residue from CH_2Cl_2–*n*-hexane at −30 °C gave dark orange crystals of **3** (0.29 g, 38%).

(c) η-$C_5H_5Fe(CO)[-C(=NC_6H_{11})C\{NHC(CH_3)_3\}=C(H)C(NHC_6H_{11})-]$ (5). (i) From η-$C_5H_5Fe(CO)[CNC(CH_3)_3]CH_3$. A mixture of η-$C_5H_5Fe(CO)[CNC(CH_3)_3]CH_3$ (0.28 g, 1.13 mmol) and $C_6H_{11}NC$ (0.27 g, 2.4 mmol) was heated in benzene at reflux. After 10 h, the solvent was removed in vacuo and the residue was chromatographed on alumina. Elution with *n*-hexane gave a pale yellow band of the unreacted starting material (0.01 g). Elution with benzene gave a yellow solution. Removal of the solvent and crystallization of the residue from CH_2Cl_2–*n*-hexane at −30 °C gave **5** (0.13 g, 25%) as orange-yellow crystals.

(ii) From η-$C_5H_5Fe(CO)[-C(=NC_6H_{11})C(CH_3)=NC(CH_3)_3]$. A solution of η-$C_5H_5Fe(CO)[-C(=NC_6H_{11})C(CH_3)=NC(CH_3)_3]$ (0.36 g, 1.0 mmol) and $C_6H_{11}NC$ (0.33 g, 3.0 mmol) in benzene (25 mL) was heated to reflux. After 20 h, the analogous workup to that described above gave **5** (0.18 g, 38%).

(d) η-$C_5H_5Fe(CO)[-C(=NC_6H_{11})C(NHC_6H_{11})=C(H)C\{NHC(CH_3)_3\}-]$ (6). A mixture of η-$C_5H_5Fe(CO)[-C(=NC_6H_{11})C(CH_3)=NC_6H_{11}]$ (0.25 g, 0.66 mmol), $(CH_3)_3CNC$ (0.17 g, 2.0 mmol), and benzene (10 mL) charged in a sealed tube was kept at 70 °C for 31 h. The solvent was removed in vacuo, and the residue was chromatographed on alumina. Elution with CH_2Cl_2–THF (10:1) gave a yellow orange band. The solution was concentrated to dryness and the residue was crystallized from *n*-hexane at −30 °C to give reddish brown crystals of **6** (0.15 g, 47%).

Reaction of η-$C_5H_5Fe(CO)[CNC(CH_3)_3]CH_3$ with $(CH_3)_3CNC$. A mixture of η-$C_5H_5Fe(CO)[CNC(CH_3)_3]CH_3$ (0.44 g, 1.78 mmol), $(CH_3)_3CNC$ (0.46 g, 5.5 mmol), and benzene (12 mL) was kept in a sealed tube at 70 °C for 30 h. The reaction mixture was purified by chromatography on alumina. Elution with *n*-hexane–benzene (10:1) gave a yellow band, from which the starting material (0.06 g) was recovered. Elution with CH_2Cl_2 gave a yellow-orange band. Removal of the solvent and crystallization of the residue from *n*-hexane–benzene yielded **8** (0.059 g, 10%). Elution with CH_2Cl_2–THF (10:1) gave unknown yellow crystals (0.029 g).

Anal. Calcd for $C_{17}H_{26}N_2OFe$: C, 61.83; H, 7.94; N, 8.48. Found: C, 61.71; H, 7.93; N, 8.45. The proton NMR spectrum in $CDCl_3$ consists of six singlets at τ 8.86, 8.90 [$NC(CH_3)_3$], 8.51 [$=NC(CH_3)_3$], 7.80, 7.53 (CH_3), and 5.38 (C_5H_5).

Reaction of η-$C_5H_5Fe(CO)[CNC(CH_3)_3]Ph$ with $C_6H_{11}NC$. A solution of η-$C_5H_5Fe(CO)[CNC(CH_3)_3]Ph$ (0.10 g, 0.32 mmol) and $C_6H_{11}NC$ (0.22 g, 2 mmol) in benzene (20 mL) was refluxed for 14 h. The solvent was removed under reduced pressure and the residue was chromatographed on alumina. The first elution with *n*-hexane–benzene (2:1) gave a mixture of unreacted cyclohexyl isocyanide and the starting material (trace). The second elution with CH_2Cl_2–THF (5:1) gave a yellow solution. Removal of the solvent and crystallization from CH_2Cl_2–*n*-hexane at −30 °C gave a yellow solid of **9** (0.025 g, 12%).

Anal. Calcd for $C_{31}H_{41}N_3OFe$: C, 70.56; H, 7.83; N, 7.97. Found: C, 70.41; H, 7.70; N, 8.00. The infrared spectrum (in benzene) showed the absorptions at 2122 (N≡C), 1940 (C≡O), 1672, 1614, and 1574 (C=N) cm^{-1}. The proton NMR spectrum in $CDCl_3$ consists of two singlets at τ 8.68 [$NC(CH_3)_3$] and 5.86 (C_5H_5), a broad signal at τ 6.1–6.7 (C_6H), and two complex signals at τ 7.75–8.95 (C_6H_{10}) and 2.2–2.6 (Ph).

Compound **10** was obtained from the reaction of η-$C_5H_5Fe(CO)(CNC_6H_{11})C_6H_4Cl$-*p* and $C_6H_{11}NC$ by the analogous procedures to those described above.

Anal. Calcd for $C_{33}H_{42}N_3OClFe$: C, 67.41; H, 7.20; N, 7.15. Found: C, 67.20; H, 7.00; N, 7.25. The infrared spectrum (in benzene) showed peaks at 2135 (N≡C), 1945 (C≡O), 1670, 1620, and 1575 (C=N) cm^{-1}. The proton NMR spectrum in $CDCl_3$ consists of a singlet at τ 5.63 (C_5H_5), a broad signal at τ 6.0–6.9 (C_6H), and two complex signals at τ 7.8–9.0 (C_6H_{10}) and 1.9–2.8 (C_6H_4).

Polymerization of Cyclohexyl Isocyanide. A mixture of $C_6H_{11}NC$ (0.33 g, 3 mmol), **10** (0.7 g, 0.1 mmol), and toluene (10 mL) was charged in a sealed tube and kept at 120 °C for 20 h. The resulting pale yellow solid (0.19 g) was filtered off and washed with benzene and methanol. The infrared spectrum of the solid was in good agreement with that of the authentic cyclohexyl isocyanide polymer.[7]

Attempted Reaction of η-$C_5H_5Fe(CO)(CNC_6H_{11})COCH_2Ph$ or η-$C_5H_5Fe(CO)_2[C(CH_2Ph){=}NC_6H_{11}]$ with $C_6H_{11}NC$. The title reactions were carried out in THF or benzene at reflux for 8–15 h. Evaporation of the solvent resulted in quantitative recovery of the starting material.

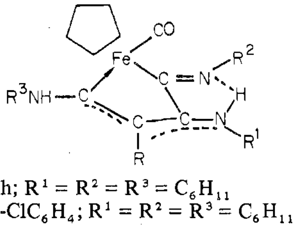
Attempted Reactions of the Cyclic Carbene Complexes with Bases. Solutions of **1** and PPh_3 or $C_6H_{11}NC$ in benzene were kept at 80 °C for 10–30 h. Evaporation of the solvent revealed (IR spectroscopy) no detectable amount of a base-containing product in the residue of each compound.

Results and Discussion

Formation of Cyclic Carbene and Imino Complexes. The carbonyl(cyclohexyl isocyanide)-η-cyclopentadienylbenzyliron derivatives η-$C_5H_5Fe(CO)(CNC_6H_{11})CH_2R$ (R = Ph or p-ClC_6H_4) reacted with $C_6H_{11}NC$ in benzene or THF at reflux to give the stable reddish brown crystalline compounds (**1** or **2**), analyzing as 1:2 compounds of the two reactants. The reaction of η-$C_5H_5Fe(CO)(PPh_3)CH_3$ with $C_6H_{11}NC$ produced the similar type of complex **3**, although η-$C_5H_5Fe(CO)_2CH_3$ gave only the acetyl complex,[14] η-$C_5H_5Fe(CO)(CNC_6H_{11})COCH_3$. Compound **3** was also obtained from the reaction of bisimino complex η-$C_5H_5Fe(CO)[\text{-}C({=}NC_6H_{11})C(CH_3){=}NC_6H_{11}]$ with $C_6H_{11}NC$ in benzene at 70 °C.

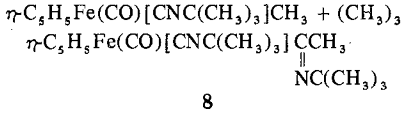
Compounds which contain two different N-alkyl substituted imino groups can be prepared. When reactions of η-$C_5H_5Fe(CO)[CNC(CH_3)_3]R$ (R = $PhCH_2$ or CH_3) or η-$C_5H_5Fe(CO)(CNCH_2Ph)CH_2Ph$ with $C_6H_{11}NC$ were run under similar conditions, the 1:2 adduct (**4**, **5**, or **6**) was formed. Treatment of η-$C_5H_5Fe(CO)[\text{-}C({=}NC_6H_{11})C(CH_3){=}NC_6H_{11}]$ with $(CH_3)_3CNC$ in benzene at 70 °C gave **7**. The infrared spectra of these compounds showed a strong absorption in the range from 1880 to 1933 cm^{-1} assignable to a carbonyl stretching frequency. These compounds also exhibited two weak bands due to the N–H stretching, a sharp band in the range from 3270 to 3400 cm^{-1}, and a relatively broad one from 3180 to 3290 cm^{-1}. The broad absorption suggested the presence of a N···H hydrogen bond.[15] This absorption shifted to 2500–2800 cm^{-1} on deuteration. In the proton NMR spectra the resonance at τ ca. 3.2 due to the NH protons disappeared on treatment with D_2O.

It was determined by x-ray crystallography that the molecular architecture of **7** has a five-membered carbene structure containing an iron atom and that there exists the electron delocalization in the N(H)–C–C(R)–C–N(H) system.[10,16] The presence of a hydrogen bond was also confirmed by the shorter H(N)···N distance (2.29(3) Å) than that of van der Waals radii (2.7 Å) and the planarity of the five-membered ring system, N-C-C-N-H. Accordingly, analogous structures were assigned to this type of complex.



1, R = Ph; $R^1 = R^2 = R^3 = C_6H_{11}$
2, R = p-ClC_6H_4; $R^1 = R^2 = R^3 = C_6H_{11}$
3, R = H; $R^1 = R^2 = R^3 = C_6H_{11}$
4, R = Ph; $R^1 = (CH_3)_3C$; $R^2 = R^3 = C_6H_{11}$
5,[17] R = Ph; $R^1 = (CH_3)_3C$; $R^2 = R^3 = C_6H_{11}$
6, R = Ph; $R^1 = PhCH_2$; $R^2 = R^3 = C_6H_{11}$
7, R = H; $R^1 = R^2 = C_6H_{11}$; $R^3 = (CH_3)_3C$

Compound η-$C_5H_5Fe(CO)[CNC(CH_3)_3]CH_3$ gave a 1:1 addition compound, η-$C_5H_5Fe(CO)[CNC(CH_3)_3][C(CH_3){=}NC(CH_3)_3]$ (**8**), without forming a carbene complex, when treated with bulky *tert*-butyl isocyanide in benzene at 70 °C (eq 3). The infrared spectrum of **8** showed three strong



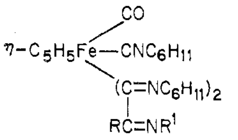
$$\eta\text{-}C_5H_5Fe(CO)[CNC(CH_3)_3]CH_3 + (CH_3)_3CNC \rightarrow \eta\text{-}C_5H_5Fe(CO)[CNC(CH_3)_3]\underset{\underset{\displaystyle NC(CH_3)_3}{\|}}{C}CH_3 \qquad (3)$$

8

bands at 2120 (N≡C), 1945 (C≡O), and 1634 (C=N) cm^{-1}. The proton NMR spectrum was shown as a mixture of two isomers, which differ by the orientation of the $=NC(CH_3)_3$ group. The *tert*-butyl group may assume either cis or trans orientation to the methyl group with respect to the C=N double bond. The ratio of two isomers is 3.5:1. The presence of the analogous type of isomers has been reported in the related compounds of iron,[18] molybdenum,[19] and palladium.[5] The steric requirement of both coordinated and incoming isocyanides appears to be a factor to control of the reactivity.

When aryl iron complexes, η-$C_5H_5Fe(CO)(CNR)C_6H_4X$-p (X = H or Cl), were treated with cyclohexyl isocyanide in THF at reflux, multiple insertion occurred to produce the trisimino complexes [**9** (R = p-ClC_6H_4; $R^1 = C_6H_{11}$) and **10** (R = Ph; $R^1 = (CH_3)_3C$], characterized by the presence of an absorption at ca. 2130 cm^{-1} due to a coordinated isocyanide group (eq 4).

$$\eta\text{-}C_5H_5Fe(CO)(CNR^1)R + 3C_6H_{11}NC \longrightarrow$$



(4)

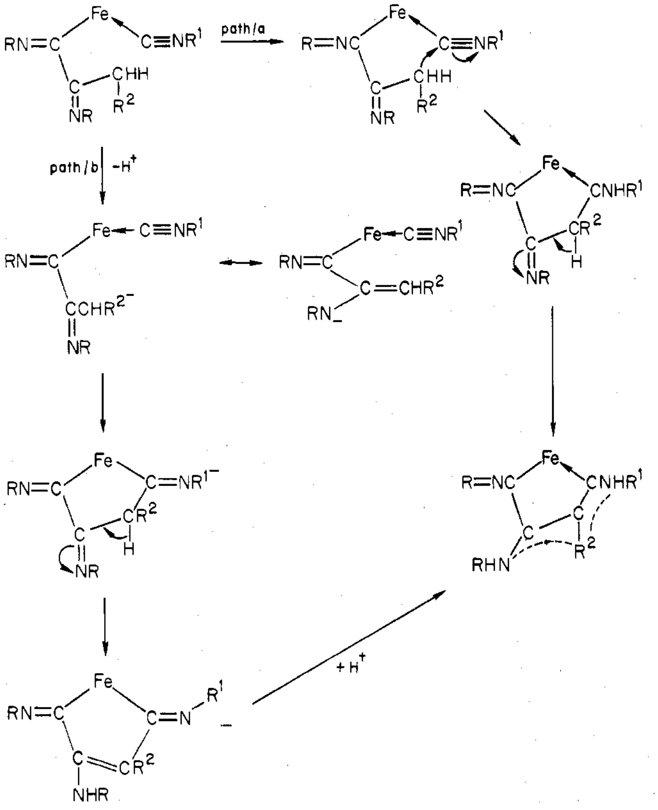
9 or **10**

Insertion Mechanism. Insertion of carbon monoxide into a transition metal σ bond is a well-known phenomenon.[20] Mechanistic studies have been conducted in a variety of metal alkyl complexes. Such reactions are generally believed to involve a migration of an alkyl group onto a coordinated carbonyl ligand. Much work on analogous insertion reactions of isocyanides has been reported.[3,4] Recently, mechanistic studies on the insertion of isocyanide into alkyl(aryl)–platinum[21] and –palladium[5,22] complexes and the photoassisted insertion of isocyanide into alkyliron complexes[9] have been performed. These reactions are suggested to proceed with ligand replacement or by direct coordination to the metal with expansion of the metal coordination number, followed by subsequent migration of an alkyl group to a coordinated isocyanide.

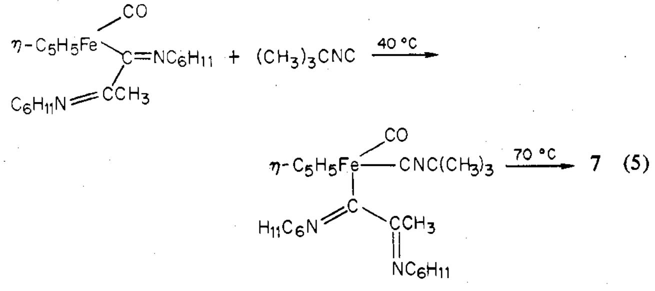
We have already described that the reaction of a benzyl derivative of dicarbonyl-η-cyclopentadienyliron with cyclohexyl isocyanide gives a cyclic carbene complex but the methyl or phenyl derivative gives only the acyl complex.[10,14,16] The former reaction is assumed to arise from an initial displacement of CO with isocyanide to give η-$C_5H_5Fe(CO)(CNC_6H_{11})CH_2C_6H_4X$-p. This process is supported by the fact that η-$C_5H_5Fe(CO)(CNR^1)R$ reacts smoothly with isocyanide to produce a carbene complex, although η-$C_5H_5Fe(CO)(CNC_6H_{11})COCH_2Ph$ or η-$C_5H_5Fe(CO)_2[C(CH_2Ph){=}NC_6H_{11}]$ remains unchanged. Thus, the direction of reaction between η-$C_5H_5Fe(CO)_2R$ and isocyanide (either formation of a cyclic carbene or an acyl complex) is determined by either a substitution reaction of carbon monoxide with isocyanide or an insertion of carbon monoxide. This may be related to bond strength of an iron–carbon σ bonds. It has generally been known that the benzyl–metal linkage is stronger than methyl- or phenyl–metal.[20]

For the purpose of obtaining some information on the subsequent steps for the multiple insertion mechanism, the

Scheme I. Two Possible Routes for Formation of Cyclic Carbene Complexes (the η-$C_5H_5(CO)$ group has been omitted for clarity)



reaction of the bisimino complex η-$C_5H_5Fe(CO)[-C(=NC_6H_{11})C(CH_3)=NC_6H_{11}]$ with $(CH_3)_3CNC$ was run in benzene at 40 °C. This compound underwent release of coordination of a nitrogen atom and filling of the vacant position with an entering isocyanide, thus converting it to **11**. On heating **11** at 70 °C, the cyclic carbene complex **7** was formed (eq 5).

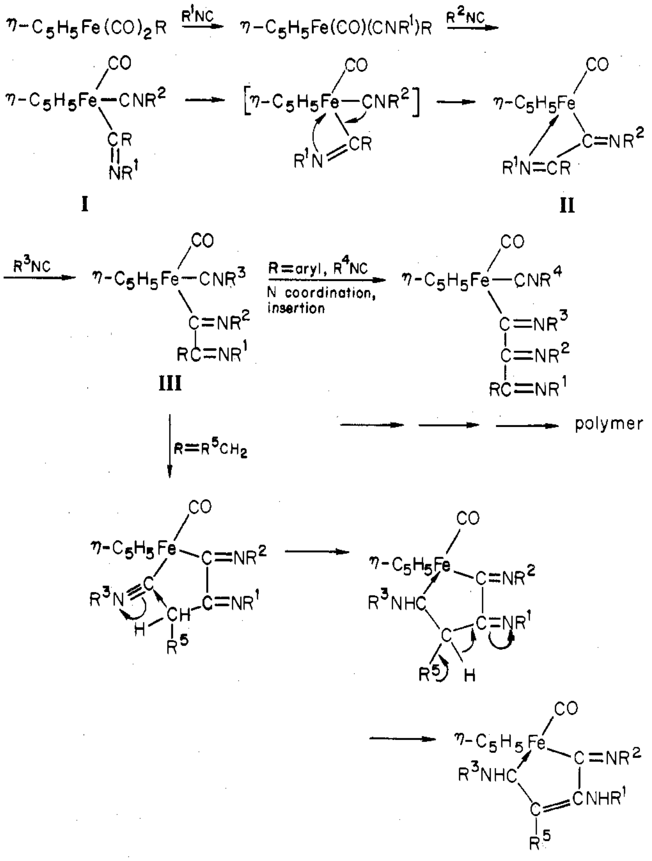


(5)

11

Among various possible pathways for formation of the carbene complex from **11**, two possible routes may be considered (Scheme I). Path a consists of a nucleophilic attack of an acidic C–H group activated by the neighboring imino groups on the carbon atom of a coordinated isocyanide. This mechanism is analogous to that postulated for the reactions of the protic substances such as amines, alcohols, and thiols with a coordinated isocyanide ligand in the isocyanide metal complexes to give the carbene complexes.[23-25] Finally, the reaction is completed by a transfer of another proton to an imino nitrogen atom. Path b involves an initial deprotonation from an acidic C–H group, followed by a nucleophilic attack of a resulting carbanion to the slightly polarizable carbon atom of a coordinated isocyanide. The anion then undergoes a proton shift to an imino nitrogen atom and again gains a proton to give a final product. This may be compared with the postulated mechanism for the insertion reactions of acetylenes

Scheme II. Proposed Mechanism of the Reactions Leading to Formation of the Cyclic Carbene Complexes and Polymerization of Isocyanide



with hydridobis(triphenylphosphine)-η-cyclopentadienylruthenium.[26]

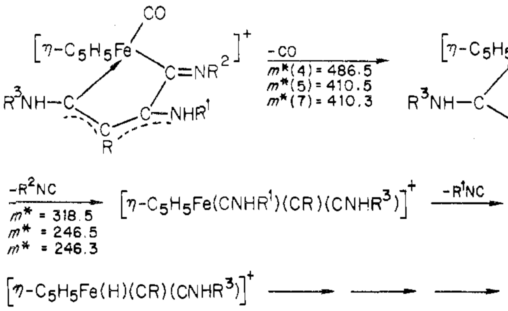
In the attempts to examine the two possible routes, compound **11** was treated in the presence of bases such as $(C_2H_5)_3N$ or $NaOCH_3$. No acceleration of the reaction was observed. Variation of the solvents had a relatively small effect on the reaction rate. Accordingly, we feel that path a is preferable over path b, although there is no direct precedent for this type of reaction.

No further insertion of isocyanide molecules to a cyclic carbene complex occurred, depending on the higher stability of the five-membered ring structure. A similar trend has been observed in the palladium complex.[5] However, the trisimino complex **9** catalyzed polymerization of cyclohexyl isocyanide in toluene at 120 °C (eq 6).

$$2nC_6H_{11}NC \xrightarrow{9} \left[\underset{NC_6H_{11}}{\underset{\|}{C}}-\!\!-\!\!-\underset{NC_6H_{11}}{\underset{\|}{C}}\right]_n \tag{6}$$

Based on the isolated complexes, their related reactions, and some speculations, the mechanism of the reaction leading to the formation of the carbene complexes and the polymerization of isocyanide may be depicted as Scheme II. A driving force from I to II may be intramolecular coordination of lone pair electrons of the imino nitrogen to the iron. The isocyanide insertion assisted by an analogous type of intramolecular coordination has already been noted in the reaction of η-$C_5H_5Co(PPh_3)(PhC{\equiv}CPh)$ with isocyanide to give η-$C_5H_5Co[-C(=NR)C(Ph)=C(Ph)C(=NR)-]$.[27] Compound III is formed by replacement of N coordination with an incoming isocyanide. Several attempts to isolate II and III from the reaction system were unsuccessful and led to only the formation of the carbene complex. Compound II was

Scheme III. Degradation Path of Cyclic Carbene Complexes



obtained from a photochemical reaction between isocyanide and η-$C_5H_5Fe(CO)(CNR^1)R$.[9] Compound III was isolated from the reaction of II with isocyanide under mild conditions. The aforementioned results show a rapid addition of the C–H bond to a coordinated isocyanide. In the case of no interaction between the acidic proton and a coordinated isocyanide, the reaction proceeds generally with displacement of a coordinated isocyanide with an incoming one, followed by insertion of a coordinated isocyanide. Repetition of this process leads to the polymerization of isocyanide. An important factor leading to formation either of the carbene complex or of the trisimino complex is due to whether or not hydrogens exist in the α position of the alkyl group in complex η-$C_5H_5Fe(CO)(CNR^1)R$.

Mass Spectra of Cyclic Carbene Complexes. There is a variety of studies on the mass spectra of transition metal alkyl and acyl complexes,[28-32] but few on the imino complexes.[8,9] We found that the mass spectra of the carbene complexes exhibited metastable ions to permit elucidation of a part of the fragmentation scheme.

The parent ion, M(**5**) (*m/e* 465, relative intensity 26), in the mass spectrum of **5** loses a carbonyl group, giving the carbonyl-free ion $[M(\mathbf{5}) - CO]^+$ (*m/e* 437, relative intensity 16). The loss of $C_6H_{11}NC$ from this ion occurs then to give the ion $[M(\mathbf{5}) - CO - C_6H_{11}NC]^+$ (*m/e* 328, relative intensity 100). This ion undergoes successive losses of $(CH_3)_2C{=}CH_2$ and HNC to give $[M(\mathbf{5}) - CO - C_6H_{11}NC - (CH_3)_2C{=}CH_2 - HNC]^+$ (*m/e* 245, relative intensity 12). Although the process to eliminate the $C_6H_{11}NC$ group from the ion (*m/e* 328) is also observed, the probability appears to be very low because of the relative intensity ratio of $[M(\mathbf{5}) - CO - C_6H_{11}NC - (CH_3)_3CNC]^+/[M(\mathbf{5}) - CO - C_6H_{11}NC - C_6H_{11}NC]^+ \simeq 10$. On the other hand, the parent ion M(**7**) (*m/e* 465, relative intensity 35) of **7**, being an isomer of **5**, undergoes the stepwise losses of carbonyl and $C_6H_{11}NC$ groups to give $[M(\mathbf{7}) - CO - C_6H_{11}NC]^+$ (*m/e* 328, relative intensity 21).

The mass spectra of two isomers (**5** and **7**) suggest that the first loss of isocyanide from the carbene complexes arises from a cleavage of the metal–carbon σ bond. Facile cleavage of the metal–carbon σ bond has been observed in the mass spectra of alkyl complexes.[8,9,31,32] The subsequent loss appears to occur with elimination of isocyanide from the N-substituted amino group of the β position.

Following these spectra, the degradation of the carbene complexes may be illustrated as Scheme III.

A similar behavior is observed in the spectrum of **4**. The stepwise losses of carbonyl and $C_6H_{11}NC$ groups from the parent ion M(**4**) (*m/e* 541, relative intensity 35) occur to give $[M(\mathbf{4}) - CO - C_6H_{11}NC]^+$ (*m/e* 404, relative intensity 100). The loss of $(CH_3)_3CNC$ from this ion occurs then giving $[M(\mathbf{4}) - CO - C_6H_{11}NC - (CH_3)_3CNC]^+$ (*m/e* 321, relative intensity 21). A salient feature in the spectra of the carbene complexes prepared here is that the base peak is $[M - CO - R^2NC]^+$.

Registry No. **1**, 57016-60-1; **2**, 57016-61-2; **3**, 64056-95-7; **4**, 59617-70-8; **5**, 64056-88-8; **6**, 64056-89-9; **7**, 52346-57-3; **8**, 64056-90-2; **9**, 52346-61-9; **10**, 64082-11-7; η-$C_5H_5Fe(CO)(CNC_6H_{11})CH_2Ph$, 51567-70-5; η-$C_5H_5Fe(CO)(PPh_3)CH_3$, 12100-51-5; η-$C_5H_5Fe(CO)[CNC(CH_3)_3]CH_3$, 57545-68-3; η-$C_5H_5Fe(CO)[{-}C({=}NC_6H_{11})C(CH_3){=}NC(CH_3)_3]$, 57437-19-1; η-$C_5H_5Fe(CO)[{-}C({=}NC_6H_{11})C(CH_3){=}NC_6H_{11}]$, 52346-55-1; η-$C_5H_5Fe(CO)[CNC(CH_3)_3]Ph$, 64056-91-3; η-$C_5H_5Fe(CO)(CNC_6H_{11})C_6H_4Cl$-*p*, 51567-76-1; $C_6H_{11}NC$, 931-53-3; $(CH_3)_3CNC$, 7188-38-7.

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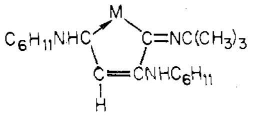
(17) Compound **5** is an isomer of **7**. Two possible structures (**5** and **5a**) may



5a

be considered, where M = η-$C_5H_5Fe(CO)$. Structure **5** received our preference by the fact that the complex was in complete agreement with that obtained from the reaction between η-$C_5H_5Fe(CO)[{-}C({=}NC_6H_{11})C(CH_3){=}NC(CH_3)_3]$ and $C_6H_{11}NC$.
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