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Note

# Photo-assisted preparation of double isocyanide insertion complexes of $\eta^5$ -cyclopentadienyliron(II) bearing only isocyanide: the molecular structure of $(\eta^5-C_5H_5)Fe(XyINC)_2[C(=NXyI)C(=NXyI)CH_3$ $(XyINC = 2,6-Me_2C_6H_3NC)$

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#### Abstract

Reaction of  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>Fe(CO)<sub>2</sub>CH<sub>3</sub> (1) with xylyl isocyanide in toluene at reflux gave  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>Fe(CO)(XylNC)COCH<sub>3</sub> (**5a**) (Xyl = 2,6-(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), whereas photochemical reaction underwent double insertion of isocyanide molecules into an iron–carbon bond to give a bis-imino type complex ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Fe(XylNC)<sub>2</sub>[C(=NXyl)C(=NXyl)CH<sub>3</sub>] (**6a**), determined by an X-ray analysis. © 1999 Elsevier Science S.A. All rights reserved.

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# 1. Introduction

It is well-known that carbon monoxide inserts into the metal-carbon  $\sigma$ -bonds to give acyl or aroyl complexes and that the ultraviolet irradiation of these acyl or aroyl complexes eliminates CO to regenerate the corresponding alkyl or aryl derivatives [1]. This latter process is particularly important when applied to those systems which can not eliminate CO under thermal conditions. A variety of insertion reactions of isocyanide, isoelectronic with carbon monoxide, into the metal-carbon or metal-hydride bonds have been documented [2].

We have previously reported that  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>Fe(CO)<sub>2</sub>CH<sub>3</sub> (1) reacted readily with alkyl isocyanide (RNC) such as cyclohexyl or t-butyl isocyanide at room temperature (r.t.) to produce the corresponding acyl complexes,  $\eta^5-C_5H_5Fe(CO)(CNR)COCH_3$  (2) [3], whereas reactions at reflux gave the cyclic carbene complexes  $\eta^5-C_5H_5Fe(CO)[\kappa C(=NR)C(NHR)=CH-\kappa C-(NHR)]$  (3) accompanying novel multiple insertion of isocyanide molecules [4]. When the photochemical reactions of  $(\eta^5-C_5H_5)Fe(CO)_2CH_3$  in the presence of cyclohexyl isocyanide were carried out, the double insertion of isocyanide into an iron-carbon  $\sigma$ -bond occurred to give a four-membered bis-imino cyclic complex  $(\eta^5-C_5H_5)Fe(CO)[\kappa C(=NC_6H_{11})-C(=\kappa NC_6H_{11})CH_3]$  (4) containing a N-coordination [5]. The photo-assisted insertion reaction is one of the most significant features in the isocyanide chemistry as well as the multiple insertion, different from carbon monoxide.

We found that the photochemical reaction of **1** with aromatic isocyanide bearing methyl groups at the two, six-positions yielded new double insertion complexes containing only isocyanide ligand.

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# 2. Experimental

All reactions were carried out under nitrogen atmosphere. ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>CH<sub>3</sub> [6], and xylyl (XylNC) and mesityl isocyanides (MesNC) [7] were prepared according to the literature. Benzene, hexane and toluene were distilled over CaH<sub>2</sub> and THF was distilled over LiAlH<sub>4</sub>. The infrared and electronic absorption spectra were measured on FT/IR-5300 and U-best 30 spectrometers, respectively. NMR spectroscopy was carried out on a Bruker AC250. <sup>1</sup>H NMR spectra were measured at 250 MHz using tetramethylsilane as an internal reference. The mass spectra were measured on a HITACHI GC-MS M-80 spectrometer. A photochemical reaction was carried out with an USIO high-pressure mercury lamp (100 W).

# 2.1. Thermal reaction of 1 with xylyl isocyanide

A mixture of 1 (0.50 g, 2.60 mmol) and xylyl isocyanide (1.77 g, 13.4 mmol) in toluene (20 ml) was refluxed for 7 h and the solvent was removed in vacuo and the residue was chromatographed on deactivated alumina (contain 10% H<sub>2</sub>O), using hexane and benzene as eluents. Two bands (yellow and dark violet) were observed. The first band was eluted with hexane and the second one with benzene. Eluting with hexane gave yellow-orange crystals of  $(\eta^5-C_5H_5)Fe(CO)(XyINC)COCH_3$  (5a) (0.672g, 80.2%), by recrystallization from benzene-hexane. Upon work-up of the second eluate a trace of dark violet residue was obtained and identified as known  $[(\eta^5 C_5H_5$ )<sub>2</sub>Fe(CO)<sub>2</sub>]<sub>2</sub> from the infrared spectrum. **5a**: Mass: m/z 322 (M<sup>+</sup>). IR (Nujol): 2100 (N=C), 1950 (C=O), 1647 (C=O) cm<sup>-1</sup>. <sup>1</sup>H NMR(CDCl<sub>3</sub>):  $\delta$  2.38 (s, o-Me), 2.57 (s, Me), 4.75 (s, Cp), 6.9-7.1 (m, Ph) ppm. Anal. Calc. for C<sub>17</sub>H<sub>17</sub>NO<sub>2</sub>Fe: C, 63.18; H, 5.30; N, 4.33. Found: C, 63.00; H, 5.55; N, 4.71%.

# 2.2. Photochemical reaction of 1 with xylyl isocyanide

A mixture of 1 (0.30 g, 1.56 mmol) and xylyl isocyanide (0.823 g, 6.27 mmol) in THF (20 ml) was irradiated at r.t. with a 100-W high-pressure mercury lamp. After 8 h, the solvent was removed in vacuo and the residue was chromatographed on deactivated alumina (contain 10%) H<sub>2</sub>O), using benzene as the eluent. Four bands (yellowbrown, pink-yellow-brown, yellow-brown and dark brown) were observed. Eluting with benzene gave a yellow-brown solution. Removal of the solvent and crystallization of the residue gave dark brown crystals of **6a** (0.633 g, 56.7%). Products from the other eluates could not be identified, because of their trace amount. Mass: *m*/*z* 659 (*M*<sup>+</sup>). IR (Nujol): 2083, 2004 (N≡C), 1639, 1572 (C=N) cm<sup>-1</sup>. UV–Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  354 nm (log  $\varepsilon$  4.22). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.57 (s, Me, 3H), 2.05, 2.09 (s, *o*-Me, inserted, 6H), 2.25 (s, o-Me, terminal, 12H), 4.84 (s, Cp),

6.3–7.0 ppm. *Anal.* Calc. for  $C_{42}H_{44}N_4Fe$ : C, 76.35; H, 6.71; N, 8.48. Found: C, 76.51; H, 6.77; N, 8.53%.

A mesityl isocyanide complex ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Fe-(MesNC)<sub>2</sub>[C(=NMes)C(=NMes)Me] (**6b**) (53%) was also obtained according to a procedure similar to that for **6a**. IR (Nujol): 2085, 2027 (NC), 1637, 1581 (C=N) cm<sup>-1</sup>. UV–Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  350 (4.15), 295 (4.25) nm. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.87 (s, Me, 6H), 2.07 (s, *o*-Me, 12H), 2.23 (s, Me, 15H), 2.26(s, Me, 6H), 6.4–6.9 (m, Ph). *Anal*. Calc. for C<sub>42</sub>H<sub>44</sub>N<sub>4</sub>Fe: C, 77.08; H, 7.31; N, 7.82. Found: C, 76.55; H, 7.28; N, 7.17%.

# 2.3. Data collection

Complex 6a was recrystallized from benzene-hexane. Cell constants (a = 14.201(5), b = 21.05(1), c =12.318(7) Å, V = 3683(6) Å<sup>3</sup>, Z = 4) were determined from 25 reflections on a Rigaku four-circle automated diffractometer AFC5S. The crystal parameters along with data collection parameters are summarized in Table 1. Data collection was carried out on a Rigaku AFC5S diffractometer. Intensities were measured by the  $2\theta - \omega$  scan method using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71069$  Å). Throughout the data collection the intensities of the three standard reflections were measured every 150 reflections as a check of the stability of the crystals and no decay was observed. Intensities were corrected for Lorentz and polarization effects. Linear absorption coefficient is  $4.4 \text{ cm}^{-1}$ , and the absorption correction was made with  $\psi$  empirical rotation. Transmission factors are in the range from 0.96 to 1.00. Atomic scattering factors were taken from the usual tabulation of Cromer and Waber [8]. Table 1

$C_{1}$
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Formula	$C_{42}H_{44}N_4Fe$
Molecular weight	660.68
Color	red
Crystal dimensions (mm)	$0.30 \times 0.20 \times 0.40$
Crystal system	orthorhombic
Space group	$P2_12_12_1$ (no. 19)
a (Å)	14.201(5)
b (Å)	21.05(1)
c (Å)	12.318(7)
$V(Å^3)$	3683(6)
Z	4
$D_{\rm calc}$ (g cm <sup>-3</sup> )	1.191
$\mu$ (cm <sup>-1</sup> )	4.40
F(000)	1400
No. reflections	6695
No. data $(I > 3.0\sigma(I))$	3575
No. variables	424
$R; R_{w}^{a}$	0.051; 0.053
GOF <sup>b</sup>	1.54

<sup>a</sup>  $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$  and  $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w |F_o|^2]^{1/2}$  ( $w = 1/\sigma^2(F_o)$ ).

<sup>b</sup> GOF =  $[\Sigma w(|F_o| - |F_c|)^2 / \Sigma (N_o - N_v)]^{1/2}$ , where  $N_o = no.$  of data,  $N_v = no.$  of variables.

Anomalous dispersion effects were included in  $F_{\text{calc}}$  [9]; the values of  $\Delta f'$  and  $\Delta f''$  were those of Creagh and McAuley [10]. All calculations were performed using a Digital VAX Station 3100 M38 computer using the TEXSAN-TEXRAY program system [11].

# 2.4. Determination of the structures

The structure of **6a** was solved by Patterson methods and refined by using the full-matrix least-squares methods. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were calculated at the ideal positions with the C-H distance of 0.95 Å. The final refinement converged to R = 0.051 and  $R_w = 0.053$ . Number of variables and goodness-of-fit (GOF) are 424 and 1.54, respectively. Final difference Fourier syntheses showed peaks at heights up to 0.44 e A<sup>-3</sup>.

# 3. Results and discussion

When a mixture of  $(\eta^5-C_5H_5)Fe(CO)_2CH_3$  (1) and excess XylNC was refluxed in toluene for 6 h, yelloworange crystals, formulated as  $(\eta^5-C_5H_5)Fe(CO)_2$ -(XylNC)CH<sub>3</sub> (5a) from the mass spectroscopy were obtained in 80% yield (Eq. (1)). The IR spectrum showed three characteristic bands at 2100, 1950 and 1647 cm<sup>-1</sup>. The bands at 2100 and 1950 cm<sup>-1</sup> suggested the presence of terminal isocyanide and carbonyl groups, respectively. The last one is assumed to be due to an acetyl group. The <sup>1</sup>H NMR spectrum showed three singlets at  $\delta$  2.38, 2.57, and 4.75 ppm consisting of a 6:3:5 intensity ratio, assignable to o-methyl protons of xylyl isocyanide, acetyl and cyclopentadienyl groups, respectively. From these spectroscopic results 5a was identified as an acetyl complex. Formation of any cyclic carbene complexes was not observed.

$$(\eta^{5}-C_{5}H_{5})Fe(CO)_{2}CH_{3} + XyINC$$
  

$$\rightarrow (\eta^{5}-C_{5}H_{5})Fe(CO)(XyINC)COCH_{3}$$
(1)

A mixture of **1** and excess XyINC in THF was irradiated with UV radiation for 8 h at r.t. and the mixture was chromatographed on alumina, from which dark brown crystals formulated as  $(\eta^5-C_5H_5)Fe-(XyINC)_4CH_3$  (**6a**) from the mass spectrum of m/z =659 were isolated (Eq. (2)). Complex **6a** was also prepared from the photochemical reaction of **5a** in the presence of xylyl isocyanide.





Fig. 1. Crystal structure of  $(\eta^5-C_5H_5)Fe(XylNC)_2[C(=NXyl)-C(=NXyl)Me]$  (6a).

The infrared spectrum of **6a**  $(R = 2.6 - (CH_3)_2C_6H_3)$ showed two sharp bands at 2083 and 2004  $\text{cm}^{-1}$  due to the terminal isocyanide groups and two bands at 1639 and 1572 cm<sup>-1</sup> due to the C–N double bonds. The <sup>1</sup>H NMR spectrum showed four singlets due to methyl protons at  $\delta$  1.57, 2.05, 2.09, and 2.25 ppm consisting of an intensity ratio of 1:2:2:4. The first one is assigned to the  $C-CH_3$  group, the last one to the terminal isocyanide groups, and the other two to the inserted isocyanide groups. On the basis of these results the complex is assumed to have a bis-imino type structure with two isocyanide molecules inserted doubly into a Fe-C bond. A similar double-insertion product 6b  $(R = 2,4,6-(CH_3)_3C_6H_2)$  was prepared by using mesityl isocyanide and characterized spectroscopically (see Section 2). These complexes are the first examples of the imino-type complexes of iron constructed by only isocvanide molecules.

In an attempt to confirm the detailed structure an X-ray analysis was carried out and was in good agreement with the spectroscopic results. The molecule displayed a piano-stool structure whereby the iron atom was surrounded by two terminal isocyanide ligands and a bis-imino group (Fig. 1). The selected bond lengths and angles are shown in Table 2. The Fe-C (terminal isocyanide) bonds of 1.786(7) and 1.808(7) Å are shorter than those found in tris-imino palladium complex [12] and the average Fe-C (terminal isocyanide) bond length (1.820 Å) in Fe(t-BuNC)<sub>5</sub> [13]. The Fe-C(3) bond length of 1.985(6) Å is longer than that (1.960(3) Å) [4b] of the cyclic carbene complex 3, due to structural difference between the open-chain and cyclic form. The Fe-C3-N3 angle of 134.6(5)° larger than other Fe-C3-C4 (116.6°) and C4-C3-N3 Table 2

236

Selected bond lengths (Å) and angles (°) of  $(\eta^5 - C_5H_5)Fe(XylNC)_2[(C = NXyl)_2Me]$  (6a)

Fe(1)-C(1)	1.786(7)	Fe(1)–C(2)	1.808(7)
Fe(1)-C(3)	1.985(6)	C(1) - N(1)	1.149(7)
C(2)–N(2)	1.175(7)	C(3)–N(3)	1.275(7)
C(3)–C(4)	1.527(9)	C(4)–C(5)	1.483(9)
C(4)–N(4)	1.252(7)		
C(1)-Fe(1)-C(2)	92.7(3)	C(1)-Fe(1)-C(3)	93.2(3)
C(2)-Fe(1)-C(3)	97.6(3)	Fe(1)-C(1)-N(1)	176.1(6)
Fe(1)-C(2)-N(2)	172.9(6)	Fe(1)-C(3)-N(3)	134.6(5)
Fe(1)-C(3)-C(4)	116.6(7)	C(1)-N(1)C(11)	176.4(7)
C(2)–N(2)–C(21)	164.8(7)	C(3)–N(3)–C(31)	126.2(6)
C(4)–N(4)–C(41)	120.4(6)	C(4)-C(3)-N(3)	108.5(5)
C(3)-C(4)-C(5)	115.5(6)	C(3)-C(4)-N(4)	119.7(6)
N(4)-C(4)-C(5)	124.8(6)		~ /

(108.5°) angles, minimizing steric repulsion between the C21-C26 and C31-C36 planes. In fact the dihedral angle between these two planes is nearly parallel  $(13.9^{\circ})$ . The dihedral angle between the C11–C16 and C41-C46 planes is perpendicular (87.0°). The torsion angles of FeC(3)C(4)C(5) and N(3)C(3)C(4)N(4) are -107.3(6) and  $-104.6(6)^{\circ}$ , being smaller than those  $(-155.4 \text{ and } -159.6(8)^\circ)$  found in the planar bisimino type complex,  $Cl(Et_3P)_2PdC \equiv C - C(=NPh)C$ -(=NPh)Pd(PEt<sub>3</sub>)Cl [14], responsible for the difference of the stereochemistry between two complexes. These torsion angles are assumed to be a minimum model for helical polymers of isocyanide. The C-N double and triple bond lengths are usual. The Fe-C-N bond and C-N-C angles are nearly linear except the C(2)-N(2)-C(21) bond angle (164.8(7)°).

#### 4. Conclusion

Thermal reaction of 1 with aromatic isocyanide bearing the methyl groups at the two- and six-positions at r.t. or at reflux underwent a usual carbonyl insertion to form an acetyl complex. The photochemical reaction gave the open-chain double insertion product 6 without forming a four-membered N-coordination complex such as 4. The photo-assisted insertion of isocyanide was revealed to be one of the significant features in the transition-metal chemistry of isocyanide. The different reactivities depending on the substituents of isocyanide also suggest the versatility of the isocyanide chemistry.

## 5. Supplementary material

A listing of thermal parameters, bond lengths, bond angles and torsion angles, and tables of observed and calculated structure factors are available from the Cambridge Structural Database on quoting the CCDC No. 112956.

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