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The Synthesis and Characterization of Mixed Isocyanide Complexes of Cyclopentadienyliron

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The alkylation of η^5-$C_5H_5Fe(CO)(CN)(CNR)$ complexes with primary, secondary, and tertiary alkyl iodides, R'I ($R \neq R'$) produces the mixed isocyanide species [η^5-$C_5H_5Fe(CO)(CNR)(CNR')$]I. Infrared and NMR spectra of the new complexes are discussed. The effect of metal coordination on the ^{13}C spectra of cationic and neutral isocyanide complexes is considered. The use of the chiral alkyl iodides, sec-butyliodide and α-phenylethyliodide, results in configurationally non-labile diastereomers which, in the case of compounds of the latter, can be detected by ^1H and ^{13}C NMR spectra.

Introduction

Interest in transition metal isocyanide complexes has heightened in recent years, resulting in the synthesis of compounds having a wide variety of ligand environments [1]. While in many cases research has sought to capitalize on the similar bonding characteristics of these ligands with the more widely studied carbonyl derivatives, unusual reactions of coordinated isocyanides themselves have elicited considerable attention.

As a result of our own research interests in complexes derived from the reactions of coordinated isocyanides [2], we have recently prepared a series of mixed isocyanides of the form [η^5-$C_5H_5Fe(CO)(CNR)(CNR')$] I. Although a number of series of cyclopentadienyl complexes having two or three isocyanide groups are known [3–5], only one complex, [η^5-$C_5H_5Co(CN)(CNMe)(CNEt)$]$^+$I$^-$, having nonequivalent isocyanide ligands has been reported [6]. The inclusion of chiral isocyanide substituents makes this a particularly interesting series, since the asymmetry of tetrahedrally-coordinated metals predicts diastereomeric products. This report describes the synthesis of several of these complexes and their characterization by infrared and NMR spectroscopy.

Results and Discussion

In contrast to analogous cobalt [6], manganese [4], and molybdenum [3] cyclopentadienyl complexes, dialkylation of coordinated cyanides in K[η^5-$C_5H_5Fe(CO)(CN)_2$] has been observed to occur readily under relatively mild conditions, using alkyl bromides or iodides. To obtain mixed isocyanide complexes, the neutral monoalkylated compounds η^5-$C_5H_5Fe(CO)(CN)(CNR)$ were prepared using equimolar quantities of K[η^5-$C_5H_5Fe(CO)(CN)_2$] and RI, as described by Coffey [5]. Infrared and NMR spectra confirmed the presence of cyano and isocyano groups (see Table IV, Experimental Section). The monoalkylated complexes were easily separated from traces of the unreacted potassium salt and the dialkylated species, [η^5-$C_5H_5Fe(CO)(CNR)_2$] I, by chromatography on alumina.

Alkylation of the second cyanide was achieved by treating the neutral complexes with an excess of the desired alkyl iodide in acetonitrile. For a given complex, alkylation reactions of secondary alkyl halides were significantly slower than those having tertiary or primary groups, reflecting opposing S_N1 (t-butyl) and S_N2 (methyl) reactivity sequences. In the alkylation of η^5-$C_5H_5Fe(CO)(CN)(CNCH_3)$ with RI, reactivity decreased in the series

$$R = \text{t-Bu} \gg \text{Me} > \text{Et} \simeq \text{n-Pr} \gg \text{i-Pr} \simeq \text{s-Bu}$$

Reactions were monitored by infrared spectra which are summarized in Table I. As a result of the increase in positive charge on the complex accompanying alkylation, carbonyl stretching frequencies of the dialkylated complexes were approximately 20 cm^{-1} higher than those of the neutral analogs. However, the frequencies were insensitive to the nature of the isocyanide substituents.

In the C–N stretching region alkylation was observed by the loss of terminal cyanide absorptions and the appearance of two intense bands corresponding to isocyanide C–N stretching modes. These bands were also at higher frequencies than those of the neutral isocyanides and, as is frequently found in cationic complexes, the values were also higher than

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TABLE I. Infrared Spectra in C≡O and C≡NR Stretching Regions.

Compound	ν(CO)^a	ν(CNR)^a	
η^5-$C_5H_5Fe(CO)(CNCH_3)(CNCH_2CH_3)^+$	2019	2225	2193
η^5-$C_5H_5Fe(CO)(CNCH_3)(CNCH_2CH_2CH_3)^+$	2021	2223	2194
η^5-$C_5H_5Fe(CO)(CNCH_3)(CNCH(CH_3)_2)^+$	2021	2224	2184
η^5-$C_5H_5Fe(CO)(CNCH_3)(CNCH(CH_3)CH_2CH_3)^+$	2021	2223	2182
η^5-$C_5H_5Fe(CO)(CNCH_3)(CNCH(CH_3)C_6H_5)^+$	2022	2225	2180
η^5-$C_5H_5Fe(CO)(CNCH_3)(CNC(CH_3)_3)^+$	2022	2222	2178
η^5-$C_5H_5Fe(CO)(CNCH_2CH_3)(CNCH_2CH_2CH_3)^+$	2021	2217	2188
η^5-$C_5H_5Fe(CO)(CNCH_2CH_3)(CNCH(CH_3)_2)^+$	2020	2215	2183
η^5-$C_5H_5Fe(CO)(CNCH(CH_3)_2)(CNCH(CH_3)C_6H_5)^+$	2020	2204	2176

^{a}Spectra recorded in $CHCl_3$.

TABLE II. Proton Nuclear Magnetic Resonance Data^a.

$CpFe(CO)(CNR)(CNR')^+$	Cp	CNR^b	CNR'^{b}		
$CpFe(CO)(CNCH_3)(CNCH_2CH_3)^+$	5.27 s	3.72 s	4.00 q	(7.3)	NCH_2-
			1.47 t	(7.3)	-CH_3
$CpFe(CO)(CNCH_3)(CNCH_2CH_2CH_3)^+$	5.27 s	3.72 s	3.90 t	(6.6)	NCH_2-
			1.85 m		-CH_2-
			1.06 t	(7.3)	-CH_3
$CpFe(CO)(CNCH_3)(CNCH(CH_3)_2)^+$	5.25 s	3.72 s	4.40 m		NCH-
			1.48 d	(6.7)	-CH_3
$CpFe(CO)(CNCH_3)(CNCH(CH_3)CH_2CH_3)^+$	5.27 s	3.73 s	4.15 m		NCH-
			1.72 m		-CH_2-
			1.47 d	(6.7)	$NC(CH_3)$
			1.05 t	(7.3)	-CH_3
$CpFe(CO)(CNCH_3)(CNCH(CH_3)C_6H_5)^+$	5.28 s	3.70 s	7.41 m		C_6H_5
	5.27 s	3.67 s	5.47 q	(6.8)	NCH-
			1.80 d	(6.8)	-CH_3
$CpFe(CO)(CNCH_3)(CNC(CH_3)_3)^+$	5.22 s	3.71 s	1.60 s		-CH_3
$CpFe(CO)(CNCH_2CH_3)(CNCH_2CH_2CH_3)^+$	5.27 s	4.02 q	3.91 t	(6.5)	NCH_2-
		1.46 t	1.84 m		-CH_2-
			1.06 t	(7.3)	-CH_3
$CpFe(CO)(CNCH_2CH_3)(CNCH(CH_3)_2)^+$	5.26 s	4.02 q	4.38 m		NCH-
		1.46 t	1.49 d	(6.7)	-CH_3
$CpFe(CO)(CNCH(CH_3)_2)(CNCH(CH_3)C_6H_5)^+$	5.30 s	4.39 q	7.40 m		C_6H_5
	5.29 s	1.46 d	5.59 q	(6.7)	NCH-
		1.41 d	5.54 q	(6.7)	NCH-
			1.81 d	(6.7)	-CH_3

^{a}Chemical shifts (δ) relative to TMS in $CDCl_3$ at room temperature. ^{b}Splittings are given in Hz as s, singlet; d, doublet; t, triplet; m, multiplet.

those of the free ligand [7]. Also, a decrease in the stretching frequency accompanied an increase in the number of alkyl substituents on the carbon α to the nitrogen, as has been observed in the uncoordinated ligands [7]. Of particular interest was a marked increase of 6–10 cm^{-1} in the half-width of bands in the two complexes containing α-phenylethyl isocyanide. This most likely results from the overlap of diastereomeric bands in these complexes and is further illustrated by the NMR spectra discussed below. Although diastereomers are also expected for the sec-butyl isocyanide complex, no increase in

TABLE III. Carbon-13 Nuclear Magnetic Resonance Data[a].

$CpFe(CO)(CNR)(CNR')^+$	δ CO	δ C^0NR	δ Cp	δ CNR	δ CNR'	
$CpFe(CO)(CNCH_3)(CNCH_2CH_3)^+$	211.28	147.2	84.99	33.46	42.21	NCH_2-
					15.13	-CH_3
$CpFe(CO)(CNCH_3)(CNCH_2CH_2CH_3)^+$	211.35	147.7	84.90	32.99	48.22	NCH_2-
					22.56	-CH_2-
					10.94	-CH_3
$CpFe(CO)(CNCH_3)(CNCH(CH_3)_2)^+$	211.33	147.6	85.11	33.32	50.94	NCH-
					23.37	-CH_3
$CpFe(CO)(CNCH_3)(CNCH(CH_3)CH_2CH_3)^+$	211.00	147.4	84.66	32.75	56.37	NCH-
		146.6			29.40	-CH_2-
					20.64	$NC(CH_3)$
					9.74	-CH_3
$CpFe(CO)(CNCH_3)(CNCH(CH_3)C_6H_5)^+$	211.17	147.3	85.52	33.21	138.36	C_1
					129.62	C_2, C_6
					125.90	C_3, C_5
					129.20	C_4
					58.80	NCH-
					24.83	-CH_3
$CpFe(CO)(CNCH_3)(CNC(CH_3)_3)^+$	211.28	147.4	85.28	33.21	60.66	NC-
					31.06	-CH_3
$CpFe(CO)(CNCH_2CH_3)(CNCH_2CH_2CH_3)^+$	211.04	147.6	84.14	41.24	47.47	NCH_2
		147.0		14.16	21.83	-CH_2-
					10.09	-CH_3
$CpFe(CO)(CNCH_2CH_3)(CNCH(CH_3)_2)^+$	211.24	147.4	84.78	41.86	50.85	NCH-
				14.89	23.04	-CH_3
$CpFe(CO)(CNCH(CH_3)_2(CNCH(CH_3)C_6H_5)^+$	211.52	147.5	84.69	50.59	137.62	C_1
				22.70	137.56	C_1
					128.60	C_2, C_6
					124.98	C_3, C_5
					128.12	C_4
					57.75	NCH-
					24.08	-CH_3
					23.90	-CH_3

[a] Chemical shifts relative to TMS in $CDCl_3$ at room temperature.

band-width was observed in this complex, a result which is consistent with our inability to detect diastereomers in this complex in either ^1H or ^{13}C NMR spectra.

The mixed isocyanide complexes were characterized by their ^1H and ^{13}C NMR spectra, summarized in Tables II and III. Where necessary, assignments were made by selective (^1H) or off-resonance (^{13}C) decoupling. In general these spectra reflected consistent chemical shift patterns within the series of complexes synthesized. Changes in the identity of the isocyanide substituents, as expected, had a negligible effect on the magnetic environments of the other ligands in the complex. A closer look at the carbon-13 spectra is appropriate due to the relatively small number of ^{13}C spectra of coordinated isocyanides reported in the literature [8] and the opportunity in this series of complexes to compare coordination effects in closely related isocyanides. Resonances attributable to the isocyano carbon (δ C^0) were observed as broad signals at about 147 ppm. Detection of the signals was aided by the use of 0.05 *M* $Cr(acac)_3$ as a relaxation reagent. In only two cases (see Table III) was resolution sufficient to identify two distinct C^0 signals. In each complex these resonances occur 6–10 ppm upfield from those of either the neutral isocyanide complexes or the free ligand, an observation that has been found to be characteristic of a number of cationic complexes [8]. Although large upfield shifts of C^0 in Cu^I isocyanide complexes have been attributed to coordination effects on the paramagnetic shielding term [9], the presence of significant d_π–π^* backbonding produces downfield shifts that may offset this effect and even

TABLE IV. NMR and IR Data of Neutral Isocyanide Complexes.

CpFe(CO)(CN)(CNR)	$^1H^a$	$^{13}C^a$	$\nu(cm^{-1})^b$
$CpFe(CO)(CN)(CNCH_3)$	4.84 s Cp 3.46 s NCH_3	215.29 CO 156.9 CNR 137.8 CN 83.07 Cp 30.93 NCH_3	2195 CNR 2103 CN 2001 CO
$CpFe(CO)(CN)(CNCH_2CH_3)$	4.84 s Cp 3.74 q NCH_2- 1.43 t -CH_3	214.58 CO 154.8 CNR 137.4 CN 82.17 Cp 39.69 NCH_2- 14.41 -CH_3	2180 CNR 2103 CN 2000 CO
$CpFe(CO)(CN)(CNCH(CH_3)C_6H_5)$	7.39 m C_6H_5 5.06 q NCH- 4.85 s Cp 1.72 d -CH_3	215.18 CO 154.5 CNR 138.34 C_1 137.5 CN 129.56 C_2, C_6 125.60 C_3, C_5 128.96 C_4 82.75 Cp 56.72 NCH- 24.65 -CH_3	2163 CNR 2101 CN 2000 CO

^{a}Chemical shifts (δ) relative to TMS in $CDCl_3$ at room temperature. ^{b}Spectra recorded in $CHCl_3$.

yield slightly higher chemical shifts in coordinated isocyanides [8]. The upfield ^{13}C shifts of the cationic isocyanide C^0 carbons compared to those of the neutral complexes (Table IV) thus reflect a decrease in d_π–π^* backbonding, an observation consistent with the increase in ν C–N noted in infrared spectra of the former.

Saturated alkyl carbon atoms directly bonded to nitrogen (C^1) exhibited consistent downfield shifts of 5–6 ppm relative to the uncoordinated isocyanide. Smaller deshieldings of 1–3 ppm have been noted for similar nuclei in Cu^1 isocyanide complexes [9]. Deshielding of this nature can most likely be attributed to the increased withdrawing properties of the N–C group on coordination. As expected, this effect is greatest in cationic complexes. Thus, C^1 resonances of the neutral isocyanide species, though shifted downfield, were consistently 1–3 ppm upfield relative to their cationic analogs. The spectra showed the chemical shifts of the remaining carbon nuclei to be unaffected by coordination to the metal.

Complexes containing α-phenylethylisocyanide were observed as diastereomers in both ^1H and ^{13}C spectra under a number of solvent conditions. An example is seen in the ^1H spectrum of the methylisocyanide derivative reproduced in Figure 1. Resonances were most clearly separate in ^1H spectra, where a doubling of expected signals was observed for a number of protons including those of the chiral isocyanide and the remaining ligands (see Table II).

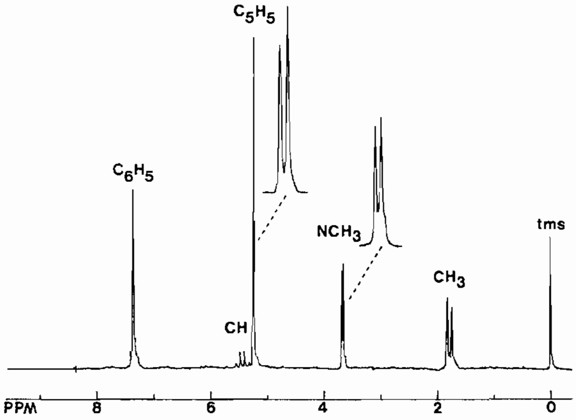

Figure 1. Room temperature 90 MHz ^1H Spectrum of $[\eta^5\text{-}C_5H_5Fe(CO)(CNCH_3)(CNCH(CH_3)C_6H_5)]I$ in $CDCl_3$.

Evidence of diastereomers was also seen in the ^{13}C spectrum of $\eta^5\text{-}C_5H_5Fe(CO)(CNCH(CH_3)_2)(CNCH(CH_3)C_6H_5)^+$, where the two carbon atoms bonded to the asymmetric carbon were each seen as two signals. However, the remaining carbon nuclei in this complex and all of the ^{13}C nuclei in $\eta^5\text{-}C_5H_5Fe(CO)(CNCH_3)(CNCH(CH_3)C_6H_5)^+$ were coincident. It is also interesting to note that the s-butylisocyanide complex, which showed no increase in C–N IR bandwidths, was not resolved as diastereomers in either ^1H or ^{13}C spectra. Differences in magnetic environments significant enough to discern diastereomers of this type in NMR spectra thus depend on both the substituents on the metal and on the chiral ligand. Although the two complexes with α-phenylethylisocyanide in this series were resolved by ^1H NMR, the same isocyanide, used by Brunner in (±)η^5-$C_5H_5Co(CNR)(C_3F_7)I$, produced diastereomers with coincident NMR spectra [10].

Although attempts to prepare mixed cyclopentadienyl isocyanide complexes by isocyanide substitution have been reported to result in extensive rearrangement in some complexes [11], we observed no behavior of this type in the iron complexes. No evidence of rearrangement of η^5-$C_5H_5Fe(CO)(CNR)(CNR')^+$ to η^5-$C_5H_5Fe(CO)(CNR)_2^+$ and η^5-$C_5H_5Fe(CO)(CNR')_2^+$ was seen. Further, the observation of non-equivalent diastereomeric NMR resonances indicates that the complexes are configurationally non-labile in solution at ambient temperatures. Separation of the diastereomers by fractional crystallization or column chromatography was not possible. All samples exhibited diastereomeric signals of equal intensity.

Experimental

All reactions were conducted under an atmosphere of prepurified nitrogen. Chromatographic separations utilized low activity alumina (Fisher A-540). All ^1H and ^{13}C NMR spectra were obtained using a Bruker WH90-DS spectrometer. Infrared spectra were recorded on a Perkin-Elmer 283 calibrated with gaseous DCl.

Potassium cyclopentadienylcarbonyldicyanoferrate(II) was prepared by literature methods [5].

Preparation of Neutral Mono-alkylated Complexes, η^5-$C_5H_5Fe(CO)(CN)(CNR)$

Neutral methyl, ethyl, and α-phenylethyl isocyanide complexes were prepared using equimolar quantities of $K[\eta^5$-$C_5H_5Fe(CO)(CN)_2]$ and the appropriate alkyl iodide in refluxing acetonitrile, as described by Coffey [5]. In a typical reaction, 3.0 g (0.013 mol) of $K[\eta^5$-$C_5H_5Fe(CO)(CN)_2]$ was dissolved in 150 ml of acetonitrile to which 0.78 ml (0.013 mol) of CH_3I was added. After 24 hours infrared spectra indicated the reaction mixture to contain predominently the monoalkylated product. In the case of ethyl and α-phenylethyl iodide addition, corresponding reaction times were 26 and 64 hours, respectively. After evaporation of the acetonitrile, the reaction mixtures were chromatographed on alumina. Using a mixture of 4/1 CH_2Cl_2/Pet. Ether, the neutral complex eluted as the first yellow band. Traces of the dialkylated product eluted as a second yellow band using 15/1 CH_2Cl_2/CH_3OH. Infrared and NMR data for the complexes are reported in Table IV. Upon spectral characterization the complexes were used without further isolation in the alkylation reactions described below.

Preparation of Cationic Mixed Isocyanide Complexes, η^5-$C_5H_5Fe(CO)(CNR)(CNR')^+$

The preparation of bis-isocyanide complexes of this series by alkylation of potassium cyclopentadienylcarbonyldicyanoferrate(II) has been described in the literature [5, 6]. Cationic complexes reported in this study were prepared by alkylating the mono-isocyanide complexes prepared above. All alkylations were conducted in refluxing acetonitrile using an excess of alkyl iodide.

Alkylation of η^5-$C_5H_5Fe(CO)(CN)(CNCH_3)$

The methylisocyanide complex was alkylated with ethyl, n-propyl, iso-propyl, sec-butyl, and tert-butyl iodides. Approximate reaction times for 90% completion of these alkylations were 36, 35, 70, 66, and 3 hours, respectively. After evaporation of the acetonitrile, the reaction mixtures were chromatographed on alumina. The unreacted methylisocyanide complex eluted with 4/1 CH_2Cl_2/petroleum ether while the desired product eluted with a 15/1 mixture of CH_2Cl_2/CH_3OH. Non-optimized yields after chromatography were 70–80%, based on the starting methylisocyanide complex. The complexes were isolated as the iodide salts, using dichloromethane and anhydrous ethyl ether. Melting points of the ethyl, isopropyl, and sec-butyl isocyanide complexes, obtained as yellow crystals, were 144°, 164°, and 130 °C, respectively. The n-propyl and tert-butyl isocyanide complexes were isolated as amber-colored oils.

Alkylation of η^5-$C_5H_5Fe(CO)(CN)(CNCH_2CH_3)$

The ethylisocyanide complex was alkylated with n-propyl and iso-propyl iodide, each requiring in excess of 144 hours for 90% completion. Isolation of the products followed the same procedure as described above and in each case yielded amber oils.

Alkylation of η^5-$C_5H_5Fe(CO)(CN)(CNCHCH_3)C_6H_5$

The α-phenylethylisocyanide complex was alkylated with methyl and isopropyl iodide. The methyl iodide reaction was 90% complete in 96 hours, however the isopropyl iodide reaction required a considerably longer reaction time and was stopped after 96 hours, when an infrared spectrum indicated the reaction to be 65% complete. Isolation of the products followed the same procedure as described above and resulted in amber oils.

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