

PHOTOCHEMICAL REACTIONS OF CATIONIC ISOCYANIDE/CARBONYL COMPLEXES OF IRON WITH SELECTED NUCLEOPHILES

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Summary

Photolysis of $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\text{CNMe})_2]\text{PF}_6$ in the presence of excess nucleophiles resulted in efficient substitution of the carbonyl ligand, generating the new isocyanide complexes $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CNMe})_2(\text{L})]\text{PF}_6$ (L = PPh₃, AsPh₃, SbPh₃, pyridine, acetonitrile, and ethylene). Similar reactions of $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{-}(\text{CNMe})]\text{PF}_6$ led to sequential replacement of both carbonyl groups with the exception of L = ethylene. No evidence of photochemical isocyanide substitution was found. The same carbonyl complexes failed to react with L thermally. In the absence of light, ethylene, pyridine, and acetonitrile complexes were found to disproportionate in the manner $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CNMe})(\text{L})_2]\text{PF}_6 \rightarrow [\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CNMe})_2(\text{L})]\text{PF}_6 \rightarrow [\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CNMe})_3]\text{PF}_6$ with the first rearrangement occurring much faster than the second. The new isocyanide complexes are characterized by their infrared and NMR (¹H, ¹³C) spectra.

Introduction

The high inherent photolability of metal-coordinated carbonyls has provided the basis for both synthetic applications and theoretical studies in many transition metal systems [1]. Substitution reactions, especially in binary metal carbonyls or cyclopentadienyl metal carbonyls, dominate most of these investigations. Photochemical studies of the substituted carbonyl complexes themselves or species containing carbonyls and other potentially labile ligands are considerably less common. Nonetheless there is a continuing interest in elucidating the relationship between specific photochemical reactivity and the electronic structure and coordination environment of the central metal. The potential for exploring these factors, coupled with the attractive possibility of synthesizing several new complexes that we had been unable to obtain thermally, led us to

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begin a study of the photochemistry of metal complexes containing both carbonyl and isocyanide ligands.

Despite the synthesis of a great many isocyanide complexes and their often-cited similarity to carbonyls, only infrequent references to photoreactions of coordinated isocyanides have appeared in the literature. For example, photochemical dissociation of coordinated isocyanide is reported by Yamamoto to contribute to reaction pathways proposed for formation of bis-imino complexes of iron [2]. Products obtained upon irradiation of $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})\text{(CNR)COCH}_3$ did indicate substitution of isocyanide although carbonyl replacement predominated by a factor of 13 [2]. In contrast, Trahanovsky reported that photolysis of $\eta^6\text{-benzonorbornadiene(isocyanide)dicarbonylchromium}$ resulted exclusively in expulsion of isocyanide rather than carbonyls in the formation of $\eta^8\text{-benzonorbornadiene}$ derivatives [3].

In the present study we report the results of irradiation of the cationic complexes $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\text{CNMe})_2]\text{PF}_6$ and $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2(\text{CNMe})]\text{PF}_6$ in the presence of excess nucleophilic ligands. The ionic nature of these species provided an additional dimension to the structure—reactivity objectives of our studies since very few examples of photochemical reactions of charged organometallic complexes are known. Also, unlike a number of other mixed carbonyl/isocyanide systems [4,5,6] the iron complexes were chosen because they exhibit high thermal stability and resist disproportionation in the absence of light.

Results

Photolysis of $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\text{CNMe})_2]\text{PF}_6$

Dichloromethane solutions of the bis methyl isocyanide complex were irradiated with UV/Vis light (> 300 nm) in the presence of a ten molar excess of acetonitrile, pyridine, or tertiary phenyl Group Vb ligands. Ethylene reactions were run by continuous bubbling of the gas through the irradiation mixture. Reactions were monitored by periodic recording of infrared spectra in the carbonyl and isocyanide stretching region. Rapid disappearance of the carbonyl stretching frequency at 2024 cm^{-1} was observed with most reactions complete within 60 minutes. Slight differences in reaction times could be attributed to variation in the flow rate of nitrogen gas, which was used to purge solutions of dissociated CO. Loss of the CO stretching band was accompanied by a shift of the two CN bands to lower frequencies. Continued irradiation produced no further changes in the infrared spectra, although extensive photolysis of the substituted products was not pursued.

Reaction mixtures were analyzed by ^1H NMR spectroscopy before the application of recrystallization or chromatography techniques. In reactions with Group Vb donors, the only product observed was the carbonyl substituted complex, $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CNMe})_2\text{L}]\text{PF}_6$. Small amounts of $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CNMe})_3]\text{PF}_6$ were formed during the acetonitrile, pyridine, and ethylene reactions. No evidence of $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\text{CNMe})\text{L}]\text{PF}_6$ or $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CNMe})\text{L}_2]\text{PF}_6$ complexes was found. The new products were characterized by their IR, ^1H , and ^{13}C spectra (Tables 1–3) and were subsequently obtained as analytically pure samples.

TABLE I
INFRARED SPECTRA IN C=O AND C≡NR STRETCHING REGIONS ^a

L	$\nu_{\text{CNR}} (\text{cm}^{-1})$	$\nu_{\text{CO}} (\text{cm}^{-1})$
[$\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CNMe})_2(\text{L})\text{]PF}_6$ Complexes		
PPh ₃	2153, 2185	
AsPh ₃	2151, 2182	
SbPh ₃	2153, 2183	
MeCN	2173, 2202	
pyridine	2154, 2187	
ethylene	2186, 2214	
[$\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\text{CNMe})(\text{L})\text{]PF}_6$ Complexes		
PPh ₃	2208	1995
AsPh ₃	2210	1995
SbPh ₃	2204	1991
MeCN	2222	2018
pyridine	2214	1999
ethylene	2246	2029
[$\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CNMe})(\text{L})_2\text{]PF}_6$ Complexes		
PPh ₃	2149	
AsPh ₃	2150	
SbPh ₃	2151	
MeCN	2180	
pyridine	2146	

^a Spectra recorded in CHCl₃ at room temperature.

TABLE 2
PROTON NUCLEAR MAGNETIC RESONANCE DATA ^a

L	C ₅ H ₅ (δ , ppm)	CNMe (δ , ppm)	L (δ)
[$\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CNMe})_2(\text{L})\text{]PF}_6$ Complexes			
PPh ₃ ^b	4.71	3.31	7.49–7.60 m
AsPh ₃	4.80	3.34	7.51–7.54 m
SbPh ₃	4.97	3.36	7.56 s
MeCN	4.67	3.69	2.36 s
pyridine	4.63	3.74	7.30 m 7.84 t 8.93 d
ethylene	5.02	3.62	3.24 s
[$\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\text{CNMe})(\text{L})\text{]PF}_6$ Complexes			
PPh ₃ ^{b,c}	4.90	3.24	7.50–6.50 m
AsPh ₃	5.27	3.37	7.47–7.67 m
SbPh ₃	5.43	3.41	7.61 s
MeCN	5.28	3.72	2.42 s
pyridine	5.17	3.77	7.41 m 7.95 t 8.87 d
ethylene	5.47	3.58	3.63 s
[$\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CNMe})(\text{L})_2\text{]PF}_6$ Complexes			
PPh ₃ ^b	4.46	3.74	7.28–7.43 m
AsPh ₃	4.60	3.63	7.24–7.46 m
SbPh ₃	4.98	3.70	7.34–7.47 m
MeCN	4.46	3.84	2.50 s
pyridine	4.53	3.99	7.31 m 7.84 t 8.93 d

^a Chemical shifts relative to TMS in acetone-*d*₆ at room temperature. ^b Cyclopentadienyl and isocyanide signals in complexes containing PPh₃ exhibited splittings of 1.5 Hz. ^c Reported in ref. 7 as the tetraphenylborate salt.

TABLE 3

CARBON-13 NUCLEAR MAGNETIC RESONANCE DATA ^a

L	$\delta(\text{Cp})$ (ppm)	$\delta(\text{CNCH}_3)^b$ (ppm)	$\delta(\text{L,CO})$	
$[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CNMe})_2(\text{L})]\text{PF}_6$ Complexes				
PPh ₃	83.12	31.54	134.71	PPh ₃
			133.24	
			131.11	
			129.20	
AsPh ₃	80.79	31.06	135.07	AsPh ₃
			132.56	
			130.64	
SbPh ₃	79.23	31.06	129.44	SbPh ₃
			135.07	
			130.88	
MeCN	80.22	31.16	130.88	NCCH ₃
			129.92	
pyridine	80.40	31.61	117.4	pyridine
			4.68	
			159.10	
$[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\text{CNMe})(\text{L})]\text{PF}_6$ Complexes				
PPh ₃	86.24	31.96	137.64	CO
			125.47	
			214.87	
			133.24	
AsPh ₃	84.66	32.03	133.15	AsPh ₃
			131.71	
			129.62	
SbPh ₃	83.06	31.54	214.13	SbPh ₃
			133.69	
			132.61	
MeCN	84.45	31.57	131.66	CO
			130.22	
			213.56	
pyridine	85.19	30.67	135.19	pyridine
			131.84	
			130.64	
ethylene	87.44	31.50	130.04	ethylene
			215.43	
			136.17	
$[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CNMe})(\text{L})_2]\text{PF}_6$ Complexes				
PPh ₃	84.04	32.58	4.41	CO
			213.89	
			159.97	
			139.71	
AsPh ₃	79.41	31.84	127.13	AsPh ₃
			136.27	
			132.82	
SbPh ₃	76.35	31.90	130.40	SbPh ₃
			130.40	
			129.26	
pyridine ^c	77.43	32.26	135.19	pyridine
			132.19	
			130.87	
			129.92	
			158.44	
			137.47	
			125.48	

^a Chemical shifts (δ) relative to TMS in acetone-*d*₆ at room temperature unless otherwise noted. Spectra of $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CNMe})_2(\text{ethylene})]\text{PF}_6$ and $[\eta^5\text{-C}_5\text{H}_5\text{-Fe}(\text{CNMe})_2(\text{NCMe})]\text{PF}_6$ were not recorded because of their low solubilities and decreased thermal stabilities. ^b Signals of isocyanide carbons (CNMe) are not included in the table but were observed as broad signals at 150–165 ppm. ^c Recorded in CDCl₃ at 223°K.

Analogous thermal reactions conducted in refluxing acetone for over 100 hours showed only traces of $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CNMe})_2\text{L}]\text{PF}_6$ (<3%) accompanied by approximately equal amounts of $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CNMe})_3]\text{PF}_6$.

Photolysis of $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2(\text{CNMe})]\text{PF}_6$

Irradiation of the dicarbonyl complex was conducted in the same manner as the bis isocyanide. In each case there was rapid conversion to $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\text{CNMe})\text{L}]\text{PF}_6$ as evidenced by the disappearance of the carbonyl bands of the starting complex (2078, 2038 cm^{-1}) and the appearance of a single CO band at lower frequency. Isolation of the monocarbonyl species which, with the exception of $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\text{CNMe})(\text{PPh}_3)]\text{BPh}_4$ [7], have not been previously reported was possible by stopping the reaction at this point. An alternative method of preparing the same complexes without appreciable quantities of $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CNMe})\text{L}_2]\text{PF}_6$ was accomplished by ligand exchange with ethylene in $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\text{CNMe})(\text{ethylene})]\text{PF}_6$. Substitution occurred when the complex was refluxed in dry acetone for several hours with an excess of the appropriate nucleophile. (The ethylene complex was the easiest of the monocarbonyl species to isolate, since conversion to $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CNMe})(\text{ethylene})_2]\text{PF}_6$ was not observed and disproportionation reactions were slow relative to initial carbonyl displacement.)

Continued irradiation of the monosubstituted complexes in all but the ethylene case resulted in rapid loss of the remaining carbonyl and conversion to products having one isocyanide and no carbonyl bands, identified as $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CNMe})\text{L}_2]\text{PF}_6$ species. Continued irradiation of $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\text{CNMe})(\text{ethylene})]\text{PF}_6$ resulted in disproportionation to $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CNMe})_2(\text{ethylene})]\text{PF}_6$ and eventually to $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CNMe})_3]\text{PF}_6$. Similar disproportionations to $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CNMe})_2\text{L}]\text{PF}_6$ complexes occurred readily in the absence of light when bis acetonitrile and bis pyridine complexes were left in solution at room temperature. Isolation of these complexes required care in both handling and storing samples at low temperatures. Spectral data for both disubstituted and monocarbonyl complexes are summarized in Tables 1–3.

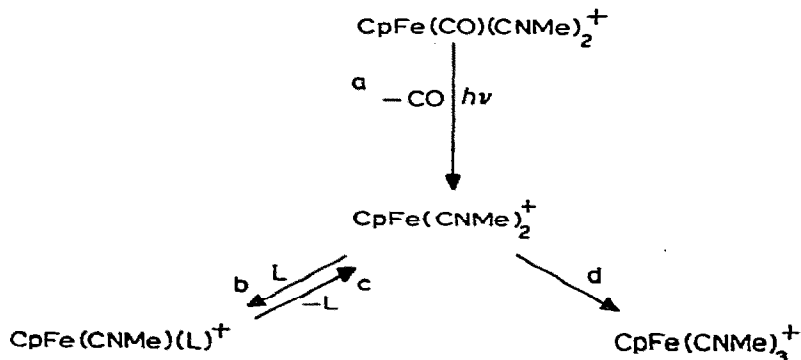
Again, attempted carbonyl substitution by thermal reaction yielded only trace amounts of monosubstituted products after prolonged heating.

Discussion

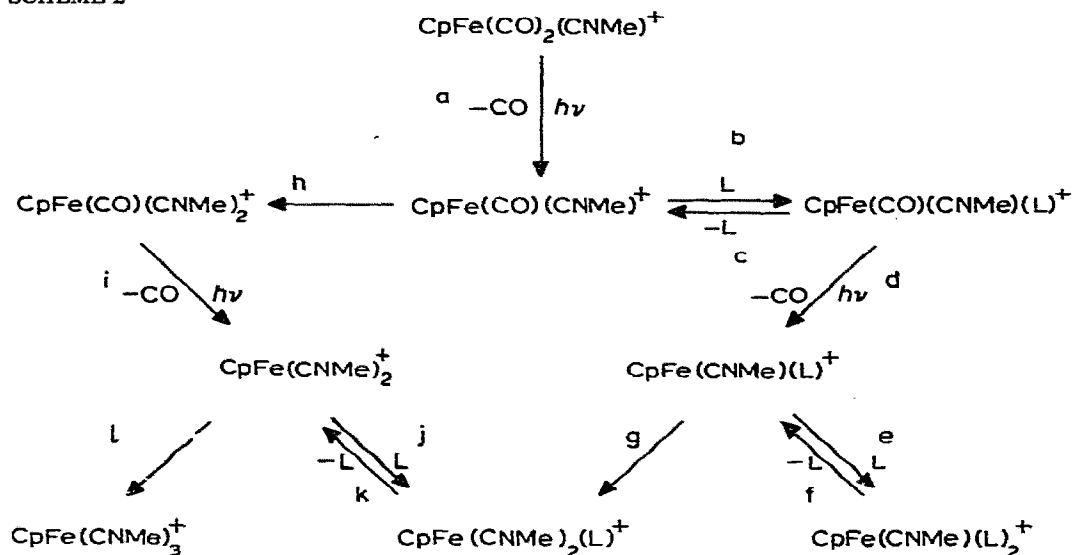
The photochemical behavior of each mixed carbonyl/isocyanide complex was characterized by rapid photolabilization of the coordinated carbonyls, permitting efficient substitution by available nucleophiles where thermal reactivity was negligible. Significantly, not one reaction gave evidence of photochemical dissociation of coordinated methyl isocyanide. Analysis of the products of these irradiations and consideration of several side reactions, observed in the absence of other nucleophiles, permitted construction of the reaction sequences outlined in Schemes 1 and 2.

The initial effect of irradiating $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\text{CNMe})_2]\text{PF}_6$ is undoubtedly photodissociation of the carbonyl, yielding the sixteen electron complex $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CNMe})_2]^+$, which is probably weakly complexed by the solvent. In the absence of any other nucleophiles this species apparently degrades, pro-

SCHEME 1



SCHEME 2



ducing free isocyanide, which rapidly adds to remaining molecules of $[\eta^5\text{-C}_5\text{H}_5\text{Fe(CNMe)}_2]^+$ to yield $[\eta^5\text{-C}_5\text{H}_5\text{Fe(CNMe)}_3]^+$ (reaction *d*). This reaction, observed by Dineen and Pauson upon photolysis of $[\eta^5\text{-C}_5\text{H}_5\text{Fe(CO)(CNMe)}_2]\text{I}$ in dioxane, has been cited as a convenient method of preparing the trisubstituted compounds [8]. Although the irradiation in dioxane is reported to take 18 hours [8], disproportionation in irradiated dichloromethane solutions was complete (for the PF_6 complex) in four hours. Formation of the tris isocyanide complex (reaction *d*, Scheme 1) does not require light. In fact, non-photolytic generation of $[\eta^5\text{-C}_5\text{H}_5\text{Fe(CNPh)}_2]^+$ by the reaction of $\eta^5\text{-C}_5\text{H}_5\text{Fe(CNPh)}_2\text{I}$ with Ag^+ has already been reported by Treichel [9] and has been shown to yield $[\eta^5\text{-C}_5\text{H}_5\text{Fe(CNPh)}_3]\text{PF}_6$ as the sole product. The tris isocyanide is a terminal product in these reactions. In our studies it was also found to be thermally and photochemically inert to further substitution.

Formation of the tris isocyanide can be effectively suppressed when another nucleophile is present to react with $[\eta^5\text{-C}_5\text{H}_5\text{Fe(CNMe)}_2]^+$ before it decomposes

(*a* → *b*). The independence of the rate of this reaction on the identity of the nucleophile is further evidence that carbonyl dissociation is the rate determining step. Thermal or photochemical dissociation of L from $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CNMe})_2\text{L}]\text{-PF}_6$ provided an additional route to the tris isocyanide complex (*c* → *d*) although in the case of tertiary Group Vb ligands this reaction was totally suppressed by the presence of excess nucleophile. Solutions of these substituted complexes in the absence of excess ligand were also thermally stable to disproportionation but did appear to dissociate L when irradiated*. Competitive production of the tris complex was greatest with ethylene as the incoming ligand. At room temperature, in the absence of light, isolated solutions of $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CNMe})_2(\text{ethylene})]\text{PF}_6$ were completely converted within 10 hours (*c* → *d*). Despite this observed thermal instability and the likelihood of photochemical olefin dissociation, continuous bubbling of ethylene through the irradiation mixture produced an 81% yield of the olefin complex. Thermal disproportionation of the pyridine and acetonitrile complexes in isolated solutions was also noted but occurred at a much slower rate.

Photochemical substitution of the dicarbonyl complex, as seen in Scheme 2, is initiated by dissociation of one carbonyl to form $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\text{CNMe})]^+$. The reaction, followed in the absence of additional nucleophiles, proceeds through the sequence *h* → *i* → *l* with $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CNMe})_3]\text{PF}_6$ as the only eventual product. The reaction sequence parallels that reported for the photochemical conversion of $\eta^5\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_2(\text{CNMe})$ to $\eta^5\text{-C}_5\text{H}_5\text{Mn}(\text{CNMe})_3$ although in the manganese series the bis isocyanide intermediate was too unstable to be detected [5]. In the present case, the bis isocyanide of iron is clearly formed as an intermediate. In the absence of light, Treichel has also shown that $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\text{CNPh})]^+$, generated by the reaction of $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\text{CNPh})\text{I}$ with Ag^+ , converts solely to $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\text{CNPh})_2]^+$ [9]. Although the stoichiometry of the photochemical disproportionations requires the formation of other products, no evidence of any other organometallic species was ever seen in solution infrared or NMR spectra. Insoluble precipitates were formed but were not analyzed.

When excess nucleophiles were present in irradiation mixtures the reaction sequence *b* → *d* → *e* predominated in most cases. Tertiary phosphine, arsine, and stibine ligands completely suppressed disproportionation pathways and afforded thermally stable disubstituted products. The analogous pyridine and acetonitrile derivatives could also be produced in significant yield but were thermally unstable, disproportionating within minutes (*f* → *g*) when isolated in room temperature solutions. Both the free ligand and $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CNMe})_2(\text{L})]\text{-PF}_6$ were detected in these solutions with further disproportionation (*k* → *l*) occurring at a much slower rate, as described previously. Irradiations of the dicarbonyl complex in the presence of ethylene gave only $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CNMe})_2(\text{ethylene})]\text{PF}_6$ and $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CNMe})_3]\text{PF}_6$ as eventual products with the disubstituted complex either thermally or photochemically too unstable to be detected.

* The photochemistry of the products was not fully investigated, however it was noted that solutions of $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CNMe})_2(\text{SbPh}_3)]\text{PF}_6$, irradiated in the presence of excess triphenylphosphine, could be completely converted to $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CNMe})_2(\text{PPh}_3)]\text{PF}_6$.

In all of the reactions the monocarbonyl was observed and could be isolated as a stable intermediate. Thermal dissociation (reaction *c*) was evident only in the case of the olefin complex but was very slow relative to further photo-induced carbonyl dissociation (*d*). Photochemical dissociation of ethylene in $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\text{CNMe})(\text{ethylene})]\text{PF}_6$ also appeared likely since, relative to other incoming nucleophiles, longer irradiation of $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2(\text{CNMe})]\text{PF}_6$ was necessary to generate the monocarbonyl complex. Significant differences in photoreaction rates of the monosubstituted complex that might be attributable to *cis* labilization effects by L were not observed.

Variations in stabilities within the series of $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CNMe})_2\text{L}]\text{PF}_6$ and $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CNMe})\text{L}_2]\text{PF}_6$ complexes appear to reflect differences in the mode of bonding of the incoming nucleophile, L. Isocyanides are stronger σ donors and weaker π acceptors than carbonyls and give rise to greater electron density on the metal. Even in these cationic complexes, significant increases in charge density of the isocyanide derivatives are evident from Mössbauer data [10]. The isocyanide complexes are therefore stabilized by ligands such as PPh_3 , AsPh_3 , and SbPh_3 which, though less π acidic than isocyanides, are capable of transferring some metal density to vacant *d* orbitals. This is particularly evident in complexes where two sites are occupied by the incoming nucleophile and only one isocyanide is present. Strong σ donors incapable of π backdonation (pyridine, acetonitrile) afford considerably less stable compounds. Ethylene, a weak σ donor with some π backbonding ability typically forms much weaker metal–ligand bonds than the other nucleophiles in this study and not surprisingly was unable to stabilize the disubstituted derivative. Differences in stability attributable to relative σ or π effects are greatly diminished by replacement of one isocyanide by a carbonyl. Thus $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\text{CNMe})\text{L}]^+$ complexes, where L = PPh_3 , AsPh_3 , SbPh_3 , pyridine, and acetonitrile, show no tendency to decompose or disproportionate in solution and, when L = ethylene, ligand exchange occurred only upon heating.

The ease of carbonyl displacement in $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2(\text{CNMe})]\text{PF}_6$ is in contrast to the general lower reactivity of the neutral dicarbonyl complexes, $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{R}$ reported in the literature [11–14]. Of the nucleophiles examined in this study only SbPh_3 (reacted with $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{SnMe}_3$) has been previously reported to photochemically replace two carbonyls [13]. Factors that account for the extent of photochemical substitution in all of these complexes cannot be easily separated and in some cases kinetic rather than thermodynamic control has been suggested [15]. However, the extent to which electronic charge on the metal effects the strength of the metal–carbonyl bond is certainly an important consideration and most likely accounts for the consistent degree of substitution of these cationic carbonyls. Replacing a carbonyl with a less π -acidic ligand strengthens the remaining metal–CO bond which appears to prohibit further substitution in many of the neutral complexes. Carbonyl stretching frequencies of $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\text{L})\text{R}$ derivatives are 40–80 cm^{-1} lower than those of $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\text{CNMe})\text{L}]^+$ cations, reflecting considerably greater $\text{M} \rightarrow \text{L}$ π donation. Significantly, Millich et al [15] report sequential displacement of both carbonyls when $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{SiMe}_3$ is photoreacted with alkyl isocyanides which, though less π acidic than carbonyls, are capable of moderate π backbonding.

Substitution of two carbonyls by predominantly σ donating ligands (pyridine, acetonitrile) also differs from the photochemistry of certain analogous manganese and rhenium complexes observed by Wrighton [16]. However, failure to observe the disubstituted complexes $\eta^5\text{-C}_5\text{H}_5\text{Mn}(\text{CO})\text{X}_2$ when X was not a reasonable π -acceptor ligand correlates with the behavior of the neutral iron complexes noted above. Reported carbonyl stretching frequencies of $\eta^5\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{X}$ derivatives are also much lower than those of $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\text{CNMe})(\text{MeCN})]\text{PF}_6$ or $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\text{CNMe})(\text{pyridine})]\text{PF}_6$.

Failure to observe isocyanide photodissociation may also be related to electronic charge. Whereas metal-carbonyl bonds are weakened by decreased charge on the metal, isocyanides, as strong σ donating ligands, stabilize metal complexes in high oxidation states and should experience enhanced L \rightarrow M bonding as positive charge increases. In chromium complexes, where dissociation of isocyanides occurred exclusively, high metal electron density, evident from low CO stretching frequencies, was cited as a determining factor for the observed photochemistry [3]. Neutral iron complexes in which Yamamoto detected isocyanide photodissociation also had greater negative charge on the metal than those in the present study [2], although comparisons are complicated by the uncertain effect of differences in the structure of the alkyl isocyanide groups.

The possible effect of wavelength variation on relative ligand photolabilities has not been investigated as yet. However, the electronic spectra of the complexes $\text{CpFe}(\text{CO})_{3-n}(\text{CNMe})_n^+$ differ only slightly, exhibiting nearly identical charge transfer bands at 240 nm and weaker absorptions at 325 ($n = 0$), 339 ($n = 1$), 355 ($n = 2$), and 365 ($n = 3$) nm. With respect to dissociation of the metal-CO bond, experiments by Folkes and Rest [14] have demonstrated that the photoreaction of $\text{CpFe}(\text{CO})_2\text{Me}$ is unaffected by changing the irradiation wavelength from $\lambda > 200$ to $\lambda > 300$ nm.

Further studies of isocyanide complexes exploring the effects of charge, wavelength, and substituent variation on relative photolabilities are in progress.

Experimental

The compounds $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\text{CNMe})_2]\text{PF}_6$ and $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2(\text{CNMe})]\text{PF}_6$ were prepared as described in the literature [7]. All reactions were run under prepurified nitrogen. Photochemical reactions utilized a 250-W General Electric sunlamp filtered through Pyrex. Solutions were purged with a vigorous stream of nitrogen during photolysis and were maintained at 3°C by a circulating water jacket. Triphenylphosphine, triphenylarsenic, and triphenylantimony were obtained from Alfa. Deaerated reagent grade solvents were used in all cases. Pyridine was redistilled prior to use. Chromatographic separations utilized low activity alumina (Fisher A-540) or florisil, where noted. Microanalyses were performed by the Kentucky Center for Energy Research Laboratory, Lexington, Kentucky and also by Galbraith Laboratories, Knoxville, Tennessee.

All ^1H and ^{13}C NMR spectra were obtained using a Bruker WH90-DS spectrometer. Infrared spectra were recorded on a Perkin-Elmer 283 spectrometer calibrated with DCl. Electronic spectra were recorded in acetonitrile using a Perkin-Elmer 571 spectrophotometer.

TABLE 4
MELTING POINTS AND ANALYTICAL DATA FOR ISOCYANIDE COMPLEXES

Compound	Mp (°C)	Exptl (calcd) analyses (%)		
		C	H	N
$[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CNMe})_2(\text{PPh}_3)]\text{PF}_6$	215–216	53.57 (53.14)	4.15 (4.29)	4.24 (4.59)
$[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CNMe})_2(\text{AsPh}_3)]\text{PF}_6$	210–211	49.70 (49.57)	3.92 (4.01)	4.08 (4.28)
$[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CNMe})_2(\text{SbPh}_3)]\text{PF}_6$	192–193	46.49 (46.25)	3.63 (3.74)	3.87 (3.99)
$[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CNMe})_2(\text{py})]\text{PF}_6$	126–127	39.83 (39.36)	3.76 (3.78)	9.72 (9.84)
$[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CNMe})_2(\text{NCMe})]\text{PF}_6$	210–211	34.29 (33.96)	3.67 (3.63)	10.69 (10.80)
$[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CNMe})_2(\text{ethylene})]\text{PF}_6$	210–212	34.92 (35.13)	3.93 (4.02)	7.44 (7.45)
$[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CNMe})(\text{PPh}_3)_2]\text{PF}_6$	163–164	62.43 (62.11)	4.59 (4.61)	1.47 (1.68)
$[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CNMe})(\text{AsPh}_3)_2]\text{PF}_6$	157–159	56.21 (56.17)	4.14 (4.17)	1.29 (1.52)
$[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CNMe})(\text{SbPh}_3)_2]\text{PF}_6$	167–168	51.10 (50.98)	3.73 (3.78)	1.22 (1.38)

Complete IR and NMR characterization of the products has been provided in Tables 1–3. Melting points and analytical data for thermally stable $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CNMe})_2(\text{L})]\text{PF}_6$ and $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CNMe})(\text{L})_2]\text{PF}_6$ derivatives are summarized in Table 4 and data for $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\text{CNMe})(\text{L})]\text{PF}_6$ intermediates are contained in Table 5.

$[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CNMe})_2(\text{SbPh}_3)]\text{PF}_6$

A solution of $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\text{CNMe})_2]\text{PF}_6$ (0.5 g, 1.3 mmol) and triphenyl-

TABLE 5
YIELDS, MELTING POINTS, AND ANALYTICAL DATA FOR MONOCARBONYL COMPLEXES

$[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\text{CNMe})(\text{L})]\text{PF}_6$ L	Mp (°C)	Yield (%)	Prep. method ^a	Exptl (calcd) analyses (%)		
				C	H	N
PPh ₃	previously reported as BPh ₄ salt (ref. 7)					
A ⁺ Ph ₃	149–151 d	44	$\Delta, \text{C}_2\text{H}_4$	48.51 (48.70)	3.55 (3.62)	2.67 (2.19)
SbPh ₃	176	40	$\Delta, \text{C}_2\text{H}_4$	45.14 (45.39)	3.22 (3.37)	2.56 (2.04)
Py	91	55	$\Delta, \text{C}_2\text{H}_4$	37.48 (27.71)	3.35 (3.16)	7.04 (6.77)
NCMe	>300	69	$\Delta, \text{C}_2\text{H}_4$	32.20 (31.94)	3.15 (2.95)	7.88 (7.45)
ethylene	180–181 d	65	$h\nu$	33.02 (33.09)	3.36 (3.33)	3.90 (3.86)

^a Preparation method was either photochemical displacement of CO from $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2(\text{CNMe})]\text{PF}_6$, ($h\nu$), or thermal substitution of ethylene in $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\text{CNMe})(\text{ethylene})]\text{PF}_6$, ($\Delta, \text{C}_2\text{H}_4$).

antimony (4.7 g, 13 mmol) in dichloromethane (300 ml) was irradiated for 45 minutes. The solution, which had changed from yellow to reddish orange, was concentrated to 5 ml and loaded on an alumina column. Excess SbPh_3 was eluted with petroleum ether and the product was eluted with a solution of 2% methanol in dichloromethane. After evaporation of chromatography solvents, a yellow-orange solid was obtained. Recrystallization from dichloromethane/ethyl ether yielded 0.70 g (76.8%) of $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CNMe})_2(\text{SbPh}_3)]\text{PF}_6$.

$[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CNMe})_2(\text{AsPh}_3)]\text{PF}_6$

The procedure was exactly the same as described above except that 4.0 g (13 mmol) of AsPh_3 was used and the final yield of $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CNMe})_2(\text{AsPh}_3)]\text{PF}_6$ was 0.7 g (82.3%).

$[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CNMe})_2(\text{PPh}_3)]\text{PF}_6$

The procedure was exactly the same as described above except that 5.6 g (21 mmol) of PPh_3 and 0.8 g (2.1 mmol) of $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\text{CNMe})_2]\text{PF}_6$ were used and the final yield of $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CNMe})_2(\text{PPh}_3)]\text{PF}_6$ was 1.9 g (92.0%).

$[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CNMe})_2(\text{py})]\text{PF}_6$

A solution of $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\text{CNMe})_2]\text{PF}_6$ (0.25 g, 0.66 mmol) and pyridine (0.53 ml, 6.6 mmol) in dichloromethane (300 ml) was irradiated for 40 minutes. Excess pyridine and the solvent were removed and the solid residue was recrystallized slowly from acetone/ethyl ether to yield 0.26 g (91.2%) of deep red crystals, identified as $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CNMe})_2(\text{py})]\text{PF}_6$.

$[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CNMe})_2(\text{NCMe})]\text{PF}_6$

A solution of $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\text{CNMe})_2]\text{PF}_6$ (0.5 g, 1.3 mmol) and acetonitrile (0.69 ml, 13.3 mmol) in dichloromethane (300 ml) was irradiated for 40 minutes. Excess acetonitrile and solvent were removed and the solid residue was recrystallized slowly from acetonitrile/ethyl ether to yield 0.47 g (89.0%) of red-orange crystals, identified as $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CNMe})_2(\text{NCMe})]\text{PF}_6$.

$[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CNMe})_2(\text{ethylene})]\text{PF}_6$

Ethylene was bubbled through a solution of $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\text{CNMe})_2]\text{PF}_6$ (0.5 g, 1.3 mmol) in dichloromethane (300 ml) and irradiated for approximately one hour. After removing the solvent, the residue was extracted with CHCl_3 (to remove $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CNMe})_3]\text{PF}_6$) and 0.45 g (90.0%) of the ethylene-substituted product recovered as a yellow powder.

$[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CNMe})(\text{SbPh}_3)_2]\text{PF}_6$

A solution of $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2(\text{CNMe})]\text{PF}_6$ (0.5 g, 1.4 mmol) and SbPh_3 (4.9 g, 14 mmol) in dichloromethane (300 ml) was irradiated for two hours, during which time the color of the solution changed from light yellow to orange. The solution was then concentrated to 5 ml and loaded on an alumina column in petroleum ether. Excess SbPh_3 was eluted with petroleum ether and the orange product band was eluted with a solution of 2% methanol in dichloromethane. After evaporation of chromatography solvents, a dark orange-red solid was obtained. Recrystallization from acetone/ethyl ether yielded 1.24 g (87.5%) of $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CNMe})(\text{SbPh}_3)_2]\text{PF}_6$.

$$[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CNMe})(\text{AsPh}_3)_2]\text{PF}_6$$

The procedure was exactly the same as described above except that 4.2 g (14 mmol) of AsPh_3 was used and the final yield of $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CNMe})(\text{AsPh}_3)_2]\text{PF}_6$ was 1.00 g (79.8%).

$$[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CNMe})(\text{PPh}_3)_2]\text{PF}_6$$

The procedure was exactly the same as described above except that 1.0 g (2.8 mmol) of $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2(\text{CNMe})]\text{PF}_5$ and 7.34 g (28 mmol) of PPh_3 were used and the final yield of $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CNMe})(\text{PPh}_3)_2]\text{PF}_6$ was 2.15 g (92.4%).

$$[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CNMe})(\text{py})_2]\text{PF}_6$$

A solution of $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2(\text{CNMe})]\text{PF}_6$ (0.5 g, 1.4 mmol) and pyridine (1.1 ml, 14 mmol) was irradiated in dichloromethane (100 ml) for forty minutes after which nitrogen was bubbled through the solution until the volume was reduced to 10 ml. At this point cold ethyl ether was added slowly, producing deep olive-colored crystals which were collected, washed with ether, and dried in vacuo. A total of 0.46 g (71.7%) of $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CNMe})(\text{py})_2]\text{PF}_6$ was obtained and was shown to be pure by ^1H NMR spectra, recorded immediately at 213° K.

$$[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CNMe})(\text{NCMe})_2]\text{PF}_6$$

The procedure was exactly the same as described for the pyridine complex except that 0.75 ml of acetonitrile was used and 0.26 g (50.0%) of dark red crystals were obtained. Although identified as $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CNMe})(\text{NCMe})_2]\text{PF}_6$ by ^1H NMR spectra (recorded immediately at 213° K), disproportionation to $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CNMe})_2(\text{NCMe})]\text{PF}_6$ was rapid even at low temperature.

Reaction of $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2(\text{CNMe})]\text{PF}_6$ with ethylene

Ethylene was bubbled through a solution of the dicarbonyl complex in dichloromethane. After approximately one hour of irradiation the infrared spectrum showed complete conversion to $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\text{CNMe})(\text{ethylene})]\text{PF}_6$. After three hours of irradiation only $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CNMe})_2(\text{ethylene})]\text{PF}_6$ and a small amount of $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CNMe})_3]\text{PF}_6$ were detected. No evidence of $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CNMe})(\text{ethylene})_2]\text{PF}_6$ was seen in infrared spectra or in NMR spectra of the reaction mixture. The yield of $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\text{CNMe})(\text{ethylene})]\text{PF}_6$ recovered after one hour of irradiation was 65%.

$[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\text{CNMe})(\text{L})]\text{PF}_6$ complexes

The carbonyl complexes were observed as intermediates in infrared and ^1H NMR spectra recorded while monitoring the irradiation of $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2(\text{CNMe})]\text{PF}_6$. They could be isolated from these reaction mixtures by chromatography on florisil, however pure samples could be more easily prepared by refluxing $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\text{CNMe})(\text{ethylene})]\text{PF}_6$ in dry acetone and an excess of L. The ethylene complex was prepared as described above. Spectra of complexes prepared by ethylene replacement were identical to those observed as intermediates in irradiation mixtures.

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