$PFe(CO)_4$, 51743-95-4; $(CH_3O)_3PFe(CO)_4$, 51743-96-5; $(C_6H_5)(CH_3)_2PFe(CO)_4$, 51743-97-6; $(n\text{-}C_4H_9)_3PFe(CO)_4$, 18474-82-3; $(C_6H_5O)_3PFe(CO)_4$, 51653-00-0; $(CH_2{=}CHCOCl)Fe(CO)_4$, 51743-98-7; $(CH_2{=}CHCOOH)Fe(CO)_4$, 51743-99-8; $(CH_2{=}CHCONC_5H_{10})Fe(CO)_4$, 51744-00-4; $(CH_2{=}CHCN)Fe(CO)_4$, 51744-01-5; $[(n\text{-}C_4H_9)_3P]_2Fe(CO)_3$, 51653-01-1; $[(CH_3O)_3P]_2Fe(CO)_3$, 19457-84-2; $[(C_6H_5O)_3P]_2Fe(CO)_3$, 20516-74-9; $[C_6H_5(OC_2H_5)C](C_6H_5)_3PFe(CO)_3$, 42947-52-4.

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Studies on Interactions of Isocyanides with Transition Metal Complexes. X.[1] Preparation and Reactions of Alkyliron Complexes Containing Isocyanide[2]

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Reactions of $\pi\text{-}C_5H_5Fe(CO)(CNR')X$ ($R' = C_6H_{11}$, $(CH_3)_3C$, $PhCH_2$; X = Cl, I) with $p\text{-}YC_6H_4MgCl$ (Y = H, Cl) give the corresponding benzyl derivative $\pi\text{-}C_5H_5Fe(CO)(CNR')CH_2C_6H_4Y\text{-}p$ whereas reactions with other Grignard reagents (*e.g.*, CH_3MgI, $i\text{-}C_3H_7MgBr$, PhMgBr) lead to decomposition. When the latter reactions are run in the presence of CO, $\pi\text{-}C_5H_5Fe(CO)(CNR')COR$ complexes ($R = CH_3$, $i\text{-}C_3H_7$, Ph, $p\text{-}ClC_6H_4$) are obtained. The former reactions under comparable conditions give both benzyl and phenylacetyl derivatives. The mechanism of these reactions is discussed. Reactions of $\pi\text{-}C_5H_5Fe(CO)(CNR')R$ ($R = PhCH_2$, $p\text{-}ClC_6H_4CH_2$, $p\text{-}ClC_6H_4$; $R' = C_6H_{11}$, $PhCH_2$) with CO undergo preferentially an isocyanide insertion to afford the corresponding iminoacyl complexes $\pi\text{-}C_5H_5Fe(CO)_2[C(R){=}NR']$. The mass spectra of the isocyanide complexes and the iminoacyl ones are also investigated.

Introduction

Reactions of carbonyl-π-cyclopentadienylalkylmetal complexes $\pi\text{-}C_5H_5M(CO)_nR$ (M = Fe, n = 2; M = Mo, n = 3) with isocyanides proceed with either carbonyl or isocyanide insertion into the metal-carbon σ bonds.[3-5] In some cases the competitive insertion proceeds to give the corresponding metal-acyl and -iminoacyl complexes. It is of particular interest to know whether CO or R'NC is inserted preferentially in some alkylmetal complexes containing both CO and R'NC ligands, when reacted with Lewis bases. Reported here in detail is an extensive investigation on the syntheses and the reactions of carbonyl(isocyanide)-π-cyclopentadienylalkyliron complexes.

Experimental Section

General Procedures and Physical Measurements. All reactions were carried out under an atmosphere of nitrogen. Melting points were taken on a Yanagimoto Model MP-S2 and a Mitamura capillary melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 521 spectrophotometer or on a Shimazu IR-27G spectrophotometer. Proton magnetic resonance spectra were obtained on JEOL C-60, JEOL C-50HL, and Varian HA-100B spectrometers, using tetramethylsilane as a reference. The mass spectra were measured on a Nippondenshi Type JPS-1S mass spectrometer with a direct-inlet system. The photochemical reactions were carried out with a Usio-Denki 450-W high-pressure mercury lamp (Type UV-453).

Materials. Isocyanides[6] were prepared by procedures described in the literature. $\pi\text{-}C_5H_5Fe(CO)_2X$ (X = Cl,[7] I[8]) were prepared according to published methods.

Preparation of Bis[carbonyl(*tert*-butyl isocyanide)-π-cyclopentadienyliron]. A mixture of $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ (2.0 g, 5.7 mmol) and *tert*-butyl isocyanide (1.0 g, 12.0 mmol) in THF (30 ml) was irradiated at 25°. After 24 hr, the solvent was removed under reduced pressure, and then the residue was chromatographed on alumina. Two bands (dark brown and dark green) were observed. The first band (benzene) afforded a trace of $(\pi\text{-}C_5H_5)_2Fe_2(CO)_3[CNC(CH_3)_3]$.[9] The work-up of the second band [benzene–CH_2Cl_2 (1:1)] gave dark green crystals (1.7 g, 67%) of $[\pi\text{-}C_5H_5Fe(CO)\{CNC(CH_3)_3\}]_2$, recrystallized from benzene–hexane. *Anal.* Calcd for $C_{11}H_{14}NOFe$: C, 56.93; H, 6.08; N, 6.03. Found: C, 56.97; H, 5.92; N, 6.17.

The compound is very stable in the solid state but decomposes in solution, especially in $CHCl_3$. The infrared spectrum (KBr) shows three strong peaks at 2055 and 2093 cm^{-1} assignable to the coordinated isocyanide groups and 1732 cm^{-1} due to the bridged carbonyl groups. This suggests that the complex has a cis structure in the solid state. The proton nmr spectrum in CS_2 consists of two singlets at τ 8.27 (CH_3) and 5.73 (C_5H_5).

This nmr behavior could be explained by having a facile, rapid cis $\rightleftarrows$ trans isomerization as well as by related compounds, *e.g.*, $[\pi\text{-}C_5H_5Fe(CO)_2]_2$[10,11] and $(\pi\text{-}C_5H_5)_2Fe_2(CO)_3[CNC(CH_3)_3]$.[11] Study on this subject will be reported in the future.

Preparation of Carbonyl(isocyanide)-π-cyclopentadienyliron Halides. Two representative examples are described below. Analytical data and spectroscopic data are summarized in Table I.

(a) $\pi\text{-}C_5H_5Fe(CO)(CNC_6H_{11})I$. A mixture of $\pi\text{-}C_5H_5Fe(CO)_2I$ (3.1 g, 10.4 mmol) and cyclohexyl isocyanide (1.2 g, 11.0 mmol) in benzene (30 ml) was refluxed for 2 hr. The reaction mixture was then chromatographed on alumina, benzene being used as an eluent. Removal of solvent and crystallization of the residue from benzene–hexane gave $\pi\text{-}C_5H_5Fe(CO)(CNC_6H_{11})I$ (3.2 g, 80%) as dark yellow crystals.

The benzyl and *tert*-butyl isocyanide derivatives were prepared by similar procedures. The chloride complex was prepared at 25°.

(b) $\pi\text{-}C_5H_5Fe(CO)[CNC(CH_3)_3]I$. A solution of iodine (0.7 g, 2.8 mmol) in benzene was added to a solution of $[\pi\text{-}C_5H_5Fe(CO)\{CNC(CH_3)_3\}]_2$ (1.1 g, 2.4 mmol) in benzene (20 ml) at 25° and stirred for 24 hr. By procedures similar to that described in (a), $\pi\text{-}C_5H_5Fe(CO)[CNC(CH_3)_3]I$ (1.1 g, 62%) was obtained.

Reactions of Carbonyl(isocyanide)-π-cyclopentadienyliron Halides with Grignard Reagents. Two representative reactions are described in detail.

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(1) Part IX: Y. Yamamoto and H. Yamazaki, *Inorg. Chem.*, **13**, 438 (1974).

(2) A part of this paper was presented at the 26th Annual Meeting of the Chemical Society of Japan, Kanagawa, Japan, April, 1972; see Preprints III, p 1041.

(3) Y. Yamamoto and H. Yamazaki, *Bull. Chem. Soc. Jap.*, **43**, 143 (1970).

(4) Y. Yamamoto and H. Yamazaki, *Inorg. Chem.*, **11**, 211 (1972).

(5) Y. Yamamoto and H. Yamazaki, *J. Organometal. Chem.*, **24**, 717 (1970).

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

(7) T. S. Piper, F. A. Cotton, and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **1**, 165 (1955).

(8) T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **2**, 38 (1956).

(9) Y. Yamamoto and N. Hagihara, *Mem. Inst. Sci. Ind. Res., Osaka Univ.*, **27**, 109 (1970).

(10) (a) E. A. C. Lucken, K. Noak, and D. F. Williams, *J. Chem. Soc. A*, 148 (1967); (b) O. A. Gansow, A. R. Burke, and W. D. Vernon, *J. Amer. Chem. Soc.*, **94**, 2550 (1972).

(11) R. D. Adams and F. A. Cotton, *J. Amer. Chem. Soc.*, **95**, 6589 (1973).

Table I. Analytical Data, Physical Properties, and Spectroscopic Data of π-$C_5H_5Fe(CO)(CNR')X$

Compd			Analysis, %						Ir,[a] cm^{-1}		Nmr,[b] τ
			C		H		N				
R	X	Mp (dec), °C	Calcd	Found	Calcd	Found	Calcd	Found	ν(N≡C)	ν(C≡O)	
C_6H_{11}	Cl	53–56	53.19	53.37	5.49	5.54	4.77	4.61	2163	1980	
C_6H_{11}	I	79–81	40.55	40.48	4.19	4.21	3.64	3.63	2154	1972	7.9–9.0 b (C_6H_{10}), 5.8–6.3 b (C_6H), 5.29 s (C_5H_5)
$(CH_3)_3C$	I	139–141	36.80	37.33	3.93	3.73	3.90	3.97	2153	1970	8.51 s (CH_3), 5.28 s (C_5H_5)
$PhCH_2$	I	73–77	42.79	42.98	3.08	3.00	3.51	3.61	2173	1968	5.25 s (C_5H_5), 4.99 s (CH_2), 2.62 s (Ph)

[a] Measured as KBr pellets. [b] Measured in $CDCl_3$.

Table II. Analytical Data and Physical Properties of π-$C_5H_5Fe(CO)(CNR')COR$

Compd			Analysis, %					
			C		H		N	
R	R'	Mp (dec), °C	Calcd	Found	Calcd	Found	Calcd	Found
$PhCH_2$	C_6H_{11}	53–55	66.86	66.91	6.14	6.30	3.71	3.70
$PhCH_2$	$(CH_3)_3C$	70–73	64.97	65.21	6.00	6.03	4.02	3.99
Ph	$(CH_3)_3C$	94.5–96.5	64.12	64.36	5.68	5.85	4.15	4.18
p-ClC_6H_4	C_6H_{11}	94–95	60.40	60.56	5.07	4.87	3.52	3.42
i-C_3H_7	C_6H_{11}	44–45	62.02	62.00	7.04	6.97	4.25	4.23
i-C_3H_7	$(CH_3)_3C$	67.5–69	59.42	59.39	6.97	6.97	4.62	4.59

Table III. Infrared and Proton Magnetic Resonances of π-$C_5H_5Fe(CO)(CNR')COR$

Compd		Ir,[a] cm^{-1}			Nmr,[b] τ	
R	R'	ν(N≡C)	ν(C≡O)	ν(C=O)	C_5H_5	Other protons
$PhCH_2$	C_6H_{11}	2108	1940	1592	5.43	8.0–9.0 b (C_6H_{10}), 5.93 s (CH_2)
$PhCH_2$	$(CH_3)_3C$	2110	1942	1580	5.46	8.58 s ($(CH_3)_3C$), 5.92 s (CH_2), 2.82 bs (Ph)
Ph	$(CH_3)_3C$	2113	1948	1593	5.24	8.62 s ($(CH_3)_3C$), 2.27–2.72 b (Ph)
p-ClC_6H_4	C_6H_{11}	2125	1945	1584	5.34	7.9–8.9 b (C_6H_{10}), 6.0–6.5 b (C_6H_4), 2.5–2.9 s (C_6H_4)
i-C_3H_7	C_6H_{11}	2029	1920	1603	5.35	9.10 d (CH_3, 7.2 Hz), 9.12 d (CH_3, 7.2 Hz), 9.0–8.0 b (C_6H_{10}), 6.88 h (CH, 7.2 Hz), 6.0–6.5 b (C_6H)
i-C_3H_7	$(CH_3)_3C$	2035	1923	1576	5.44	9.08 d (CH_3, 6 Hz), 9.07 d (CH_3, 6 Hz), 8.53 s ($(CH_3)_3C$), 6.92 h (CH, 6 Hz)

[a] Measured as KBr pellets. [b] Measured in $CDCl_3$ solution. Abbreviations: s, singlet; d, doublet; h, heptet; b, broad; c, complex; bs, apparent broad singlet.

(a) **Preparation of π-$C_5H_5Fe(CO)(CNC_6H_{11})CH_2Ph$.** To a solution of π-$C_5H_5Fe(CO)(CNC_6H_{11})I$ (2.0 g, 5.3 mmol) in a mixture of benzene (20 ml) and ether (10 ml) was added $PhCH_2MgCl$ (30 mmol) in ether (10 ml) at 0°. After stirring for 4 hr, unreacted Grignard reagent was decomposed with water. The reddish orange layer was separated and the aqueous layer was extracted twice with 5-ml portions of benzene. The combined extracts were washed with water and dried over anhydrous magnesium sulfate. The solvent was then evaporated almost to dryness under reduced pressure, and the residue was chromatographed on alumina. 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 a yellow viscous oil of π-$C_5H_5Fe(CO)(CNC_6H_{11})CH_2Ph$ (0.94 g, 52%). The compound was characterized by the infrared and proton magnetic resonance spectra. Ir (in benzene): 2136 (N≡C) and 1938 (C≡O) cm^{-1}. Nmr (in $CDCl_3$): τ 7.42 singlet (CH_2), 5.47 singlet (C_5H_5), 8.1–9.0 broad (C_6H_{10}), 6.1–6.5 broad (C_6H), and 2.3–3.4 (Ph).

Upon work-up of the second eluate a compound was obtained which was identified as known $(\pi$-$C_5H_5)_2Fe_2(CO)_3(CNC_6H_{11})$[9].

π-$C_5H_5Fe(CO)(CNR')CH_2C_6H_4Cl$-*p* compounds (R' = C_6H_{11}, $PhCH_2$) (viscous oils) were prepared according to procedures analogous to (a).

π-$C_5H_5Fe(CO)(CNC_6H_{11})CH_2C_6H_4Cl$-*p* (43%). Ir (in benzene): 2135 (N≡C) and 1940 (C≡O) cm^{-1}. Nmr (in $CDCl_3$): τ 7.37 singlet (CH_2), 5.36 singlet (C_5H_5), 8.1–8.9 broad (C_6H_{10}), 6.2–6.5 broad (C_6H), and 2.6–2.8 broad (C_6H_4).

π-$C_5H_5Fe(CO)(CNCH_2Ph)CH_2C_6H_4Cl$-*p* (40%). Ir (in benzene): 2107 (N≡C) and 1948 (C≡O) cm^{-1}. Nmr (in $CDCl_3$): τ 7.52 singlet (CH_2), 5.70 singlet (C_5H_5), 5.23 singlet (NCH_2), and 2.3–3.2 broad (C_6H_4).

(b) **Attempted Preparation of π-$C_5H_5Fe(CO)(CNR')R$ (R = CH_3, *i*-C_3H_7, Ph).** Solutions of π-$C_5H_5Fe(CO)(CNR')X$ (R' = C_6H_{11}, $(CH_3)_3C$, $PhCH_2$; X = Cl, I) in a mixture of benzene (20 ml) and ether (10 ml) were treated with excesses of CH_3MgI, *i*-C_3H_7MgBr, and PhMgBr at 0–25°. Decomposition of excess Grignard reagent followed by drying of the organic layer and chromatography on alumina revealed no detectable amount of alkyl- or arylmetal complexes.

Reactions of Carbonyl(isocyanide)-π-cyclopentadienyl Halides with Grignard Reagents in the Presence of Carbon Monoxide. Two representative reactions are described in detail. The analytical data, physical properties, and spectroscopic data of the acyl and aroyl complexes prepared here are summarized in Tables II and III.

(a) **Reaction of π-$C_5H_5Fe(CO)[CNC(CH_3)_3]I$ with CH_3MgI in the Presence of CO.** To a solution of π-$C_5H_5Fe(CO)[CNC(CH_3)_3]I$ (0.72 g, 2.0 mmol) in a mixture of benzene (20 ml) and ether (10 ml) was added 10 mmol of CH_3MgI in ether (10 ml) at 0° in a stream of carbon monoxide. After 20 min, the reaction mixture was warmed to 25° and then kept stirring for 2 hr. Excess CH_3MgI was then decomposed with water. The dark orange layer was separated and the aqueous layer was extracted twice with 5-ml portions of benzene. The combined extracts were washed with water and dried over $MgSO_4$. The solvent was evaporated to dryness *in vacuo*, and the residue was chromatographed on alumina. Two bands (dark red and yellow) were observed to develop. Each was eluted with hexane–benzene (1:2) and benzene–CH_2Cl_2 (1:2). Eluting with hexane–benzene gave known $[\pi$-$C_5H_5Fe(CO)_2]_2$. The product from the second eluate was identified as known π-$C_5H_5Fe(CO)[CNC(CH_3)_3]COCH_3$ (0.3 g, 50%).[4]

(b) **Reaction of π-$C_5H_5Fe(CO)[CNC(CH_3)_3]I$ with $PhCH_2MgCl$ in the Presence of Carbon Monoxide.** To π-$C_5H_5Fe(CO)[CNC(CH_3)_3]I$ (0.75 g, 2.1 mmol) in a mixture of benzene (20 ml) and ether (10 ml) was added 10 mmol of $PhCH_2MgCl$ in ether (10 ml) at 0° in a stream of carbon monoxide. The reaction mixture was treated as in procedure (a) except that the reaction time was extended to 4 hr. The chromatography on alumina showed three bands. They were eluted with hexane–benzene (10:1), benzene, and benzene–THF (2:1), giving yellow, dark red, and yellow eluates, respectively. The product from the first eluate was identified as known π-$C_5H_5Fe(CO)[CNC(CH_3)_3]CH_2Ph$ (0.35 g, 40%).[4] The product from the second one was identified as known $[\pi$-$C_5H_5Fe(CO)_2]_2$ (trace). The product from the last one was identified as π-$C_5H_5Fe(CO)[CNC(CH_3)_3]COCH_2Ph$ (0.12 g, 17%).

Reactions of Carbonyl(isocyanide)-π-cyclopentadienylalkyliron with Carbon Monoxide. Some representative reactions are described below. Analytical data and characterizations of the iminoacyl complexes are summarized in Tables IV and V.

(a) **Reaction of π-$C_5H_5Fe(CO)(CNC_6H_{11})CH_2Ph$ with CO.** A

Table IV. Analytical Data and Physical Properties of Iminoacyl Complexes: $\pi\text{-}C_5H_5Fe(CO)_2[C(R){=}NR']$

Compd			Analysis %							
			C		H		N		Cl	
R	R′	Mp (dec), °C	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$PhCH_2$	C_6H_{11}	94–96	66.86	66.97	6.14	5.87	3.71	3.73		
$p\text{-}ClC_6H_4CH_2$	C_6H_{11}	114–115	61.26	61.31	5.39	5.21	3.40	3.48	8.61	8.64
$p\text{-}ClC_6H_4CH_2$	$PhCH_2$	105–107	62.96	62.81	4.32	4.09	3.34	3.30	8.57	8.55
$p\text{-}ClC_6H_4$	C_6H_{11}	87–89	60.40	60.45	5.07	5.21	3.52	3.55		

Table V. Infrared and Proton Magnetic Resonances of Iminoacyl Complexes: $\pi\text{-}C_5H_5Fe(CO)_2[C(R){=}NR']$

Compd		Ir,[a] cm^{-1}		Nmr,[b] τ	
R	R′	$\nu(C{\equiv}O)$	$\nu(C{=}N)$	C_5H_5	Other protons
$PhCH_2$	C_6H_{11}	1993, 1932	1609	5.51	7.85–9.0 b (C_6H_{10}), 6.6–7.1 b (C_6H), 6.0 s (CH_2), 2.4–3.0 b (Ph)
$p\text{-}ClC_6H_4CH_2$	C_6H_{11}	2000, 1946	1607	5.42	7.9–8.9 b (C_6H_{10}), 6.6–7.1 b (C_6H), 6.02 s (CH_2), 2.74 s (C_6H_4)
$p\text{-}ClC_6H_4CH_2$	$PhCH_2$	1997, 1942	1604	5.38	5.92 s (CH_2), 5.31 s ($N\text{-}CH_2$), 2.5–3.0 c (C_6H_4)
$p\text{-}ClC_6H_4$	C_6H_{11}	2007, 1953	1598	5.12	7.8–9.2 b (C_6H_{10}), 6.5–7.1 b (C_6H), 2.99 q (C_6H_4, J_{AB} = 8.4 Hz)

[a] Measured as KBr pellets. [b] Measured in $CDCl_3$.

mixture of $\pi\text{-}C_5H_5Fe(CO)(CNC_6H_{11})CH_2Ph$ (0.50 g, 1.4 mmol) and 30 kg/cm² of CO in tetrahydrofuran (15 ml) in a 200-ml stainless steel autoclave was kept for 144 hr. Removal of the solvent and chromatography of the residue gave two bands. Each was eluted with hexane and benzene, respectively. The product from the hexane solution was known $\pi\text{-}C_5H_5Fe(CO)_2CH_2Ph$ (0.02 g).[12] The product from the benzene solution was identified as $\pi\text{-}C_5H_5Fe(CO)_2[C(CH_2Ph){=}NC_6H_{11}]$ (0.38 g, 77%).

(b) Reaction of $\pi\text{-}C_5H_5Fe(CO)(CNC_6H_{11})C_6H_4Cl\text{-}p$[13] with CO. A mixture of $\pi\text{-}C_5H_5Fe(CO)(CNC_6H_{11})C_6H_4Cl\text{-}p$ (0.40 g, 0.11 mmol) and 30 kg/cm² of CO in benzene (15 ml) was kept for 100 hr. Work-up of the reaction mixture by the procedures analogous to those described above gave unreacted $\pi\text{-}C_5H_5Fe(CO)(CNC_6H_{11})C_6H_4Cl\text{-}p$ (0.06 g) and $\pi\text{-}C_5H_5Fe(CO)_2[C(C_6H_4Cl\text{-}p){=}NC_6H_{11}]$ (0.08 g, 27%).

(c) Attempted Reactions of Carbonyl(*tert*-butyl isocyanide)-π-cyclopentadienylalkyliron with CO. Solutions of $\pi\text{-}C_5H_5Fe(CO)[CNC(CH_3)_3]R$ (R = $PhCH_2$,[4] Ph[13]) and 20–30 kg/cm² of CO in benzene or THF were kept for 140–167 hr at 25°. Evaporation of the solvent revealed (ir spectroscopy) no detectable amount of iminoacyl complexes in the residue of each compound, and resulted in recovery of about 65–85% starting material. Reaction between $\pi\text{-}C_5H_5Fe(CO)[CNC(CH_3)_3]CH_2Ph$[4] (0.5 g, 1.50 mmol) and CO in THF (10 ml) was also carried out at 70–75° for 7 hr; again no iminoacyl complex could be detected.

Photochemical Reaction of Dicarbonyl-π-cyclopentadienyl(1-*N*-cyclohexylimino-2-phenylethyl)iron. A solution of $\pi\text{-}C_5H_5Fe(CO)_2[C(CH_2Ph){=}NC_6H_{11}]$ (0.65 g, 1.72 mmol) in THF (20 ml) was irradiated at 25° with a 450-W high-pressure mercury lamp. After 21 hr, the reaction mixture was chromatographed on alumina. Three bands (yellow, dark violet, and pale yellow) were observed and eluted with hexane, benzene–hexane (3:1) and benzene–CH_2Cl_2 (1:2), respectively. The product from the first band was identified as $\pi\text{-}C_5H_5Fe(CO)(CNC_6H_{11})CH_2Ph$ (0.10 g, 17%). The product from the second band was identified as known $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ (0.03 g, 10%). The product from the third band was identified as the unreacted starting material (0.04 g).

Attempts at Replacement of CO in Dicarbonyl-π-cyclopentadienyl-(1-*N*-cyclohexylimino-2-phenylethyl)iron with Bases. Solutions of $\pi\text{-}C_5H_5Fe(CO)_2[C(CH_2Ph){=}NC_6H_{11}]$ and PPh_3 or $C_6H_{11}NC$ in benzene or THF were refluxed for 8 hr. Evaporation of the solvent revealed (ir spectroscopy) no detectable amount of the decarbonylated product in the residue of each reaction mixture and led to recovery of starting material.

Attempted Decarbonylation of Carbonyl(isocyanide)-π-cyclopentadienylphenylacetyliron. When solutions of $\pi\text{-}C_5H_5Fe(CO)(CNC_6H_{11})COCH_2Ph$ (*ca.* 0.5 g) in 50 ml of benzene or THF were heated at reflux for 6–10 hr, *ca.* 80–90% starting material was recovered.

Attempted Carbonylation of Dicarbonyl-π-cyclopentadienylbenzyliron. A mixture of $\pi\text{-}C_5H_5Fe(CO)_2CH_2Ph$ (*ca.* 0.3 g) and 40 kg/cm² of CO in benzene was kept for 105 hr at 25°. Evaporation of the solvent resulted in recovery of starting material.

Results and Discussion

Reactions of Carbonyl(isocyanide)-π-cyclopentadienyliron Halides with Grignard Reagents. Treatment of $\pi\text{-}C_5H_5Fe(CO)(CNC_6H_{11})I$ with a large excess of benzylmagnesium chloride in a benzene–ether mixture gives a yellow-orange solution. The work-up of the solution affords a yellow oil, identified as $\pi\text{-}C_5H_5Fe(CO)(CNC_6H_{11})CH_2Ph$. The analogous benzyl derivatives are also prepared in a similar manner (eq 1; R = Ph, $C_6H_4Cl\text{-}p$; R′ = C_6H_{11}, $(CH_3)_3C$, $PhCH_2$; X = Cl, I).

$$\pi\text{-}C_5H_5Fe(CO)(CNR')X + RCH_2MgCl \rightarrow \pi\text{-}C_5H_5Fe(CO)(CNR')CH_2R + MgClX \qquad (1)$$

In contrast, the reactions of $\pi\text{-}C_5H_5Fe(CO)(CNR')X$ with methyl-, ethyl-, isopropyl-, or phenylmagnesium halide under comparable conditions result in decomposition without giving the desired alkyl or aryl derivatives. We believe that the alkyl or aryl products as well as the benzyl derivatives, if formed, should have sufficient stability for detection and isolation under these conditions. In fact, some of these compounds are obtained through decarbonylation of the corresponding acyl or aroyl complexes.[13,14]

Reactions of nucleophilic reagent such as Grignard reagent or alkyllithium with zerovalent metal carbonyls have been reported.[15-17] They furnished an attack of the carbanion on the carbon atom of coordinated CO group. Piper and Wilkinson have reported that treatment of Grignard reagent with $\pi\text{-}C_5H_5M(CO)_nX$ (M = Fe, n = 2; M = Mo or W, n = 3; X = Cl, Br, or I) leads to considerable decomposition with formation of tars.[18] They suggested that the reactions leading to decomposition proceeded *via* an attack of Grignard reagent on the coordinated CO group. We could expect the similar pathway in our reaction. Thus in the reactions

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(12) J. P. Bibler and A. Wojcicki, *J. Amer. Chem. Soc.*, 88, 4862 (1966).

(13) The compound is prepared by the photochemical decarbonylation of the corresponding aroyl complex. Studies on this complex and the related reactions will be described in a successive paper.

(14) For example, $\pi\text{-}C_5H_5Fe(CO)[CNC(CH_3)_3]CH_3$ is obtained from the photoassisted decarbonylation of the corresponding acetyl compound.

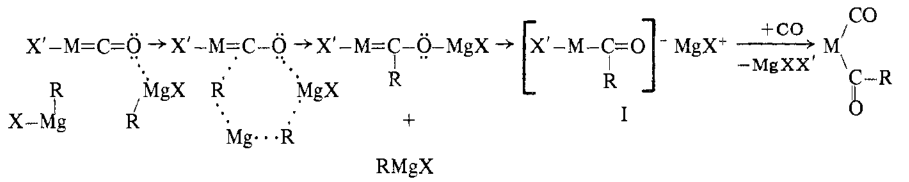
(15) M. Y. Darensbourg, H. L. Conder, D. J. Darensbourg, and C. Hasday, *J. Amer. Chem. Soc.*, 95, 5919 (1973).

(16) E. O. Fischer and A. Maasbol, *Angew. Chem., Int. Ed. Engl.*, 3, 580 (1964).

(17) G. R. Dobson and J. R. Paxson, *J. Amer. Chem. Soc.*, 95, 5925 (1973).

(18) T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 3, 104 (1956).

Scheme I. Proposed Mechanism for the Reaction of π-$C_5H_5Fe(CO)(CNR')X'$ with RMgX[a]



[a] The terminal isocyanide group and the cyclopentadienyl ligand are omitted for clarity.

with Grignard reagent, an initial attack would occur preferably on the carbon monoxide group rather than on the iron atom and lead to the formation of coordinatively unsaturated species, which will result in decomposition.

In the attempts to examine this hypothesis, the reactions of π-$C_5H_5Fe(CO)(CNR')I$ ($R' = C_6H_{11}$, $(CH_3)_3C$) with RMgX ($R = CH_3$, i-C_3H_7, Ph, C_6H_4Cl-p) were run in the presence of carbon monoxide. They give the corresponding acyl or aroyl complex in fairly good yield (eq 2).

$$\pi\text{-}C_5H_5Fe(CO)(CNR')I + RMgX + CO \rightarrow \pi\text{-}C_5H_5Fe(CO)(CNR')COR + MgIX \qquad (2)$$

The analogous reaction with benzyl or p-chlorobenzylmagnesium chloride gives both benzyl and phenylacetyl derivatives (eq 3).

$$2\pi\text{-}C_5H_5Fe(CO)(CNR')I + 2RCH_2MgX + CO \rightarrow \pi\text{-}C_5H_5Fe(CO)(CNR')CH_2R + \pi\text{-}C_5H_5Fe(CO)(CNR')COCH_2R + 2MgIX \qquad (3)$$

It is substantiated by the following points that two compounds obtained by the eq 3 are the direct products. First, the yields of the benzyl compound are relatively constant in the presence and absence of carbon monoxide, and the relative yields of both compounds are scarcely dependent on the length of time when the reactions were run for a long time (Table VI). Second, decarbonylation of the phenylacetyl complex to the benzyl one is not observed even in THF at reflux. Treatment of π-$C_5H_5Fe(CO)(CNC_6H_{11})CH_2Ph$ with carbon monoxide in the presence and absence of $PhCH_2MgCl$ (at 25° and for 4 hr) leads also to recovery of the unreacted material. These results indicate that there has occurred no interconversion between the benzyl and phenylacetyl complexes under the reaction conditions in question. Similar behavior has been observed in the reaction of the cationic $[\pi$-$C_5H_5Fe(CO)_3]PF_6$ with C_6F_5Li to give both π-$C_5H_5Fe(CO)_2COC_6F_5$ and π-$C_5H_5Fe(CO)_2C_6F_5$.[19]

The mechanism of the reactions leading to formation of the acyl complex may be explained in terms of the action of 1 mol of the Grignard reagent on a complex comprised of 1 mol of the Grignard reagent and the isocyanide complex, by analogy to the postulated mechanism[20] for the reaction of ketone with Grignard reagent (Scheme I). The reaction proceeds with elimination of MgXX' and coordination of free carbon monoxide, or displacement of X' with CO in the intermediate I, thus converting it to the final complex. No attempts to examine different reactivity between benzyl and other Grignard reagent were made at present.

It is not surprising that an attack of RMgX on the CO ligand occurs more favorably than that on the isocyanide ligand. It may be interpreted by ease of an initial electrophilic attack of MgX^+ on the oxygen molecule of the terminal carbonyl group compared with that on the nitrogen molecule of the coordinated isocyanide[21] and by the less steric requirement of carbon monoxide relative to isocyanide.

Table VI. Effect of Reaction Time on Yields of π-$C_5H_5Fe(CO)(CNC_6H_{11})CH_2Ph$ and π-$C_5H_5Fe(CO)(CNC_6H_{11})COCH_2Ph$ in Reactions of π-$C_5H_5Fe(CO)(CNC_6H_{11})I$ with $PhCH_2MgCl$[a]

		%	
No.	Time, hr	Benzyl complex	Phenylacetyl complex
1[b]	2	50	
2[b]	4	52	
3[c]	2	51	33
4[c]	3	50	35

[a] Solvent benzene (20 ml)–ether (10 ml); reaction temperature 0–10°; iodide complex:$PhCH_2MgCl \approx 1{:}5$. [b] Reaction in the absence of CO. [c] Reaction in the presence of CO.

In the proton nmr spectra of π-$C_5H_5Fe(CO)(CNR')R$ and π-$C_5H_5Fe(CO)(CNR')COR$ the chemical shifts of the cyclopentadienyl ring protons occur at higher field than those of the corresponding signals for the parent alkyl or aroyl complexes. This is the effect expected by substitution of the more weakly π-accepting isocyanide ligand for the CO ligand. The nmr spectra of π-$C_5H_5Fe(CO)(PPh_3)CH_2Ph$[22] and π-$C_5H_5Fe(CO)(PPh_3)COCH_2Ph$[23] have been known to display the AB type quartet for the methylene protons, arising from the presence of an asymmetric moiety in the compounds in question. The methylene protons of benzyl and phenylacetyl derivatives of isocyanide show a sharp or a relatively sharp singlet. This nmr behavior can be explained by (1) a rapid exchange process or more likely (2) an accidental degeneracy of the two benzylic methylene proton resonances. The two methyl proton resonances show magnetic nonequivalence in the nmr spectra of π-$C_5H_5Fe(CO)(CNC_6H_{11})COCH(CH_3)_2$ and π-$C_5H_5Fe(CO)[CNC(CH_3)_3]COCH(CH_3)_2$.

Reactions of Carbonyl(isocyanide)-π-cyclopentadienylalkyliron Complexes with Carbon Monoxide. Direct carbonylation and isocyanide insertion of noncarbonyl-alkylmetal complexes have been shown for $M(L)_2(X)R$, where M = Pd or Pt, L = tertiary phosphine, X = halogen, and R = alkyl or aryl.[24-26]

It is of particular interest in comparison with the direct insertion to study whether carbon monoxide or isocyanide

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(19) P. M. Treichel and R. L. Shubkin, *Inorg. Chem.*, 6, 1328 (1967).

(20) C. G. Swain and H. B. Boyles, *J. Amer. Chem. Soc.*, 73, 870 (1951).

(21) I. Ugi, "Isonitrile Chemistry," Academic Press, New York, N. Y., 1971, p 222.

(22) J. W. Faller and A. S. Anderson, *J. Amer. Chem. Soc.*, 91, 1550 (1969).

(23) H. Brunner, H.-D. Schindler, E. Schmidt, and M. Vogel, *J. Organometal. Chem.*, 24, 515 (1970).

(24) (a) P. M. Treichel, K. P. Wagner, and R. W. Hess, *Inorg. Chem.*, 12, 1471 (1973); (b) Y. Yamamoto and H. Yamazaki, *Bull. Chem. Soc. Jap.*, 44, 1873 (1971).

(25) G. Booth and J. Chatt, *J. Chem. Soc. A*, 634 (1966).

(26) Y. Yamamoto and H. Yamazaki, *Inorg. Chem.*, 13, 438 (1974).

inserts favorably into the metal–carbon σ bond in the transition metal complexes coordinated by both ligands. Carbonyl(isocyanide)-π-cyclopentadienylalkyliron, π-$C_5H_5Fe(CO)(CNR')R$, is the best candidate to investigate this subject. Reaction of π-$C_5H_5Fe(CO)(CNR')R$ with CO is expected to give either π-$C_5H_5Fe(CO)_2[C(R){=}NR']$ or π-$C_5H_5Fe(CO)(CNR')COR$.

The reaction of π-$C_5H_5Fe(CO)(CNC_6H_{11})CH_2Ph$ with 20–30 kg/cm^2 of carbon monoxide was run in benzene, THF, or CH_3CN. The solution was chromatographed on alumina and the work-up of the yellow eluate gives a 1:1 adduct identified as π-$C_5H_5Fe(CO)_2[C(CH_2Ph){=}NC_6H_{11}]$. No formation of the acyl complexes is observed. The infrared spectrum of the iminoacyl complex shows two terminal carbonyl absorptions at 1998 and 1941 cm^{-1}. In addition to these, the spectrum shows a strong peak at 1609 cm^{-1}, attributable to the carbon–nitrogen double bond. The proton nmr spectrum exhibits two sharp singlets at τ 5.51 and 6.00 assignable to the C_5H_5 and benzylic methylene protons and three broad signals due to the phenyl proton (*ca.* τ 2.5), α proton of the cyclohexyl group (*ca.* τ 6.85), and other cyclohexyl protons (*ca.* τ 8.4), respectively. Similar iminoacyl complexes, π-$C_5H_5Fe(CO)_2[C(R){=}NR']$ ($R = p$-ClC_6H_4, p-$ClC_6H_4CH_2$; $R' = C_6H_{11}, PhCH_2$), are prepared from the reaction of π-$C_5H_5Fe(CO)(CHR')R$ with CO. The related complex π-$C_5H_5Fe(CO)_2[C(C_6F_5){=}NCH_3]$ has been obtained by the reaction of $[\pi$-$C_5H_5Fe(CO)(CNCH_3)_2]PF_6$ with C_6F_5Li.[27] π-$C_5H_5Fe(CO)[CNC(CH_3)_3]CH_2Ph$ having a bulky isocyanide ligand does not undergo an isocyanide insertion, presumably because of steric influence.

Treichel, *et al.*, have reported that decarbonylation of π-$C_5H_5Fe(CO)(CNCH_3)[C(C_6F_5){=}NCH_3]$ takes place under thermal conditions to afford π-$C_5H_5Fe(CNCH_3)_2C_6F_5$.[27] On the contrary, no thermal decarbonylation of π-$C_5H_5Fe(CO)_2[C(CH_2Ph){=}NC_6H_{11}]$ is observed. When this compound is irradiated with a mercury lamp, extraction of CO occurs to give π-$C_5H_5Fe(CO)(CNC_6H_{11})CH_2Ph$ (eq 4).

$$\pi\text{-}C_5H_5Fe(CO)_2[C(CH_2Ph){=}NC_6H_{11}] \underset{CO}{\overset{h\nu,\,-CO}{\rightleftarrows}} \pi\text{-}C_5H_5Fe(CO)(CNC_6H_{11})CH_2Ph \qquad (4)$$

Thus, this reaction is reversible. All attempts at replacement of CO in this complex with PPh_3 and $C_6H_{11}NC$ in benzene at reflux prove unsuccessful, although π-C_5-$H_5Fe(CO)_2COR$ undergoes displacement of CO to produce π-$C_5H_5Fe(CO)(L)COR$, when allowed to react with PPh_3 and $R'NC$[28] on heating. The alkynylmetal complex π-$C_5H_5Fe(CO)(CNC_6H_{11})C{\equiv}CPh$ does not lead to an insertion reaction, probably due to greater strength of the metal–alkynyl bond.

Treatment of π-$C_5H_5Fe(CO)_2CH_2Ph$ with carbon monoxide under comparable conditions fails to give the carbonylation product. Insertion reaction of CO into π-$C_5H_5Fe(CO)_2CH_3$ has ultimately been provided under 2000 psi of CO at 125°.[29] In contrast to this, the aforementioned migration of the alkyl group on the isocyanide ligand in π-$C_5H_5Fe(CO)(CNR')R$ occurs under relatively milder conditions. Furthermore, the migration on the isocyanide ligand proceeds preferentially rather than on the carbon monoxide ligand.

The effect of length of reaction times on the yields of the product was investigated. It would appear that the relative rate of isocyanide insertion in the complexes in question decreases in the orders $PhCH_2NC > C_6H_{11}NC >> (CH_3)_3CNC$ for the isocyanide and p-$ClC_6H_4CH_2 > PhCH_2 > p$-$ClC_6H_4$ for the alkyl group, respectively (Table VII). The result relating to the isocyanide group seems in general accord with the postulate that the reaction rate is enhanced by an electron-withdrawing ligand.[30] Such an effect is noted in the isocyanide insertion of the alkylplatinum complex.[24a] The effect associated with the alkyl group is in contrast to that observed in the carbonylation of $RMn(CO)_5$ with CO.[31] The reaction also depends on solvents employed and increases with the dielectric constant of solvent; the order is $CH_3CN > THF > C_6H_6$. Analogous trends have been observed in carbonylation of π-$C_5H_5Fe(CO)_2R$ with phosphorus ligands[30] and sulfonylation with SO_2.[32]

Table VII. Effect of Reaction Time on Yields of Iminoacyl Complexes: π-$C_5H_5Fe(CO)_2[C(R){=}NR']$[a]

Compd				
R	R'	Time, hr	Solvent	Yield, %
p-$ClC_6H_4CH_2$	C_6H_{11}	24	C_6H_6	10
p-$ClC_6H_4CH_2$	C_6H_{11}	24	THF	15
p-$ClC_6H_4CH_2$	C_6H_{11}	90	C_6H_6	42
p-$ClC_6H_4CH_2$	C_6H_{11}	140	C_6H_6	63
p-$ClC_6H_4CH_2$	$PhCH_2$	100	C_6H_6	67
$PhCH_2$	C_6H_{11}	100	C_6H_6	38
$PhCH_2$	C_6H_{11}	150	C_6H_6	59
$PhCH_2$	C_6H_{11}	144	THF	77
$PhCH_2$	C_6H_{11}	140	CH_3CN	83
p-ClC_6H_4	C_6H_{11}	100	C_6H_6	27

[a] CO pressure *ca.* 30 kg/cm^2; 15 ml of solvent; reaction temperature 25°; *ca.* 1–1.5 mmol of complex.

Mass Spectra of Isocyanide Complexes and Iminoacyl Complexes. There are many studies on the mass spectra of the metal-alkyl complexes[33-35] but few examples of the metal complexes containing isocyanide ligands. We investigated the fragmentation schemes of the alkyl isocyanide complexes and the iminoacyl ones. Some of the degradation processes are supported by the observation of the metastable ions.

(a) π-$C_5H_5Fe(CO)(CNR')R$ and π-$C_5H_5Fe(CO)(CNR')COR$. The mass spectra of the acetyl and methyl derivatives are so similar that they appear to be those of the same compound except the parent ion of the acetyl compound. The parent ion (*m/e* 275, relative intensity (ri) 21) in the spectrum of π-$C_5H_5Fe(CO)[CNC(CH_3)_3]COCH_3$ undergoes stepwise losses of carbonyl groups, giving the carbonyl-free ion $C_5H_5Fe[CNC(CH_3)_3]CH_3^+$ (*m/e* 219, ri 43). The losses of $CH_2{=}C(CH_3)_2$ and the methyl group occur then to form $C_5H_5Fe(CNH)^+$ (*m/e* 148, ri 100). The structure with a hydrogen isocyanide ligand for the ion $C_5H_5Fe(CNH)^+$ is suggested by the loss of HNC to give the $C_5H_5Fe^+$ (*m/e* 121, ri 84) ion, followed finally by loss of C_5H_5 to furnish the iron ion. This process is supported by the observation of

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[27] P. M. Treichel and J. P. Stenson, *Inorg. Chem.*, 8, 2563 (1969).

[28] Y. Yamamoto and H. Yamazaki, unpublished results.

[29] T. H. Coffield, J Kozikowski, and R. J. Closson, *Chem. Soc., Spec. Publ.*, No. 13, 126 (1959).

[30] (a) J. B. Bibler and A. Wojcicki, *Inorg. Chem.*, 5, 889 (1966); (b) M. L. H. Green and C. R. Hurley, *J. Organometal. Chem.*, 10, 188 (1967); (c) M. Green and D. J. Westlake, *J. Chem. Soc. A*, 367 (1971); (d) I. Douck and G. Wilkinson, *ibid.*, 2604 (1967); (e) A. Wojcicki, *Advan. Organometal. Chem.*, 11, 87 (1973).

[31] F. Calderazzo and F. A. Cotton, *Proc. Int. Conf. Coord. Chem.*, 296 (1962).

[32] (a) S. E. Jacobson and A. Wojcicki, *J. Amer. Chem. Soc.*, 93, 2535 (1971); (b) A. Wojcicki, *Accounts Chem. Res.*, 4, 344 (1971); (c) A. Wojcicki, *Advan. Organometal. Chem.*, 12, 31 (1974).

[33] M. I. Bruce, *Advan. Organometal. Chem.*, 6, 274 (1968).

[34] M. Cais and M. L. Lupin, *Advan. Organometal. Chem.*, 8, 211 (1970).

[35] J. Muller, *Angew. Chem., Int. Ed. Engl.*, 11, 653 (1972).

a metastable ion at *m/e* 98.5 ($121^2/148 = 98.9$). The presence of the ion bearing a hydrogen isocyanide ligand has been noted in the spectra of $C_5H_5Mn(CO)_2(CNC_6H_{11})$[36] and $C_5H_5Fe(CO)(NCCF_3)[C(CF_3)=NH]$.[37] π-$C_5H_5Fe(CO)[CNC(CH_3)_3]COCH_2Ph$ breaks down *via* two different pathways. In the first pathway the loss of a benzyl group occurs to afford $C_5H_5Fe(CO)_2[CNC(CH_3)_3]^+$ (*m/e* 260, ri 42). This ion loses two carbonyls and $CH_2=C(CH_3)_2$ stepwise to $C_5H_5Fe(CHN)^+$ (*m/e* 148, ri 37). The second pathway is of particular interest. A salient feature of this process involves the simultaneous loss of two carbonyl groups, although losses of two carbonyl groups occur stepwise in the mass spectra of the other acyl isocyanide complexes, π-$C_5H_5Fe(CO)(CNR')COR$, prepared here.

Thus the loss of 2 CO from the parent ion occurs, affording $C_5H_5Fe[CNC(CH_3)_3]CH_2Ph$ (*m/e* 295, ri 7). This transition is confirmed by the observation of a metastable ion at *m/e* 247.5 ($295^2/351 = 247.9$) and the high-resolution mass spectrum of this complex.[38] Some examples of the simultaneous loss of carbonyl groups have been noted in the mass spectra of several arenemetal complexes.[33,34] The successive losses of the $CH_2=C(CH_3)_2$ and HNC groups occur from the ion (*m/e* 295), finally giving the iron ion.

(b) π-$C_5H_5Fe(CO)_2[C(R)=NR']$. Many examples of decarbonylation of metal carbonyl derivatives, resulting in the absence of the parent peak in the mass spectrometer have been noted.[39-41] An example among such compounds is observed in the mass spectra of the iminoacyl complexes.

In the spectrum of π-$C_5H_5Fe(CO)_2[C(CH_2Ph)=NC_6H_{11}]$, the loss of CO from the highest ion $C_5H_5Fe(CO)[C(CH_2Ph)=NC_6H_{11}]^+$ (*m/e* 349, ri 22) occurs to give $C_5H_5Fe[C(CH_2Ph)=NC_6H_{11}]^+$ (*m/e* 321, ri 75). This ion appears to break down *via* two pathways. In the first the successive losses of C_6H_{11} and CN occur to form $C_5H_5FeCH_2Ph^+$ (*m/e* 212, ri 100). This loses the $PhCH_2$ and C_5H_5 groups to give Fe^+. In the second the loss of $PhCH_2$ occurs, affording $C_5H_5Fe(CNC_6H_{11})^+$ (*m/e* 230, ri 66). The mass spectrum of π-$C_5H_5Fe(CO)_2[C(CH_2C_6H_4Cl\text{-}p)=NC_6H_{11}]$ gives a fragmentation pattern similar to that of the benzyl derivative.

In the spectrum of π-$C_5H_5Fe(CO)_2[C(C_6H_4Cl\text{-}p)=NC_6H_{11}]$ the second path leading to formation of the ion $C_5H_5Fe(CNC_6H_{11})^+$ from $C_5H_5Fe[C(C_6H_4Cl\text{-}p)=NC_6H_{11}]^+$ (*m/e* 341, ri 35) is not detectable. The successive losses of CO, C_6H_{11}, and CN from the highest ion $C_5H_5Fe(CO)[C(C_6H_4Cl\text{-}p)=NC_6H_{11}]^+$ (*m/e* 369, ri 58) occur to form $C_5H_5FeC_6H_4Cl\text{-}p^+$ (*m/e* 232, ri 19).

Registry No. $[\pi\text{-}C_5H_5Fe(CO)\{CNC(CH_3)_3\}]_2$, 51567-87-4; π-$C_5H_5Fe(CO)(CNC_6H_{11})I$, 36644-63-0; π-$C_5H_5Fe(CO)[CNC(CH_3)_3]I$, 51567-85-2; π-$C_5H_5Fe(CO)(CNC_6H_{11})CH_2Ph$, 51567-70-5; π-$C_5H_5Fe(CO)(CNC_6H_{11})CH_2C_6H_4Cl\text{-}p$, 51567-76-1; π-$C_5H_5Fe(CO)(CNCH_2Ph)CH_2C_6H_4Cl\text{-}p$, 51567-77-2; π-$C_5H_5Fe(CO)[CNC(CH_3)_3]COCH_2Ph$, 51567-72-7; π-$C_5H_5Fe(CO)_2[C(CH_2Ph)=NC_6H_{11}]$, 51567-81-8; π-$C_5H_5Fe(CO)_2[C(C_6H_4Cl\text{-}p)=NC_6H_{11}]$, 51567-80-7; π-$C_5H_5Fe(CO)(CNC_6H_{11})Cl$, 51567-74-9; π-$C_5H_5Fe(CO)(CNCH_2Ph)I$, 51567-84-1; π-$C_5H_5Fe(CO)(CNC_6H_{11})COCH_2Ph$, 51567-73-8; π-$C_5H_5Fe(CO)[CNC(CH_3)_3]COPh$, 51567-71-6; π-$C_5H_5Fe(CO)(CNC_6H_{11})COC_6H_4Cl\text{-}p$, 51567-75-0; π-$C_5H_5Fe(CO)(CNC_6H_{11})COC_3H_7\text{-}i$, 51567-78-3; π-$C_5H_5Fe(CO)[CNC(CH_3)_3]COC_3H_7\text{-}i$, 51567-79-4; π-$C_5H_5Fe(CO)_2[C(CH_2C_6H_4Cl\text{-}p)=NC_6H_{11}]$, 51567-83-0; π-$C_5H_5Fe(CO)_2[C(CH_2C_6H_4Cl\text{-}p)=NCH_2Ph]$, 51567-82-9; $[\pi\text{-}C_5H_5Fe(CO)_2]_2$, 12154-95-9; π-$C_5H_5Fe(CO)_2I$, 12078-28-3; $PhCH_2MgCl$, 6921-34-2; CO, 630-08-0.

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(36) J. Muller and M. Herberhold, *J. Organometal. Chem.*, 13, 399 (1968).

(37) R. B. King and K. H. Pannell, *J. Amer. Chem. Soc.*, 90, 3984 (1968).

(38) The metastable ion at *m/e* 247.5 corresponds to the 2 CO or the $CH_2=C(CH_3)_2$ fragment. The exact mass of *m/e* 295 was counted as *m/e* 295.098, identical with that of the ion $C_5H_5Fe[CNC(CH_3)_3]CH_2Ph^+$ (*m/e* 295.102). For comparison the exact mass of the ion $C_5H_5Fe(CO)_2(CNH)CH_2Ph^+$ is *m/e* 295.030.

(39) R. B. King, *J. Amer. Chem. Soc.*, 90, 1417 (1968).

(40) R. B. King, *J. Amer. Chem. Soc.*, 85, 1584 (1963).

(41) E. K. von Gustorf, M. C. Henry, and D. J. MeAdoo, *Justus Liebigs Ann. Chem.*, 707, 190 (1967).

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Nature of the Electronic Ground State in Tris(2-chlorophenanthroline)iron(II) Perchlorate and Related Complexes

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The orbital and spin ground states of $[Fe(2\text{-}Cl(phen))_3](ClO_4)_2$ (phen = phenanthroline) and related high-spin ferrous complexes have been studied using Mossbauer spectroscopy. The temperature dependence of the Mossbauer spectrum of $[Fe(2\text{-}Cl(phen))_3](ClO_4)_2$ over the range 300–4.2°K indicates the system to have a ground *spin quintet* contrary to the results of a recent susceptibility study in which a high-spin to low-spin equilibrium is assumed. Magnetically perturbed Mossbauer spectra of the 2-Cl complex as well as the high-spin form of $[Fe(phen)_2(NCS)_2]$ show these compounds to have a *negative* principal component (V_{zz}) of the electric field gradient tensor. This result is consistent with previous Mossbauer and magnetic studies of $[Fe(phen)_2X_2]$ complexes ($X^- = Cl^-, N_3^-$) and is interpreted in terms of an electron in d_{z^2} corresponding to an *orbital* (^2A) *singlet* ground term.

The purpose of this work is the elucidation of both the orbital and spin ground states of certain high-spin ferrous (diimine) complexes which have been the subject of several recent studies.

Spin Ground State

Extensive data[1] exist establishing that nearly all six-coordinate iron(II) complexes of the type $[Fe(phen)_3]^{2+}$ and $[Fe(bipy)_3]^{2+}$ have diamagnetic (^1A) ground states. This same

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(1) R. L. Collins, R. Pettit, and W. A. Baker, Jr., *J. Inorg. Nucl. Chem.*, 28 1001 (1966).