Journal of Organometallic Chemistry, 140 (1977) 203—210

THE STEREOSPECIFICITY OF PROTON ADDITION TO CYCLOHEPTATRIENEIRON TRICARBONYL

MAURICE BROOKHART *, KARIN J. KAREL

Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27514 (U.S.A.)

and LEWIS E. NANCE

Department of Chemistry, University of North Carolina at Wilmington, Wilmington, North Carolina 28401 (U.S.A.)

(Received May 9th, 1977)

Summary

Proton addition to cycloheptatrieneiron tricarbonyl to give the cycloheptadienyliron tricarbonyl cation has been shown to occur exclusively *exo* to iron in trifluoroacetic acid and sulfuric acid. The stereospecificity was determined by an ^{1}H NMR analysis of the cycloheptadienyl-d_2-iron tricarbonyl cation formed from reaction of the specifically labeled *exo*-cycloheptatriene-d_1-iron tricarbonyl complex with trifluoroacetic acid-d_1 and sulfuric acid-d_2.

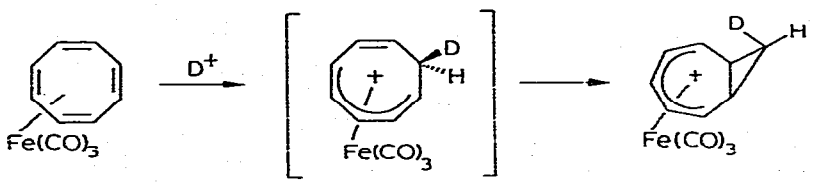
Introduction

In an effort to understand the reactions of low-valent transition metal complexes with simple electrophiles, the protonation reactions of several polyolefin-iron tricarbonyl complexes have been examined in various acid media [1—14]. Some general patterns of such reactions have emerged. When the organic ligand is a simple diene with no uncomplexed double bonds, protonation appears to occur with *endo* (*cis* to iron) stereochemistry [1]. In strong acids with poorly coordinating anions a cationic σ,π-allyliron hydride is formed [2—5]; strongly coordinating anions (X^-) such as bromide and chloride lead to neutral, covalent π-allyliron—X tricarbonyl derivatives [6].

When iron is bound to a diene unit of a conjugated triene or tetraene ligand, such as cyclooctatrieneiron tricarbonyl, cyclooctatetraeneiron tricarbonyl, and cyclononatetraeneiron tricarbonyl, protonation usually occurs at the β-carbon

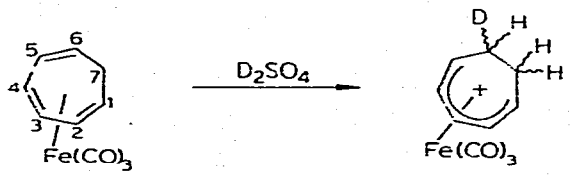
* To whom correspondence should be addressed.

of the uncomplexed double bond to give directly pentadienyliron tricarbonyl cations [8—11]. The stereochemistry of protonation in most of these cases has not been thoroughly investigated, but for cyclooctatetraeneiron tricarbonyl, (I) deuteration in D_2SO_4 clearly occurs with *exo* stereochemistry [8—10], leading ultimately to the stereospecifically deuterated species II.



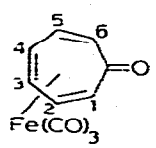
(I) (II)

The deuteration of cycloheptatrieneiron tricarbonyl (III), has been carried out in D_2SO_4 and shown to be stereospecific [8]; however, since *exo* and *endo* resonances in the resulting cycloheptadienyliron tricarbonyl cation (IV) could not be assigned with certainty it was unclear whether deuteration occurred with *exo* or *endo* stereochemistry *.



(III) (IV)

An exception to these generalizations appears to be troponeiron tricarbonyl (V) studied by Eisenstadt [12] and Hunt [13]. Both observed *exo* protonation in trifluoroacetic acid, and based on deuterium labeling results reported by Hunt [13] protonation apparently occurs at the bound carbon, C(1) **.



(V)

In view of the unexpected result for protonation of V and the general lack of data concerning the stereochemistry of protonation of iron tricarbonyl complexes of simple cyclic triene and tetraene complexes, we felt it was important

---

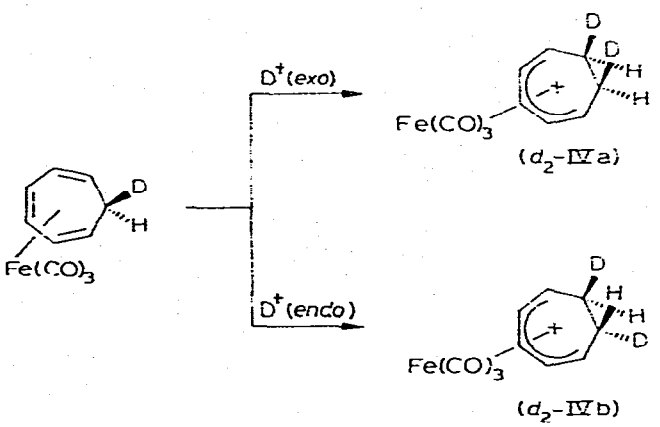
* In fact, Wilkinson [8] assigned the highest field resonance in IV to the *endo* protons based on other model systems. This led to the assignment of stereospecific *endo* protonation. However, as we show later in the paper the resonance for the *exo* protons occurs at highest field and thus *exo* stereospecificity is indicated.

** Eisenstadt [12b] has recently offered an alternative explanation based on low temperature studies in HSO_3F. In addition, protonation of V is further complicated by the fact that kinetically controlled oxygen protonation occurs initially [14].

to establish unequivocally the stereochemistry of protonation of cycloheptatrieneiron tricarbonyl (III). In this paper we report the results of such studies.

Results and discussion

The method for determining the stereochemistry of protonation of cycloheptatrieneiron tricarbonyl (III) is based on the observation of Maltz [15] that treatment of III with CH_3O^-/CH_3OD results in stereospecific exchange and production of *exo*-d_1-III. If *exo*-d_1-III is subject to stereospecific deuteration then two possibilities obtain. If *exo* deuteration applies, the *diexo*-d_2 ion IVa is formed, whereas *endo* deuteration results in the *exo*-d_1-*endo*-d_1 ion IVb. Since Wilkinson [8] has demonstrated that the *exo* and *endo* resonances are easily



resolved (even though specific *exo* and *endo* assignments cannot be made with certainty) ions IVa and IVb will be easily distinguished. At high fields ion IVa will exhibit only a two-proton *endo* signal, while ion IVb will exhibit two signals in a 1/1 ratio for the single *exo* proton and the single *endo* proton.

The validity of this interpretation relies on a correct stereochemical assignment by Maltz [15] of the d_1-III. Since this assignment was based on expected differences in the C—H infrared stretching frequencies of the 7-*endo* and 7-*exo* hydrogens of III, we felt this should be verified by other methods which we here describe before discussing the protonation results.

A detailed proton NMR study was carried out on III and extensive decoupling experiments were performed. Chemical shifts and coupling constant data are summarized in Tables 1 and 2. In general, free methylene groups contained in otherwise cyclic conjugated metal complexes are tilted out of the plane of the ring away from the metal. Such distortion results in increased vicinal coupling of the *endo* proton with the adjacent ring protons (in this case (H(1) and H(6)) relative to the *exo* proton. This difference in coupling has been used previously in assigning stereochemistry [13,16]. In the present case the differences are small but using this criterion the *exo* proton is assigned to the resonance at δ 1.89 ppm ($J_{7\,exo,1}$ 3.4 Hz, $J_{7\,exo,6}$ 3.5 Hz) and the *endo* proton to the resonance at δ 2.12 ppm ($J_{7\,endo,1}$ 4.3 Hz, $J_{7\,endo,6}$ 4.2 Hz). This assignment is in accord with Maltz's assignment of *exo* deuterium in d_1-III in that base-catalyzed deuteri-

TABLE 1

^{1}H NMR CHEMICAL SHIFT ASSIGNMENTS FOR COMPOUNDS III AND IV

Compound	Medium	Temperature	Chemical shifts[a]						
			H(1)	H(2,3)	H(4)	H(5)	H(6)	H(7X)	H(7N)
III	C_6D_6	Amb.	2.89	4.59—4.74	2.72	5.68	5.03	1.89	2.12
7-*exo*-d_1-III	C_6D_6	Amb.	2.89	4.59—4.74	2.72	5.68	5.03	—	2.12
			H(1,5)	H(2,4)	H(?)	H(6N,7N)	H(6X,7X)		
IV	TFA/CD_2Cl_2	0°C	4.98[b]	6.00	7.11	2.69	1.87		
d_2-IV[c]	d_1-TFA/CD_2Cl_2	0°C	4.98[b]	6.00	7.11	2.69	[c]		
	D_2SO_4/$CDCl_3$	Amb.	4.96[d]	5.97	7.10	2.70	[c]		

[a] Chemical shifts in δ (ppm) relative to internal C_6HD_5 (δ 7.27) unless otherwise stated. [b] C_2HDCl_2 (δ 5.28) used as internal reference. [c] A small residual signal appears at ca. δ 1.9. [d] $CHCl_3$ (δ 7.27) used as internal reference.

TABLE 2

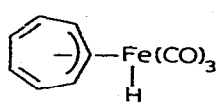
COUPLING CONSTANTS[a] FOR COMPOUNDS III AND IV

III in C_6D_6	IV in TFA
$J_{1,6}$ = 1.4 or 0.9	$J_{1,2} = J_{4,5}$ = 9.2
$J_{1,7X}$ = 3.4; $J_{1,7N}$ = 4.3	$J_{1,3} = J_{3,5}$ = 1.4
$J_{4,5}$ = 7.9	$J_{2,3} = J_{3,4}$ = 6.4
$J_{4,6}$ = 0.9 or 1.4	$J_{1,7N} = J_{5,6N} \cong 6.6$ [b]
$J_{5,6}$ = 10.6	$J_{6N,7N} \cong 10$ [b]
$J_{5,7X}$ = 2.6; $J_{5,7N}$ = 1.9	
$J_{6,7X}$ = 3.5; $J_{6,7N}$ = 4.2	
$J_{7X,7N}$ = 22.0	

[a] Coupling constants in hertz. [b] Based on analysis of the AA'XX' system (H(1), H(5), H(6N), H(7N) in d_2-IVa.

um exchange results in disappearance of the signal at δ 1.89 ppm.

A second and more convincing method used to verify the stereochemistry of d_1-III was to subject the complex to thermal isomerization. From previous studies on polyolefin-iron carbonyls it was clear that hydrogen migration in this complex could occur and that the general mechanism for migration would involve metal attack at the *endo*-hydrogen to yield a π-allyl iron hydride species such as VI which could collapse back to III [17]. Such a mechanism applied to *exo*-d_1-III would result in deuterium scrambling to all other positions except



(VI)

the *endo* position. If the d_1-complex were to have the opposite stereochemistry (i.e., *endo*-d_1-III) then rearrangement via this mechanism would result in no deuterium scrambling to other sites (the iron bound deuterium would always return to the *endo* position) and thus no ^1H would be incorporated into the *endo* site.

When *exo*-d_1-III is heated to 72°C, deuterium is observed to scramble by watching ^1H incorporation into the δ 1.89 ppm position ($t_{1/2}$ ca 7 h). The intramolecular nature of this process was confirmed by using ^2H NMR to follow the incorporation of deuterium into sites H(1)—H(6).

Thus, assuming a π-allyliron hydride mechanism these results also indicate *exo* stereochemistry for d_1-III. Since ^1H NMR, IR and thermal isomerization results all suggest the same stereochemistry, the initial *exo* assignment by Maltz can be accepted with certainty.

Protonation results

Treatment of d_1-III with degassed d_1-TFA results in formation of a cycloheptadienyl-d_2-iron tricarbonyl cation which shows four resonances with integration ratios of 1/2/2/2 at δ (ppm) 7.11 (H(3), triplet of triplets), 6.00 (H(2), H(4) doublet of doublets), 4.98 (H(1), H(5) (br) triplet) and δ (ppm) 2.69 (br, unresolved). A small residual band appears at δ 1.87 ppm. The absence of the

δ 1.87 ppm band and the presence of a two proton resonance at δ 2.69 ppm clearly indicate that deuteration has occurred stereospecifically *exo* resulting in formation of ion IVa as outlined above. The two proton signal at δ 2.69 ppm can then be assigned to the H(6), H(7) *endo* protons and the almost undetectable signal at δ 1.87 ppm to the residual ^{1}H in the *exo* positions *. Coupling constants and chemical shifts are summarized in Tables 1 and 2. The shifts are similar to ones reported for this ion by Wilkinson [8]; measured J values are in accord with those reported for IV [8] and are consistent with values reported for other pentadienyliron tricarbonyl cations [9—13]. From integration of the residual ^{1}H signal at δ 1.87 ppm it can be estimated that the stereospecificity of protonation in d_1-TFA is ⩾ 95% **. Similar experiments were carried out in D_2SO_4 with similar results except that deuteration appeared to be somewhat less stereospecific (ca. ⩾90%).

The results reported here for cycloheptatrieneiron tricarbonyl and those reported previously for cyclooctatetraeneiron tricarbonyl support the general idea that protonation of the free double bond of conjugated cyclic triene- and tetraene-iron tricarbonyl complexes occurs stereospecifically *trans* to iron. How general this feature of proton addition to related complexes will prove to be must await further experimental results.

Experimental

General. All materials were handled under an atmosphere of dried, oxygen-free nitrogen gas. ^{1}H NMR spectra were recorded on a Varian XL-100 FT-NMR spectrometer.

Cycloheptatrieneiron tricarbonyl

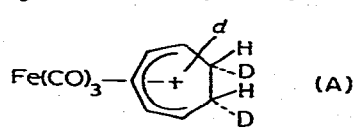
Freshly distilled cycloheptatriene (6.3 g, 68 mmol) and $Fe(CO)_5$ (8.9 g, 46 mmol) were photolyzed in degassed benzene (150 ml) for 12 h using a 450 W Hanovia medium-pressure mercury are lamp. The dark red solution was filtered through Celite, concentrated under reduced pressure, and then chromatographed under nitrogen on an activity III Al_2O_3 column (2.8 × 30 ml) with degassed hexane. The first yellow band to elute is the desired cycloheptatrieneiron tricarbonyl (ca. 12% yield) identical with that previously prepared [18].

7-exo-Deuterocycloheptatrieneiron tricarbonyl

Cycloheptatrieneiron tricarbonyl (1.4 g, 6 mmol) was added to 15 ml of 0.1 M

---

* A referee has suggested that if the *exo/endo* assignments in IV are incorrect and if *endo* exchange coupled with scrambling of the *exo-d* into the ring occurs, then the observed species would be the d_3-ion (A) which is specifically *endo* dideuterated. (Such an exchange and *endo* deuterium incor-



(A)

poration occur for cyclohexadiene iron tricarbonyl, see ref. 1a). This possibility is ruled out by the observation that deuteration of III in d_1-TFA results in incorporation of only a single deuterium indicating no exchange.

** Approximate corrections were made for the residual ^{1}H in the d_1-TFA and in d_1-III; it was assumed there was no isotope effect in the protonation reaction.

sodium methoxide in methanol-d_1 and stirred for 5.5 h. The reaction was quenched with saturated aqueous NH_4Cl. The deuterated complex was extracted with ether, dried over K_2CO_3, concentrated and the residual orange oil distilled under vacuum to give ca. 0.98 g (70%) of the 7-*exo*-d_1-III.

Protonation of cycloheptatrieneiron tricarbonyl with trifluoroacetic acid (TFA)

TFA and CD_2Cl_2 were degassed in Schlenk tubes on a vacuum line by freeze-pump-thaw cycles. TFA (0.3 ml) was pipetted into a cooled (—78°C) 5 mm NMR tube which had been sealed to a female 14/20 glass joint and flushed with N_2. Approximately 50 mg of complex was dissolved in 0.2 ml of degassed CD_2Cl_2 and pipetted onto the frozen TFA. The TFA was allowed to thaw while the mixture was stirred with a glass rod. The sample was then frozen in liquid nitrogen and sealed under vacuum.

Deuteration of 7-exo-deuterocycloheptatrieneiron tricarbonyl with d_1-TFA

The above procedure was repeated, using the deuterated cycloheptatriene complex and d_1-TFA.

Deuteration of cycloheptatrieneiron tricarbonyl with deutero-sulfuric acid

Degassed D_2SO_4 (0.3 ml) was pipetted into an N_2-filled NMR tube (modified as described above), and cooled to 0°C. Approximately 50 mg of complex in 0.2 ml of degassed $CDCl_3$ were added. The sample was stirred, frozen in liquid nitrogen and sealed under vacuum.

Thermal isomerization of 7-exo-d_1-III

The 7-*exo*-d_1-III complex (ca. 50 mg) and degassed C_6D_6 (0.5 ml) were pipetted into an NMR tube (modified as described above). The sample was further degassed by three freeze-pump-thaw cycles and sealed under vacuum. Integration of the NMR spectrum showed no *exo*-hydrogen. The NMR tube was wrapped in aluminum foil and placed in an oil bath for 1 h at 52°C, then 2 h at 72°C. Integration of the resulting spectrum showed ca. 25% incorporation of ^1H into the *exo* site. Scrambling increased to ca. 60% after an additional 6 h at 72°C.

Acknowledgment

Acknowledgment is made to the National Science Foundation (Grant MPS75-01239) and the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

References

1 (a) T.H. Whitesides and R.W. Arhart, J. Amer. Chem. Soc., 93 (1971) 5296; (b) T.H. Whitesides, R.W. Arhart and R.W. Slaven, ibid., 95 (1973) 5792.
2 M. Brookhart and D.L. Harris, Inorg. Chem., 13 (9174) 1540.
3 T.H. Whitesides and R.W. Arhart, Inorg. Chem., 14 (1975) 209.
4 M. Brookhart, T.H. Whitesides and J.H. Crockett, Inorg. Chem., 15 (1976) 1550.
5 D.A.T. Young, J.R. Holmes and H.D. Kaesz, J. Amer. Chem. Soc., 91 (1969) 6968.
6 (a) F.J. Impastato and K.G. Ihrman, J. Amer. Chem. Soc., 83 (1961) 3726; (b) G.F. Emerson, J.E. Mahler and R. Pettit, Chem. Ind. (London) (1964) 836; (c) D.H. Gibson and D.K. Erwin, J. Organometal. Chem., 86 (1975) C31.

7 (a) D.H. Gibson and R.L. Vonnahme, J. Amer. Chem. Soc., 94 (1972) 5090; (b) J. Chem. Soc., Chem. Commun., (1972) 1021.
8 A. Davison, W. McFarlane, L. Pratt and G. Wilkinson, J. Chem. Soc., (1962) 4821.
9 W. McFarlane, L. Pratt and G. Wilkinson, J. Chem. Soc., (1963) 2162.
10 (a) M. Brookhart, E.R. Davis and D.L. Harris, J. Amer. Chem. Soc., 94 (1972) 7853; (b) M. Brookhart and E.R. Davis, Tetrahedron Lett., (1971) 4349.
11 E.J. Reardon and M. Brookhart, J. Amer. Chem. Soc., 95 (1972) 4311.
12 (a) A. Eisenstadt and S. Winstein, Tetrahedron Lett., (1971) 613; (b) A. Eisenstadt, J. Organometal. Chem., 97 (1975) 443.
13 D.F. Hunt, G.C. Farrant and G.T. Rodeheaver, J. Organometal. Chem., 38 (1972) 349.
14 M. Brookhart, C.P. Lewis and A. Eisenstadt, J. Organometal. Chem., 127 (1977) C14.
15 H. Maltz and B.A. Kelley, J. Chem. Soc., Chem. Commun., (1971) 1390.
16 T.H. Whitesides and R.W. Arhart, J. Amer. Chem. Soc., 93 (1971) 5296.
17 T.H. Whitesides and J.P. Neilan, J. Amer. Chem. Soc., 98 (1976) 63 and ref. therein.
18 R. Burton, L. Pratt and G. Wilkinson, J. Chem. Soc., (1961) 594.