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PHOTOCHEMICAL REACTION BETWEEN CYCLOHEXYL ISOCYANIDE AND π-CYCLOPENTADIENYLDICARBONYLTRIMETHYLSILYLIRON(II)

TZE-MING CHAN *, JOHN W. CONNOLLY ***, CARL D. HOFF ** and FRANK MILLICH ***

Polymer and Inorganic Divisions, Department of Chemistry, University of Missouri-K.C., Kansas City, MO 64110 (U.S.A.)

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Summary

The photoreaction between $C_5H_5Fe(CO)_2Si(CH_3)_3$ (I) and cyclohexyl isocyanide leads to the sequential replacement of both carbonyl groups by the isocyanide. Both the racemic monosubstituted product, $C_5H_5Fe(CO)(C_6H_{11}NC)$-$Si(CH_3)_3$ (II) and the disubstituted product, $C_5H_5Fe(C_6H_{11}NC)_2Si(CH_3)_3$ (III) have been isolated and characterized. Photoreaction between the disubstituted product III and $C_5H_5Fe(CO)_2Si(CH_3)_3$ in a sealed tube gives the monosubstituted product, II. Thermal initiation of the above reactions failed. The disubstituted product III is stable under both the thermal and photochemical conditions used; thus, insertion of isocyanide into Fe—Si bond was observed not to occur.

Introduction

Isocyanide ligands have been used extensively in organotransition metal chemistry [1—3]. Insertion of the isocyanide ligand into metal—carbon bonds, leading to iminoacyl ligands is a common reaction [4,5].

Adams recently reported the synthesis by the salt elimination method [6—8] of a series of compounds having the formula $(\pi\text{-}C_5H_5)Mo(CO)_{3-x}(CNCH_3)_xR$, where R = $Ge(C_6H_5)_3$, $Sn(CH_3)_3$ and $Pb(C_6H_5)_3$; however, no compound with a transition metal bonded to silicon was obtained. The synthesis and some reactions of the first organotransition metal isocyanides containing a transition metal to a Group IV metal bond, silicon, are reported in this paper. Both the preparation of such compounds and the possible occurrences of insertion reactions are of

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* This paper is taken from the Masters thesis of T.M. Chan, Chemistry Department, U.M.K.C., 1977. Present address: Department of Chemistry, Purdue University, Lafayette, IN 47907 (U.S.A.).

** Present address: Department of Chemistry, University of Georgia, Athens, GA 30602 (U.S.A.).

*** To whom communications should be addressed.

interest. Special interest is derived where multiple insertions can occur which may lead to oligo- and poly-isocyanides [9—11].

Experiments and results

All reactions were carried out under nitrogen atmosphere. Infrared spectra were recorded with a Perkin—Elmer 621 spectrometer. Proton NMR spectra were recorded with a Varian T60 spectrometer. Mass spectra were conducted at 70 eV electron energies with a Nuclide 12-90-G spectrometer. Microanalyses were performed by Schwarzkoff Microanalytical Laboratory, Woodside, New York. Photoreactions were carried out by using a Rayonet Srinivasan—Griffin Reactor which is equipped with ten 3500 Å photolysis lamps. Optical rotation was measured with a O.C. Rudolph polarimeter and a sodium lamp.

Bis[dicarbonylcyclopentadienyliron(II)] was purchased from Alfa Inorganics, and trimethylchlorosilane from General Electric Silicon Products Department. Cyclohexyl isocyanide was prepared by the procedure of Walborsky and Niznik [12]. Compound I was prepared according to the procedure of Wilkinson, Piper and Lemal [13].

Photoreaction between $C_5H_5Fe(CO)_2Si(CH_3)$ and $C_6H_{11}NC$

Compound I (4.7 g, 0.0188 mol) and $C_6H_{11}NC$ (8.2 g, 0.075 mol) were dissolved in 50 ml of benzene, under nitrogen, in a Schlenk tube connected to an exit bubbler and the mixture was irradiated with ultraviolet. Samples (0.8 ml) of the solution mixture were withdrawn periodically, and the reaction was monitored by NMR. Products $C_5H_5Fe(CO)(C_6H_{11}NC)Si(CH_3)_3$ (II) and then $C_5H_5Fe(C_6H_{11}NC)_2Si(CH_3)_3$ (III) have separate signals for the methyl and the C_5H_5 groups, and the relative amounts of the three organometallic compounds at different times were determined from their integration curves. The results are shown in Fig. 1.

Isolation and characterization of $C_5H_5Fe(CO)(C_6H_{11}NC)Si(CH_3)_3$ and $C_5H_5Fe(C_6H_{11}NC)_2Si(CH_3)_3$

Compound I (5.5 g, 0.022 mol) and $C_6H_{11}NC$ (8.8 g, 0.08 mol) were dissolved in 75 ml of benzene and irradiated until the C_5H_5 signal of the starting material disappeared (in about 72 h). Benzene and most of the excess cyclohexyl isocyanide were removed by evacuation at 0.5 Torr. The brown oil (8.6 g) obtained was applied on a Woelm 200 neutral alumina column (2.5 × 15 cm). The orange-yellow band was eluted with hexane, which upon evaporation gave a mixture of II and III (1/3.8 ratio) and a small amount of cyclohexyl isocyanide. The mixture (6.6 g) was then applied to a Woelm Silica Gel Column (2.5 × 50 cm) and developed with a hexane/benzene gradient eluent. Compound II eluted first (0.65 g, 9.0%), and then III (3.3 g, 36.4%) was obtained. The IR, NMR, elemental analytical and mass spectral data are summarized in Tables 1—4. Compound II is a racemic modification since its solution in benzene (0.1 g/ml, 1 dm) showed an optical rotation of α_D^{23} 0.00 ± 0.05°.

Reaction between $C_5H_5Fe(CO)_2Si(CH_3)_3$ and $C_5H_5Fe(C_6H_{11}NC)_2Si(CH_3)_3$

Compounds I and III were dissolved in about 1 ml of benzene and sealed

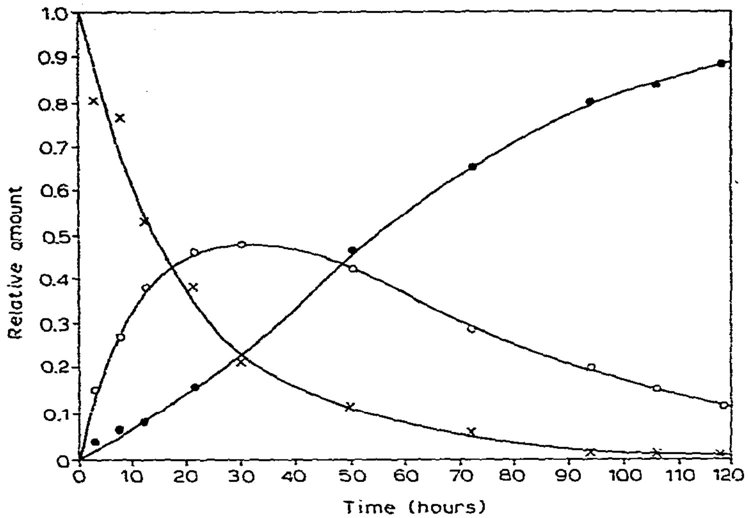

Fig. 1. Progress of the photoreaction of a 4/1 molar mixture of $C_6H_{11}NC$ and $C_5H_5Fe(CO)_2Si(CH_3)_3$ in benzene at 42°C, as monitored by the intensity of NMR peaks of C_5H_5; X = $C_5H_5Fe(CO)_2Si(CH_3)_3$, ○ = $C_5H_5Fe(CO)(C_6H_{11}NC)Si(CH_3)_3$, ● = $C_5H_5Fe(C_6H_{11}NC)_2Si(CH_3)_3$.

in an NMR tube. The solution was then heated at 80°C for 6 h and no change in the NMR spectrum of the solution occurred. The solution was then irradiated with ultraviolet and after ca. 1 h of photolysis, the presence of II was detected, and its concentration increased with time.

Attempted reaction between $C_5H_5Fe(C_6H_{11}NC)_2Si(CH_3)_3$ and $C_6H_{11}NC$

Compound III and $C_6H_{11}NC$ in 1/4 ratio were heated in refluxing benzene and in tetrahydrofuran. In both cases the solution mixture was monitored by IR and no change occurred in 24 h. Compound III was recovered from the reaction mixture.

TABLE 1

INFRARED ABSORPTION FREQUENCIES OF COMPOUNDS II AND III

Compound	ν(CN) or ν(CO)[a] (cm^{-1})	Other absorption bands[b] (cm^{-1})
II	2089s (ν(CN)) 1932vs (ν(CO))	3100(sh), 2940s, 2890(sh), 2960m, 1450w, 1369w, 1260w, 1230m, 810s, 738m
III	1920—2060(br)s (ν(CN))	3100(sh), 2940s, 2860m, 1449m, 1359m, 1322m, 1220m, 821s, 801s, 732m

[a] Measured in hexane solution; the frequencies were read directly from the wavenumber counter; possible error is 1 cm^{-1}. [b] Absorption frequencies obtained from spectra taken of liquid films; frequencies are read from the spectra; possible error is 2 cm^{-1}; (sh), shoulder; w, weak; m, medium; s, strong; vs, very strong; br, broad.

TABLE 2

NMR DATA FOR COMPOUNDS II AND III [a]

Compound	$CDCl_3$ solution	Assignment
II	5.55s	C_5H_5
	9.70s	$Si(CH_3)_3$
	7.8—9.0br	C_6H_{10}
	6.2—6.6br	C_6H
III	5.75s	C_5H_5
	9.75s	$Si(CH_3)_3$
	7.8—9.0br	C_6H_{10}
	6.1—6.5br	C_6H

[a] Chemical shifts are reported in ppm on the τ scale with TMS (= 10.0 ppm) as the internal standard; possible error is 0.02 ppm. [b] s, singlet; br, broad.

TABLE 3

ELEMENTAL ANALYTICAL DATA (found (calcd.) (%)) [a] FOR COMPOUNDS II AND III

	Compound II	Compound III
C	58.00	63.96
	(58.04)	(64.10)
H	7.73	8.95
	(7.55)	(8.74)
N	4.01	6.62
	(4.23)	(6.80)
Fe	16.59	13.27
	(16.86)	(13.54)
Si	8.26	6.41
	(8.49)	(6.82)

[a] Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, New York.

TABLE 4

MASS SPECTRAL DATA FOR COMPOUNDS II AND III

Compound	*m/e*	Rel. intensity	Probable ion
II	331	14	$C_5H_5Fe(CO)(C_6H_{11}NC)Si(CH_3)_3$
	303	15	$C_5H_5Fe(C_6H_{11}NC)Si(CH_3)_3$
	230	9.5	$C_5H_5Fe(C_6H_{11}NC)$
	220	96	$C_5H_5Fe(CN)Si(CH_3)_3$
	148	42	$C_5H_5Fe(CNH)$
	121	72	C_5H_5Fe
	73	(100)	$Si(CH_3)_3$
	56	27	Fe
III	412	17	$C_5H_5Fe(C_6H_{11}NC)_2Si(CH_3)_3$
	329	29	$C_5H_5Fe(C_6H_{11}NC)(CN)Si(CH_3)_3$
	303	36	$C_5H_5Fe(C_6H_{11}NC)Si(CH_3)_3$
	274	19	—
	230	21	$C_5H_5Fe(C_6H_{11}NC)$
	220	(100)	$C_5H_5Fe(CN)Si(CH_3)_3$
	148	57	$C_5H_5Fe(CNH)$
	121	55	C_5H_5Fe
	73	57	$Si(CH_3)_3$
	56	12	Fe

Discussion

Yamamoto and coworkers have reported that alkyl(π-cyclopentadienyl)iron dicarbonyl compounds react with organic isocyanides both thermally and photochemically [14—18]. We find that π-cyclopentadienyldicarbonyltrimethylsilyliron(II) does not react with cyclohexyl isocyanide in boiling benzene. However, when the reaction mixture is irradiated with 3500 Å light at room temperature the carbonyl ligands are successively replaced by cyclohexyl isocyanide (eq. 1).

$$\underset{\text{(I)}}{\pi\text{-}C_5H_5Fe(CO)_2Si(CH_3)_3} + C_6H_{11}NC \xrightarrow{h\nu} \underset{\text{(II)}}{\pi\text{-}C_5H_5Fe(CO)(C_6H_{11}NC)Si(CH_3)_3} + CO \tag{1a}$$

$$\text{II} + C_6H_{11}NC \xrightarrow{h\nu} \underset{\text{(III)}}{\pi\text{-}C_5H_5Fe(C_6H_{11}NC)_2Si(CH_3)_3} + CO \tag{1b}$$

Compounds II and III were isolated and characterized by their elemental analysis, IR and proton NMR spectra, and mass spectra, as described in the experimental section. In one experiment, the reaction mixture was analyzed while the photolysis proceeded. The results, shown in Fig. 1, show that the replacement of the carbonyl ligands is successive.

The replacement of both carbonyl ligands by cyclohexyl isocyanide in this reaction requires some comment. The reaction of alkyl(π-cyclopentadienyl)iron dicarbonyl with alkyl isocyanides, either thermally or photochemically, results in the replacement of only one carbonyl [14]. Similarly, King and Pannell [19] found that prolonged irradiation of I with excess of the monodentate ligands, $P(C_6H_5)_3$ and $P(OC_6H_5)_3$ did not lead to the replacement of both carbonyl groups. Bidentate ligands $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ and *cis*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$ did replace both carbonyls, however. These results are consistent with the idea that replacing a carbonyl ligand with a less π-acidic ligand strengthens the remaining metal—CO bonds.

However, Cullen, Sams and Thompson have reported that in the photochemical reactions of π-$C_5H_5Fe(CO)_2Sn(CH_3)_3$ with $(C_6H_5)_3Sb$ and with methylphenylphosphines both mono- and di-substituted products result, whereas only monosubstituted derivatives result on reaction with $(C_6H_5)_3P$ and with $(C_6H_5)_3As$ [20].

According to the IR investigations by Horrocks and Taylor [21], an alkyl isocyanide is a better π-acceptor than triphenylphosphine and weaker than triphenylphosphite. Consequently, the relative strengths of the Fe—CO bond of the monosubstituted compounds, $C_5H_5Fe(CO)(L)Si(CH_3)_3$, with different ligands L, should vary in the order: $P(C_6H_5)_3 > C_6H_{11}NC > P(OC_6H_5)_3$.

The experimental results of King [19] and of Cullen [20] and coworkers and of this study point to the fact that the Fe—CO bond strength is not the only factor controlling the substitution reaction under ultraviolet irradiation; that is, in some cases it appears that the reaction is kinetically rather than thermodynamically controlled *.

The experimental results of this study also reflect on a difference between

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* We thank one of the referees for this suggestion.

the reactivities of Fe—alkyl and Fe—Si bonds. The reactions between $C_5H_5Fe(CO)_2CH_3$ and $C_5H_5Fe(CO)_2CH_2C_6H_5$ with $C_6H_{11}NC$ lead to the formation of isocyanide insertion products [17]. In this study, under both thermal and photochemical conditions, no insertion into the Fe—Si bond is observed. This might be explained by a difference in the strengths of the Fe—Si and Fe—C bonds. The transition metal—silicon σ-bond generally has been considered to be substantially stronger than the corresponding metal—carbon bond, presumably due to the metal-to-metal d_π—d_π bonding [22].

The CO stretching frequencies of a series of compounds with the general formula $C_5H_5Fe(CO)(L)Si(CH_3)_3$, formed by monosubstitution of a carbonyl in $C_5H_5Fe(CO)_2Si(CH_3)_3$ by various ligands are listed in Table 5. These data agree with Horrocks and Taylor's findings that alkyl isocyanides have a π-acidity intermediate between $P(OC_6H_5)_3$ and $P(C_6H_5)_3$.

The NC stretching frequency in $C_5H_5Fe(CO)(C_6H_{11}NC)Si(CH_3)_3$ is 2089 cm^{-1}, which is 50 cm^{-1} lower than that of the free isocyanide. For $C_5H_5Fe(C_6H_{11}NC)_2Si(CH_3)_3$, a broad absorption peak from 1920 to 2060 cm^{-1} is obtained with maxima at 1960 and 2054 cm^{-1}, which are assigned as NC stretching frequencies. The absorption frequency is 80 to 120 cm^{-1} lower than that of the free ligand (2140 cm^{-1}). In both cases, the lowering in frequency indicates a substantial amount of backdonation to the NC antibonding orbital, especially for the disubstituted product. The extent of lowering in NC stretching frequency is similar to that in $Ni(CNC_6H_5)_4$, in which the two fundamental NC stretching modes are 70 and 125 cm^{-1} lower than that of the free isocyanide [23].

For the series $C_5H_5Fe(CO)_2Si(CH_3)_3$, $C_5H_5Fe(CO)(C_6H_{11}NC)Si(CH_3)_3$ and $C_5H_5Fe(C_6H_{11}NC)_2Si(CH_3)_3$, the chemical shift of the C_5H_5 and $Si(CH_3)_3$ signals increased steadily when carbonyl is replaced by $C_6H_{11}NC$, which is expected. These results support the IR evidence which indicated that replacing CO with RNC increases the electron density on the iron.

Compounds I and III interchange ligands when excited photochemically but not thermally (eq. 2). The details of this interesting reaction warrant further investigation.

$$\underset{\text{(I)}}{\pi\text{-}C_5H_5Fe(CO)_2Si(CH_3)_3} + \underset{\text{(III)}}{\pi\text{-}C_5H_5Fe(CNC_6H_{11})_2Si(CH_3)_3} \xrightarrow{h\nu} 2\ \underset{\text{(II)}}{\pi\text{-}C_5H_5Fe(CO)(CNC_6H_{11})Si(CH_3)_3} \tag{2}$$

TABLE 5

INFRARED CO STRETCHING FREQUENCIES OF $C_5H_5Fe(CO)(L)Si(CH_3)_3$

Compound	ν(CO) (cm^{-1})	Reference
$C_5H_5Fe(CO)_2Si(CH_3)_3$	1999, 1946	experimental
$C_5H_5Fe(CO)[P(OC_6H_5)_3]Si(CH_3)_3$	1953	[19]
$C_5H_5Fe(CO)(C_6H_{11}NC)Si(CH_3)_3$	1932	experimental
$C_5H_5Fe(CO)[P(C_6H_5)_3]Si(CH_3)_3$	1916	[19]

Even under rather forcing conditions, i.e., refluxing in benzene and in THF in the presence of a four-fold excess of cyclohexyl isocyanide, no insertion of isocyanide into the Fe—Si bond is detected. Negative results have been reported in the past regarding insertion into the iron—silicon bonds, e.g., π-$C_5H_5Fe(CO)_2$-$Si(CH_3)_3$ does not react with sulphur dioxide at elevated temperature and pressure [24]. This also would follow as a result of a greater iron—silicon bond strength as compared to the corresponding iron—carbon bond strength.

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