Organometallic Chemistry. 11.[1] Structure of Protonated 1,3-Butadieneiron Tricarbonyl in FSO_3H–SO_2 Solution Based on Its Carbon-13 Nuclear Magnetic Resonance Spectroscopic Study

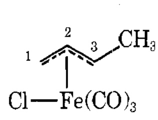
George A. Olah,* Gao Liang, and Simon H. Yu

Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106

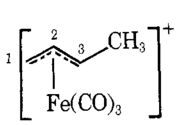
Received July 18, 1975

Protonation of 1,3-butadieneiron tricarbonyl (1) can yield different products depending on the strength of acid.[2] Addition of HCl forms covalent π-allylchloroiron tricarbonyl (2),[3] which upon treatment with silver tetrafluoroborate gives the π-allyliron tricarbonyl cation 3.[4] On the other hand, protonation by stronger acids, such as HBF_4 or $HClO_4$, produces the isomeric cation 4.[5] Interestingly, Young, Holmes, and Kaesz[6] reported the formation of a diprotonated dication 5 when 1 was treated with excess of the even stronger acid, FSO_3H. In contrast, Brookhart and Harris alternatively suggested that the diprotonated species 5 was actually better formulated as a monoprotonated σ–π complex 6.[7] Further experimental evidence supporting structure 6 has recently been provided by Whitesides and Arhart.[8]

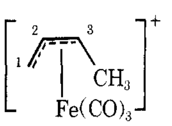
1



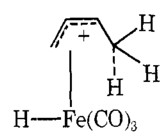
2



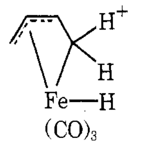
3



4



5



6

In order to clarify the structure of protonated butadieneiron tricarbonyl we now report the ^{13}C NMR spectroscopic study of the system in strong acids.

Results and Discussion

Addition of HCl or 1 equiv of FSO_3H in sulfur dioxide solution to butadieneiron tricarbonyl (1) at −60 °C affords species showing very similar ^{13}C NMR spectra (Figure 1). Table I summarizes the ^{13}C NMR carbon resonances, multiplicities, and coupling constants (J_{C-H}, in hertz) along with their assignments.[9] There are three allylic carbon resonances and one methyl resonance, based on their proton-coupled ^{13}C NMR spectra, clearly indicating protonation of the butadiene moiety to give a methylallyl system. C_3 experiences about 30 ppm more deshielding than C_1 owing in all probability to a methyl substituent effect.[10] According to the previous conclusions by Whitesides the covalent methylallylchloroiron tricarbonyl complex 2 was formed from 1 in HCl solution. The

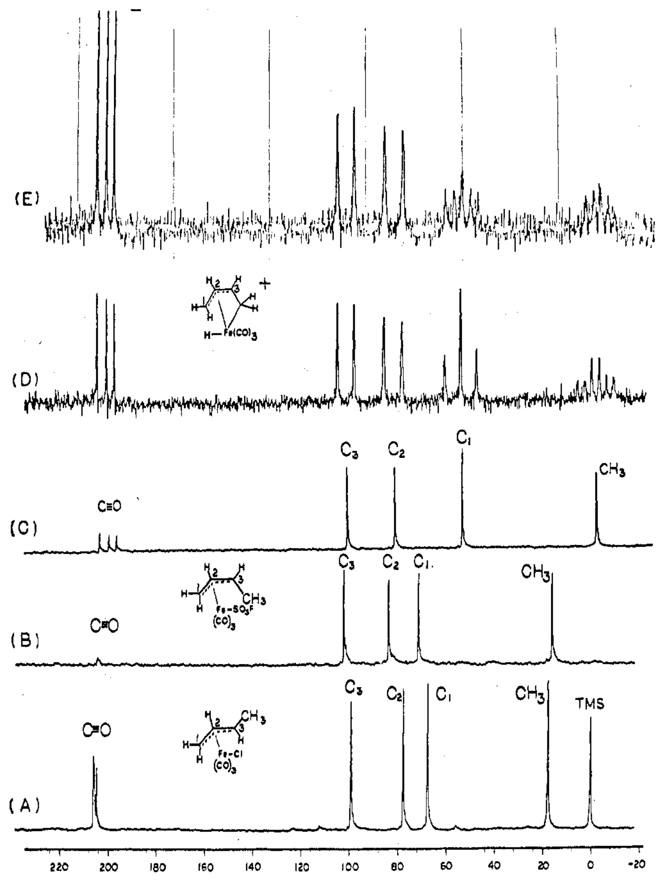


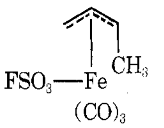
Figure 1. Carbon-13 NMR spectra of butadieneiron tricarbonyl complex in (A) HCl–SO_2 solution, proton decoupled; (B) FSO_3H (1 equiv)–SO_2 solution, proton decoupled; (C) FSO_3H (excess)–SO_2 solution, proton decoupled; (D) FSO_3H (excess)–SO_2 solution, proton coupled; (E) FSO_3D (excess)–SO_2 solution, proton coupled.

Table I. Carbon-13 NMR Parameters of Protonated 1,3-Butadieneiron Tricarbonyl in Varying Acid–SO_2 Solution [a]

Solution, °C	C_1	C_2	C_3	CO	CH_3
SO_2, −60	40.95 (t, 158.7)[b]	85.76 (d, 170.0)		209.0 (av)	
HCl–SO_2, −60	67.63 (t, 166.2)	77.71 (d, 170.0)	99.02 (d, 162.5)	205.89 205.48 204.64	17.66 (q, 127.5)
FSO_3H–SO_2, −60 (1 equiv)	70.88 (t, 168.0)	83.23 (d, 165.0)	101.38 (d, 162.5)	203.6 (av)	15.4 (q, 130.0)
FSO_3H–SO_2, −60 (excess)	53.06 (t, 165.5)	80.92 (d, 184.1)	100.29 (d, 173.9)	203.11 199.23 196.04	−2.76 (t-d, 146.5, 73.7)
FSO_3D–SO_2, −60 (excess)	52.78 (m)	80.88 (d, 182.9)	100.46 (d, 170.3)	203.22 199.35 196.16	−2.99 (m)

[a] Carbon resonances ($\delta_{^{13}C}$ are in parts per million from external $(CH_3)_4Si$ (capillary). [b] Multiplicities and coupling constants (J_{C-H}, Hz) are given in parentheses: d = doublet, t = triplet, q = quartet, t-d = triplet of doublets, m = multiplet.

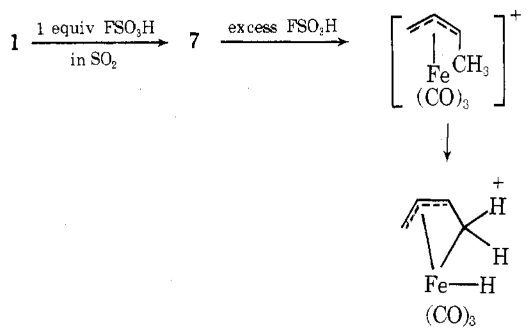
species **7** formed from **1** with 1 equiv of FSO_3H in SO_2 solution also seems to be covalently bonded because of the nearly identical nature of the ^{13}C NMR spectra for the species observed in both acid systems. Ionic species such as **3** and **4**, even if intermediately formed, are not observable under the conditions as they would be rapidly quenched by the fluorosulfate acids. As the *syn*-methylallyl cation **4** was observed in HBF_4 or $HClO_4$ solution,[4,5] the covalent species **7** is assigned to be the *syn*-methylallylfluorosulfatoiron tricarbonyl complex.



7

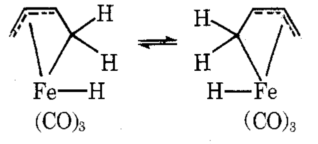
When the solution of **7** was treated with excess of FSO_3H, both the C_1 and the methyl carbon resonance were shielded by about 17 ppm. Although C_1 remains as a triplet (Figure 1D), the methyl quartet originally present in **7** now becomes a triplet of doublets indicating that the methyl carbon couples with two equivalent and a third different proton with J_{C-H} of 146.5 and 73.7 Hz, respectively. It is further noticed that the magnitudes of J_{C-H} for the methyl carbon, as well as C_2 and C_3, are substantially larger than those in **7**. The increase in coupling constant and the shielding of the methyl carbon and that of C_1 thus agrees with the formation of **6** as the $\sigma-\pi$ type complex in accordance with the suggestion of Brookhart and Harris.[7a,b] The observation of the geminal $^{13}C-Fe-^{1}H$ coupling (73.7 Hz) further substantiates the proposed structure.

The ^{13}C NMR observations are thus best interpreted in terms of initial formation (by 1 equiv of FSO_3H) of a covalent fluorosulfonic acid adduct **7** of butadieneiron tricarbonyl which upon treatment with excess of FSO_3H ionizes to give **6**.



6

Protonation of butadieneiron tricarbonyl (**1**) with excess FSO_3D in SO_2 solution at −60 °C, based on the proton-coupled ^{13}C NMR spectrum (Figure 1E), gives an ion bearing deuterium on both C_1 and methyl carbon, but not on C_2 and C_3. This observation is thus in agreement with a slow intramolecular exchange process.



Our ^{13}C NMR spectroscopic studies reinforce the conclusions reached by Brookhart[7] and Whitesides[8] that butadieneiron tricarbonyl is monoprotonated in strong acids and not diprotonated as suggested previously by Kaesz.[6]

Experimental Section

Materials. Butadieneiron tricarbonyl (**1**) was obtained from Ventron Corp. Alfa Products, and was used without further purification. Both FSO_3H and FSO_3D (Cationics, Inc.) were freshly distilled under nitrogen.

Preparation of Ions. A weighed amount of **1** in SO_2 was placed in an NMR tube at dry ice–acetone bath temperature (ca. −78 °C) under nitrogen and was dissolved in SO_2 containing a known amount of acid (equimolar or fewfold excess FSO_3H) with stirring to give an about 10% solution. Samples were immediately transferred to a precooled NMR probe for spectroscopic study.

^{1}H and ^{13}C NMR Spectroscopy. Both ^{1}H and ^{13}C NMR spectra were obtained as previously reported.[1]

Acknowledgment. Support of our work by the National Science Foundation is gratefully acknowledged.

Registry No.—**1,** 12078-32-9; **2,** 12287-49-9; **6,** 58904-55-5; **7,** 58919-15-6; HCl, 7647-01-0; FSO_3H, 7789-21-1.

References and Notes

(1) Part 10: G. A. Olah and S. H. Yu, *J. Org. Chem.*, in press.
(2) (a) R. Pettit and L. W. Haynes, "Carbonium Ions", Vol. 5, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N.Y., in press; (b) R. Pettit and G. F. Emerson, *Adv. Organomet. Chem.*, **1,** 1 (1964).
(3) (a) F. J. Impastato and K. G. Ihram, *J. Am. Chem. Soc.*, **83,** 3726 (1961); (b) E. Weiss and H. D. Murdoch, *Helv. Chim. Acta*, **45,** 1156 (1962); (c) A. N. Nesmeyanov and I. I. Kritskaya, *J. Organomet. Chem.*, **14,** 387 (1968); (d) T. H. Whitesides and R. W. Arhart, *J. Am. Chem. Soc.*, **93,** 5296 (1971).
(4) R. Pettit, G. F. Emerson, and J. E. Mahler, *Chem. Ind. (London)*, 836 (1964).
(5) R. Pettit and G. F. Emerson, *J. Am. Chem. Soc.*, **84,** 4591 (1962).
(6) (a) D. A. Young, J. R. Holmes, and H. D. Kaesz, *J. Am. Chem. Soc.*, **91,** 6968 (1969); (b) M. L. Naddox, S. H. Satfford, and H. D. Kaesz, *Adv. Organomet. Chem.*, **3,** 1 (1965).
(7) (a) M. Brookhart and D. L. Harris, *Inorg. Chem.*, **13,** 1540 (1974). (b) A reference pointed out that M. Brookhart and J. L. Crockett, Abstracts, 169th National Meeting of the American Chemical Society, Philadelphia, Pa., April 6–11, 1975, No. INOR-150, also represented this ^{13}C NMR spectrum.
(8) (a) T. H. Whitesides and R. W. Arhart, *Inorg. Chem.*, **14,** 209 (1975), and references cited therein; (b) T. H. Whitesides, R. W. Arhart, and R. W. Slaven, *J. Am. Chem. Soc.*, **95,** 5792 (1973).
(9) ^{1}H NMR spectra of these species are in accord with those previously reported. See ref 6.
(10) B. E. Mann, *Adv. Organomet. Chem.*, **12,** 135 (1974).

Alkylation of the Carbanion from Methyl Bis(ethylthio)acetate with Alkyl and Aralkyl Halides[1]

Leon M. Lerner

Department of Biochemistry, State University of New York, Downstate Medical Center, Brooklyn, New York 11203

Received December 10, 1975

Treatment of dithioacetals with strong base can result in carbanions capable of reacting with alkyl halides to give moderate to poor yields of products.[2] Corey and Seebach improved considerably upon this reaction with the introduction of the lithium salts of dithiane and its derivatives.[3] The importance of these reactions in addition to the formation of new carbon–carbon bonds stems from the convenience of utilizing the resulting bis(alkylthio)ketals to obtain ketones after hydrolysis, or methylene groups following reduction with Raney nickel. Recently a need arose in this laboratory for a two-carbon fragment that could be alkylated and act as a precursor to α-keto esters. A few years ago, a preparation of α-keto esters was reported using the carbanion from ethyl 1,3-dithiane-2-carboxylate in condensations with alkyl halides.[4] In this work ethyl 1,3-dithiane-2-carboxylate was prepared by a boron trifluoride catalyzed reaction of 1,3-propanedithiol with ethyl diethoxyacetate.

In the present report it is demonstrated that the activating effect of the ester group on the acidity of the neighboring proton is such that a simple bis(alkylthio)acetal will work equally well. Moreover, the cost of preparing the reagent as performed below is a small fraction of that required to prepare the dithiane derivative. Methyl bis(ethylthio)acetate (**1**) was