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CLEAVAGE OF IRON—2-ALKENYL AND IRON—2-ALKYNYL BONDS BY MERCURY(II) CHLORIDE

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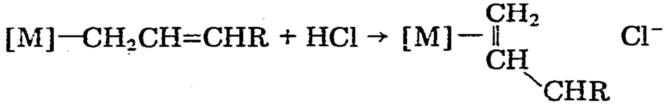
Summary

Reactions of $HgCl_2$ with η^5-$C_5H_5Fe(CO)_2R$ (R = $CH_2CH{=}CH_2$ and $CH_2C(CH_3){=}CH_2$) in THF at 25°C rapidly afford 1/1 adducts of the two reactants. These adducts were converted to the corresponding PF_6^- salts, $[\eta^5\text{-}C_5H_5Fe(CO)_2(\eta^2\text{-}CH_2{=}C(R)CH_2HgCl)]^+ PF_6^-$ (R = H and CH_3), for characterization. Slower reactions with cleavage of the iron—carbon σ bond and elimination of the R group from η^5-$C_5H_5Fe(CO)_2R$ occur for R = $CH_2CH{=}C(CH_3)_2$, $CH_2CH{=}CHC_6H_5$, and $CH_2C{\equiv}CC_6H_5$. Both elimination and 1/1 adduct formation are observed when R = $CH_2CH{=}CHCH_3$. The kinetics of the cleavage reactions are presented and possible mechanisms for both cleavage and 1/1 adduct formation are discussed.

Introduction

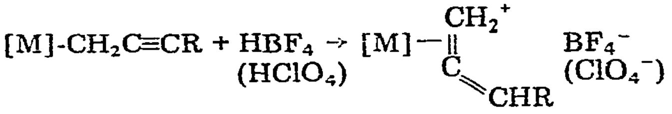
Reactions of transition metal-alkyl and -aryl compounds with mercury(II) salts have been the recent focus of extensive examinations [1—3], as have been reactions of metal-2-alkenyl and -2-alkynyl complexes with other electrophiles. Whereas the former group of reactions results in elimination of the alkyl or aryl ligand, the latter generally affords (3 + 2) cycloaddition and/or insertion products with unsaturated molecules that include SO_2, SO_3, and $(NC)_2C{=}C(CN)_2$ [4—6], and cationic *dihapto*-olefin [7,8] and *dihapto*-allene [9] complexes with protic acids.



$$[M]{-}CH_2CH{=}CHR + HCl \rightarrow [M]{-}\overset{CH_2}{\underset{\substack{CH\\ \quad\diagdown CHR}}{\|}} \qquad Cl^-$$

[M] = η^5-$C_5H_5Fe(CO)_2$; R = H, CH_3

[M] = η^5-$C_5H_5Mo(CO)_3$, η^5-$C_5H_5W(CO)_3$; R = H



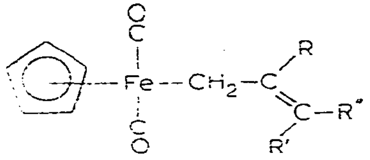
$$[M]\text{-}CH_2C{\equiv}CR + \underset{(HClO_4)}{HBF_4} \rightarrow [M]-\overset{CH_2^+}{\underset{\underset{\searrow CHR}{C}}{\|}} \quad \underset{(ClO_4^-)}{BF_4^-}$$

$[M] = \eta^5\text{-}C_5H_5Fe(CO)_2$; $R = CH_3, C_6H_5$

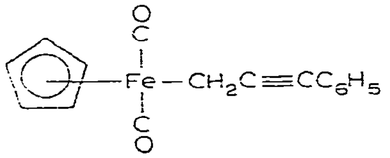
$[M] = \eta^5\text{-}C_5H_5Mo(CO)_3$; $R = C_6H_5$

Recently we have reported on the reactivity of $\eta^5\text{-}C_5H_5Fe(CO)_2R$ (R = alkyl, aryl) complexes with mercury(II) halides [10]. It was found that three distinct reaction pathways occur depending on the nature of R. Two of the paths involve electrophilic cleavage of the iron—carbon σ bond leading to the products (1) $\eta^5\text{-}C_5H_5Fe(CO)_2X$ and RHgX or (2) $\eta^5\text{-}C_5H_5Fe(CO)_2HgX$ and RX, whereas the third path involves oxidative decomposition of the iron complex.

As an extension of this study and as part of our ongoing investigation into the mechanism of reactions of organometallic compounds with electrophilic reagents, we now wish to report the reactions of $HgCl_2$ with some 2-alkenyl and 2-alkynyl complexes of iron, Ia—If. A preliminary account of this work was published earlier [11].



(Ia) $R = R' = R'' = H$
(Ib) $R = CH_3, R' = R'' = H$
(Ic) $R = R' = H, R'' = CH_3$
(Id) $R = H, R' = R'' = CH_3$
(Ie) $R = R' = H, R'' = C_6H_5$



(If)

Experimental

All organometallic reactions were conducted under an atmosphere of argon. Florisil (60—100 mesh), from Fisher, and Ventron alumina, deactivated with distilled water (6--10%), were used in chromatographic separations and purifications. Reagent grade $HgCl_2$ was used as received. Reagent grade NH_4PF_6 was recrystallized from hot methanol and dried at 70° C (~0.1 Torr) for 24 h. Tetrahydrofuran (THF), b.p. 65—66° C, was distilled from $LiAlH_4$ under Ar immediately before use. Technical grade pentane was distilled from CaH_2, b.p. 35° C. All other chemicals and solvents procured commercially were reagent grade or equivalent quality and were used without further purification.

Melting points were obtained on a Thomas—Hoover capillary melting point apparatus and are uncorrected. Proton NMR spectra were obtained on a Varian Associates A-60A spectrometer using tetramethylsilane (TMS) as an internal standard. Conductivity measurements were taken on an Industrial Instruments Co. Model RC 16B2 bridge. Infrared (IR) measurements were made on a Perkin

Elmer Model 456 or Beckman IR-9 spectrophotometer using polystyrene film for calibration. Mass spectra (MS) were recorded by Mr. C.R. Weisenberger on an A.E.I. Model MS-9 spectrometer. Elemental analyses were done by Galbraith Laboratories, Inc., Knoxville, Tenn.

The organoiron complexes η^5-$C_5H_5Fe(CO)_2R$ where R = $CH_2CH{=}CH_2$ [7], $CH_2C(CH_3){=}CH_2$ [12], $CH_2CH{=}C(CH_3)_2$ [13], $CH_2CH{=}CHC_6H_5$ [13], and $CH_2C{\equiv}CC_6H_5$ [14] were prepared by the literature methods.

Kinetic measurements of the cleavage reactions were conducted by following the disappearance of the lower frequency CO stretching absorption, $\nu_{as}(C{\equiv}O)$, of the η^5-$C_5H_5Fe(CO)_2R$ on a Beckman Model IR-9 spectrophotometer using 0.05-mm CaF_2 solution cells. Beer's law was found to hold for the $\nu_{as}(C{\equiv}O)$ absorption of these organoiron complexes over the concentration range 2×10^{-3} to 5×10^{-2} *M* in THF. Solutions of η^5-$C_5H_5Fe(CO)_2R$ and $HgCl_2$ were prepared in a dry box, mixed there, and then transferred to a thermostatted bath (25.0 ± 0.1°C) where they were magnetically stirred. Samples of the reaction solutions were withdrawn by syringe and transferred to the CaF_2 cell for periodic measurements of the absorbance of the $\nu_{as}(C{\equiv}O)$ band. All reactions were run under pseudo-first-order conditions, with the concentration of $HgCl_2$ (0.02—0.2 *M*) generally in at least 10-fold excess of that of the iron complex. For the cleavage of η^5-$C_5H_5Fe(CO)_2CH_2C{\equiv}CC_6H_5$ it was necessary to use $[HgCl_2]$ as high as 0.67 *M* to enhance the reaction rate to a measurable level. Where possible the reactions were followed for at least 3 half-lives. Pseudo-first-order rate constants, k_{obs}, were obtained by plotting $-\ln(A - A_\infty)$ vs. time, where A is the absorbance at any time during the reaction and A_∞ is the absorbance at infinite time. Since all of the cleavage reactions went to completion, A_∞ is zero. The rate constants, k_3, are reproducible to ±5%.

Reaction of η^5-$C_5H_5Fe(CO)_2CH_2CH{=}CH_2$ *(Ia) with* $HgCl_2$

A solution of Ia (0.64 g, 2.9 mmol) in THF (5 ml) was added dropwise to a slight deficiency of $HgCl_2$ (0.56 g, 2.1 mmol) in THF (20 ml) at 25°C under Ar. Immediate formation of a yellow-orange precipitate was observed. Treatment with 25 ml of THF completely dissolved the precipitate and the resulting clear yellow solution was stirred for 1 h. The solution was filtered and addition of pentane (400 ml) to the filtrate reprecipitated the yellow-orange material which was washed with acetone (5 ml) to yield 0.75 g of yellow solid. The pentane/THF filtrate was subsequently concentrated to yield another 0.22 g of product. Total yield was 95% based on a 1/1 adduct, η^5-$C_5H_5Fe(CO)_2CH_2CH{=}CH_2 \cdot HgCl_2$ (IIa); dec. 110—115°C without melting; IR (KBr pellet, cm^{-1}) 3092w, 2064vs, 2025vs, 1509m, 1428m, 1416m, 1392m, 1203w, 1112w, 1058vw, 998w, 951w, 906vw, 864m, 786w, 596m, 562m, 533m, (Nujol mull, CsI plates, cm^{-1}) 396vw, 307m. Conductivity at 25°C (1.0×10^{-3} *M* nitrobenzene solution, Λ) 13.9 cm^2 ohm^{-1}.

The yellow product was found to decompose slowly even under Ar. Its solution IR spectrum in the carbonyl stretching region was exactly the same as that of the η^5-$C_5H_5Fe(CO)_2CH_2CH{=}CH_2$ starting material, $\nu(C{\equiv}O)$ (THF, cm^{-1}) 2004vs, 1949vs.

Preparation of $[\eta^5$-$C_5H_5Fe(CO)_2(\eta^2$-$CH_2{=}CHCH_2HgCl)]^+ PF_6^-$ *(IIIa)*

To a stirred mixture of 0.25 g of IIa in acetone (25 ml) was added excess

NH_4PF_6 (0.41 g, 2.5 mmol) at 25°C. Within a few minutes the slurry turned to a bright-yellow solution and a white insoluble solid. The solution was filtered, the acetone was removed (ca. 20 Torr) from the filtrate, and the resulting yellow residue was washed with H_2O (3 × 5 ml). The residue was then redissolved in acetone (10 ml) and to the acetone solution was added an equal amount of H_2O. Reduction of the volume of the resulting solution with cooling to 0°C afforded 0.05 g (16%) of the yellow crystalline $[\eta^5\text{-}C_5H_5Fe(CO)_2(\eta^2\text{-}CH_2{=}CHCH_2HgCl)]^+ PF_6^-$ (IIIa). These crystals were collected, recrystallized from acetone, and dried (ca. 0.1 Torr); dec. 145°C without melting; $\nu(C{\equiv}O)$ (acetone, cm^{-1}) 2072vs, 2036vs. Other physical and analytical data for IIIa are furnished in Table 1. A listing of the major mass spectral peaks appears in Table 2.

Reaction of $\eta^5\text{-}C_5H_5Fe(CO)_2CH_2C(CH_3){=}CH_2$ (Ib) with $HgCl_2$

To a stirred solution of Ib (1.5 g, 6.5 mmol) in THF (2 ml) under Ar was added dropwise a deficiency of $HgCl_2$ (1.1 g, 4.1 mmol) in THF (5 ml) at 25°C. Immediate formation of precipitate was observed. The heterogeneous mixture was stirred for 1 h and then filtered. The orange precipitate was collected and washed first with THF (2 ml) and then with pentane (50 ml) to yield 1.48 g of orange powder, 71% based on a 1/1 adduct, $\eta^5\text{-}C_5H_5Fe(CO)_2CH_2C(CH_3){=}CH_2 \cdot HgCl_2$ (IIb); $\nu(C{\equiv}O)$ (Nujol mull, CsI plates, cm^{-1}) 2060 vs, 2020 vs.

Preparation of $[\eta^5\text{-}C_5H_5Fe(CO)_2(\eta^2\text{-}CH_2{=}C(CH_3)CH_2HgCl)]^+ PF_6^-$ (IIIb)

To a solution of 0.48 g of IIb in acetone (200 ml) under Ar at 25°C was added

TABLE 1

PHYSICAL AND ANALYTICAL DATA FOR CATIONIC η^2-OLEFIN—IRON COMPLEXES

Complex	IR (cm^{-1}) [a]	^1H NMR (τ, ppm) [b]	Conductivity (Λ, cm^2 ohm^{-1}) [c]	Analysis [d] (Found (calcd.)) (%)	
				C	H
IIIa	3090 w, 2064 vs, 2032 vs, 1512 m, 1424 m [e], 1388 m [e] 1195 w, 1110 w, 940 w, 864(sh), 834 vs, 596 m, 558 s, 534 m, 390 w, 307 m	4.23 (s, 5H, C_5H_5) 4.75 (m(br), 1 H, =CH) 6.28 (d [f](br), 4 H, 2 CH_2)	32.0	19.17 (20.05)	1.78 (1.68)
IIIb	3095 w, 2930 w [e], 2062 vs, 2022 vs, 1512 m, 1416 s [e] 1372 m [e], 1281 m, 1165 w, 1108 w, 1024 w, 960 w, 866 (sh), 834 vs, 596 m, 558 s, 532 m, 303 m	4.40 (s, 5 H, C_5H_5) 6.40 (s, 1 H, =CH_2) 6.85 (s, 1 H, =CH_2) 7.84 (s, 2 H, CH_2) 8.15 (s, 3 H, CH_3)	31.2	21.48 (21.55)	1.84 (1.98)

[a] Nujol mull, CsI plates, except as noted, ±5 cm^{-1}. Abbreviations: vs, very strong, s, strong; m, medium; w, weak; vw, very weak; (sh), shoulder. [b] Acetone-d_6 solution. Abbreviations: s, singlet; d, doublet; m, multiplet; (br), broad. [c] Nitrobenzene solution, 3.9×10^{-4} *M* for IIIa and 5.4×10^{-4} *M* for IIIb, at 25°C. [d] IIIa, $C_{10}H_{10}ClF_6FeHgO_2P$; IIIb, $C_{11}H_{12}ClF_6FeHgO_2P$. [e] KBr pellet. [f] J = 11 Hz.

TABLE 2

MAJOR MASS SPECTRAL PEAKS FOR $[\eta^5\text{-}C_5H_5Fe(CO)_2(\eta^2\text{-}CH_2{=}CHCH_2HgCl)]^+ PF_6^-$ (IIIa)

m/e [a]	*I* [b]	Ion [c]
278 [d] Hg	5.8	$C_3H_5HgCl^+$
212	7.6	$[Fe]Cl^+$
202 Hg	100	Hg^+
190	5.9	$[Fe]C_3H_5^+ - CO$
186	14	$(C_5H_5)_2Fe^+$
184	11	$[Fe]Cl^+ - CO$
162	26	$[Fe]C_3H_5^+ - 2\ CO$
156	45	$[Fe]Cl^+ - 2\ CO$
149	11	$[Fe]^+ - CO$
122	7.9	$[Fe]H^+ - 2\ CO$
121	45	$[Fe]^+ - 2\ CO$
107	98	PF_4^+
104	23	?
101 Hg	18	Hg^{2+}
91	17	$FeCl^+$
88	12	?
85	28	?
76	27	$C_3H_5Cl^+$
66	20	$C_5H_6^+$
65	32	$C_5H_5^+$
56	18	Fe^+

[a] 70 eV, source temperature 100°C. Hg = mercury isotopic pattern. [b] Intensities relative to *m/e* 202. [c] $[Fe] = \eta^5\text{-}C_5H_5Fe(CO)_2$. Cl = ^{35}Cl isotope. Other significant ions of lesser abundance include $C_5H_5HgCl^+$, $HgCl_2^+$, $HgCl^+$, $C_3H_5Hg^+$, and $[Fe]^+$. [d] Exact mass: Found 277.97894. $C_3H_5{}^{35}Cl^{202}Hg^+$ calcd. 277.97859.

a solution of NH_4PF_6 (1.0 g, 6.1 mmol) in acetone (25 ml). A white precipitate formed immediately. Solvent was in part removed to reduce the volume to 25 ml, the mixture was filtered, and H_2O (10 ml) was added to the filtrate. Further reduction of the volume of the solution to ca. 10 ml yielded 0.11 g (19%) of the yellow-orange crystalline powder $[\eta^5\text{-}C_5H_5Fe(CO)_2(\eta^2\text{-}CH_2{=}C(CH_3)CH_2HgCl)]^+ PF_6^-$ (IIIb). These crystals were collected, washed with H_2O (2 ml), and dried (ca. 0.1 Torr). Physical and analytical data for IIIb are furnished in Table 1. A listing of the major mass spectral peaks appears in Table 3.

Reaction of $\eta^5\text{-}C_5H_5Fe(CO)_2CH_2CH{=}CHCH_3$ (Ic) with $HgCl_2$

A solution of Ic (1.2 g, 5.2 mmol) and $HgCl_2$ (1.0 g, 3.7 mmol) in THF (25 ml) under Ar was stirred for 3 h at 25°C to yield a yellow precipitate. The solvent was then removed (ca. 20 Torr) and the excess Ic was extracted from the residue into pentane. Subsequent extraction of the residue with $CHCl_3$ afforded 0.99 g (65%) of $\eta^5\text{-}C_5H_5Fe(CO)_2HgCl$ and a trace amount of $\eta^5\text{-}C_5H_5Fe(CO)_2Cl$. The remainder of the yellow residue was first washed with acetone (50 ml) and then recrystallized from THF (50 ml) to yield 0.11 g of yellow powder, 6% based on a 1/1 adduct, $\eta^5\text{-}C_5H_5Fe(CO)_2CH_2CH{=}CHCH_3 \cdot HgCl_2$ (IIc); IR (Nujol mull, CsI plates, cm^{-1}) 3100 m, 2079 vs, 2040 vs, 1509 vw, 1150 vw, 1094 vw, 1062 vw, 1004 vw, 960 vw, 872 m, 598 m, 564 s, 534 m, 315 vw.

TABLE 3

MAJOR MASS SPECTRAL PEAKS FOR $[\eta^5\text{-}C_5H_5Fe(CO)_2(\eta^2\text{-}CH_2{=}C(CH_3)CH_2HgCl)]^+PF_6^-$ (IIIb)

m/e [a]	*I* [b]	Ion [c]
292 Hg	13	$C_4H_7HgCl^+$
272 Hg	69	$HgCl_2^+$
257 Hg	4.4	$C_4H_7Hg^+$
237 Hg	6.6	$HgCl^+$
212	11	$[Fe]Cl^+$
202 Hg	100	Hg^+
186	2.2	$(C_5H_5)_2Fe^+$
184	13	$[Fe]Cl^+ - CO$
162	4.4	$[Fe]C_3H_5^+ - 2\,CO$
156	75	$[Fe]Cl^+ - 2\,CO$
121	16	$[Fe]^+ - 2\,CO$
101 Hg	11	Hg^{2+}
91	33	$FeCl^+$
90	29	?
86	16	?
69	6.6	?
66	8.9	$C_5H_6^+$
65	20	$C_5H_5^+$
57	69	FeH^+
56	220	Fe^+

[a] 70 eV, source temperature 85°C. Hg = mercury isotopic pattern. [b] Intensities relative to *m/e* 202.
[c] $[Fe] = \eta^5\text{-}C_5H_5Fe(CO)_2$. Cl = ^{35}Cl isotope.

Reaction of η^5-$C_5H_5Fe(CO)_2CH_2CH{=}C(CH_3)_2$ (Id) with $HgCl_2$

A solution of Id (1.0 g, 4.1 mmol) and $HgCl_2$ (1.0 g, 3.7 mmol) in THF (25 ml) under Ar at 25°C was stirred for 1 h. No precipitation was observed. The THF was removed and the residue was washed with pentane. Subsequent extraction of the residue with CH_2Cl_2 gave a bright yellow solution which was filtered. Removal of the CH_2Cl_2 (ca. 20 Torr) afforded 1.49 g (99%) of the yellow-orange crystalline η^5-$C_5H_5Fe(CO)_2HgCl$; mp. 115° C (dec.); $\nu(C{\equiv}O)$ (THF, cm^{-1}) 2006 vs, 1959 vs.

To a stirred solution of Id (0.10 g, 0.41 mmol) in acetone-d_6 (2 ml) under Ar at 25°C was added $HgCl_2$ (0.41 g, 1.5 mmol). After 10 min the solvent and volatile products were pumped off and collected at −196°C. Analysis by ^1H NMR spectroscopy revealed $(CH_3)_2C{=}CHCH_2Cl$ to be only product present with the solvent.

Reaction of η^5-$C_5H_5Fe(CO)_2CH_2CH{=}CHC_6H_5$ (Ie) with $HgCl_2$

A solution of Ie (0.10 g, 0.34 mmol) and $HgCl_2$ (2.0 g, 7.4 mmol) in THF (10 ml) was stirred under Ar at 25°C for 2 h. No precipitation was observed. Analysis of the solution by IR spectroscopy showed the reaction to be complete and the primary iron-containing product to be η^5-$C_5H_5Fe(CO)_2HgCl$ (>97%). A trace amount of η^5-$C_5H_5Fe(CO)_2Cl$ (<3%) was also noted, $\nu(C{\equiv}O)$ (THF, cm^{-1}) 2048 vs, 2000 vs.

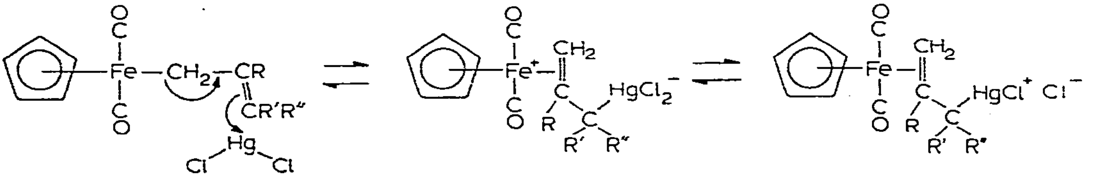
Reaction of η^5-$H_5Fe(CO)_2CH_2C{\equiv}CC_6H_5$ (If) with $HgCl_2$

A solution of If (0.24 g, 0.83 mmol) and $HgCl_2$ (0.27 g, 1.0 mmol) in THF (5 ml) was stored under Ar in a sealed flask at 25°C. IR spectroscopy showed the reaction to be complete in 55 h and revealed the absence of η^5-$C_5H_5Fe(CO)_2HgCl$, the only detectable iron carbonyl product being η^5-$C_5H_5Fe(CO)_2Cl$. A small amount of precipitate (0.04 g) composed of Hg_2Cl_2 and an iron-containing decomposition material was also present. The filtrate of the reaction mixture was concentrated to ca. 5 ml and chromatographed on a Florisil column eluting first with benzene and then with 3/1 (v/v) CH_2Cl_2/acetone to yield 0.13 g of a semicrystalline white solid identified as $C_6H_5C{\equiv}CCH_2HgCl$, m.p. 106—108°C (dec.) (in a sealed tube, with sublimation) (lit. [15] m.p. 108°C), and 0.12 g (67%) of η^5-$C_5H_5Fe(CO)_2Cl$, m.p. 87°C (dec.).

Results and discussion

The 2-alkenyliron complexes Ia and Ib react very rapidly with $HgCl_2$ in THF at 25°C to yield 1/1 adducts of the two reactants. Complex Ic reacts with $HgCl_2$ in this manner more slowly and to a lesser degree. The primary reaction of Ic and the nearly exclusive reactions of Id and Ie with $HgCl_2$ are scission of the iron—carbon σ bond with the formation of η^5-$C_5H_5Fe(CO)_2HgCl$ and the allyl chloride. There is no observable formation of 1/1 adducts between Id or Ie and $HgCl_2$. The 2-alkynyl complex If and $HgCl_2$ react with cleavage of the iron—carbon σ bond to afford η^5-$C_5H_5Fe(CO)_2Cl$ and $C_6H_5C{\equiv}CCH_2HgCl$ and, to a small extent, with oxidative decomposition of If and reduction of $HgCl_2$ to Hg_2Cl_2.

The mercuration of Ia, Ib, and Ic affords products that are formulated as the η^2-olefin-iron complexes IIa, IIb, and IIc, respectively. These products appear to result from electrophilic attack at the double bond of the 2-alkenyl ligand by $HgCl_2$, leading to the addition of the $HgCl_2$ to the carbon-3 and to the accompanying rearrangement of the η^1-alkenyl to η^2-olefin.

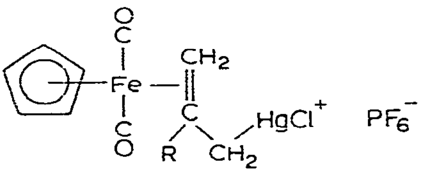


(IIa) R = R′ = R″ = H
(IIb) R = CH_3, R′ = R″ = H
(IIc) R = R′ = H, R″ = CH_3

The infrared spectra (Nujol mull or KBr pellet) of the adducts IIa—IIc show high carbonyl stretching frequencies (2079—2060 and 2040—2020 cm^{-1}), indicative of a positive charge at the iron atom [7,8,16], as well as absorptions due to the stretching of a coordinated carbon—carbon double bond (~1500 cm^{-1}) and a mercury—chlorine bond (~300 cm^{-1}). The adducts are insoluble in CH_2Cl_2, $CHCl_3$, benzene, and saturated hydrocarbons, slightly soluble in acetone, and moderately soluble in THF. Conductivity measurements on a nitrobenzene solution of IIa show it to be less than a 1/1 electrolyte in this medium [7,8,17], consistent with the proposed equilibria involving Ia and the dipolar and ionic structures of IIa (vide supra). The formation of IIa seems to be easily reversible as evidenced by the exclusive appearance of the carbonyl stretching frequencies of Ia upon dissolution of IIa in THF.

The proposed mode of addition of $HgCl_2$ to Ia—Ic is strictly analogous to the protonation of transition metal—2-alkenyl complexes [7,8]. It also parallels the formation of the recently detected [16] zwitterionic intermediates in the reaction of these same iron complexes with SO_2.

The adducts IIa and IIb were converted to the respective PF_6^- salts for complete characterization. These latter salts are insoluble in CH_2Cl_2, $CHCl_3$, and benzene, moderately soluble in THF and H_2O, and soluble in acetone. Their formulation as IIIa and IIIb rests on the physical and analytical data set out in Table 1 and on the mass spectrometric data given in Tables 2 and 3.



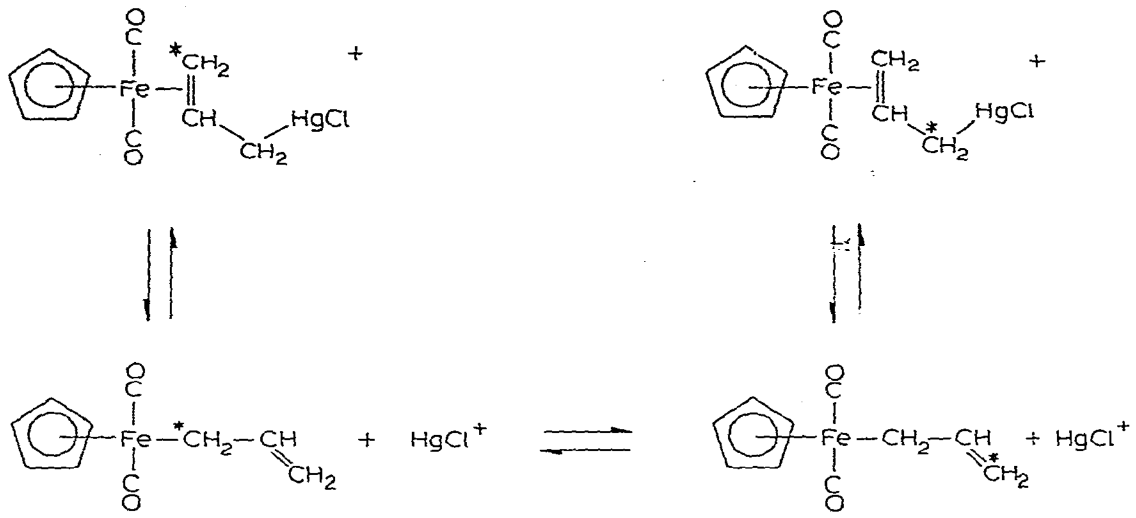
(IIIa) R = H
(IIIb) R = CH_3

As observed for the adducts IIa and IIb, the PF_6^- salts IIIa and IIIb possess high carbonyl stretching frequencies (2064—2062 and 2032—2022 cm^{-1}, Nujol mull), which point to the presence of a positively charged η^5-$C_5H_5Fe(CO)_2$ species. These high $\nu(C\equiv O)$ values persist (2072, 2036 cm^{-1}) upon dissolution of IIIa in acetone. In addition important infrared absorptions occur which are assigned to ν(C—H) of the C_5H_5 ring (~3100 cm^{-1}), ν(C=C) of the coordinated double bond (1512 cm^{-1}), and ν(Hg—Cl) (~300 cm^{-1}). Although no parent ions are detected in the mass spectra of IIIa and IIIb, peaks corresponding to the ions $CH_2{=}C(R)CH_2HgCl^+$ (R = H and CH_3) are observed with moderate relative intensities. The conductivities of the two salts in nitrobenzene compare favorably with those found for other, related organoiron 1/1 electrolytes [7,8, 17].

The ^1H NMR spectra of IIIa and IIIb show the resonance of the C_5H_5 protons at fields comparable to those for the corresponding resonance of various η^5-$C_5H_5Fe(CO)_2(\eta^2\text{-olefin})^+$ complexes [7,8,16]. The remainder of the spectrum of IIIa bears a close resemblance to that of an AX_4 spin system. Accordingly it consists of a broad multiplet centered at τ 4.75 ppm (relative intensity 1) and a broad doublet (J 11 Hz) at τ 6.28 ppm (relative intensity 4). This pattern is very similar to that reported for allylmercury chloride, $CH_2{=}CHCH_2HgCl$, in dimethyl sulfoxide-d_6 in the presence of trace amounts of $HgCl_2$, i.e. τ 3.98 and 6.36 ppm (relative intensities 1/4) and J 11 Hz [18]. Such an equilibration of the —CH_2— and =CH_2 protons may in the case of IIIa also result from the presence of catalytic amounts of $HgCl_2$; a reasonable mechanism for the exchange is depicted in Scheme 1.

The exchange of the allylic termini in Ia would have to be catalyzed by the dissociated $HgCl^+$ (or $HgCl_2$ impurities), since such equilibration is slow on the NMR time scale in the absence of mercury(II) [5]. Mechanisms involving reversible dissociation of $CH_2{=}CHCH_2HgCl$ from IIIa to give [η^5-$C_5H_5Fe(CO)_2$(sol-

SCHEME 1



vent)]$^+$ are considered unlikely because the generated cation would afford η^5-$C_5H_5Fe(CO)_2Cl$ in the presence of chloride. No η^5-$C_5H_5Fe(CO)_2Cl$ was observed in the preparation of IIIa from IIa.

In contrast to the behavior of IIIa, the ^{1}H NMR spectrum of IIIb is consistent with the assigned static structure of the cation in solution. The reason for this difference is not clear. If the proposed mechanism for IIIa is indeed operative, this would suggest that the dissociation of HgCl$^+$ from IIIb does not proceed as readily as that from IIIa. This is because without added mercury(II), deuterium-labeled Ib undergoes more rapid allylic 1,3 shifts than similarly labelled Ia [5,19]. Hence Ib might be expected also to equilibrate very fast in the presence of mercury(II).

The rate data for the cleavage reactions of Id, Ie, and If with ca. 10-fold excess of $HgCl_2$ in THF at 25°C are presented in Table 4. The corresponding data for the complexes η^5-$C_5H_5Fe(CO)_2CH_3$ and η^5-$C_5H_5Fe(CO)_2C(CH_3)_3$, reported earlier [10], are included for comparison. These reactions proceed

TABLE 4

RATE DATA FOR THE REACTIONS OF η^5-$C_5H_5Fe(CO)_2R$ WITH $HgCl_2$ IN THF AT 25°C

R	Reaction path [a] (Scheme 2)	k_3 (M^{-2} sec^{-1})	Rel. k_3	$\nu(C\equiv O)$ (cm^{-1}) [b]
$C(CH_3)_3$ [c]	2	9.3×10^{-3}	1030	1996, 1938
$CH_2CH{=}C(CH_3)_2$	2	6.6×10^{-3}	730	2000, 1944
$CH_2CH{=}CHC_6H_5$	2	1.3×10^{-3}	140	2000, 1948
CH_3 [c]	1	4.6×10^{-4}	51	2005, 1948
$CH_2C{\equiv}CC_6H_5$	1 [d]	1.8×10^{-5} (9.0×10^{-6}) [e]	2(1) [e]	2006, 1958

[a] Minor reaction paths are excluded; see text. [b] Measured in THF solution, ±1 cm^{-1}. [c] Data from ref. 10. [d] Alternatively, $HgCl_2$ may attack the 2-alkynyl ligand; see text. [e] Adjusted rate constants to compensate for the high concentration of $HgCl_2$ used; see text.

by one of the three paths described previously [10] and depicted below; the fourth path is the addition of $HgCl_2$ to the 2-alkenyl ligand (Scheme 2). Because of the occurrence of two competing reactions (paths 2 and 4) between Ic and $HgCl_2$, no attempt was made at obtaining rate constants for this cleavage.

SCHEME 2

$$\eta^5\text{-}C_5H_5Fe(CO)_2R + HgCl_2 \rightarrow \eta^5\text{-}C_5H_5Fe(CO)_2Cl + RHgCl \qquad (1)$$

$$\eta^5\text{-}C_5H_5Fe(CO)_2R + HgCl_2 \rightarrow \eta^5\text{-}C_5H_5Fe(CO)_2HgCl + RCl \qquad (2)$$

$$\eta^5\text{-}C_5H_5Fe(CO)_2R + HgCl_2 \rightarrow \text{“Fe-containing material”} + \tfrac{1}{2}\ Hg_2Cl_2 + 2\ CO + \text{organic products} \qquad (3)$$

$$\eta^5\text{-}C_5H_5Fe(CO)_2CH_2C(R){=}CR'R'' + HgCl_2 \rightarrow [\eta^5\text{-}C_5H_5Fe(CO)_2(\eta^2\text{-}CH_2{=}C(R)C(R')(R')HgCl)]^+\ Cl^- \qquad (4)$$

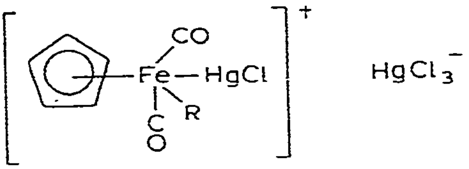
All reactions were found to obey the rate expression:

$$-\frac{d[\eta^5\text{-}C_5H_5Fe(CO)_2R]}{dt} = k_{obs}[\eta^5\text{-}C_5H_5Fe(CO)_2R]$$

giving good linear plots of $-\ln A$ vs. time. No induction period was observed in any of these reactions. The cleavage of each of Id and Ie by $HgCl_2$ was further found to exhibit a second-order dependence on $HgCl_2$ and to obey a third-order rate expression overall:

$$-\frac{d[\eta^5\text{-}C_5H_5Fe(CO)_2R]}{dt} = k_3[\eta^5\text{-}C_5H_5Fe(CO)_2R][HgCl_2]^2$$

Thus these reactions, and very likely that of Ic with $HgCl_2$ by path 2, seem to be strictly analogous to the scission of the η^5-$C_5H_5Fe(CO)_2R$ where R = $C(CH_3)_3$ or $CH(CH_3)C_6H_5$ by HgX_2 [10]. The resulting products, η^5-$C_5H_5Fe(CO)_2HgCl$ and the allyl chloride, are apparently formed by heterolysis of the Fe—R bond in the postulated intermediate IV and rapid capture by chloride of the dissociating allyl carbonium ion [10]. The intermediate IV is proposed to result from initial electrophilic attack of $HgCl_2$ at the iron in η^5-$C_5H_5Fe(CO)_2R$ leading to the formation of a 1/1 adduct and subsequent abstraction of chloride from this adduct by a second molecule of $HgCl_2$ [10]. Significantly, the cleavage by path 2 is generally considerably faster than that by path 1 (Table 4); this point was considered earlier [10].



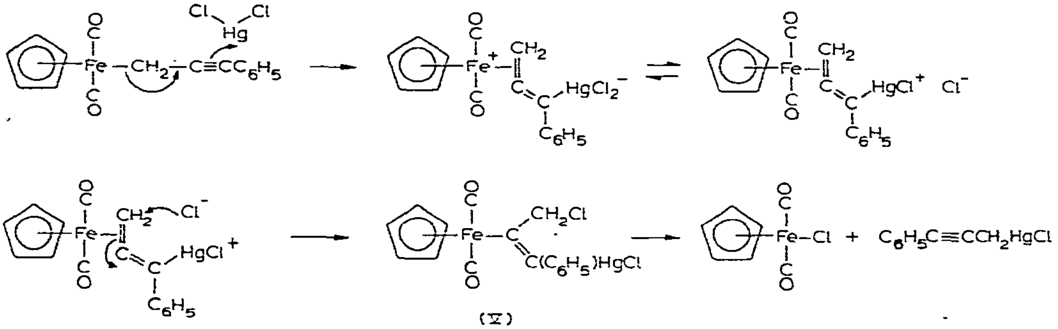
(IV)

The cleavage of If by $HgCl_2$ is much slower than that of Id or Ie and proceeds primarily by what appears to be path 1, with minor reactivity by path 3. If path

1 is indeed operative, then the rather slow rate of this reaction may be ascribed to both the relatively low electron density at the iron and the apparent inability of the $CH_2C{\equiv}CC_6H_5$ ligand to dissociate off as a carbonium ion. The lower amount of electron density at the metal is evidenced by the higher carbonyl stretching frequencies of If relative to Id and Ie (Table 4). The reaction of If with $HgCl_2$ was in fact found to proceed too slowly to use a wide enough range of concentrations of $HgCl_2$ for accurate measurement of the rate dependence on $[HgCl_2]$. However, the cleavage of the η^5-$C_5H_5Fe(CO)_2R$ alkyl and aryl complexes by path 1 has been previously found invariably to obey third-order kinetics, second-order in $HgCl_2$ [10]. Accordingly, the reaction in point is assumed also to be third-order overall, and on this basis the rate constant k_3 has been calculated. Furthermore, as reported earlier [10] for the cleavage reactions of η^5-$C_5H_5Fe(CO)_2R$, the use of an $HgCl_2$ concentration of ca. 0.67 M leads to an approximate 2-fold rate enhancement over that obtained by employing $HgCl_2$ concentrations in the range 0.02—0.2 M. Since in the scission of If 0.67 M concentrations of $HgCl_2$ were employed, an adjusted rate constant has been calculated which is corrected for the expected change in rate. This rate constant, given in parentheses in Table 4, is thought to provide a more meaningful comparison with the data obtained at the lower concentrations of $HgCl_2$ than does the unadjusted rate constant.

There is, however, an alternative path for the above reaction which cannot be dismissed on the basis of available evidence (Scheme 3). Here electrophilic attack of $HgCl_2$ at the triple bond of the 2-alkynyl ligand would lead to the formation of an η^2-alleneiron zwitterion in equilibrium with the corresponding ionic species. This equilibrium is strictly analogous to that proposed for the η^2-olefin-iron complexes II (vide supra). Attack of chloride at the terminal carbon of the coordinated allene is then expected to afford V. Such a reaction is amply precedented in the literature; for example, $[\eta^5\text{-}C_5H_5Fe(CO)_2(\eta^2\text{-}CH_2{=}C{=}CHC_6H_5)]^+$ reacts in this manner with a variety of nucleophiles [9a]. Finally, intermediate V is expected to undergo conversion to η^5-$C_5H_5Fe(CO)_2Cl$ with elimination of C_9H_7HgCl. The organomercury fragment C_9H_7HgCl would most likely be expelled as $CH_2{=}C{=}C(C_6H_5)HgCl$, which subsequently isomerizes to the isolated $C_6H_5C{\equiv}CCH_2HgCl$ in the presence of $HgCl_2$. In support of this proposed alternative path is the report [20] that $[P(C_6H_5)_3]_2ClPt[C(CH_2Cl){=}CH_2]$ decomposes to $Pt[P(C_6H_5)_3]_2Cl_2$ and C_3H_4 at 40°C in $CHCl_3$. As further evidence,

SCHEME 3



$[\eta^5\text{-}C_5H_5Fe(CO)_2(\eta^2\text{-}CH_2{=}C{=}CHC_6H_5)]^+ BF_4^-$ reacts with NaI in acetone at 25° C to yield $\eta^5\text{-}C_5H_5Fe(CO)_2I$ [9a].

The final point of discussion addresses itself to possible factors that determine whether cleavage of the iron—carbon σ bond (Scheme 2, paths 1—3) or formation of the 1/1 adduct (path 4) occurs in the reactions of these 2-alkenyl complexes with $HgCl_2$. The rapid addition of $HgCl_2$ to Ia and Ib indicates that path 4 is the most favorable course of reaction of $HgCl_2$ with 2-alkenylmetal complexes containing a sterically unencumbered allylic carbon—carbon double bond. A slower, two-path (2 and 4) reaction of Ic likely results from partial steric inhibition to electrophilic attack by $HgCl_2$ at the double bond of the 2-alkenyl ligand in this complex. This steric inhibition increases further with the presence of two CH_3 groups (Id) or one C_6H_5 group (Ie) on the carbon-3 of the 2-alkenyl; now the reaction with $HgCl_2$ proceeds still more slowly and exclusively by path 2. Irrespective of the mechanism, the observed slow reaction between If and $HgCl_2$ is consistent with the lower susceptibility of the carbon—carbon triple bond in the 2-alkynyl complexes than of the carbon—carbon double bond in the 2-alkenyl complexes toward attack by various electrophiles [21].

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