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 π -Allyliron Carbonyl Complexes

BY RICHARD F. HECK AND CHARLES R. BOSS

RECEIVED JANUARY 29, 1964

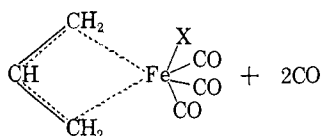
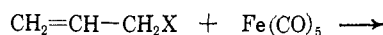
Allylic halides and iron pentacarbonyl react at room temperature under the influence of ultraviolet light to give π -allyliron tricarbonyl halides. *cis*-4-Chloro-2-buten-1-ol reacts to give a chlorine-free iron complex which appears to be the bicyclic complex 1-hydroxymethyl- π -allylcarboxyiron tricarbonyl lactone.

Introduction

π -Allyliron tricarbonyl derivatives have been prepared by the action of strong acids on π -1,3-dieneiron tricarbonyls,^{1,2} by the reaction of allylic iodides with iron pentacarbonyl at 40°,³ and by the reaction of iron enneacarbonyl with allylic halides at 40°.⁴ This paper reports another π -allyliron tricarbonyl halide synthesis which is more convenient to carry out than the previous ones.

Results

Ultraviolet irradiation of pentane solutions of allylic halides and iron pentacarbonyl at room temperature or below gives π -allyliron tricarbonyl halides. The reactions can be carried out in Pyrex glassware. Ordinarily the reagents were combined in a capped nitro-

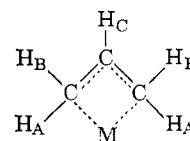


gen-filled bottle and irradiated for a few hours to several days while being cooled with a slow stream of tap water running over the bottles. The reactions became slower with time because minor amounts of decomposition products, mainly ferrous halides, deposited on the walls of the containers and shut out the light. The course of the reaction could be conveniently followed by removing a small sample of the reaction mixture and taking its infrared spectrum. All of the π -allyliron carbonyl derivatives had intense carbonyl bands at about 4.8 μ which were easily distinguished from the band of iron carbonyl itself. Isolation of the π -allyliron tricarbonyl halides was accomplished by centrifuging off the insoluble material and cooling the pentane solution in Dry Ice. The products normally crystallized readily from these solutions. Another recrystallization or two from pentane gave analytically pure products. The mother liquors from the first crystallizations could be irradiated again to give higher yields. The halides prepared by this reaction are listed in Table I. All of the products gave satisfactory carbon and hydrogen analyses. The yields were usually about 20–30% in 48 hr. and they gradually increased with longer irradiation.

We also found, as Murdoch and Weiss reported,⁴ that the chloride groups were readily replaced from

the π -allyliron tricarbonyl chlorides by iodide ion. π -Allyliron tricarbonyl chloride and 1-methyl- π -allyliron tricarbonyl chloride reacted very rapidly with lithium iodide in acetone to produce high yields of the corresponding iodides. It is interesting that the iodide exchange reactions produced the same isomeric π -allyl complexes as were obtained directly from the allylic iodides and iron carbonyl.

The n.m.r. spectra of these complexes were obtained, and the results are given in Table II. The spectrum of π -allyliron tricarbonyl chloride shows excellent resolution and contains a multiplet and two doublets in an area ratio of 1:2:2. This type of spectrum arises from a structure



where $J_{AB} \sim 0$. Similar results have been obtained for many π -allyl transition metal complexes and are considered to be very strong evidence for such a structure.^{1,5,6} The corresponding bromide gave similar peaks, but the resolution was not as good. The 115–135 c.p.s. region was more complex than in the chloride.

As Plowman and Stone had reported,³ we also found the π -allyliron tricarbonyl iodide n.m.r. spectrum unusual and very similar to theirs. The spectrum was the same whether the compound was prepared from the corresponding chloride (a "normal" π -allyl complex) and lithium iodide or from allyl iodide and iron pentacarbonyl. We assume with Stone and Plowman³ that a monomer-dimer equilibrium exists. Based on trends of the anisotropic effect of the ligands in these complexes, we make the assignments for the monomer given in Table II. Drawing an analogy with previous results of $\text{CH}_2=\text{CH}-\text{CH}_2-\text{Mn}(\text{CO})_5$ we assign our 235-c.p.s. doublet to $\text{Fe}-\text{CH}_2-$ and the unresolved 37-c.p.s. peak to $=\text{CH}-$ in the dimer postulated by Stone and Plowman.³ The relative areas indicate the iodide contains approximately equal amounts of π - and σ -allyl groups. The corresponding bromide appears to be largely a π -allyl monomer with a minor amount of σ -dimer also present.

The 2-methyl- π -allyliron tricarbonyl chloride and the corresponding iodide produce three singlets in a 2:2:3 ratio. These results would be expected for a normal π -bonded complex; there are no extraneous peaks or unusual features in the n.m.r. spectrum of this iodide complex.

(1) F. J. Impastato and K. G. Ihrman, *J. Am. Chem. Soc.*, **83**, 3726 (1961).

(2) G. F. Emerson and R. Pettit, *ibid.*, **84**, 4591 (1962).

(3) R. A. Plowman and F. G. A. Stone, *Z. Naturforsch.*, **17b**, 575 (1962).

(4) H. D. Murdoch and E. Weiss, *Helv. Chim. Acta*, **45**, 1927 (1962).

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(6) J. C. W. Chien and H. C. Dehm, *ibid.*, **82**, 4429 (1960).

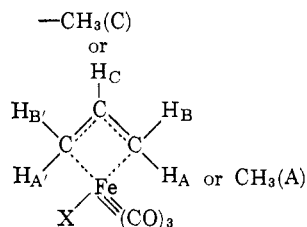
TABLE I

 π -ALLYLIRON TRICARBONYL HALIDES PREPARED FROM ALLYLIC HALIDES AND IRON CARBONYL

Allylic halide	Product	M.p. (dec.), °C.	Lit. m.p., °C.
CH ₂ =CHCH ₂ Cl	π -C ₃ H ₅ Fe(CO) ₃ Cl	81-83	88-89 ^a
CH ₂ =CHCH ₂ Br	π -C ₃ H ₅ Fe(CO) ₃ Br	92.5-93	86-87 ^a
CH ₂ =CHCH ₂ I	π -C ₃ H ₅ Fe(CO) ₃ I	97-98	98, ^b 85-86 ^a
CH ₃ CH=CHCH ₂ Cl	1-CH ₃ - π -C ₃ H ₄ Fe(CO) ₃ Cl	57.5-58.0	58 ^{a,c}
CH ₃ CH=CHCH ₂ Br	1-CH ₃ - π -C ₃ H ₄ Fe(CO) ₃ Br	32-33	34.5 ^a
CH ₂ =CHCHBrCH ₃			
CH ₂ =C(CH ₃)CH ₂ Cl	2-CH ₃ - π -C ₃ H ₄ Fe(CO) ₃ Cl ^d	98-99	
CH ₃ OCOCH=CHCH ₂ Br	1-CH ₃ OCO- π -C ₃ H ₄ Fe(CO) ₃ Br	72-73	65 ^a

^a See ref. 4. ^b See ref. 3. ^c See ref. 1. ^d Anal. Calcd. for C₇H₇O₃ClFe: C, 36.49; H, 3.06. Found: C, 36.67; H, 3.22.

TABLE II

N.M.R. PARAMETERS OF π -ALLYLIRON TRICARBONYL HALIDES

Compound	Chemical shift in c.p.s. from benzene (60 Mc.)							
	X	H _A	H _{A'}	H _B	H _{B'}	H _C	CH ₃ (A)	CH ₃ (C)
π -Allyl	Cl	195		116		80		
π -Allyl	Br	176		120		~120 (?)		
π -Allyl	I	151 ^a		128 ^a		~120		
2-Methyl- π -allyl	Cl	194		126				270
2-Methyl- π -allyl	I	159		140				265
1-Methyl- π -allyl	Cl		208	~135	129	87	263	
1-Methyl- π -allyl	Br		198	~115	136	~100	268	

^a Assignments on peaks of complex group and trends in anisotropic effects of ligands.

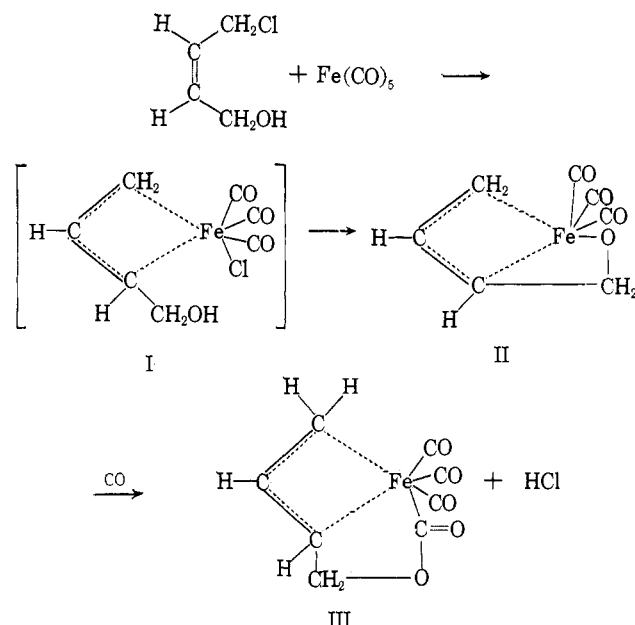
The n.m.r. spectra of 1-methyl- π -allyliron tricarboxyl chloride and the corresponding bromide indicate that both have a normal π -bonded structure, and that the only isomer was the one with the methyl group directed toward the metal. These results agree with those of Impastato and Ihrman¹ for 1-methyl- π -allyliron tricarboxyl chloride, and similar results were obtained by Chien and Dehm⁶ for 1-methyl- π -allylpalladium chloride. A footnote in a paper by Murdoch and Weiss⁴ states that this assignment is incorrect but the reasons were not given. We believe ours is correct because the higher field, more widely spaced doublet decreases in size when a terminal methyl group is added. This peak has been assigned to the protons toward the metal because the peak is at higher field,⁶ these protons are *trans* to the proton on the center carbon atom, and J_{trans} is larger than J_{cis} in ethylenic compounds.

The reaction of *cis*-4-chloro-2-buten-1-ol with iron pentacarbonyl proceeded unexpectedly in that the product isolated was not a halide. The product, pale yellow prisms of m.p. 118.2-118.6°, isolated in about 5% yield, had a very strong, unusual carbonyl band in its infrared spectrum at 6.0 μ in addition to the usual π -allyliron tricarboxyl bands at 4.8-5.0 μ . Analyses indicated an empirical formula of C₈H₆O₅Fe for the compound.

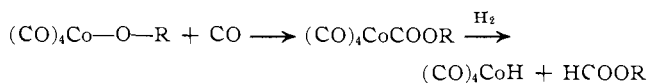
The n.m.r. spectrum consists of four peaks which are found at 95, 147, 165, and 213 c.p.s. from benzene.

The resolution was poor, but these peaks appear to be a broad singlet (area 2), a sharp singlet (area 2), an unresolved multiplet (area 1) and a doublet with $J \approx 10$ c.p.s. (area 1), respectively.

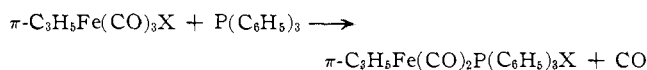
The data are consistent with, and appear to us to be best explained by, structure III. Presumably the normal π -allyl complex I is formed first, then ester



formation between the alcohol group and the chlorine group takes place by elimination of hydrogen chloride, forming II, followed by carbon monoxide insertion between the iron and the oxygen group to give III. The insertion of carbon monoxide into a metal-oxygen group is not without precedent. Carbomethoxymercuric acetate, for example, is formed from a methanol solution of mercuric acetate and carbon monoxide, possibly by way of a methoxymmercuric acetate.⁷ Formate esters are one of the products produced in the reaction of alcohols with carbon monoxide and hydrogen.⁸ Probably they are formed by the insertion of carbon monoxide into the cobalt alkoxide group followed by hydrogenation.



The π -allyliron tricarbonyl halides react readily with triphenylphosphine, producing 1 mole of carbon monoxide and π -allyliron dicarbonyl triphenylphosphine halides. The π -allyliron dicarbonyl triphenylphosphine



chloride complex, although almost certainly formed, is too unstable to be isolated and purified. Both the bromide and iodide give stable, crystalline, dark red to brown monotriphenylphosphine derivatives.

The rates of reaction of the π -allyliron tricarbonyl halides with triphenylphosphine were measured in order to compare the reactivity and mechanism of reaction of these π -allyliron complexes with those of the π -allylcobalt tricarbonyls.⁹ The π -allyliron tricarbonyl bromide and iodide appear to react with triphenylphosphine in a second-order reaction, depending upon both the iron complex concentration and the phosphine concentration. At 0° in ether solution the rate of the bromide reaction is 0.41 l./mole/sec. and the iodide rate is 2.8×10^{-2} l./mole/sec. Thus, the bromide is about 15 times more reactive than the iodide. The chloride is more reactive than the bromide under the same conditions, but the second-order reaction rate constants decreased markedly with time during the first 30% of the reaction. The rate constant decreased from 4.2 to 0.8 l./mole/sec. and then remained fairly constant for the remainder of the reaction at about 0.7 l./mole/sec. The final value is about 1.7 times faster than that of the bromide. Since the product from the chloride reaction was so unstable, we did not investigate the kinetics further. It is clear that π -allyliron tricarbonyl halides are quite different from the π -allylcobalt tricarbonyls in their mechanism of reaction with triphenylphosphine, the former reacting by a second-order mechanism and the latter by a first-order mechanism.⁹

Experimental

General Method for the Preparation of π -Allyliron Tricarbonyl Halides.—Into heavy-walled Pyrex bottles, which were capped

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(9) R. F. Heck, *J. Am. Chem. Soc.*, **85**, 655 (1963).

with self-sealing rubber-lined caps and filled with nitrogen, 50 ml. of pentane, 5 ml. of iron pentacarbonyl, and 5 ml. of the allylic halide were injected with a hypodermic syringe. The solution was mixed and the bottle placed in a pan of tap water through which cold water was continually and slowly flowing. The solution was then irradiated with a 100-w. G.E. H100-A4 lamp placed from 1 to 2 in. above the liquid. Generally 2 or 3 days of irradiation gave 20–30% conversions to the π -allyl complexes. Longer irradiation times gave higher yields. The solutions were then centrifuged in the same bottles and the clear reaction mixtures were removed by syringe and placed in another nitrogen-filled bottle. On cooling to -80° , the products crystallized. The supernatant liquid was then removed and either put in another bottle for further irradiation or discarded, and the solid was recrystallized one or more times from pentane.

2-Methyl- π -allyliron Tricarbonyl Iodide.—A solution of 0.5 g. of anhydrous lithium iodide in 5 ml. of acetone was mixed with a solution of 0.42 g. of 2-methyl- π -allyliron tricarbonyl chloride in 2 ml. of acetone under nitrogen. After standing for 3 hr., the solvent was evaporated *in vacuo* at room temperature and the product was extracted from the residue with three or four portions of pentane. On cooling to -80° , the extracts deposited glistening dark red prisms of the iodide. Two more crystallizations from ether-pentane gave material of m.p. 103.5–104.0° (gas evolution), (lit.³ m.p. 100°. *Anal.* Calcd. for $\text{C}_7\text{H}_7\text{O}_3\text{FeI}$: C, 26.12; H, 2.19. Found: C, 26.33; H, 2.39.

π -Allyliron tricarbonyl iodide was prepared in a similar manner from the chloride.

The Reaction of *cis*-4-Chloro-2-buten-1-ol with Iron Pentacarbonyl.—Into a nitrogen-filled, heavy-walled tube, capped with a self-sealing rubber-lined cap, 5 ml. of methylene chloride, 1.0 ml. of iron pentacarbonyl, and 1.0 ml. of *cis*-4-chloro-2-buten-1-ol¹⁰ were injected. The solution was irradiated and cooled as described above for 48 hr. The solution was then centrifuged and the liquid was separated and placed in another nitrogen-filled tube. The solid residue was extracted twice more with a few milliliters of methylene chloride. The combined extracts were evaporated to an oil. Addition of 5 ml. of ether to the residue and cooling to -80° gave a crystalline product. Two more recrystallizations from ether-methylene chloride gave pale yellow prisms of m.p. 118.2–118.6° dec. in about 5% yield. *Anal.* Calcd. for $\text{C}_8\text{H}_8\text{O}_3\text{Fe}$: C, 40.38; H, 2.54; Fe, 23.47. Found: C, 40.47; H, 2.81; Fe, 21.4, 21.5.

The infrared spectrum in chloroform had bands at 3.35 (m), 3.49 (w), 4.80 (vs), 4.93 (vs), 4.98 (vs), 6.00 (vs), 6.70 (w), 6.83 (w), 7.22 (w), 7.31 (m), 8.09 (m), 8.63 (m), 9.43 (vs), 10.00 (vs), 10.15 (vs), 10.68 (m), and 11.64 μ (w).

π -Allyliron Dicarbonyl Triphenylphosphine Bromide.—In a 100-ml. reaction flask attached to a gas buret¹¹ was placed 0.52 g. (2 mmoles) of π -allyliron tricarbonyl bromide. The apparatus was flushed with ether-saturated carbon monoxide at 0°, and 10 ml. of ether was added by means of a hypodermic syringe through a rubber stopper on the reaction flask. When the solution reached equilibrium with the gas phase, 3.0 ml. of 1.0 M triphenylphosphine in ether solution at 0° was added. In about 1 min. 56 ml. or 1.86 mmoles of gas was evolved and an orange crystalline complex separated from the solution. The solid was separated and recrystallized several times from methylene chloride-pentane at -80° . Orange-red prisms of m.p. 117–118° dec. were obtained. *Anal.* Calcd. for $\text{C}_{23}\text{H}_{20}\text{O}_2\text{PBrFe}$: C, 55.79; H, 4.07. Found: C, 55.58; H, 4.15. In chloroform solution the complex had carbonyl bands at 4.94 (vs) and 5.09 μ (vs).

The kinetics of the reaction were determined by observing the rate of gas evolution under conditions similar to those described, but with more dilute solutions.

π -Allyliron Dicarbonyl Triphenylphosphine Iodide.—This complex was prepared exactly as described for the bromide above, using 0.62 g. (2 mmoles) of the π -allyliron tricarbonyl iodide instead of the bromide. In 10 min. 1.82 mmoles of gas was evolved. The product obtained was recrystallized three times from methylene chloride-pentane to give shiny brown plates, m.p. 121–122° dec. *Anal.* Calcd. for $\text{C}_{23}\text{H}_{20}\text{O}_2\text{PIFe}$: C, 50.95; H, 3.72. Found: C, 50.95; H, 3.81. The infrared spectrum in chloroform had carbonyl bands at 4.97 (vs) and 5.09 μ (vs).

If the corresponding chloride is prepared in the same way,

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the reaction mixture has carbonyl bands at 4.90 (vs) and 5.06 μ (vs). Attempts to isolate the product led to yellow crystals which decomposed as they were being purified.

N.m.r. Spectra.—The n.m.r. spectra were obtained using a Varian Associates 12-in. electromagnet and a frequency of 60

Mc. All samples were sealed in *vacuo* in 5 mm. o.d. glass sample tubes. They were studied at 30° as solutions in CDCl_3 . Chemical shifts, referred to external benzene, were obtained by the usual side-band technique using a Hewlett-Packard wide-range oscillator, Model 200CD.

[CONTRIBUTION FROM THE ORGANICS DIVISION, OLIN MATHIESON CHEMICAL CORPORATION, NEW HAVEN, CONNECTICUT]

Solvolysis Reactions in Chlorine Trifluoride and Bromine Pentafluoride: Preparation of the Tetrafluorochlorates and Hexafluorobromates of Potassium, Rubidium, and Cesium¹

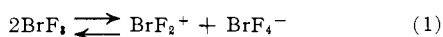
BY E. DOW WHITNEY,² RICHARD O. MACLAREN, CHARLES E. FOGLE, AND THOMAS J. HURLEY

RECEIVED JANUARY 25, 1964

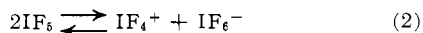
Solvolysis reactions of alkali metal fluorides in chlorine trifluoride and bromine pentafluoride at 100° resulted in the formation of the respective alkali metal tetrafluorochlorates and hexafluorobromates; the compounds KClF_4 , RbClF_4 , CsClF_4 , KBrF_6 , RbBrF_6 , and CsBrF_6 have been prepared. All of the above materials are powerful oxidizing agents, react violently with water, liberate iodine from aqueous iodide solutions, and interact explosively with common organic solvents.

Introduction

Halogen fluorides are a particularly interesting class of compounds from the standpoint of their unusual composition and great chemical reactivity. The fluorides are usually quite easy to prepare, their physical and chemical properties have been studied extensively, and several reviews on the subject have been published.³⁻⁷ Particular interest has been shown in the self-ionization of many of the halogen fluorides, and in the polyhalide salts resulting from the dissolution of metal halides in them. Indeed, many of the halogen fluorides act as solvents for the formation of a new class of acids and bases brought about *via* solvolysis reactions. Thus, bromine trifluoride and iodine pentafluoride have been shown by Emeléus and Woolf⁸ to act as ionizing solvents according to the following equilibria



and



Compounds containing the BrF_2^+ or IF_4^+ ions are thus considered as acids, whereas those containing BrF_4^- or IF_6^- ions are bases. Through solvolysis reactions in the above halogen fluorides, the bases KBrF_4 , AgBrF_4 , $\text{Ba}(\text{BrF}_4)_2$, and KIF_6 have been prepared.⁹⁻¹¹ No stable addition compounds of the type $\text{M}(\text{IF}_6)$ could be formed, however, when the alkali fluorides,

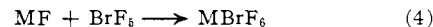
NaF , KF , or RbF , were mixed with iodine heptafluoride at room temperature.¹²

Although the tetrafluorohalates of cesium, rubidium, and potassium have been prepared through direct reaction of elementary fluorine with the corresponding alkali metal halides,¹³⁻¹⁷ there has been no report in the literature of bases of the type MClF_4 or MBrF_6 being formed as the result of solvolysis reactions in chlorine trifluoride or bromine pentafluoride, respectively.

In this paper are reported the results of solvolysis reactions between the fluorides of potassium, rubidium, and cesium, and the halogen fluorides, ClF_3 and BrF_5 , leading to the formation of the corresponding tetrafluorochlorates or hexafluorobromates, respectively. Our results can best be explained by the general reactions



and



To our knowledge this constitutes the first reported synthesis of bases containing the hexafluorobromate (BrF_6^-) ion, *i.e.*, compounds of the type MBrF_6 .

Experimental

Materials.—Anhydrous HF and 99% ClF_3 were obtained from the Matheson Co., Inc. Bromine pentafluoride and IF_5 were obtained from the General Chemical Division, Allied Chemical and Dye Corp. Prior to use, the halogen fluorides (except for IF_5) were allowed to distil under vacuum through a bed of NaF pellets maintained at 100° in a Monel pipe heated by means of a Fisher combustion tube furnace. In this manner HF impurities, and in the case of BrF_3 traces of BrF_5 , were removed. BrF_5 and ClF_3 were then fractionated under vacuum to remove traces of F_2 , and in the latter case Cl_2 and ClF if present. Fractionation was accomplished by a series of trap-to-trap distillations at -78°

(1) This work was supported by the Advanced Research Projects Agency and monitored by the Bureau of Naval Weapons, Department of the Navy, Contract NOrd 18210.

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