REACTIONS OF COORDINATED PROPARGYL AND ALLENE LIGANDS IN CYCLOPENTADIENYLIRON DICARBONYL COMPLEXES*

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Summary

Reactions of η^5-$C_5H_5Fe(CO)_2CH_2C\equiv CR$ (R = CH_3, C_6H_5, and CH_2Fe-$(CO)_2(\eta^5$-$C_5H_5))$ with HBF_4 in acetic anhydride yield $[\eta^5$-$C_5H_5Fe(CO)_2(\eta^2$-$CH_2=C=CHR)]^+BF_4^-$. The resultant cationic iron-η^2-allene complexes react with a wide range of nucleophiles (Nu) to give the following types of behavior: (a) addition of Nu to carbon-1 of the η^2-allene fragment (with $NaBH_4$, $(C_2H_5)_2NH$, and $P(C_6H_5)_3$, inter alia), (b) addition of Nu to carbon-2 of the η^2-allene fragment (with $NaOCH_3$), (c) addition of Nu to the carbonyl carbon (with $NaOC_2H_5$), (d) deprotonation of the iron-η^2-allene cation to the parent propargylic complex (with $N(C_2H_5)_3$), and (e) nonselective reactions to yield a mixture of products (with CH_3Li). Of these, the most common is behavior (a); together with the protonation of η^5-$C_5H_5Fe(CO)_2CH_2C\equiv CR$ it stimulates the two-step (3 + 2) cyclo-addition reactions between electrophilic molecules and these iron-propargyl complexes.

Introduction

Transition metal-propargyl complexes react with a variety of unsaturated, electrophilic molecules to afford (3 + 2) cycloaddition products [1,2]. A very attractive mechanism for these reactions encompasses the initial formation of a dipolar metal-η^2-allene complex and its subsequent closure to the cycloadduct, as depicted in Scheme 1. Analogous dipolar metal-η^2-olefin species, from reactions of transition metal-σ-allyl complexes with these same unsaturated electrophiles, have been recently detected and intercepted [2,3]. However, similar direct evidence for the metal-η^2-allene intermediates is lacking and may prove to be difficult to obtain. Accordingly, when the unsaturated electrophile E=Nu is SO_2, the formation of the metal-vinyl cycloadduct from the appropriate propargylic complex takes place very rapidly and no intermediate could be observed [4].

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SCHEME 1

$$M \stackrel{-}{\equiv} CH_2$$
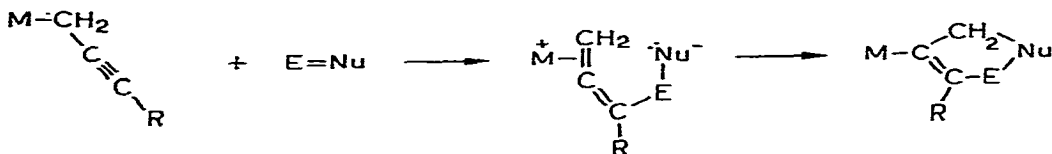
This apparent failure to detect metal-η^2-allene dipolar species prompted us to design reactions that would simulate the sequence in Scheme 1. Accordingly we undertook an investigation of protonation of the propargylic complexes, a re-action which was expected to be analogous to the first step of Scheme 1. Subse-quent treatment of the resulting products with nucleophiles was to mimic the second step. Derivatives of the extensively studied η^5-cyclopentadienyliron di-carbonyl were selected for this investigation.

Protonation reactions of η^5-$C_5H_5Fe(CO)_2R'$ where R' is a 2-unsaturated, carbon-bonded ligand such as $CH_2CH=CH_2$ [5], C_5H_5 [6], $CH(R)C\equiv N$ [7], and $CH_2C(R)=O$ [8] have been reported. Attack by the proton results in a rearange-ment of the $R'H$ fragment to the η^2-ligand, $CH_2=CHCH_3$, C_5H_6, $CH(R)=C=NH$, and $CH_2=C(R)OH$, respectively. The formation of η^2-ketenimine cationic com-plexes, $[\eta^5$-$C_5H_5Fe(CO)_2(\eta^2$-$CH(R)=C=NH)]^+X^-$, strongly resembles the first step in Scheme 1.

The addition of nucleophiles (Nu) to cationic complexes of the type $[\eta^5$-$C_5H_5Fe(CO)_2L]^+X^-$ has been shown to produce a wide variety of novel products. When L is CO, addition to the carbonyl carbon occurs for such nucleophiles as, for example, NH_3 [9], NH_2NH_2 [10], N_3^- [10], and alkoxides [11]. Attack at the thiocarbonyl carbon occurs with many of these same nucleophiles when L = CS [12]. Nucleophilic addition to complexes with L = $CH_2=CHR$ produces compounds of the type η^5-$C_5H_5Fe(CO)_2CH_2CH(R)Nu$ (Nu = OCH_3 [13], $P(C_6H_5)_3^+$ [14] and H [15]). Recently this last reaction type has been extended to nucleo-philes which are themselves organometallic complexes [14].

No similar additions to cationic η^2-allene complexes have yet been shown to occur. However, certain short-lived palladium-, platinum-, and iridium-η^2-allene complexes are thought to undergo intramolecular nucleophilic attack as evidenced by the resulting products [16-18].

In this paper we report full details of our study on the protonation of η^5-$C_5H_5Fe(CO)_2CH_2C\equiv CR$ to yield $[\eta^5$-$C_5H_5Fe(CO)_2(\eta^2$-$CH_2=C=CHR)]^+X^-$ and on reactions with nucleophiles of the generated cationic complexes. Initial re-sults of this investigation were communicated earlier [19].

Results and discussion

Protonation of the propargylic complexes

When η^5-$C_5H_5Fe(CO)_2CH_2C\equiv CR$ (R = CH_3, C_6H_5, and $CH_2Fe(CO)_2(\eta^5$-$C_5H_5)$) are treated with HBF_4 in acetic anhydride, new organoiron complexes result. They are air-stable orange or yellow solids that dissolve readily in acetone and methanol, but less readily in chloroform or dichloromethane. Their spectro-scopic properties and electrical conductivities are given in Table 1. The molar conductivities in nitrobenzene are consistent with an ionic, 1/1 electrolyte na-

ture of these compounds in solution [20], and the high values of $\nu(C\equiv O)$ indicate that the constituent iron carbonyl species are cationic [5].

The ^{1}H NMR spectra of the products with R = CH_3 and C_6H_5 compare well with those reported for metal complexes containing an η^2-allene ligand [21,22]. Particularly noteworthy are the values of the coupling constant ^4J which are appreciably lower (4-4.5 Hz) than those for free allenes (6-7 Hz) [23]. This lowering likely arises from nonlinearity of the η^2-allene fragment [24] as depicted in Ia.

(Ia)   (Ib)

A, R = CH_3
B, R = C_6H_5
C, R = $CH_2Fe(CO)_2(\eta^5-C_5H_5)$

Following the initial, preliminary communication of these results by us [19] and others [25], Rosenblum [26] has shown that $[\eta^2\text{-}C_5H_5Fe(CO)_2(\eta^2\text{-}CH=C=CHCH_3)]^+$ exists as a mixture of two isomeric forms at equilibrium in nitromethane at 50°C. These isomers were assigned structures IAa and IAb. However, in the present work the isolated compounds were never heated above room temperature and only one isomer, most likely Ia, was observed.

Reactions of the cationic allene complexes with nucleophiles

Treatment of $[\eta^5\text{-}C_5H_5Fe(CO)_2(\eta^2\text{-}CH_2=C=CHR)]^+BF_4^-$ with various nucleophiles (Nu) at ambient temperatures has resulted in the following types of behavior: (a) addition of Nu to carbon-1 ($H_2C=$) of the η^2-allene fragment, (b) addition of Nu to carbon-2 of the η^2-allene fragment, (c) addition of Nu to the

TABLE 1

SPECTROSCOPIC DATA AND ELECTRICAL CONDUCTIVITY FOR $[\eta^5\text{-}C_5H_5Fe(CO)_2(\eta^2\text{-}CH_2=C=CHR)]^+BF_4^-$

R	IR $\nu(C\equiv O)$ (cm^{-1})[a]	^{1}H NMR (τ ppm)[b]				Λ_M(ohm^{-1}cm^2)[c]
		C_5H_5	$H_2C=$	$HC=$	R	
CH_3	2087, 2053	4.06s	6.76d[d]q[e]	3.15q[f]t[d]	7.74d[f]t[e]	29.4
C_6H_5	2088, 2054	3.98s	6.12d[g]	2.51[h]	2.51s	27.4
		(4.27s)	(6.42d[i])	(2.68t[i])	(2.54s)	
$CH_2Fe(CO)_2$-$(\eta^5\text{-}C_5H_5)$	2068s, 2017, 1959s			[j]		26.0

[a] In acetone solution. All absorptions are very intense unless otherwise noted; s, strong. [b] In CDCl$_3$ (or CF$_3$CO$_2$H) solution. Abbreviations: s, singlet; d, doublet; t, triplet; dq, doublet of quartets; qt, quartet of triplets; dt, doublet of triplets. [c] In ca. $10^{-3}M$ nitrobenzene solution. [d] $^4J(CH_2—CH)$ = 4.1 Hz. [e] $^5J(CH_3—CH_2)$ = 2.9 Hz. [f] $^3J(CH_3—CH)$ = 6.9 Hz. [g] ^4J = 4 Hz. [h] Separate signal not observed; assumed to be covered by the C_6H_5 resonance. [i] $^4J \sim$ 4.5 Hz. [j] Not measured.

TABLE 2

^{1}H NMR SPECTRA OF η^{5}-C$_5$H$_5$Fe(CO)$_2$C(CH$_2$Nu)=CHR

R	Nu	Isomer	Chemical shift (τ ppm)[a]					Coupling constants (Hz)
			C$_5$H$_5$	CH$_2$C	HC=	R	Nu	
CH$_3$	H	A	5.21s	7.86m	3.97m	8.30dq	7.86m	$^{5}J(CH_3-CH_3) = 1.3$; $^{3}J(CH_3-CH) = 6.7$
		B[c]	or 5.27s	or 8.01m	or 4.55m	8.30dq	or 8.01m	$^{5}J(CH_3-CH_3) = 1.3$; $^{3}J(CH_3-CH) = 6.7$
C$_6$H$_5$	H	A	5.18s	7.70d	2.75q	2.71s	7.70d	$^{4}J(CH_3-CH) = 1.6$
		B[d]	5.33s	7.64d	2.75q	2.71s	7.64d	$^{4}J(CH_3-CH) = 1.6$
CH$_3$	N(C$_2$H$_5$)$_2$		5.18s	6.08s(br)	3.77q	8.23d	7.53q, 8.01t	$^{3}J(CH_3-CH) = 6.5$; $^{3}J(CH_3-CH_2) = 7.5$
C$_6$H$_5$	N(C$_2$H$_5$)$_2$	A	5.47s	6.81d	2.73f	2.73m	7.42q, 8.08t	$^{4}J(CH_2-CH) = 1.4$; $^{3}J(CH_3-CH_2) = 7.0$
		B[e]	5.21s	6.88d	2.73f	2.73m	7.61q, 9.13t	$^{4}J(CH_2-CH) = 1.4$; $^{3}J(CH_3-CH_2) = 7.0$
CH$_3$	P(C$_6$H$_5$)$_3$$^{+}$		4.90s	5.35d(br)	4.01m	8.35dd	2.4-2.8m(br)	$^{2}J(CH_2-P) = 14$; $^{3}J(CH_3-CH) = 6.5$; $^{5}J(CH_3-P) = 5$
C$_6$H$_5$	P(C$_6$H$_5$)$_3$$^{+}$		4.97s	5.52d(br)	2.21 or 2.33f	2.33s(br)	2.21s(br)	$^{2}J(CH_2-P) = 14$
C$_6$H$_5$	OCH$_3$		5.34s	5.91d	3.03s	2.71s	6.59s	$^{4}J(CH_2-CH) = 1.4$
CH$_3$	OH[b]		5.09s	5.80s(br)	3.63q	8.17d	h	$^{3}J(CH_3-CH) = 7$
C$_6$H$_5$	OH		5.39s	5.71s(br)	2.52s(br)	2.82s	h	
C$_6$H$_5$	OC(O)CH$_3$		5.28s	5.23d	2.53m	2.73s	7.90s	

[a] In CDCl$_3$ solution. Abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; (br) broad; dd, doublet of doublets; dq, doublet of quartets. [b] Sample supplied by J.P. Williams. [c] Assignment precluded by the 1/1 ratio of isomers. [d] A/B isomer ratio ca. 2/1. [e] A/B isomer ratio ca. 2/1. [f] Separate signal not observed; assumed to be covered by the C$_6$H$_5$ resonance. [g] Signal not observed.
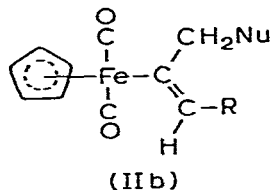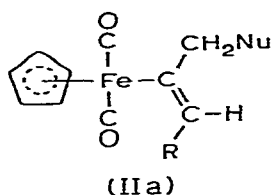
TABLE 3

INFRARED $\nu(C{\equiv}O)$ ABSORPTIONS OF η^5-$C_5H_5Fe(CO)_2C(CH_2Nu){=}CHR$

R	Nu	Frequency $(cm^{-1})^a$
CH_3	H	2013, 1955
CH_3	$N(C_2H_5)_2$	2011, 1953
CH_3	$P(C_6H_5)_3^+$	2016, 1959
CH_3	OH^b	2017, 1962
CH_3	N_3	2019, 1965
C_6H_5	H	2016, 1960
C_6H_5	$N(C_2H_5)_2$	2014, 1959
C_6H_5	$P(C_6H_5)_3^+$	2018, 1963
C_6H_5	OCH_3	2017, 1963
C_6H_5	OH	2018, 1965
C_6H_5	$OC(O)CH_3$	2020, 1966
C_6H_5	I	2018, 1965
C_6H_5	NHC_6H_5	2016, 1962
C_6H_5	$P(OCH_3)_3^+$	2022, 1968

^{a} In $CHCl_3$ solution. All absorptions are very intense. ^{b} Sample supplied by J.P. Williams.

carbonyl carbon, (d) deprotonation of the iron-η^2-allene cation to the parent propargylic complex, and (e) nonselective reactions to yield a mixture of products.

Of the above, the most common was the addition of Nu to carbon-1 of the η^2-allene fragment. Thus, $NaBH_4$, $(C_2H_5)_2NH$, and $P(C_6H_5)_3$ afforded isolable metal-vinyl products of type II (A and B: Nu = H, $N(C_2H_5)_2$, and $P(C_6H_5)_3^+$). They were characterized by elemental analysis and ^1H NMR, infrared, and mass

(IIa)   (IIb)

A, R = CH_3
B, R = C_6H_5

spectroscopy. The ^1H NMR and infrared $\nu(C{\equiv}O)$ spectra of these and other complexes of structure II are given in Tables 2 and 3, respectively.
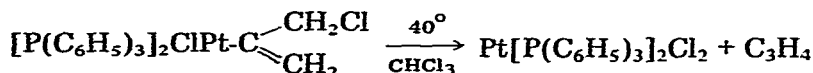
Nucleophilic additions to a cation Ia would be expected to proceed from the side opposite the metal and thus to yield vinyl complexes in which the iron is cis to the group R (IIa). However, it is apparent from the ^1H NMR spectra that three products (A: Nu = H; B: Nu = H and $N(C_2H_5)_2$) were isolated as mixtures of geometric isomers, IIa and IIb. It has not been possible to ascertain the stereochemistry of any of these complexes, since in general the coupling constant $^4J(CH_2{-}CH)$ is approximately the same (ca 1.5 ± 0.3 Hz) for both cis and trans isomers of $R(CH_2X)C{=}CHR'$ [27]. The observed presence of two geo-

metric isomers may be best ascribed to partial isomerization of Ia to Ib in solution and to a stereospecific reaction of each iron-η^2-allene cation with the nucleophile. However, a nonspecific addition to Ia alone cannot be ruled out.

The reaction of I with triphenylphosphine merits comment, since tertiary phosphines generally coordinate readily to low-valent transition metals. The observed addition of $P(C_6H_5)_3$ to the hydrocarbon ligand rather than to the iron is however not unprecedented. Similar reactions have been reported recently for cationic iron complexes containing coordinated η^2-olefin [14], η^3-allyl [28], η^4-cyclobutadiene [29], η^5-cyclohexadienyl [30], and η^5-cycloheptadienyl [30] ligands.

The addition of NaN_3, $C_6H_5NH_2$, and $P(OCH_3)_3$ to I afforded impure metal-vinyl products of type II (A: Nu = N_3; B: Nu = C_6H_5NH and $P(OCH_3)_3^+$), as inferred from the infrared $\nu(C\equiv O)$ and/or mass spectra. Attempts at purification of these unstable complexes proved unsuccessful.

When iodide ion is added as the nucleophile to IB, the major product isolated is the iodo complex, η^5-$C_5H_5Fe(CO)_2I$. However, an unstable material, characterized as IIB (Nu = I) by infrared spectroscopy, is apparently the initial product; it spontaneously decomposes to η^5-$C_5H_5Fe(CO)_2I$ at room temperature. A similar decomposition has been noted for a platinum(II) complex [31]:

$$[P(C_6H_5)_3]_2ClPt-C{\overset{\text{CH}_2\text{Cl}}{\underset{\text{CH}_2}{\big<}}} \quad \xrightarrow[\text{CHCl}_3]{40^\circ} \quad Pt[P(C_6H_5)_3]_2Cl_2 + C_3H_4$$

Although simple addition to the terminal carbon of the η^2-allene ligand is observed with many nucleophiles, other types of adducts were also found. Methoxide ion in methanol adds to IB to afford a vinylic complex of structure IIB (Nu = OCH_3), but the major product IIIB, apparently results from a nucleo-
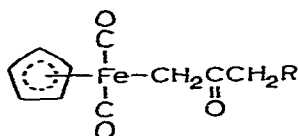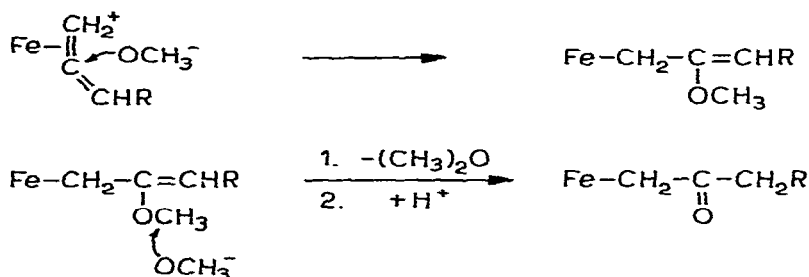

(III) A, R = CH_3
       B, R = C_6H_5

philic addition to carbon-2 of the η^2-allene moiety. The identity of the latter complex was established from its ^{1}H NMR spectrum which shows four singlets of relative intensities 5/5/2/2, and through cleavage with gaseous HCl to give η^5-$C_5H_5Fe(CO)_2Cl$ and the known [32] ketone $CH_3C(O)CH_2C_6H_5$. The cationic η^2-allene complex IA yielded only IIIA upon treatment with $NaOCH_3$.

The formation of III may proceed via intermediacy of η^5-$C_5H_5Fe(CO)_2$-$CH_2C(OCH_3)=CHR$, a subsequent attack on the latter by methoxide to eliminate $(CH_3)_2O$, and abstraction of a proton from the solvent (Scheme 2). This sequence is an adaptation of the mechanism proposed by Clark and Chisholm [33] for the formation of a platinum(II)-acyl complex.

An alternative pathway to III would involve a nucleophilic attack of hydroxide present in solution on carbon-2 of the η^2-allene fragment. However, this

SCHEME 2

$$Fe-\overset{CH_2^+}{\underset{\overset{\|}{C}}{\underset{CHR}{\underset{\|}{C}}}}OCH_3^- \longrightarrow Fe-CH_2-\underset{\overset{|}{OCH_3}}{C}=CHR$$

$$Fe-CH_2-\underset{\underset{\overset{|}{OCH_3}}{OCH_3}}{\overset{|}{C}}=CHR \quad \xrightarrow[\text{2.} \quad +H^+]{\text{1.} \quad -(CH_3)_2O} \quad Fe-CH_2-\underset{\overset{\|}{O}}{C}-CH_2R$$

possibility is considered unlikely since IB in acetone adds hydroxide in a "normal" fashion to yield IIB (Nu = OH).

Surprisingly, the reaction of IB with $NaOC_2H_5$ in ethanol affords complex IV which was characterized by infrared, ^1H NMR, and mass spectroscopy, as shown in the Experimental section. The infrared spectrum in chloroform exhibits only a single $\nu(C\equiv O)$ band, at 1969 cm^{-1}, as well as a $\nu(C=O)$ absorption of the $CO_2C_2H_5$ moiety at 1702 cm^{-1}. By comparison, complexes of the type η^5-$C_5H_5Fe(CO)(\eta^3$-allyl) typically show a single $\nu(C\equiv O)$ band at 1950-1940 cm^{-1} [5,34]. The ^1H NMR spectrum of IV contains resonances at τ 8.16, 5.88, and 4.04 ppm which are consistent with the presence of protons H_a, H_b, and H_c of the η^3-allyl fragment. However, it could not be determined whether the isolated compound is the *syn* (IVa) or the *anti* (IVb) isomer, or a mixture of the two.

(IVa)   (IVb)
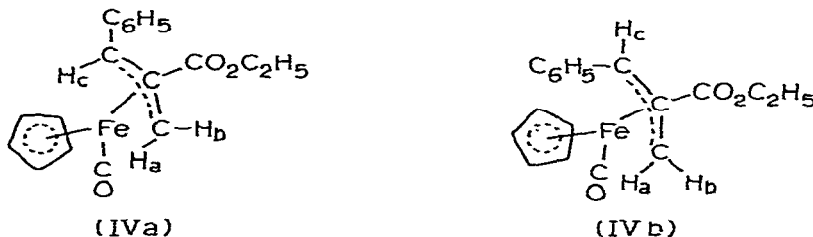
Roustan et al. [35] have recently shown that η^5-$C_5H_5Mo(CO)_3CH_2C\equiv CR$ and $Mn(CO)_5CH_2C\equiv CR$, but not η^5-$C_5H_5Fe(CO)_2CH_2C\equiv CR$, react with alcohols to afford similar η^3-allyl complexes. In the present case it is likely that the initial attack of ethoxide on the carbonyl carbon is followed by a migration of the carboethoxy group thus formed onto carbon-2 of the η^2-allene moiety (Scheme 3).

Methyllithium reacts with IB in a nonselective fashion to give a mixture of products that includes $CH_2=C=CHC_6H_5$, η^5-$C_5H_5Fe(CO)_2CH_2C\equiv CC_6H_5$, and η^5-$C_5H_5Fe(CO)_2CH_3$. In contrast, the strong base triethylamine was found only to deprotonate IB regenerating η^5-$C_5H_5Fe(CO)_2CH_2C\equiv CC_6H_5$. Rosenblum [36] has recently shown that $[\eta^5$-$C_5H_5Fe(CO)_2(\eta^2$-olefin)]$^+$ cations can be similarly deprotonated by triethylamine.

Finally, it was noted that acetic acid and water (under the acidic conditions of an alumina column) add to η^5-$C_5H_5Fe(CO)_2CH_2C\equiv CC_6H_5$ to yield IIB (Nu = $OC(O)CH_3$ and OH, respectively). A similar addition of acetic acid to $Mn(CO)_4$-$[P(C_6H_5)_3]CH_2C\equiv CH$ was reported earlier by Haszeldine et al. [37]. These pro-

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SCHEME 3
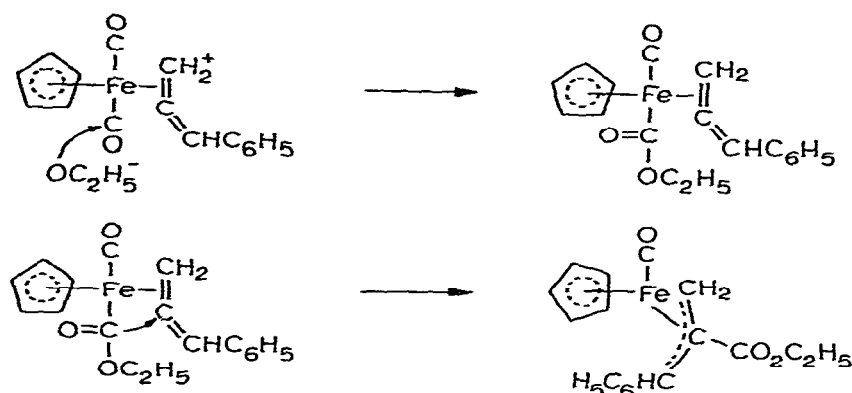
ducts may be considered to arise from protonation of the propargyl complex and a nucleophilic attack on the incipient η^2-allene fragment by the conjugate base. As already mentioned above, the same addition product of water (IIB: Nu = OH) is formed (although in low yield) in a two-step process that involves protonation with HBF$_4$ of η^5-C$_5$H$_5$Fe(CO)$_2$CH$_2$C≡CC$_6$H$_5$ followed by treatment of the resultant IB with NaOH. However, attempts to synthesize the addition product of acetic acid (IIB: Nu = OC(O)CH$_3$) by treatment of IB with NaOC-(O)CH$_3$ proved unsuccessful. It may be that acetate ion is not a strong enough nucleophile to add to the iron-η^2-allene cation in an intermolecular manner.

Conclusion

The protonation of the iron-propargyl complexes and the above-ncted nucleophilic additions to carbon-1 of the resultant iron-η^2-allene cations simulate the two steps of the transformation depicted in Scheme 1. They thus lend credence to the proposed mechanism for the cycloaddition between these same propargyl complexes and electrophiles of the type E=Nu, e.g., SO$_2$, SO$_3$, (CN)$_2$-C=C(CN)$_2$, and (CF$_3$)$_2$CO. However, two points are apropbs in connection with this analogy. First, not all nucleophiles add to carbon-1 of the iron-η^2-allene cations, the strongest bases reacting by addition to carbon-2 or the carbonyl carbon, abstraction of the proton, or in a more complex fashion. Second, factors other than those implied here may contribute significantly to the mechanism, as well as to the rate, of the (3 + 2) cycloaddition reactions in point. One of these is certainly the geometry of the η^2-allene ligand in the dipolar intermediate which appears ideally suited to ring closure.

Experimental

The propargyl complexes η^5-C$_5$H$_5$Fe(CO)$_2$CH$_2$C≡CR (R = CH$_3$ [38], C$_6$H$_5$ [39], and CH$_2$Fe(CO)$_2$(η^5-C$_5$H$_5$) [40]), Mn(CO)$_5$CH$_2$C≡CC$_6$H$_5$ [41], η^5-C$_5$H$_5$Mo(CO)$_3$-CH$_2$C≡CC$_6$H$_5$ [41], and η^5-C$_5$H$_5$W(CO)$_3$CH$_2$C≡CC$_6$H$_5$ [41] were prepared by the literature methods. Tetrahydrofuran (THF) and pentane were distilled from LiAlH$_4$ and CaH$_2$, respectively. All other chemicals and solvents procured commercially were reagent grade and were used without further purification.

All reactions were conducted under an atmosphere of dry nitrogen. Ventron alumina deactivated with 6-10% H_2O was used as the support for column chromatography. Melting points were taken on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were performed by Dr. F. Pascher, Microanalytisches Laboratorium, Bonn, W. Germany.

Conductivity measurements were made using an Industrial Instruments Co. Model RC 16B2 conductivity bridge and a cell with platinum electrodes. ^{1}H NMR spectra were recorded with a Varian Associates A-60A spectrometer using tetramethylsilane as an internal standard. All infrared $\nu(C\equiv O)$ values in Tables 1 and 3 were obtained using a Beckman IR-9 spectrophotometer; routine infrared spectra were recorded with a Perkin—Elmer Model 337 spectrophotometer. Mass spectra (70 eV) were obtained by Mr. C.R. Weisenberger with an AEI Model MS-9 spectrometer; the intensities relative to that of $C_5H_5Fe^+$ being 100 are given in parentheses.

Preparation of [η^5-$C_5H_5Fe(CO)_2(\eta^2$-$CH_2=C=CHCH_3)$]$^+BF_4^-$

Aqueous 48% HBF₄ (1.50 ml, ca. 12.5 mmol) was carefully added to acetic anhydride (10 ml) at 0°C. (Caution: This dehydration is quite exothermic!). The resulting mixture was then introduced slowly with stirring into a solution of η^5-$C_5H_5Fe(CO)_2CH_2C\equiv CCH_3$ (2.36 g, 10.3 mmol) in 20 ml of acetic anhydride at 0°C. Slow addition of 125 ml of ether afforded a yellow precipitate* which was washed with 30 ml of THF and 3 × 50 ml of ether to leave 2.15 g (66% yield) of a light yellow solid. Crystallization from CH_2Cl_2 gave yellow microcrystals which did not melt below 300°C in air, but rather slowly turned to an amorphous straw-colored solid as an orange liquid distilled from the crystals.

Anal. Found: C, 41.17; H, 3.65. $C_{11}H_{11}BF_4FeO_2$ calcd.: C, 41.57; H, 3.49%.

Preparation of [η^5-$C_5H_5Fe(CO)_2(\eta^2$-$CH_2=C=CHC_6H_5)$]$^+BF_4^-$

An aqueous solution of 48% HBF₄ (0.50 ml, 4.2 mmol) was added slowly with ice-cooling to 3.0 ml of acetic anhydride. This solution was then introduced dropwise with stirring to η^5-$C_5H_5Fe(CO)_2CH_2C\equiv CC_6H_5$ (0.82 g, 2.8 mmol) dissolved in 4 ml of acetic anhydride at 0°C. Slow addition of 100 ml of ether produced a yellow precipitate which was washed with 2 × 10 ml of THF and 20 ml of ether to yield 0.73 g (69%) of a light cream-yellow powder. Crystallization from 1/3 (v/v) acetone/CH_2Cl_2 by slow concentration at ca. 20 Torr afforded golden yellow crystals, m.p. 143-143.5°C.

Anal. Found: C, 50.31; H, 3.39. $C_{16}H_{13}BF_4FeO_2$ calcd.: C, 50.58; H, 3.45%.

Preparation of [η^5-$C_5H_5Fe(CO)_2(\eta^2$-$CH_2=C=CHCH_2Fe(CO)_2(\eta^5$-$C_5H_5)$]$^+BF_4^-$

Aqueous HBF₄ (0.40 ml, ca. 3.2 mmol) was carefully added to 4 ml of acetic anhydride at 0°C. This solution was then introduced dropwise with stirring into η^5-$C_5H_5Fe(CO)_2CH_2C\equiv CCH_2Fe(CO)_2(\eta^5$-$C_5H_5)$ (0.64 g, 1.6 mmol) dissolved in 10 ml of acetic anhydride at 0°C. The resulting solution was treated slowly with 200 ml of ether to yield an orange gum. Washing with 25 ml of THF left 0.37 g (48% yield) of a light orange solid, m.p. ca. 85°C (dec.).

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* Additional ether gave a red oil.

Attempted preparation of other η^2-allene complexes

Attempts at obtaining η^2-CH$_2$=C=CHC$_6$H$_5$ derivatives of manganese, molybdenum and tungsten by the addition of dehydrated HBF$_4$ to the corresponding complexes MCH$_2$C≡CC$_6$H$_5$ (M = Mn(CO)$_5$, η^5-C$_5$H$_5$Mo(CO)$_3$, and η^5-C$_5$H$_5$W(CO)$_3$) were unsuccessful. Only very impure oils could be isolated from the reaction mixtures.

Preparation of η^5-C$_5$H$_5$Fe(CO)$_2$C(CH$_3$)=CHCH$_3$

A suspension of [η^5-C$_5$H$_5$Fe(CO)$_2$(η^2-CH$_2$=C=CHCH$_3$)]$^+$BF$_4^-$ (0.30 g, 0.95 mmol) and NaBH$_4$ (0.038 g, 1.0 mmol) in 15 ml of THF was stirred at 25°C for 20 h. The resulting red solution was evaporated to dryness and the residue was extracted with 2 × 30 ml of pentane. The extracts were combined and eluted over a 2.5 × 10 cm column of alumina with pentane. A bright yellow band was collected and concentrated to 0.03 g (ca 10% yield) of a yellow oil. ^{1}H NMR spectroscopy indicated the presence of two isomers of the title compound in approximately equal amounts. The mass spectrum (150°C) included peaks at *m/e* 232 (P, 10), 204 (P — CO, 33), and 176 (P — 2CO, 88).

Continued elution with CH$_2$Cl$_2$ removed a dark red band. Concentration of the effluent yielded 0.15 g (90%) of [η^5-C$_5$H$_5$Fe(CO)$_2$]$_2$.

Preparation of η^5-C$_5$H$_5$Fe(CO)$_2$C(CH$_3$)=CHC$_6$H$_5$

A suspension of [η^5-C$_5$H$_5$Fe(CO)$_2$(η^2-CH$_2$=C=CHC$_6$H$_5$)]$^+$BF$_4^-$ (1.06 g, 2.79 mmol) and NaBH$_4$ (0.030 g, 0.82 mmol) in 75 ml of THF was stirred for 3.5 h at 25°C. Filtration removed the unreacted materials (0.43 g) and gave an orange-red solution. This filtrate was concentrated to dryness and the residue was extracted with a minimum of pentane. The extract was eluted over a 2.5 × 12 cm column of alumina with pentane. A yellow band was collected and concentrated to an orange-yellow oil which solidified within 1 h (0.34 g, 42% yield). A second, narrow red band of [η^5-C$_5$H$_5$Fe(CO)$_2$]$_2$ was discarded. The ^{1}H NMR spectrum of the yellow-orange solid indicated a ca. 4/1 mixture of geometric isomers. Several more chromatographies on alumina, discarding the very front of the eluted yellow band, and two crystallizations from pentane, discarding the more soluble isomer, eventually gave yellow-orange needles of the title compound as a ca. 20/1 mixture of isomers, m.p. 76-77°C. The mass spectrum (150°C) included peaks at *m/e* 294 (P, 7), 266 (P—CO, 18), and 238 (P — 2CO, 93).

Anal. Found: C, 64.67; H, 4.60. C$_{16}$H$_{14}$FeO$_2$ calcd.: C, 65.34; H, 4.80%.

Preparation of η^5-C$_5$H$_5$F(CO)$_2$C(CH$_2$N(C$_2$H$_5$)$_2$)=CHCH$_3$

Diethylamine (0.40 ml, ca. 3.9 mmol) was added dropwise to a suspension of [η^5-C$_5$H$_5$Fe(CO)$_2$(η^2-CH$_2$=C=CHCH$_3$)]$^+$BF$_4^-$ (0.30 g, 0.95 mmol) in 50 ml of pentane at 25°C and the mixture was stirred for 1 h. Filtration removed an orange solid which was identified as unreacted [η^5-C$_5$H$_5$Fe(CO)$_2$(η^2-CH$_2$=C= CHCH$_3$)]$^+$BF$_4^-$ (0.14 g). The orange-red filtrate was concentrated to 20 ml and eluted with pentane over a 2.5 × 8 cm column of alumina. A single yellow band was collected and concentrated to an orange oil (0.12 g, 43% yield) which could not be induced to crystallize. The mass spectrum (150°C) included peaks at *m/e* 303 (P, 3), 275 (P — CO, 21), and 247 (P — 2CO, 37).

Preparation of η^5-$C_5H_5Fe(CO)_2C(CH_2N(C_2H_5)_2)=CHC_6H_5$

Diethylamine (0.20 ml, ca. 1.9 mmol) was added dropwise to a stirred suspension of $[\eta^5$-$C_5H_5Fe(CO)_2(\eta^2$-$CH_2=C=CHC_6H_5)]^+BF_4^-$ (0.42 g, 1.1 mmol) in 30 ml of pentane at 25°C. After 30 min of stirring an additional 0.20 ml of diethylamine was introduced and the mixture was stirred again for 30 min. Filtration removed the unreacted iron-η^2-allene complex and gave an orange solution. This solution was concentrated to an orange oil which was then redissolved in a minimum of pentane. The pentane solution was eluted over a 2.5 × 8 cm column of alumina to produce a single yellow band which was collected and concentrated to an orange-yellow oil (0.20 g, 49% yield). This sample was shown by ^{1}H NMR spectroscopy to be composed of two isomers in a ca. 7/3 ratio. The mass spectrum (150°C) included peaks at m/e 365 (P, 2), 337 (P — CO, 5), 309 (P — 2CO, 11), and 280 (P — 2CO — C_2H_5, 13). Attempts to crystallize the oil were unsuccessful.

Preparation of $[\eta^5$-$C_5H_5Fe(CO)_2C(CH_2P(C_6H_5)_3)=CHCH_3]^+BF_4^-$

A solution of $[\eta^5$-$C_5H_5Fe(CO)_2(\eta^2$-$CH_2=C=CHCH_3)]^+BF_4^-$ (0.30 g, 0.95 mmol) in 5 ml of acetone was added to triphenylphosphine (0.25 g, 0.95 mmol) dissolved in 5 ml of acetone and the resultant mixture was stirred for 5 min at 25°C. Evaporation of the acetone at ca. 20 Torr gave a red-orange gum. This gum was washed with 10 ml of benzene and then dissolved in 25 ml of CH_2Cl_2. The solution was filtered and the filtrate was evaporated to a sticky glass (0.44 g, 88% yield). This material was dissolved in 20 ml of CH_2Cl_2 and the solution was diluted slowly with 90 ml of pentane. Most of the material precipitated as an orange-red oil, but 0.07 g of yellow needles, m.p. 188-189°C (dec.), slowly crystallized from the supernatant solution. Attempted crystallization of the oil was not successful.

Anal. (Yellow needles) found: C, 59.86; H, 4.50. $C_{29}H_{26}BF_4FeO_2P$ calcd.: C, 60.04; H, 4.52%.

Preparation of $[\eta^5$-$C_5H_5Fe(CO)_2C(CH_2P(C_6H_5)_3)=CHC_6H_5]^+BF_4^-$

A solution of triphenylphosphine (0.21 g, 0.80 mmol) in 5 ml of CH_2Cl_2 was added to a suspension of $[\eta^5$-$C_5H_5Fe(CO)_2(\eta^2$-$CH_2=C=CHC_6H_5)]^+BF_4^-$ (0.30 g, 0.79 mmol) in 25 ml of CH_2Cl_2 at 25°C. Within 15 sec the solids dissolved to form a clear, golden-yellow solution. This solution was concentrated to a viscous oil which upon further vacuum treatment (ca. 0.1 Torr, 25°C, 1 h) afforded a glassy foam (0.51 g, 100% yield).

The glass was dissolved in 20 ml of CH_2Cl_2 and pentane was added slowly until the solution became slightly cloudy. Filtration and further dilution with pentane afforded yellow microcrystals (0.07 g), m.p. 177°C (dec.). Concentration of the second filtrate gave an oil and a small amount of amorphous solid. Upon vacuum pumping the oil formed a glass. The total yield of the title compound was 0.35 g (69%). The second crop of material was shown by ^{1}H NMR spectroscopy to contain a slight impurity which could not be removed by repeated recrystallizations from CH_2Cl_2.

Preparation of η^5-$C_5H_5Fe(CO)_2CH_2C(O)CH_2CH_3$

A solution of $NaOCH_3$ (2.0 mmol) in 30 ml of CH_3OH was added to $[\eta^5$-

$C_5H_5Fe(CO)_2(\eta^2\text{-}CH_2=C=CHCH_3)]^+BF_4^-$ (0.49 g, 1.5 mmol) in 6 ml of methanol at 25°C. The mixture was immediately evaporated to a red-orange paste which was then dissolved in 30 ml of 1/4 (v/v) CH_2Cl_2/pentane and chromatographed on a 2.5 × 12 cm column of alumina. A dark red band was eluted off with the same solvent mixture and concentrated to a red gum identified as $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$ (ca. 0.02 g, 7% yield).

Elution with pure CH_2Cl_2 gave a yellow effluent which was concentrated to an orange oil (0.17 g, 45% yield) identified as $\eta^5\text{-}C_5H_5Fe(CO)_2CH_2C(O)CH_2CH_3$. The mass spectrum (60°C) included peaks at m/e 248 (P, 1.2), 220 (P — CO, 6), and 192 (P — 2CO, 29); metastable peak at m/e 195.2 (248 → 220).

Preparation of $\eta^5\text{-}C_5H_5Fe(CO)_2C(CH_2OCH_3)=CHC_6H_5$ and $\eta^5\text{-}C_5H_5Fe(CO)_2CH_2C$-$(O)CH_2C_6H_5$

A solution of $NaOCH_3$ (3.5 mmol) in 2 ml of CH_3OH, freshly prepared from Na and CH_3OH, was slowly added to $[\eta^5\text{-}C_5H_5Fe(CO)_2(\eta^2\text{-}CH_2=C=CHC_6H_5)]^+$ BF_4^- (1.03 g, 2.72 mmol) in 10 ml of absolute methanol at 25°C. After stirring for 15 min the mixture was evaporated to dryness and the residue was dissolved in 75 ml of 1/4 (v/v) CH_2Cl_2/pentane. This was eluted over a 2.5 × 14 cm column of alumina with the same solvent mixture, and a yellow-orange band was collected and concentrated to an orange oil (0.14 g, 16% yield) characterized as $\eta^5\text{-}C_5H_5Fe(CO)_2C(CH_2OCH_3)=CHC_6H_5$. The mass spectrum (60°C) included peaks at m/e 324 (P, 0.5), 296 (P — CO, 3), and 268 (P — 2CO, 8).

A deep red-violet band was eluted next. Concentration of the effluent afforded a red solid (0.13 g, 27% yield), identified as $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$.

Finally, elution with 1/1 (v/v) CH_2Cl_2/pentane removed a bright yellow band which was collected and concentrated to an orange oil (0.48 g, 57% yield) characterized as $\eta^5\text{-}C_5H_5Fe(CO)_2CH_2C(O)CH_2C_6H_5$. Slow evaporation of a pentane solution of this complex gave a yellow solid, m.p. 64-66°C. The mass spectrum (100°C) included peaks at m/e 310 (P, 0.3), 294 (P — CO, 1), and 254 (P — 2CO, 14).

Reaction of $\eta^5\text{-}C_5H_5Fe(CO)_2CH_2C(O)CH_2C_6H_5$ with HCl

Hydrogen chloride gas was passed through a solution of $\eta^5\text{-}C_5H_5Fe(CO)_2$-$CH_2C(O)CCH_2C_6H_5$ (0.16 g, 0.52 mmol) in 25 ml of $CHCl_3$. After 1 h this HCl-saturated solution was set aside overnight and then evaporated to dryness. The residue, identified by ${}^1H$ NMR and infrared spectroscopy as a ca 1/1 mixture of η^5-$C_5H_5Fe(CO)_2Cl$ and $CH_3C(O)CH_2C_6H_5$, was dissolved in CCl_4 and the resultant solution was filtered and placed in sunlight for 3.5 h to decompose the iron complex. A green solid was then filtered off and the filtrate was concentrated to a straw-colored oil (0.045 g, 65% yield) which was identified as nearly pure $CH_3C(O)CH_2C_6H_5$ [32]. ${}^1H$ NMR (τ(ppm) $CDCl_3$): 2.70s (C_6H_5 and $CHCl_3$), 6.30s (CH_2), 7.85s (CH_3); infrared (neat, cm^{-1}); 3035w, 2915m, 1710vs, 1595w, 1490s, 1445s, 1410w, 1350m-s, 1226w, 1158m, 1093m, 1076w, 1031w-m, 738m-s, 696s.

Preparation of $\eta^5\text{-}C_5H_5Fe(CO)_2C(CH_2OH)=CHC_6H_5$

(A). By addition of NaOH to $[\eta^5\text{-}C_5H_5Fe(CO)_2(\eta^2\text{-}CH_2=C=CHC_6H_5)]^+BF_4^-$.
Aqueous NaOH (1.0 mmol in 2.0 ml of H_2O) was added dropwise to a solution

of $[\eta^5\text{-}C_5H_5Fe(CO)_2(\eta^2\text{-}CH_2=C=CHC_6H_5)]^+BF_4^-$ (0.38 g, 1.0 mmol) in 10 ml of acetone. The resultant solution quickly turned to a brown suspension. Pentane (75 ml) was then added and the mixture was dried over $MgSO_4$ and filtered to give a brown solution. Evaporation of this solution afforded a brown oil which was dissolved in a minimum of CH_2Cl_2 and rapidly eluted with pentane over a 2.5 × 6 cm column of alumina. A dirty brown-green band was eluted off and discarded. Elution with CH_2Cl_2 yielded a broad yellow band which was collected and concentrated to a dark yellow oil. This oil was crystallized from 1 ml of CH_2Cl_2 by slowly adding 50 ml of pentane and then evaporating half of the solvent. The remaining solvent was decanted and the solid was washed with pentane and air-dried to afford a cream-yellow product (0.04 g, 13% yield), m.p. 101-102°C. The mass spectrum (100°C) included peaks at m/e 282 (P − CO, 14), 264 (P − CO − H_2O, 4), 254 (P − 2CO, 39) and 236 (P − 2CO − H_2O, 50).

(B). By hydration of $\eta^5\text{-}C_5H_5Fe(CO)_2CH_2C{\equiv}CC_6H_5$ on alumina. The method used is an adaptation of that discovered by J.P. Williams in this laboratory for $\eta^5\text{-}C_5H_5Fe(CO)_2CH_2C{\equiv}CCH_3$.

A solution of $\eta^5\text{-}C_5H_5Fe(CO)_2CH_2C{\equiv}CC_6H_5$ (0.25 g, 0.80 mmol) in 20 ml of pentane was eluted half way down a 2.5 × 6 cm column of alumina. The column was set aside for 30 min and then the yellow band was eluted to the bottom of the column with more pentane. The column was again set aside for 30 min and then washed with pentane to furnish a yellow solution. Concentration of this solution gave 0.15 g (60% recovery) of $\eta^5\text{-}C_5H_5Fe(CO)_2CH_2C{\equiv}CC_6H_5$. Subsequent elution with CH_2Cl_2 gave a red-orange effluent which was concentrated to an oil. The oil was washed with pentane to yield a light tan solid (0.04 g, 15% yield), m.p. 100-102°C. The infrared and ^1H NMR spectra of this complex were identical with those of the material prepared by method A.

Preparation of $\eta^5\text{-}C_5H_5Fe(CO)_2C(CH_2OC(O)CH_3)=CHC_6H_5$

A solution of $\eta^5\text{-}C_5H_5Fe(CO)_2CH_2C{\equiv}CC_6H_5$ (0.39 g, 1.3 mmol) in 5 ml of glacial acetic acid was stirred for 70 min and then diluted with pentane and neutralized with aqueous $NaHCO_3$. The pentane layer was dried over $MgSO_4$, filtered, and eluted over a 2.5 × 8 cm column of alumina with pentane. A yellow band was collected and concentrated to a yellow oil (ca. 0.1 g, 25% yield). ^1H NMR spectroscopy indicated an impurity absorbing at τ 7.70 ppm which could not be removed by further chromatography. The mass spectrum (60°C) included peaks at m/e 352 (P, 0.2), 324 (P − CO, 0.4), and 296 (P − 2CO, 6).

Preparation of $\eta^5\text{-}C_5H_5Fe(CO)(\eta^3\text{-}CH_2C(CO_2C_2H_5)CHC_6H_5)$

A solution of $NaOC_2H_5$ (0.75 mmol) in ethanol (1.50 ml) was added dropwise to a suspension of $[\eta^5\text{-}C_5H_5Fe(CO)_2(\eta^2\text{-}CH_2=C=CHC_6H_5)]^+BF_4^-$ (0.27 g, 0.71 mmol) in 20 ml of ethanol. The solids quickly dissolved to produce a deep orange solution which was stirred for an additional 15 min. The ethanol was evaporated to form an orange gum, the gum was dissolved in 70 ml of pentane, and the resultant orange solution was filtered and concentrated to a sticky orange solid. This was washed with 2 ml of cold pentane and air dried to afford orange crystals (0.16 g, 67% yield), m.p. 90-93°C. The crystals were dissolved in a minimum of 1/1 (v/v) CH_2Cl_2/pentane and the resulting solution was eluted

over a 3 × 4 cm column of alumina with the same solvent mixture. A single yellow-orange band was collected and concentrated to an orange oil. Crystallization from pentane gave golden yellow crystals (0.14 g), m.p. 95.5-97.5°C. ^{1}H NMR (τ(ppm) CDCl$_3$): 3.11 m (C$_6$H$_5$), 4.04s (br) (CH), 5.52s (C$_5$H$_5$), 5.76q (J = 7.0 Hz, CH$_2$CH$_3$), 5.88m (CH), 8.16d (J = 2 Hz, CH), 8.64t (J = 7.0 Hz, CH$_3$). Infrared (CHCl$_3$, cm^{-1}): 1969 vs ν(C≡O). The mass spectrum (90°C) included peaks at m/e 338 (P, 8), 310 (P − CO, 98), 293 (P − OC$_2$H$_5$, 2), and 281 (P − COC$_2$H$_5$, 6).

Anal. Found: C, 62.77; H, 5.36. C$_{18}$H$_{18}$FeO$_3$ calcd: C, 63.93; H, 5.37%.

Deprotonation of [η^5-C$_5$H$_5$ Fe(CO)$_2$(η^2-CH$_2$=C=CHC$_6$H$_5$)]$^+$BF$_4^-$

Triethylamine (0.16 ml, ca. 1.1 mmol) was added to a suspension of [η^5-C$_5$H$_5$Fe(CO)$_2$(η^2-CH$_2$=C=CHC$_6$H$_5$)]$^+$BF$_4^-$ (0.37 g, 1.0 mmol) in 35 ml of CH$_2$Cl$_2$ at 25°. The mixture appeared to redden immediately as all the solids dissolved. The resultant solution was evaporated to a red-orange gum, the gum was extracted with 3 × 20 ml of pentane, and the extracts were filtered through 2 cm of alumina. Concentration of the filtrate gave orange crystals (0.09 g, 30% yield) of η^5-C$_5$H$_5$Fe(CO)$_2$CH$_2$C≡CC$_6$H$_5$.

Addition of NaI to [η^5-C$_5$H$_5$Fe(CO)$_2$(η^2-CH$_2$=C=CHC$_6$H$_5$)]$^+$BF$_4^-$

A solution of NaI (0.13 g, 0.88 mmol) in 10 ml of acetone was added dropwise to a solution of the title iron compound (0.29 g, 0.76 mmol) in 10 ml of acetone as the color changed from orange to brown. After stirring for an additional 10 min the mixture was evaporated to a red gum. An infrared spectrum of this gum showed the major carbonyl-containing product to be η^5-C$_5$H$_5$Fe(CO)$_2$I The gum was treated with CH$_2$Cl$_2$ and the resulting solution was filtered to remove a white solid, mainly NaBF$_4$. The filtrate was eluted over a 2.5 × 6 cm column of alumina with CH$_2$Cl$_2$, and an initial gray-brown band was collected and concentrated to a brown oil. Infrared and mass spectroscopy indicated this sample to be somewhat impure η^5-C$_5$H$_5$Fe(CO)$_2$I (ca. 0.11 g, 48% yield). Continued elution with CH$_2$Cl$_2$ gave a yellow effluent which upon concentration yielded a small amount of brown tar (ca. 0.02 g). An infrared spectrum (CHCl$_3$) indicated this material to be a fairly pure dicarbonyl species (ν(C≡O) 2018 and 1965 cm^{-1}); however, the compound decomposed rather quickly either as an oil or in solution to produce η^5-C$_5$H$_5$Fe(CO)$_2$I. A mass spectral determination (60°C) likewise indicated decomposition to η^5-C$_5$H$_5$Fe(CO)$_2$I, P (e.g., peaks at m/e 304 (P, 30), 276 (P − CO, 30), and 248 (P − 2CO, 32)).

Addition of other nucleophiles to [η^5-C$_5$H$_5$Fe(CO)$_2$(η^2-CH$_2$=C=CHR)]$^+$BF$_4^-$

The addition of NaN$_3$ and C$_6$H$_5$NH$_2$ to the appropriate iron-η^2-allene complex afforded η^5-C$_5$H$_5$Fe(CO)$_2$C(CH$_2$Nu)=CHR (R = CH$_3$, Nu = N$_3$; R = C$_6$H$_5$, Nu = C$_6$H$_5$NH) as impure oils. The mass spectrum of η^5-C$_5$H$_5$Fe(CO)$_2$C(CH$_2$N$_3$)=CHCH$_3$ (150°C) showed peaks at m/e 273 (P, 0.1), 245 (P − CO or P—N$_2$, 3), and 217 (P − 2CO or P − CO − N$_2$, 18); that of η^5-C$_5$H$_5$Fe(CO)$_2$C(CH$_2$NHC$_6$H$_5$)=CHC$_6$H$_5$ (150°C) revealed peaks at m/e 385 (P, 4), 357 (P − CO, 4), and 329 (P − 2CO, 27). Attempts at purification of these rather unstable materials were unsuccessful. Similarly, the addition of P(OCH$_3$)$_3$ to [η^5-C$_5$H$_5$Fe(CO)$_2$(η^2-CH$_2$=C=CHC$_6$H$_5$)]$^+$BF$_4^-$ yielded impure [η^5-C$_5$H$_5$Fe(CO)$_2$C(CH$_2$P(OCH$_3$)$_3$)=CHC$_6$H$_5$)]$^+$-

BF_4^-. The infrared $\nu(C\equiv O)$ absorptions of these three complexes are given in Table 3.

Attempted addition of CH_3Li to $[\eta^5\text{-}C_5H_5Fe(CO)_2(\eta^2\text{-}CH_2=C=CHC_6H_5)]^+BF_4^-$

A 2.13 M solution of CH_3Li in ether (1.0 ml) was diluted with 30 ml of THF and 24 ml (1.7 mmol of CH_3Li) of this mixture was added over a 45 min period to a stirred suspension of $[\eta^5\text{-}C_5H_5Fe(CO)_2(\eta^2\text{-}CH_2=C=CHC_6H_5)]^+BF_4^-$ (0.56 g, 1.5 mmol) in 50 ml of THF at 0°C. The solids dissolved to form a wine red solution which was stirred for an additional 20 min and then evaporated to a red oil. The oil was dissolved in a minimum of 2/1 (v/v) $CHCl_3$/pentane and this solution was eluted over a 2.5 × 15 cm column of alumina with pentane. An initial yellow band was collected and concentrated to 0.076 g of a yellow oil. This material was shown by ^1H NMR spectroscopy to be a mixture that included phenylallene and $\eta^5\text{-}C_5H_5Fe(CO)_2CH_2C\equiv CC_6H_5$. Elution with $CHCl_3$ removed a dark red band which was concentrated to a red gum characterized as $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$ (0.052 g).

In two other, similar reactions, small amounts of $\eta^5\text{-}C_5H_5Fe(CO)_2CH_3$ were formed as indicated by the ^1H NMR resonances at τ 5.31 and 9.83 ppm.

Acknowledgements

References

1   A. Wojcicki, Ann. N.Y. Acad. Sci., 239 (1974) 100.
2   M. Rosenblum, Acc. Chem. Res., 7 (1974) 122.
3   L.S. Chen, S.R. Su and A. Wojcicki, J. Amer. Chem. Soc., 96 (1974) 5655.
4   L.S. Chen, unpublished observations.
5   M.L.H. Green and P.L.I. Nagy, J. Chem. Soc., (1963) 189.
6   M.L.H. Green and P.L.I. Nagy, Z. Naturforsch. Part B, 18 (1963) 162.
7   J.K.P. Ariyaratne and M.L.H. Green, J. Chem. Soc., (1963) 2976.
8   J.K.P. Ariyaratne and M.L.H. Green, J. Chem. Soc., (1964) 1.
9   J. Ellermann, H. Behrens and H. Krohberger, J. Organometal. Chem., 46 (1972) 119.
10 R.J. Angelici and L. Busetto, J. Amer. Chem. Soc., 91 (1969) 3197.
11 L. Busetto and R.J. Angelici, Inorg. Chim. Acta., 2 (1968) 391.
12 L. Busetto, M. Graziani and U. Belluco, Inorg. Chem., 10 (1971) 78.
13 L. Busetto, A. Palazzi, R. Ros and U. Belluco, J. Organometal. Chem., 25 (1970) 207.
14 A. Rosan, M. Rosenblum and J. Tancrede, J. Amer. Chem. Soc., 95 (1973) 3062.
15 W.P. Giering and M. Rosenblum, J. Organometal. Chem., 25 (1970) C17.
16 P.M. Maitlis, The Organic Chemistry of Palladium, Vol. I, Academic Press, New York, N.Y., 1971, pp. 188-191; Vol. II, pp. 41-42.
17 M.H. Chisholm, H.C. Clark and D.H. Hunter, J. Chem. Soc. D, (1971) 809.
18 J. Schwartz, D.W. Hart and B. McGiffert, J. Amer. Chem. Soc., 96 (1974) 5613.
19 D.W. Lichtenberg and A. Wojcicki, J. Amer. Chem. Soc., 94 (1972) 8271.
20 J. Lewis, R.S. Nyholm, C.S. Pande and M.H.B. Stiddard, J. Chem. Soc., (1963) 3600.
21 S. Otsuka, A. Nakamura and K. Tani, J. Organometal. Chem., 14, (1968) P30.
22 K. Vrieze, H.C. Volger, M. Gronert and A.P. Praat, J. Organometal. Chem., 16 (1969) P19
23 L.M. Jackman and S. Sternhell, Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry, 2nd Ed., Pergamon Press, New York, N.Y., 1969, pp. 328-330.
24 T.G. Hewitt, K. Anzenhofer, and J.J. DeBoer, Chem. Commun., (1969) 312; T. Kashiwagi, N. Yasuoka, N. Kasai and M. Kukudo, Chem. Commun., (1969) 317; P. Racenelli, G. Pantini, A. Immirzi, G. Allegra and L. Porri, Chem. Commun., (1969) 361.

25 J. Benaim, J.-Y. Merour, and J.-L. Roustan, C.R. Acad. Sci. Ser. C. 272 (1971) 789.

26 S. Raghu and M. Rosenblum, J. Amer. Chem. Soc., 95 (1973) 3060.

27 H. Rottendorf, S. Sternhell and J.R. Whilmshurst, Aust. J. Chem., 18 (1965) 1759; D.F. Ewing and K.A.W. Parry, J. Chem. Soc. B, (1970) 970.

28 T.H. Whitesides, R.W. Arhart and R.W. Slaven, J. Amer. Chem. Soc., 95 (1973) 5792.

29 A. Efraty, J. Potenza, S.S. Sandhu, Jr., R. Johnson, M. Mastropaolo, R. Bystrek, D.Z. Denney and R.H. Herber, J. Organometal. Chem., 70 (1974) C24.

30 J. Evans, D.V. Howe, B.F.G. Johnson and J. Lewis, J. Organometal. Chem., 61 (1973) C48.

31 J. Lukas, J.P. Visser and A.P. Kouwenhoven, J. Organometal. Chem., 50 (1973) 349.

32 Sadtler NMR Spectra, No. 1855; Aldrich Library of Infrared Spectra, No. 627A.

33 M.H. Chisholm and H.C. Clark, J. Amer. Chem. Soc. 94 (1972) 1532; M.H. Chisholm and D.A. Couch, J. Chem. Soc. Chem. Commun., (1974) 42.

34 M.L.H. Green and M.J. Smith, J. Chem. Soc. A, (1971) 3220; J.-Y. Merour, C. Charrier, J.-L. Roustan and J. Benaim, C.R. Acad. Sci., Ser. C, 273 (1971) 285.

35 J.-L. Roustan, C. Charrier, J.-Y. Merour, J. Benaim and C. Giannotti, J. Organometal. Chem., 38 (1972) C37.

36 W.P. Giering, S. Raghu, M. Rosenblum, A. Cutler, D. Ehntholt and R.W. Fish, J. Amer. Chem. Soc., 94 (1972) 8251.

37 W.D. Bannister, B.L. Booth, R.N. Haszeldine and P.L. Loader, J. Chem. Soc. A. (1971) 930.

38 J.E. Thomasson, P.W. Robinson, D.A. Ross and A. Wojcicki, Inorg. Chem., 10 (1971) 2130.

39 J.-L. Roustan and P. Cadiot, C.R. Acad. Sci., Ser. C, 268 (1969) 734.

40 R.B. King, Inorg. Chem., 2 (1962) 531.

41 J.-L. Roustan and C. Charrier, C.R. Acad. Sci., Ser. C, 268 (1969) 2113.