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STUDIES ON INTERACTION OF ISOCYANIDE WITH TRANSITION METAL COMPLEXES

XI*. PHOTOCHEMICAL REACTIONS OF ISOCYANIDE COMPLEXES OF IRON

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Summary

The photochemical reaction of π-$C_5H_5Fe(CO)(CNC_6H_{11})COCH_3$ (I) gave the heterocyclic compound π-$C_5H_5Fe(CO)[(C{=}NC_6H_{11})_2(CH_3)]$ (II) involving *N*-coordination to the iron atom. The analogous complex is obtained by the photo-induced reaction of π-$C_5H_5Fe(CO)_2CH_3$ with $C_6H_{11}NC$. A similar reaction of π-$C_5H_5Fe(CO)[CNC(CH_3)_3]CH_3$ with $C_6H_{11}NC$ gave π-$C_5H_5Fe(CO)$-$[(C{=}NC_6H_{11})\{C{=}N(CH_3)_3\}(CH_3)]$ (IV) involving different *N*-substituted imino groups. The possible pathways leading to formation of II are discussed. The mass spectra of these complexes were also investigated.

Introduction

It is known that the ultraviolet irradiation of transition metal acyl or aroyl complexes leads to elimination of CO, furnishing alkyl or aryl derivatives [2]. This process is particularly important when applied to those systems which do not eliminate CO under thermal conditions.

We recently reported that the photochemical reaction of π-$C_5H_5Fe(CO)_2$-$[C(CH_2Ph){=}NC_6H_{11}]$ proceeds with elimination of CO to give π-$C_5H_5Fe(CO)$-$(CNC_6H_{11})CH_2Ph$ [3]. We now have found that the photochemical reaction of π-$C_5H_5Fe(CO)(CNC_6H_{11})COCH_3$ leads to elimination of carbon monoxide and insertion of cyclohexyl isocyanide into the resulting methyl—iron σ-bond, although no reaction occurs under thermal conditions. Reported here are our investigations on the scope of this reaction and related reactions.

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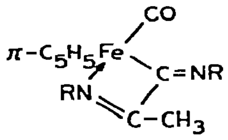
* For part X see ref. 1.

Results and discussion

When a solution of π-$C_5H_5Fe(CO)(CNC_6H_{11})COCH_3$ (I) in benzene was irradiated for 12 h under a nitrogen atmosphere with a mercury lamp, three products were formed. The first compound to elute upon chromatography of the products on alumina was identified as π-$C_5H_5Fe(CO)_2CH_3$, the second a small amount of $[\pi\text{-}C_5H_5Fe(CO)_2]_2$. The third compound was confirmed to be II (14% yield) on the basis of its mass spectrum, spectroscopic studies and the inert gas rule.



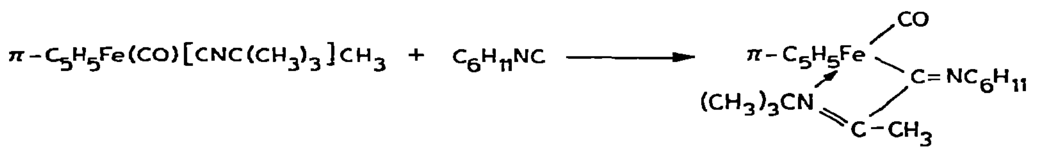
(II) R = C_6H_{11}

(III) R = $(CH_3)_3C$

The photochemical reaction of I in the presence of $C_6H_{11}NC$ increased the yield of II. A similar reaction of π-$C_5H_5Fe(CO)_2CH_3$ with an excess of $C_6H_{11}NC$ gave II in better (62%) yield. The infrared spectrum of II has a single sharp terminal carbonyl band at 1919 cm^{-1}, higher than the value of $\nu(CO)$ found for the cyclic compound containing an *N*-coordinated ligand, π-$C_5H_5Fe(CO)COCH_2$-$CH_2N(CH_3)_2$ (1890 cm^{-1}) [4]. Two other strong peaks at 1632 and 1592 cm^{-1} are assigned to two carbon—nitrogen double bonds. The proton NMR spectrum shows two singlets at 1.74 (CH_3) and 4.46 (C_5H_5) ppm, and two broad resonances at 1.50 (C_6H_{10}) and 2.85 (C_6H) ppm.

The photo-induced reaction of π-$C_5H_5Fe(CO)[CNC(CH_3)_3]COCH_3$ gave π-$C_5H_5Fe(CO)[CNC(CH_3)_3]CH_3$ as main product (63%), and small amounts of π-$C_5H_5Fe(CO)_2CH_3$ and the bis-imino type complex III (4% yield), showing the steric influence of the bulky isocyanide. The ratio of the products (π-$C_5H_5Fe(CO)$-$[CNC(CH_3)_3]CH_3/\pi$-$C_5H_5Fe(CO)_2CH_3$) derived from acetyl complex was ca. 13/1, showing that elimination of CO is much preferred to that of isocyanide. When π-$C_5H_5Fe(CO)[CNC(CH_3)_3]CH_3$ was irradiated in the presence of $(CH_3)_3CNC$ a slight increase of the yield (to 10%) of III was observed.

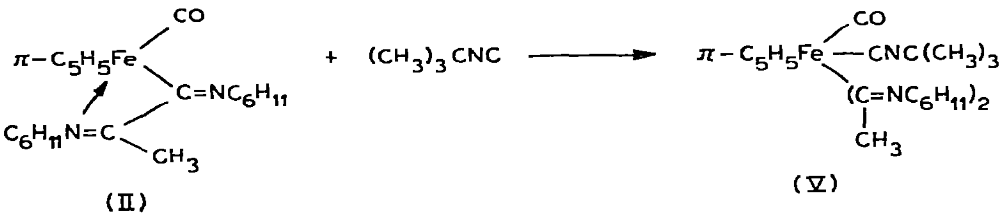
Irradiation of π-$C_5H_5Fe(CO)[CNC(CH_3)_3]CH_3$ in the presence of $C_6H_{11}NC$ gave the bis-imino type complex IV involving two different *N*-alkyl substituted groups (eqn. 1).



(1)

(IV)

The reaction of II with tert-butyl isocyanide in benzene at 40° resulted in release of *N*-coordination to give V, characterized by the presence of the terminal isocyanide band in the infrared spectrum (eqn. 2) [5]. The mass spectrum and the proton NMR spectrum were in good agreement with the proposed structure.

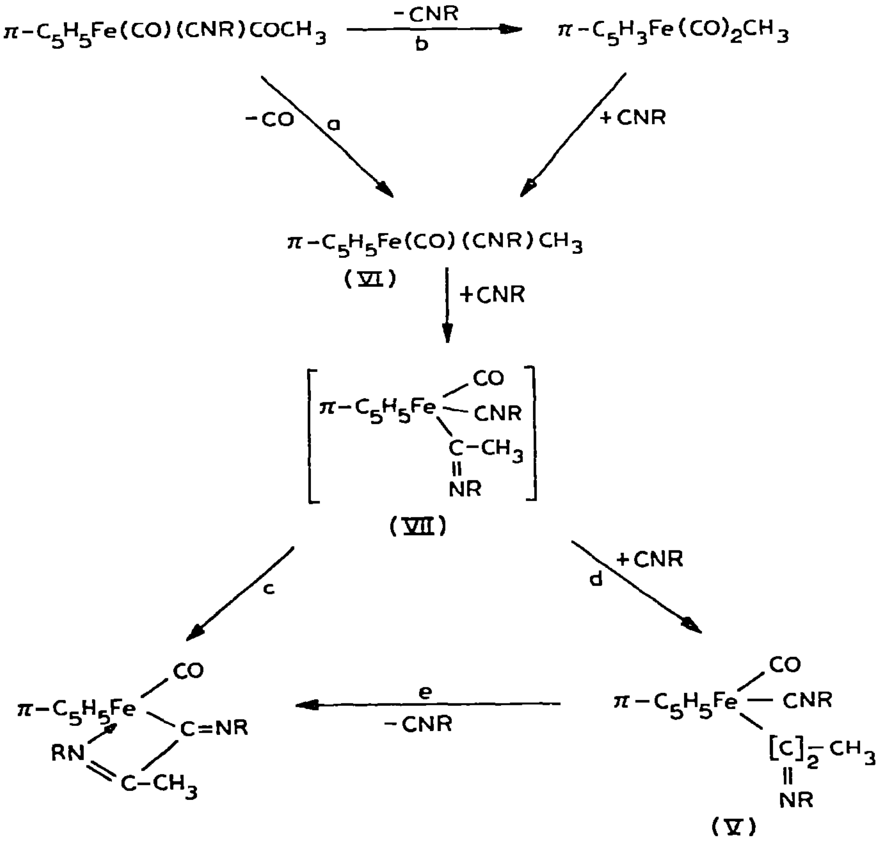


(2)

The series of aforementioned reactions suggest the mechanism, illustrated in Scheme 1. The reaction course consists of an initial formation of π-$C_5H_5Fe(CO)(CNR)CH_3$ (VI) resulting from decarbonylation of the acyl complex. The intermediate VI is isolated in the case of R = $(CH_3)_3C$. The replacement of a coordinated isocyanide by isocyanide eliminated by pathway b will give an unisolable complex VII. Two possible pathways for further reaction may be considered. In the first, c, the reaction proceeds with insertion of the coordinated isocyanide into the iron—carbon σ-bond, involving the intramolecular *N*-coordination of the imino nitrogen. Another route (d → e) consists of an initial formation of V through the reaction of VII with an incoming isocyanide, accomplished by the elimination of the coordinated isocyanide and coordination of the imino

SCHEME 1

MECHANISM FOR FORMATION OF BIS-IMINO TYPE COMPLEX



nitrogen. The photochemical reaction of V leads to recovery of starting material, showing that the cyclic complex is not the product of elimination of isocyanide from V. We thus could rule out the route (d → e).

Mass spectra

The parent ion [*m/e* 330, relative intensity (*I*) 12] in the mass spectrum of III undergoes stepwise loss of carbon monoxide and $(CH_3)_3CNC$ to give the carbonyl-free ion $C_5H_5Fe[CNC(CH_3)_3]CH_3^+$ (*m/e* 219, *I* 100). The loss of a neutral $(CH_3)_2C{=}CH_2$ fragment from this ion occurs then to afford $C_5H_5Fe(CNH)(CH_3)^+$ (*m/e* 163, *I* 99). This appears to break down further via two pathways. In the first, successive losses of CH_3 and HNC fragments occur to give $C_5H_5Fe^+$ (*m/e* 121, *I* 57). The second fragmentation process is loss of hydrogen to form the ion $C_5H_5Fe(CN)(CH_3)^+$ (VIII) (*m/e* 162, *I* 90), which is supported by the observation of a metastable ion at *m/e* 161.3 (161.0). Two possible structures for VIII are illustrated as follows:

$C_5H_5Fe(CN)(CH_3)^+$	$C_5H_5Fe(CNCH_3)^+$
(VIIIa)	(VIIIb)

Structure VIIIb bearing a methyl isocyanide ligand appears to be preferable to VIIIa because of the occurrence of one-step loss of the CH_3NC group, which is also supported by the observation of a metastable ion at *m/e* 90.5 (90.4).

In the mass spectrum of IV successive losses of CO and $C_6H_{11}NC$ groups from the parent ion (*m/e* 356, *I* 9) occur to give $C_5H_5Fe[CNC(CH_3)_3](CH_3)^+$ (*m/e* 219, *I* 52). This ion loses the $(CH_3)_2C{=}CH_2$, CH_3 and HNC fragments to give the $C_5H_5Fe^+$ ion (*m/e* 121, *I* 38). No transition of $(CH_3)_3CNC$ from $C_5H_5Fe[C{=}NC_6H_{11})\{C{=}NC(CH_3)_3\}(CH_3)]^+$ (*m/e* 328, *I* 16) is observed. This result shows that the initial loss of RNC arises from the *N*-substituted imino methylene group bound to iron. A facile cleavage of the metal—carbon bond has been observed in the mass spectra of various transition metal complexes [3,7,8].

Experimental

General procedures and physical measurements

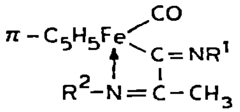
The preparation and all handling of organometallic compounds were carried out under nitrogen. Melting points were taken on a Mitamura capillary melting point apparatus and were uncorrected. The infrared spectra were recorded on Shimazu IR-27G spectrophotometer. The proton NMR spectra were obtained on JEOL C-60HL and Varian HA-100B spectrophotometers, using tetramethylsilane as a reference. The mass spectra were measured on Nippon-denshi Type JPS-1S mass spectrometer with direct-inlet system. All photochemical reactions were carried out in a quartz flask with Ushiodenshi 450W (Type UV-453) and with Riko-kagaku 400W high-pressure mercury lamp (Type UVL-400HA).

Materials

Isocyanides were prepared by published procedures [8], as were the organoiron compounds, π-$C_5H_5Fe(CO)(CNR)COCH_3$ (R = C_6H_{11} and $(CH_3)_3C$) [9].

TABLE 1

PROPERTIES OF BIS-IMINO TYPE COMPLEXES



Compound		Mol. wt. [a]	IR[b] (cm^{-1})			Proton NMR spectrum (ppm, CDCl$_3$)	
	R^1	R^2		ν(C=O)	ν(C=N)		C$_5$H$_5$	Other resonances
II	C$_6$H$_{11}$	C$_6$H$_{11}$	382	1919	1632	1592	4.46 s	0.1-2 1 (c, C$_6$H$_{10}$), 2.64-3.05 (b, C$_6$H) 1.74 (s, CH$_3$)
III	(CH$_3$)$_3$C	(CH$_3$)$_3$C	330	1918	1632	1587	4.41 s	1.14 (s, (CH$_3$)$_3$C), 1.30 (s, (CH$_3$)$_3$), 1.83 (s, CH$_3$)
IV	C$_6$H$_{11}$	(CH$_3$)$_3$C	356	1915	1633	1580	4.44 s	1.13 (s, (CH$_3$)$_3$C), 1.76 (s, (CH$_3$), 0.8-2.2 (c, C$_6$H$_{10}$), 2.70-3.10 (b, C$_6$H)

[a] From mass spectrum. [b] Measured in benzene.

Photochemical reaction of π-$C_5H_5Fe(CO)(CNC_6H_{11})COCH_3$

(a). A solution of π-$C_5H_5Fe(CO)(CNC_6H_{11})COCH_3$ (0.80 g, 2.7 mmol) in benzene (20 ml) was irradiated at 25° for 12 h. The solvent was evaporated under reduced pressure and the residue was chromatographed on Sumitomo activated alumina (KCG-30). Three bands were observed (yellow, reddish-violet, and reddish-brown). They were eluted with n-hexane, benzene and benzene—dichloromethane (8/1), respectively. The first eluate gave the known π-$C_5H_5Fe(CO)_2CH_3$ (0.06 g, 22%). The second gave [π-$C_5H_5Fe(CO)_2]_2$ (0.01 g). The third gave the bis-imino type complex II, π-$C_5H_5Fe(CO)[(C{=}NC_6H_{11})_2(CH_3)]$, (0.08 g, 14%; m.p. 122-125° (dec.). Found: C, 65.80; H, 7.48; N, 7.36. $C_{21}H_{30}FeN_2O$ calcd.: C, 65.97; H, 7.91; N, 7.33%.)

(b). A mixture of π-$C_5H_5Fe(CO)(CNC_6H_{11})COCH_3$ (0.80 g, 2.7 mmol) and $C_6H_{11}NC$ (0.33 g, 3.0 mmol) in benzene (30 ml) was irradiated at 25° for 12 h. The work-up of the reaction mixture gave II (0.36 g, 35%).

Photochemical reaction of π-$C_5H_5Fe(CO)_2CH_3$ and $C_6H_{11}NC$

A mixture of π-$C_5H_5Fe(CO)_2CH_3$ (1.0 g, 5.2 mmol) and $C_6H_{11}NC$ (2.2 g, 20 mmol) in benzene (30 ml) was irradiated at 25° for 13 h. The work-up of the reaction mixture gave II (1.23 g, 62%).

Photochemical reaction of π-$C_5H_5Fe(CO)[CNC(CH_3)_3]COCH_3$

A solution of π-$C_5H_5Fe(CO)[CNC(CH_3)_3]COCH_3$ (1.0 g, 3.6 mmol) in benzene (30 ml) was irradiated at 25°. After 12 h, the solvent was removed under reduced pressure, and the residue was chromatographed on alumina. Four bands (pale yellow, yellow, reddish-violet and brown) were observed. The work-up of the first eluate (n-hexane) gave π-$C_5H_5Fe(CO)_2CH_3$ (0.03 g, 5%). That of second eluate (n-hexane—benzene 5/1) gave π-$C_5H_5Fe(CO)[CNC(CH_3)_3]CH_3$ (0.56 g, 63%; m.p. 57-59° (dec.)) as yellow crystals. IR (KBr): 2118 (N≡C) and 1922 (C≡O) cm^{-1}. Proton NMR (CDCl$_3$): —0.06 (s, CH$_3$), 1.44 (s, (CH$_3$)$_3$C), and 4.62 (s, C$_5$H$_5$) ppm. Found: C, 58.27; H, 6.94; N, 5.67. $C_{12}H_{17}FeNO$ calcd.: C, 58.33; H, 6.93; N, 5.67%.

The work-up of the third eluate (benzene) afforded a trace of $[\pi\text{-}C_5H_5Fe(CO)_2]_2$. The last eluate (benzene—dichloromethane, 2/1) gave $\pi\text{-}C_5H_5Fe(CO)[(C{=}NC(CH_3)_3)_2(CH_3)]$ (III) (0.02 g, 4%, m.p. 115-120° (dec.)) as brown crystals. Found: C, 61.49; H, 8.02; N, 8.22. $C_{17}H_{26}FeN_2O$ calcd: C, 61.83; H, 7.94; N, 8.48%.

Photochemical reaction of $\pi\text{-}C_5H_5Fe(CO)[CNC(CH_3)_3]CH_3$ *with* $(CH_3)_3CNC$

A solution of $\pi\text{-}C_5H_5Fe(CO)[CNC(CH_3)_3]CH_3$ (0.75 g, 3.0 mmol) and $(CH_3)_3CNC$ (0.33 g, 4.0 mmol) in benzene at 25° was irradiated for 10 h. The work-up of the reaction mixture gave III (0.11 g, 10%).

Photochemical reaction of $\pi\text{-}C_5H_5Fe(CO)[CNC(CH_3)_3]CH_3$ *with* $C_6H_{11}NC$

$\pi\text{-}C_5H_5Fe(CO)[(C{=}NC_6H_{11})\{C{=}NC(CH_3)_3\}(CH_3)]$ (9%, m.p. 97-100° (dec.)) was obtained by irradiation of $\pi\text{-}C_5H_5Fe(CO)[CNC(CH_3)_3]CH_3$ and $C_6H_{11}NC$ in benzene at 25° for 8 h. Found: C, 62.35; H, 8.42; N, 8.41. $C_{18}H_{28}FeN_2O$ calcd.: C, 62.80; H, 8.20; N, 8.14%.

Reaction of $\pi\text{-}C_5H_5Fe(CO)[(C{=}NC_6H_{11})_2(CH_3)]$ *(II) with* $(CH_3)_3CNC$

A mixture of II (0.76 g, 2.0 mmol) and $(CH_3)_3CNC$ (0.25 g, 3.0 mmol) in benzene (30 ml) was kept at 40° for 5 h. The solvent was removed under reduced pressure. The residue was chromatographed on alumina. Elution with benzene gave the starting material II (0.15 g). Elution with benzene—dichloromethane (2/1) gave V (0.43 g, 47%). IR (benzene): 2108 (N≡C) 1938 (C≡O), 1672, 1624 (C=N) cm^{-1}. Proton NMR ($CDCl_3$): 1.46 (s, $(CH_3)_3C$), 1.0-2.4 (b, C_6H_{10}), 2.08 (s, CH_3), 3.04-3.4 (b, C_6H), 4.3-4.6 (C_6H) and 4.70 (s, C_5H_5) ppm. Found: C, 66.53; H, 8.09; N, 9.01. $C_{26}H_{39}FeN_3O$ calcd.: C, 67.09; H, 8.45; N, 9.13%.

Photochemical attempt to eliminate isocyanide from V

A solution of $\pi\text{-}C_5H_5Fe(CO)[CNC(CH_3)_3][(C{=}NC_6H_{11})_2(CH_3)]$ (0.50 g) in benzene (20 ml) was irradiated at 25°. After 7 h, the work-up of the reaction mixture revealed (IR spectroscopy) no detectable amount of II.

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