Studies on Interaction of Isocyanide with Transition Metal Complexes. XIII.[1) Preparation of Carbene Complexes of Nickel, Iron, and Cobalt through Protonation of Monoimino and Polyimino Type Complexes

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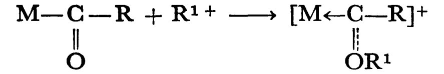
Reactions of η-$C_5H_5Ni(CNR^1)[C(R){=}NR^1]$ ($R{=}CH_3$, p-ClC_6H_4; $R^1{=}C_6H_{11}$, $(CH_3)_3C$) and η-$C_5H_5Fe(CO)_2$-$[C(CH_2C_6H_4X$-$p){=}NC_6H_{11}]$ (X=H, Cl) with HBF_4 gave the cationic carbene complexes, η-$C_5H_5Ni(CNR^1)$-$[C(R)NHR^1]BF_4$ and η-$C_5H_5Fe(CO)_2[C(CH_2C_6H_4X$-$p)$ $NHC_6H_{11}]BF_4$. η-$C_5H_5Co[-C({=}NR)-CPh{=}CPh-C({=}NR)-]$ (**1a**; $R{=}2,6$-$(CH_3)_2C_6H_3$: **1b**; $R{=}p$-$CH_3C_6H_4$) reacted with HBF_4 to give η-$C_5H_5Co[-C(NHR)-CPh{=}CPh-C({=}NR)-]BF_4$ (**2a**, **b**). Compound **2a** exists as two isomers, induced by the restricted rotation about the C–N bond. Treatment of **1a** with HCl gave η-$C_5H_5Co[-C(NHR)-CPh{=}CPh-C({=}NR)-]Cl$ (**3b**). The H(N) proton showed some fluxional behavior in its proton NMR spectrum. Reaction of **1b** with CF_3COOH gave the dicationic complex η-$C_5H_5Co[-C(NHR)-CPh{=}CPh-C(NHR)-](CF_3COO)_2$ **4b**. Compound **2** reacted with R^1NC($R^1{=}(CH_3)_3C$, $2,6$-$(CH_3)_2C_6H_3$) to give η-$C_5H_5Co(CNR^1)[-C({=}NR)-CPh{=}CPh-C({=}NR)-]$**5**. Reaction of **5** with HBF_4 gave again the cationic carbene complex η-$C_5H_5Co(CNR^1)[-C(NHR)-CPh{=}CPh-C({=}NR)-]BF_4$.

Since the current interest of the metal-stabilized carbene complexes started with the preparation of $W[C(OCH_3)Ph](CO)_5$,[2) several preparative methods of the carbene complexes have been reported.[3–5) Among them, the acetyl complexes of iron, molybdenum, and ruthenium are known to take up a proton or a carbonium ion to give the corresponding cationic carbene complexes, when reacted with protic acids or trialkyloxonium salt (Eq. (1)).[6,7)



$$\mathrm{M{-}\underset{\displaystyle O}{\overset{}{\underset{\|}{C}}}{-}R} + \mathrm{R^{1+}} \longrightarrow \mathrm{[M{\leftarrow}\underset{\displaystyle OR^1}{\underset{\vdots}{C}}{-}R]^+} \qquad (1)$$

One would expect that more facile protonation of the imino type complex in comparison with the acetyl derivative may occur because of the higher inherent basicity of nitrogen over oxygen. Treichel *et al.* reported briefly that the reaction of $Pt(PPh_3)_2I[C(Ph){=}NCH_3]$ with NH_4^+ produced $Pt(PPh_3)_2I[C(Ph)NHCH_3]^+$.[8) Lappart and coworkers reported recently that treatment of rhodium complexes with imidoyl chloride in the presence of hydrogen chloride gave the carbene complexes.[9,10) This reaction has been believed to proceed with protonation of the imino complex formed as the unstable intermediate.

We report in this paper that the imino type compounds of nickel,[11) iron,[12,13) and cobalt[14) react readily with protic acids to give stable cationic carbene complexes.

Experimental

All reactions were carried out under an atmosphere of nitrogen. Melting points were taken on a Mitamura capillary melting point apparatus, and are uncorrected. Infrared spectra were recorded on a Shimadzu IR-27G spectrophotometer. Proton magnetic resonance spectra were obtained on JEOL C-60HL or Varian HA-100B spectrometers, using tetramethylsilane as an internal reference. Isocyanides[15) were prepared by procedures described in the literature. The organometallic complexes, η-$C_5H_5Ni(CNR^1)[C(R){=}NR^1]$ ($R{=}CH_3$, Ph or p-ClC_6H_4; $R^1{=}C_6H_{11}$ or $(CH_3)_3C$),[11) η-$C_5H_5Fe(CO)_2[C(CH_2C_6H_4X$-$p){=}NC_6H_{11}]$ (X=H or Cl)[12), η-$C_5H_5Fe(CO)[-C({=}NC_6H_{11})$-$C(NHR^1)$-$C(R)$-$C(NHR^2)]$ (R=H or Ph; $R^1{=}C_6H_{11}$ or $CH_3)_3C$; $R^2{=}(CH_3)_3C$ or $C_6H_{11})$[13) and η-$C_5H_5Co[-C({=}NR)-CPh{=}CPh-C({=}NR)-]$ ($R{=}(CH_3)_3C$, p-$CH_3C_6H_4$ or $2,6$-$(CH_3)_2C_6H_3$)[14), were prepared according to the published methods.

Preparation of Carbene Complexes. *(a) η-$C_5H_5Ni(CNC_6H_{11})[C(C_6H_4Cl$-p$)NHC_6H_{11}]BF_4$.* A mixture of η-$C_5H_5Ni(CNC_6H_{11})[C(C_6H_4Cl$-$p){=}NC_6H_{11})$ [0.22 g, 0.5 mmol), 42% HBF_4 (3 ml) and benzene (15 ml) was stirred for 1 hr at room temperature. The reddish orange solution changed to dark yellow. The benzene layer was separated and the aqueous layer was extracted twice with CH_2Cl_2 (5 ml). The combined extracts were washed with water and dried over anhydrous magnesium sulfate. The solvent was evaporated almost to dryness under reduced pressure, and the residue was crystallized from CH_2Cl_2–n-hexane at −30 °C to give the dark yellow crystalline material (0.22 g, 82%). Other nickel carbene complexes were also prepared according to procedures similar to those described above.

(b) η-$C_5H_5Fe(CO)_2[C(CH_2Ph)NHC_6H_{11}]BF_4$. A mixture of η-$C_5H_5Fe(CO)_2[C(CH_2Ph){=}NC_6H_{11}]$ (0.7 g, 1.9 mmol), 42% HBF_4 (2 ml) and benzene (15 ml) was stirred for 2 hr at room temperature. Yellow crystalline material was separated. Methylene chloride was added to dissolve the crystals. The organic layer was washed with water and dried over $MgSO_4$. The solvent was removed *in vacuo* and the residue was crystallized from CH_2Cl_2–n-hexane at −30 °C to give yellow crystals (0.77 g, 85%). Other iron carbene complexes were also prepared according to procedures similar to those described above.

(c) η-$C_5H_5Co[-C\{{=}NC_6H_3(CH_3)_2$-$2,6\}$-$CPh{=}CPh$-$C\{NHC_6H_3(CH_3)_2$-$2,6$-$\}$-$]BF_4$. A mixture of η-$C_5H_5Co[-C\{{=}NC_6H_3(CH_3)_2$-$2,6\}$-$CPh{=}CPh$-$C\{{=}NC_6H_3(CH_3)_2$-$2,6\}-]$ (0.18 g, 0.32 mmol), 42% HBF_4 (1 ml) and benzene was stirred at room temperature for 1 hr. The resulting orange crystals were filtered and washed with ether (0.18 g, 86%).[16)

(d) η-$C_5H_5Co[-C({=}NC_6H_4CH_3$-p$)$-$CPh{=}CPh$-$C(NHC_6H_4CH_3$-p$)$-$]Cl$. A mixture of η-$C_5H_5Co[-C({=}NC_6H_4CH_3$-$p)$-$CPh{=}CPh$-$C({=}NC_6H_4CH_3$-$p)$-$]$ (0.16 g, 0.3 mmol) and 6M-HCl (4 ml) was kept at room temperature for 2 hr. The orange layer changed to pale yellow. The resulting brown crystalline solid was filtered off, washed with water, and then extracted with benzene. After drying over Na_2SO_4, the solvent was removed under reduced pressure, and the residue was crystallized from n-hexane to give the title compound (0.095 g, 56%) as brown crystals.

(e) η-$C_5H_5Co[-C(NHC_6H_4CH_3$-p)-CPh=CPh-$C(NHC_6H_4CH_3$-p)-]$(CF_3COO)_2$. To a solution of **1b** (0.12 g, 0.22 mmol) in CH_2Cl_2 (2 ml) was added CF_3COOH (0.2 ml) at room temperature. The resulting dark brown solution was concentrated to 1 ml under reduced pressure, and *n*-hexane was added. The dark brown crystals (0.17 g, 85%) were filtered off.

Reaction of η-$C_5H_5Ni(CNC_6H_{11})[C(Ph)NHC_6H_{11}]BF_4$ with CH_3ONa. A mixture of the carbene complex (0.075 g, 0.13 mmol), CH_3ONa (0.1 g), and CH_3OH (10 ml) was stirred at room temperature for 30 min. The solution changed rapidly from dark yellow to reddish brown. The solvent was evaporated, and the residue was dissolved with CH_2Cl_2. The solution was washed with water and dried over Na_2SO_4. Removal of the solvent and crystallization of the residue from benzene-*n*-hexane gave η-$C_5H_5Ni(CNC_6H_{11})$ [C(Ph)=NC_6H_{11}] (0.84 g, 83%).

Analogous procedures were applied for the deprotonation reactions of the iron and cobalt carbene complexes.

*Reaction of **2a** with $(CH_3)_3CNC$.* A mixture of **2a** (0.25 g, 0.38 mmol) and *tert*-butyl isocyanide (0.83 g, 1.0 mmol) in THF (15 ml) was kept at room temperature for 20 hr, followed by removal of the solvent and dark orange crystals of **5a** (0.19 g, 73%; mp 234—236 °C (decomp. with melting)). The infrared spectrum consisted of 2153-(N≡C), 1623(C=N), and 1584 cm^{-1}(C–N). The proton NMR spectrum in $CDCl_3$ showed four singlets at 1.48(s, $(CH_3)_3$), 2.17(CH_3), 2.23(CH_3), and 4.41(C_5H_5) ppm, and a complex signal at *ca.* 7.00 (C_6H_5 and C_6H_3) ppm. Found: C, 77.65; H, 6.41; N, 6.34%. Calcd for $C_{42}H_{42}N_3Co$: C, 77.88; H, 6.54; N, 6.49%.

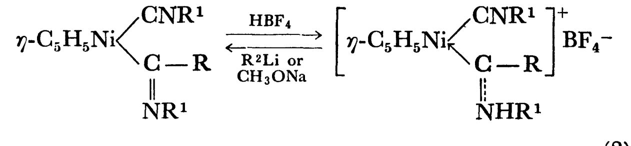
Kinetic Analysis. The methods developed by Gutowsky and Holm was applicable for the determination of the kinetic parameters.17) The difference between the chemical shifts of the methyl protons of the two isomers at various temperatures are listed in Table 1.

TABLE 1. CHEMICAL SHIFT DIFFERENCES FOR METHYL PROTONS IN **2a** AT VARIOUS TEMPERATURES

Temp. (°C)	$\delta\omega_e$ (cycles s^{-1})
−10	43
28	37
36	33
45	30
48	26.5
52	22
59	14

Results and Discussion

Nickel Carbene Complexes. Imino type complexes of nickel react with an excess of HBF_4 in benzene or CH_2Cl_2 at room temperature to produce the cationic carbene complexes (Eq. (2)), which undergo deprotonation by alkyllithium or CH_3ONa to recover the parent imino type complexes.



$$\eta\text{-}C_5H_5Ni(CNR^1)[C(R)=NR^1] \underset{R^2Li\ \text{or}\ CH_3ONa}{\overset{HBF_4}{\rightleftarrows}} [\eta\text{-}C_5H_5Ni(CNR^1)[C(R)NHR^1]]^+BF_4^- \quad (2)$$

These compounds are freely soluble in methylene chloride and acetone, but less soluble in benzene. The infrared spectra show the strong NH-stretching bands at 3300—3100 cm^{-1}, which shift to 2700—2500 cm^{-1} on deuteration. The isocyanide absorptions are observed in the range of 2200—2500 cm^{-1}, which are 40—70 cm^{-1} higher than those for the neutral parent compounds.

The proton NMR spectra of these complexes indicate the presence of isomers. The spectrum of η-$C_5H_5Ni[CNC(CH_3)_3][C(Ph)NHC(CH_3)_3]BF_4$ shows a pair of signals for each of the following: C_5H_5, $(CH_3)_3CN$=, and $(CH_3)_3CNH$– protons (the isomer ratio 3 : 1). This is reasonably explained in terms of the orientation of the N–H group. The hydrogen atom could assume either a *cis* or a *trans* orientation to the metal group with respect to the C–N bond, as follows:

cis *trans*

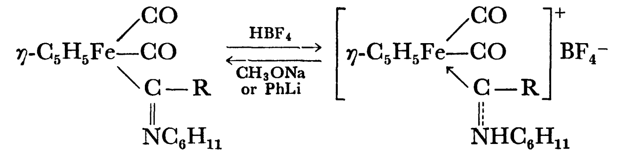
M=η-$C_5H_5Ni(CNR^1)$

Analogous isomerism was observed in the [(*p*-chlorophenyl)(*N-tert*-butylamino)]carbene complex (the isomer ratio 1.7 : 1). The [(alkyl or aryl)(*N*-cyclohexylamino)]carbene complexes, however, do not show the presence of isomers. This may arise from the bulkiness of the *N*-substituted group.

We have no direct means to distinguish between the two isomers. However, it is known that the predominant isomer in the metal carbene complexes is generally the one with the least steric interaction within the carbene groups.4,5) Examination of molecular models of the carbene complexes suggested that the *cis* isomer had less steric interaction than the *trans* isomer.

The ratio between *cis* and *trans* isomers does not depend on the solvents and temperatures (≤100 °C), showing restricted rotation about the C_{carb}–nitrogen bond (Table 3). Evidence of restricted rotation about C_{carb}–heteroatom bonds has also been obtained, *e.g.*, in the series *trans*-[MX{C(NHR)Q}L_2]ClO_4 (where M= Pt or Pd; R=Ph or *p*-$CH_3C_6H_4$; Q=PhNH, EtNH, CH_3O or EtO; L=PEt_3, $PPhMe_2$, or $AsMe_3$; X=Cl or Br).18,19)

Iron Carbene Complexes. The reaction of η-$C_5H_5Fe(CO)_2[C(CH_2C_6H_4X$-*p*)=$NC_6H_{11}$] (X=H or Cl) with HBF_4 proceeds with protonation at the imino nitrogen atom to give the cationic carbene complex in nearly quantitative yield, which was characterized by the infrared N–H stretching frequency. The reaction of this compound with CH_3ONa or PhLi occurs readily with deprotonation to regenerate the parent imino type complex (Eq. (3)).



$$\eta\text{-}C_5H_5Fe(CO)_2[C(R)=NC_6H_{11}] \underset{CH_3ONa\ \text{or}\ PhLi}{\overset{HBF_4}{\rightleftarrows}} [\eta\text{-}C_5H_5Fe(CO)_2[C(R)NHC_6H_{11}]]^+BF_4^- \quad (3)$$

The proton NMR spectra of the carbene complexes at room and low temperatures (≥−60 °C) do not

TABLE 2. ANALYTICAL AND SPECTROSCOPIC DATA OF NICKEL CARBENE COMPLEXES, η-$C_5H_5Ni(CNR)[C(R^1)NHR]BF_4$

R	R^1	Yield (%)	Mp$^{a)}$ (°C)	Analyses, Found (Calcd)			IR $(cm^{-1})^{b)}$		
				C	H	N	N-H	C≡N	C-N
C_6H_{11}	Ph	78	113—115	60.98	6.40	$5.14^{c)}$	3246	2199	1572
				(60.83)	(6.62)	(5.25)	3146		
C_6H_{11}	p-ClC_6H_4	82	151—153	57.25	5.83	$5.06^{c)}$	3246	2200	1577
				(57.14)	(6.04)	(4.94)	3148		
C_6H_{11}	CH_3	78			h)		3235	2231	1575
							3143		
$(CH_3)_3C$	Ph	69	135—138	55.54	6.31	6.20	3233	2175	
				(55.44)	(6.42)	(6.16)	3143		
$(CH_3)_3C$	p-ClC_6H_4	61	157—159	51.56	5.66	5.63	3248	2171	1578
				(51.54)	(5.77)	(5.72)	3152		

R	NMR (ppm) in $CDCl_3^{d)}$	
	C_5H_5	Other signals
C_6H_{11}	5.38	2.22—1.05(c, C_6H_{10}), 4.02—3.70(b, C_6H), 4.80—4.44(b, C_6H) 7.6—7.3(c, m-, p-H), 8.0—7.78(c, o-H), 10.18—9.7(b, NH)
C_6H_{11}	5.37	2.30—1.1(c, C_6H_{10}), 4.03—3.6(b, C_6H), 4.89—4.45(b, C_6H) 7.64(q, J_{AB}=8.4 Hz, $C_6H_4)^{e)}$, 10.3—9.8(b, NH)
C_6H_{11}	5.42	2.16—1.2(c, C_6H_{10}), 2.63(s, CH_3), 4.0—3.7(b, C_6H) 4.54—4.07(b, C_6H), 10.7—9.4(b, NH)
$(CH_3)_3C$	$5.37^{f)}$ 5.26	1.42(s, $(CH_3)_3CN$), 1.77(s, $(CH_3)_3CN(H)$), 8.04—7.30(c, Ph) 1.46(s, $(CH_3)_3CN$), 1.53(s, $(CH_3)_3CN(H)$), 10.35—9.4(b, NH)
$(CH_3)_3C$	$5.36^{g)}$ 5.24	1.43(s, $(CH_3)_3CN$), 1.76(s, $(CH_3)_3CN(H)$), 7.64(q, J_{AB}=9 Hz, $C_6H_4)^{e)}$ 1.45(s, $(CH_3)_3CN$), 1.52(s, $(CH_3)_3CN(H)$), 10.8—9.74(b, NH)

a) Decomposed on melting. b) KBr disk. c) 1/3 C_6H_6 is contained. d) c=complex, b=broad, s=singlet, q=quartet. e) Center of AB quartet. f) Isomer ratio (in $CDCl_3$); 3 : 1. g) Isomer ratio; 1.74 : 1 (in $CDCl_3$), 1.7 : 1 (in DMSO). h) Pure product was not obtained.

TABLE 3. ISOMER RATIO OF η-$C_5H_5Ni[CNC(CH_3)_3]$-$[C(R)NHC(CH_3)_3]BF_4$

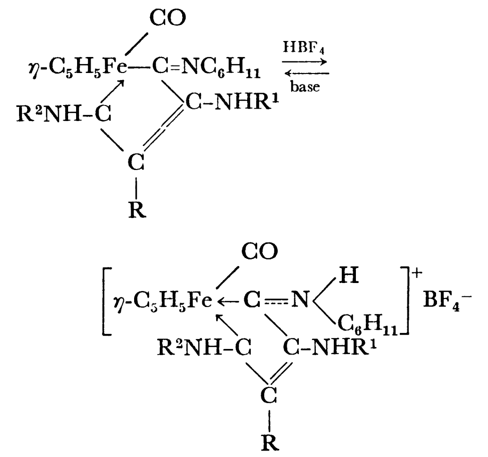
R	Temp. (°C)	Solvent$^{a)}$	Isomer ratio
Ph	25	$CDCl_3$	3 : 1
Ph	25	DMSO	2.9 : 1
Ph	63	DMSO	3 : 1
p-ClC_6H_4	25	$CDCl_3$	1.74 : 1
p-ClC_6H_4	25	DMSO	1.7 : 1
p-ClC_6H_4	56	DMSO	1.8 : 1
p-ClC_6H_4	84	DMSO	1.8 : 1

a) DMSO=$(CD_3)_2SO$.

show the presence of any isomers. Consideration of molecular models indicates that the predominant isomer is the *cis* form similar to the above mentioned nickel complexes.

The two C–O stretching frequencies appear within the range 1958—2043 cm^{-1}, 43—26 cm^{-1} higher than the value of $\nu(CO)$ of the parent complexes. They decrease in the order CO, RNC, PPh_3, and $C(CH_2Ph)$-NHC_6H_{11} for L in the complexes $[\eta$-$C_5H_5Fe(CO)_2L]X$ ($X=BF_4$ or PF_6), as shown in Table 5. The decrease is probably comparable with the order of the enhanced donor property of L.

The cyclic neutral monoamino carbene complexes react also with HBF_4 to give the cationic bisamino carbene derivatives (Eq. 4).



(4)

The infrared spectra show the NH-stretching frequencies in the range 3654—3097 cm^{-1}. In the proton NMR spectra the resonances due to the NH groups appear at *ca.* 6.7 (2H) and 9.8 (1H) ppm as two broad signals.

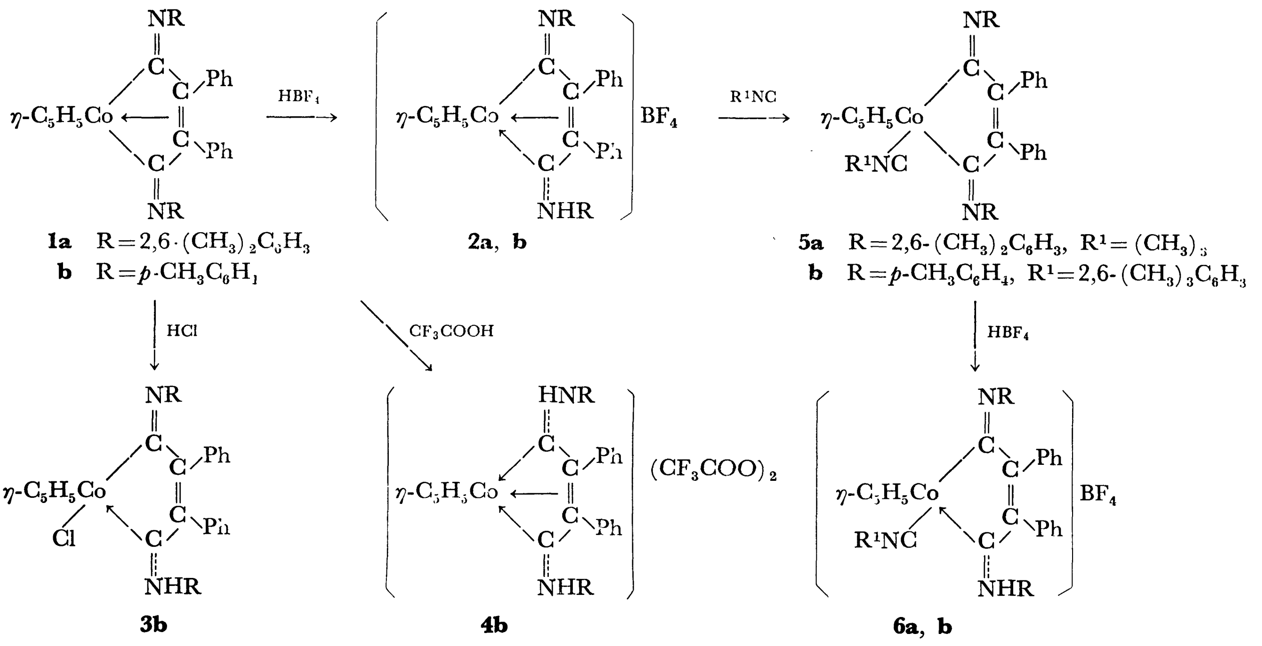
Diamino carbene complexes lose a proton again to regenerate the parent complexes by treatment with

TABLE 4. ANALYTICAL AND SPECTROSCOPIC DATA OF IRON CARBENE COMPLEXES [η-$C_5H_5Fe(CO)(L)]BF_4$

L	Yield (%)	Mp (°C)	Analysis Found (Calcd) C	H	N	IR (cm^{-1})[a] N-H	C≡O
$(CO)\{C(CH_2Ph)NHC_6H_{11}\}$	85	122—123	54.45 (54.23)	5.26 (5.20)	3.08 (3.01)	3275 3180	2042 1959
$(CO)\{C(CH_2C_6H_4Cl$-$p)NHC_6H_{11}\}$	92	134—136	50.67 (50.49)	4.61 (4.64)	2.92 (2.80)	3226 3118	2043 1958
$[(CNHC_6H_{11})\{CNHC(CH_3)_3\}(CPh)(CNHC_6H_{11})]$	63	151—153	59.42 (61.06)	7.01 (7.05)	6.53 (6.68)	3654 3540 3215 3097	1923
$[(CNHC_6H_{11})(CNHC_6H_{11})(CH)\{CNHC(CH_3)_3\}]$	70	207—209	56.38 (56.45)	7.25 (7.29)	7.38 (7.60)	3418 3374 3283	1928

L	NMR (ppm)[b] C_5H_5	Other signal
$(CO)\{C(CH_2Ph)NHC_6H_{11}\}$	4.77	2.3—1.0(b, C_6H_{10}), 4.55—4.05(b, C_6H), 4.43(s, CH_2), 7.6—7.16(c, Ph)
$(CO)\{C(CH_2C_6H_4Cl$-$p)NHC_6H_{11}\}$	4.67	2.3—1.0(b, C_6H_{10}), 4.55—4.0(b, C_6H_4), 4.45(s, CH_2), 7.55—7.1(c, C_6H_4)
$[(CNHC_6H_{11})\{CNHC(CH_3)_3\}(CPh)(CNHC_6H_{11})]$	5.30	1.05(s, $(CH_3)_3$), 2.3—0.8(b, C_6H_{10}), 4.35—3.8(b, C_6H), 7.7—7.4 and 7.25—7.05(c, Ph), 8.1—7.8(b, NH, 2H), 10.2—9.85(b, NH)
$[(CNHC_6H_{11})(CNHC_6H_{11})(CH)\{CNHC(CH_3)_3\}]$	5.48	1.47(s, $CH_3)_3$), 2.3—1.0(b, C_6H_{10}), 3.6—2.88(C_6H), 4.32—3.9(b, C_6H), 6.02(s, CH_3), 6.86—6.57(b, NH), 7.50—7.22(b, NH), 10.06—9.67(b, NH)

a) KBr disk. b) Measured in CD_3COCD_3. b=broad. s=singlet. c=complex.



Scheme 1. Reaction of cobalt complexes.

TABLE 5. INFRARED SPECTRA OF [η-$C_5H_5Fe(CO)_2L$]X

L	X	$\nu_{C=O}$ (cm^{-1})[a]	Ref.[b]
CO	PF_6	2120, 2070	1
CH_3NC	PF_6	2079, 2037	2
PPh_3	PF_6	2055, 2010	1
PPh_3	BF_4	2057, 2014	3
$C(CH_2R)NHC_6H_{11}$	BF_4	2043, 1958	This paper

a) Measured in CH_2Cl_2. b) 1) P. M. Treichel, R. L. Shubkin, K. W. Barnett, and D. Reichard, *Inorg. Chem.*, **5**, 1177 (1966). 2) R. J. Angelici, P. A. Christian, B. D. Dombek, and G. A. Pfeffer, *J. Organometal. Chem.* **67**, 287 (1974). 3) B. D. Dombek and R. J. Dombek and R. J. Angelici, *Inorg. Chim. Acta*, **7**, 345 (1973).

CH_3ONa or NaOH.

Cobalt Carbene Complexes. The reaction of organocobalt complexes are summarized in Scheme I. η-Cyclopentadienyl-2,5-di(*N*-2,6-dimethylphenylimino)-3,4-diphenylcobaltacyclopentene (**1a**) takes up readily a proton to give the cationic carbene complex (**2a**), when reacted with a large excess of HBF_4 in benzene or NH_2Cl_2 at room temperature. The infrared spectrum shows three bands at 1769 (C=N), 1630 (C=O), and 1587 (O–N) cm^{-1}, higher than those for the parent complex (**1a**). In addition to these, a new weak absorption due to the NH stretching frequency appears at 3203 cm^{-1}. The high frequency due to the C–N double bond suggests the highly strained five-membered

TABLE 6. ANALYTICAL AND SPECTROSCOPIC DATA OF COBALT COMPLEXES
η-$C_5H_5Co[-C(=NR)-PhC=CPh-C(NHR)-]BF_4$ (Type I), η-$C_5H_5Co[-C(=NR)-PhC=CPh-C(NHR)-]Cl$ (Type II), η-$C_5H_5Co[-C(NHR)-PhC=CPh-C(NHR)-](CF_3COO)_2$ (Type III), and η-$C_5H_5Co[-C(=NR)-PhC=CPh-C(NHR)-](CNR^1)BF_4$ (Type IV)

	R	R^1	Yield (%)	Mp[a] (°C)	Analyses Found (Calcd) C	H	N
	Type I						
2a	2,6-$(CH_3)_2C_6H_3$		85	210—212	67.37 (68.12)	5.01 (5.25)	4.37 (4.23)
2b	*p*-$CH_3C_6H_4$		92	—167	67.39 (67.33)	4.83 (4.84)	4.37 (4.49)
	Type II						
3b	*p*-$CH_3C_6H_4$		56	159—161	73.67 (73.36)	5.02 (5.28)	5.01 (4.89)
	Type III						
4b	*p*-$CH_3C_6H_4$		85	167—170	55.95 (56.05)	3.59 (3.67)	3.14[c] (3.19)
	Type IV						
6a	2,6-$(CH_3)_2C_6H_3$	$(CH_3)_3C$	73	123—126	69.75 (69.95)	5.20 (5.20)	5.43 (5.56)
6b	*p*-$CH_3C_6H_4$	2.6-$(CH_3)_2C_6H_3$	78	105—107	68.43 (68.58)	5.72 (5.89)	5.82 (5.71)

	IR (cm^{-1})[b] N-H	C=N	C=C	N≡C	NMR (ppm) in $CDCl_3$[d] C_5H_5	Other signals
	Type I					
2a	3203	1769	1630		5.35(s)	2.16(s, CH_3), 1.78(bs, CH_3), 2.36(bs, CH_3), 7.80—6.5(c, Ph, C_6H_3), 12.2—11.84(b, NH)
2b	3261	1758	1639		5.34(s)	2.16(bs, *p*-CH_3), 2.40(bs, *p*-CH_3), 8.00—6.8(c, Ph, C_6H_4), 12.6(b, NH)
	Type II					
3b	3260	1628	1594		4.49(s)	7.61(s, CH_3), 8.0—6.9(Ph, C_6H_4)
	Type III					
4b	3273	1772	1691		4.82(s)	2.50(s, *p*-CH_3), 7.7—7.0(c, Ph, C_6H_4), 11.2—10.8(b, NH)
	Type IV					
6a	3247	1632	1587	2192	4.73(s)	1.68(s, CH_3), 2.26(b, CH_3), 7.36—6.6(c, Ph, C_6H_3)
6b	3260	1632	1591	2152	4.47(s)	2.25(s, CH_3), 2.39(s, CH_3), 7.28—6.57(c, C_6H_3, C_6H_4)

a) Decomposed on melting. b) KBr disk. c) One mole of CF_3COOH is contained. d) s = singlet. bs = broad singlet. c = complex.

ring structure, resulting from the coordination of the C–C double bond to the cobalt atom as well as **1a**.[14] The proton NMR spectrum shows the presence of the two isomers in the ratio 2 : 1. The resonances due to the *ortho*-methyl groups occur at 2.16(s), 1.78(bs), and 2.36(bs) ppm in the relative intensity of 6 : 4 : 2, respectively. The first resonance is assignable to the methyl groups of the *N*-substituted imino group, and the latter two to those of the isomeric *N*-substituted amino one. The four structures for the compound (**2a**) are illustrated as follows:

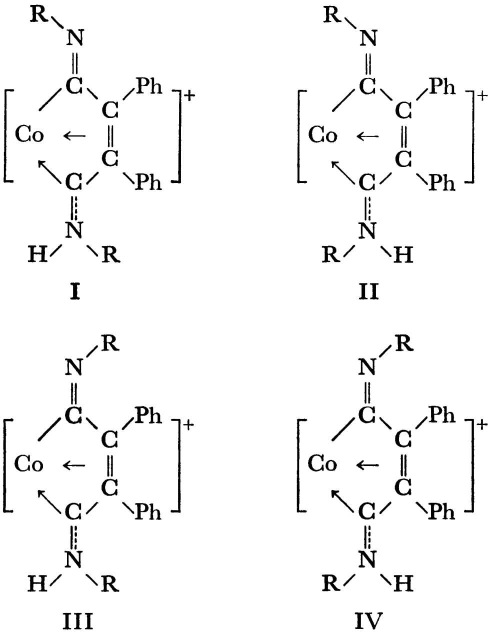


Fig. 1. Possible structures of **2a**. η-C_5H_5 and BF_4^- groups are omitted for clarity, where R is 2,6-dimethylphenyl group.

An X-ray crystallographic examination of η-C_5H_5Co-[-C(=NPh)-CPh=CPh-C(=NPh)-][14] as an analog of **1a** has shown that the *N*-phenyl group has the *cis* orientation to cobalt with respect to the C–N double bond. Accordingly, we tentatively assign two isomers to I and II. The interconversion between I and II was observed by various temperature PMR spectra. The *ortho*-methyl protons of the *N*-2,6-dimethylphenylimino group of two isomers appear at 1.78 and 2.36 ppm as relatively broad singlet at 17 °C. They became broader and their chemical shift difference became smaller on heating. At 63 °C, the spectrum consisted of one single broad signal. Finally the broad signal turned into a sharp singlet (2.06 ppm) above *ca.* 75 °C. These changes in PMR patterns are reversible.

Kinetic parameters for the rotation barrier about the C_{carb}–N bond[20] were determined by PMR line-broading technique of variable temperature PMR spectra. The approximate activation energy was 4.8 kcal/mol, and frequency factor, $1.5\times10^5\ s^{-1}$; the former value is lower than that of C_{carb}–O bond (11.5—13.8 kcal/mol) for $Cr[C(OCH_3)(C_6H_4X)](CO)_5$.[21] The relatively low activation energy, in comaprison with those of rotation barriers of organic amides (6.8—7.8 kcal/mol),[22] may be ascribed to the presence of a labile amino-proton, which leads to facile deprotonation on successive treatment with H_2O.

η-Cyclopentadienyl-2,5-di(*N*-*p*-tolylimino)-3,4-diphenylcobaltacyclopentene (**1b**) also undergoes protonation with HBF_4 to give the carbene complex (**2b**), which however shows an absence of isomers. When **1b** was allowed to react with aqueous HCl, a neutral carbene complex (**3b**) is formed. The infrared spectrum of **3b** shows three significant absorptions at 3260(NH), 1628(C=N), and 1594(C=C) cm^{-1}. The absorption due to the C–N double bond is 102 cm^{-1} lower than that (1730 cm^{-1}) for the parent compound, suggesting the absence of intramolecular coordination of the double bond to the cobalt atom. The proton NMR spectrum in $CDCl_3$ shows a sharp singlet at 2.39 ppm due to two *para*-methyl groups. The origin for this singlet may arise either (1) from an accidental degeneracy of two chemical shifts or (2) from the fluxional behavior of hydrogen in the PMR time scale. The *para*-methyl groups in the PMR spectrum of this complex in CD_3COCD_3 retain a sharp singlet resonance, whereas **2b** shows two respective singlets at 2.16 and 2.40 ppm for the two *para*-methyl groups. In the temperature variations of the PMR spectra of **3b**, a sharp singlet changes to a relatively broad singlet at *ca.* −35 °C, which is converted to a doublet at *ca.* −60 °C. These changes are reversible. These observations are consistent with predictions for the fluxional behavior of hydrogen. Similar behavior has been observed in the carbene complex of platinum.[23]

The compound **1b** reacts readily with CF_3COOH in CH_2Cl_2 to give **4b**. The infrared spectrum shows two bands at 3170 and 3125 cm^{-1} (NH) and three peaks at 1772, 1707, and 1691 cm^{-1} (C=O). The PMR spectrum in $CDCl_3$ shows two sharp singlets at 2.50 and 4.83 ppm due to the *para*-methyl and cyclopentadienyl groups, respectively.

When **2a** was treated with *t*-butyl isocyanide, both deprotonation and release of the coordinated double bond occur to give **5a**, characterized by the absence of ν(NH) and the presence of ν(N≡C) at 2152 cm^{-1}. The compound **5a** takes up a proton again to give the cationic carbene complex (**6a**), when treated with HBF_4. The analogous type of complex (**6b**) is obtained by the reaction of **5b** with HBF_4. The infrared spectra of these compounds (**6a** and **6b**) show the absorption at 3267 (for **6a**) and 3260 cm^{-1} (for **6b**) due to the N–H stretching frequency. The C=N stretching frequencies appear at 1632 and 1634 cm^{-1}, respectively. They are within the range of the normal carbon–nitrgon double bonds, suggesting the absence of coordination of the carbon–carbon double bond to the cobalt atom.

In their PMR spectra the four *ortho*-methyl groups for **6a** and the two *para*-metnyl ones for **6b** show a broad singlet at 2.26 ppm and a sharp singlet at 2.38 ppm, respectively. The respective singlets are converted to doublets consisting of the relative intensity of 1 : 1 in the low temperature PMR spectra, again showing the proton exchange in the PMR time scale as well as that in the neutral complex (**3b**). The observation of the fluxional behavior arising from rapid migration of a proton seems to originate from the planarity of the five-membered ring system containing cobalt.

References

1) Part XII. K. Aoki and Y. Yamamoto, *Inorg. Chem.* in press.

2) E. O. Fischer and Maasböl, *Angew. Chem., Int. Ed. Engl.*, **3**, 580 (1964).

3) E. O. Fischer, *Pure Appl. Chem.*, **24**, 407 (1970).

4) F. A. Cotton and C. M. Lukehart, *Progr. Inorg. Chem.*, **16**, 487 (1972).

5) D. J. Cardin, B. Cetinkaya, and M. F. Lappert, *Chem. Rev.*, **72**, 545 (1972).

6) M. L. H. Green, L. C. Mitchard, and M. G. Swanwick, *J. Chem. Soc. A*, **1971**, 794.

7) E. O. Fischer and A. Riedel, *Chem. Ber.*, **101**, 156 (1968).

8) P. M. Treichel, J. J. Benedict, R. W. Hess, and J. P. Stenson, *J. Chem. Soc. D*, **1970**, 1627.

9) M. F. Lappert and A. J. Oliver, *J. Chem. Soc. Dalton*, **1974**, 65.

10) P. B. Hitchcock, M. F. Lappert, G. M. McLaughlin, and A. Oliver, *ibid.*, **1974**, 68.

11) Y. Yamamoto, H. Yamazaki, and N. Hagihara, This Bulletin, **41**, 532 (1968); *J. Organometal. Chem.*, **18**, 189 (1969).

12) Y. Yamamoto and H. Yamazaki, *Inorg. Chem.*, **13**, 2145 (1974).

13) Y. Yamamoto, K. Aoki, and H. Yamazaki, *J. Amer. Chem. Soc.*, **96**, 2647 (1974).

14) H. Yamazaki, K. Aoki, Y. Yamamoto, and Y. Wakatsuki, *ibid.*, **97**, 3546 (1975)., 22nd Symposium on Organometal. Chem. Japan. October 16—18, 1974. Preceeding p. 67.

15) I. Ugi and R. Meyer, *Chem. Ber.*, **93**, 239 (1960).

16) When the reaction mixture was washed several times with water, the resulting carbene complex was reformed to the parent one.

17) H. S. Gutowsky and R. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).

18) M. H. Chisholm and H. C. Clark, *Chem. Commun.*, **1971**, 809.

19) B. Crociani and R. L. Richards, *J. Chem. Soc. Dalton*, **1974**, 693.

20) The chelating carbene ligand of **2a** has the advantage of eliminating ambiguities or complications arising from rotation about the M–C (carb) bond.

21) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectrscopy," Vol. 1, Pergamon Press, p. 556.

22) E. O. Fischer, C. G. Kreiter, H. J. Kollmeier, J. Muller, and R. D. Fischer, *J. Organometal. Chem.*, **28**, 237 (1971).

23) W. M. Butler, J. H. Enemark, J. Parks, and A. Balch, *Inorg. Chem.*, **12**, 451 (1973).