Journal of Organometallic Chemistry, 421 (1991) 257–264
Elsevier Sequoia S.A., Lausanne
JOM 22182

Synthesis of tetracarbonyl(η^3-2-hydroxypropenylium)iron complexes

M. Frey and T.A. Jenny *
Institut de chimie organique, University of Fribourg, Fribourg (Switzerland)

(Received June 24th, 1991)

Abstract

Dehydrohalogenation of halogeno-tricarbonyl(2-hydroxypropenyl)iron complexes (**6**) with a silver tetrafluoroborate/pyridine complex gives the dimeric tricarbonyl(oxyallyl)iron complexes (**4**), or, in the presence of CO, the tetracarbonyl(2-hydroxypropenylium)iron salts (**8**). The latter complexes are soluble only in strongly polar solvents, and show unprecedentedly large *geminal* ^2J(HH) coupling constants (5.9–6.1 Hz) for the π-complexed allylic ligands. The dimeric methyl-substituted oxyallyl complex (**4b**) undergoes a facile intramolecular rearrangement followed by fragmentation to yield tricarbonyl(η^4-2-hydroxybutadiene)iron (**10**). Neither the methyl-substituted nor the cationic tetracarbonyloxyallyl complexes undergoes cycloaddition with furan.

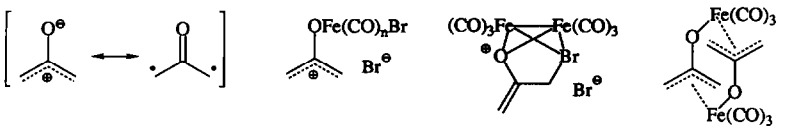
Introduction

Oxyallyl (**1**), a formal analog of trimethylenemethane, may be involved as a short-lived intermediate in well-known reactions such as the Favorski rearrangement and the cycloaddition of α,α'-dihalogenoketones to dienes under reductive conditions (Noyori reaction). We previously described [1] the synthesis of the (oxodimethylenemethane)iron dimer **4a**, a transition metal stabilized oxyallyl system, and the present work was initiated to investigate the possible involvement of π-complexed species in the latter reaction.

Noyori et al. [2] tentatively assigned enolate structure **2** to the reaction intermediate, whereas Fölisch et al. [3] proposed the dinuclear-bridged complex **3** on the basis of the X-ray structure of a closely related sulfur-containing compound. Either product could undergo loss of bromide ion to yield a free allyl cation.

The observed lack of reactivity of complex **4a** towards cycloaddition, e.g. [4 + 3] addition to furan, might be due to the low electrophilicity of the complexed ligand or insufficient stabilization of a transitorily formed unsubstituted allyl cation. In order to throw light on the matter we examined both alkyl-substituted derivatives

and cationic analogs of complex **4a**.



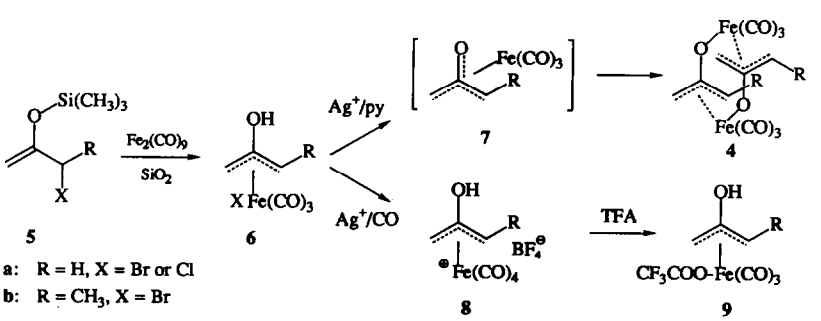
1 2 3 4a

Results and discussion

The methyl-substituted complex **4b** was synthesized in two steps by complexation of the known silyl enol ether **5b** with $Fe_2(CO)_9$ followed by dehydrohalogenation of the isolated intermediate, bromotricarbonyl(η^3-2-hydroxy-2-butenyl)iron (**6b**), by treatment with the salt [Ag(pyridine)]BF_4 generated *in situ*. Two equivalents of silver salt are required, since the precipitate consists of [Ag(pyridine)$_2$]BF_4 and only silver ions in solution remove halides. The function of the precipitated silver complex is probably simply to lower the concentration of dissolved pyridine. Most of the protecting trimethylsilyl groups were cleaved off during complexation, leaving only minor amounts of the silyl-protected complex of **6**. Complete conversion to complex **6b** occurred during work-up, including chromatography on silica gel (Scheme 1).

Complex **6b** possesses the structure shown, containing an *endo*-oriented allylic ligand and a *Z*-configurated CH_3 group. The position of the latter was deduced from the absence of a ^4J coupling between H_{syn}–C(1) and H–C(3) in the ^{1}H NMR spectrum (cf. Table 1) (*syn* and *anti* with respect to the substituent at C(2)): the ^4J coupling constant between the *syn*-hydrogens arranged in a *W*-shape in the unsubstituted complex **6a** has a value of 3.5 Hz. Assignment of the *syn*- and *anti*-hydrogens, in turn, were based on the findings that mutual NOEs are observed between (a) the signal of the OH group (5.3 ppm) and the signals of the CH_3 group (2.0 ppm) and H_{syn}–C(1) (4.16 ppm), and (b) between those of H_{anti}–C(1) (3.06 ppm) and H_{anti}–C(3) (4.09 ppm). Upon addition of Eu(fod)$_3$, there was a 1.2-fold larger displacement of the signal at 4.16 ppm (H_{syn}–C(1)) than of the signal at 3.06 ppm (H_{anti}–C(1)).

The *endo*-orientation is commonly adopted by 2-substituted allylic ligands for steric reasons. Furthermore, the observed dependence of the chemical shifts for



Scheme 1.

Table 1

^{1}H NMR data (δ (ppm), multiplicity, J (Hz))

Compound	H-C(1)		H-C(3)		H-C(4)	OH or $Si(CH_3)_3$
	anti [a]	*syn*	*anti*	*syn*		
5a (X = Cl)	4.12 (d, 1.5 Hz, 1H)	4.18 (d, 1.5 Hz, 1H)	3.58 (s, 2H)			0.16 (s, 9H)
5b	4.01 (d, 1.6 Hz, 1H)	4.16 (d, 1.6 Hz, 1H)	4.25 (q, 6.8 Hz, 1H)		1.55 (d, 6.8 Hz, 3H)	0.17 (s, 9H)
6a-$Si(CH_3)_3$	3.25 (m, 1H)	3.9 (m, 1H)	3.25 (m, 1H)	3.9 (m, 1H)		0.09 (s, 9H)
6b-$Si(CH_3)_3$	3.11 (d, 3.6 Hz, 1H)	3.71 (d, 3.6 Hz, 1H)	4.22 (q, 6.4 Hz, 1H)		1.53 (d, 6.4 Hz, 3H)	−0.01 (s, 9H)
6a (X = Cl)	2.98 (br s, 1H)	3.37 (br s, 1H)	2.98 (br s, 1H)	3.37 (br s, 1H)		3.71 (br s, 1H)
6a (X = Br)	3.10 (m, 1H)	3.29 (m, 1H)	3.10 (m, 1H)	3.29 (m, 1H)		3.36 (br s, 1H)
6b	2.88 (d, 4.3 Hz, 1H)	3.01 (d, 4.3 Hz, 1H)	3.99 (q, 6.6 Hz, 1H)		1.42 (d, 6.6 Hz, 3H)	3.39 (br s, 1H)
4a	1.70 (br s, 2H)	2.77 (br s, 2H)	1.70 (br s, 2H)	2.77 (br s, 2H)		
4b	1.22 (d, 5.3 Hz, 2H)	2.57 (d, 5.3 Hz, 2H)	2.99 (q, 6.3 Hz, 2H)		1.47 (d, 6.6 Hz, 6H)	
8a [b]	3.04 (m, 1H)	4.19 (m, 1H)	3.04 (m, 1H)	4.19 (m, 1H)		
8b [b]	2.74 (br d, 1H)	4.12 (br d, 1H)	3.9 (q, 6.4 Hz, 1H)		2.11 (d, 6.4 Hz, 3H)	
9a [b]	2.56 (br d, 1H)	4.45 (br d, 1H)	2.56 (br d, 1H)	4.45 (br d, 1H)		
9b [b]	2.3 (d, 4.4 Hz, 1H)	4.37 (d, 4.4 Hz, 1H)	3.32 (q, 6.6 Hz, 1H)		2.11 (d, 6.6 Hz, 3H)	

^{13}C NMR and IR data

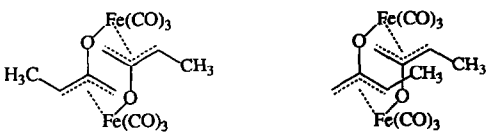
Compound	IR (ν, cm^{-1})		^{13}C NMR (δ (ppm), multiplicity [^1J(CH) (Hz)])				
	C≡O	C–O	C≡O	C(1)	C(2)	C(3)	C(4)
4a	2093, 2082, 2011, 1982	1514	209.6, 207.9	44.6	168	44.6	
6a (X = Cl)	2094, 2029, 2004	1352	205.2, 204.7	54.3 (dd) [167,158]	148.1 (s)	54.3 (dd) [167,158]	
6a (X = Br)	2094, 2029, 2004	1352	207, 206.5	51.4 (dd) [165, 157.5]	148.1 (s)	51.4 (dd) [165,157.5]	
6b	2090, 2040, 2020, 2000	1600	207.6, 206.6, 206.5	48.7 (dd) [164.7, 156.9]	146.2 (s)	68.9 (d) [163.9]	13.6 (q) [128.2]
8a			194.6, 195.6, 198.5	40.8 (t) [163.7]	155.1 (s)	40.8 (t) [163.7]	
9a			205.7, 206.1	54.2	153.3	54.2	
9b	2130, 2040, 2020	1625	197.2, 197.8, 200.1, 200.7	39.8 (t) [163]	153.9 (s)	63.2 (d) [159.7]	15.9 (q) [130]

[a] *syn* and *anti* with respect to the substituent on C(2). [b] Solvent: TFA-*d*.

the *syn*- and *anti*-hydrogens on the electronegativity of the ligand X in all complexes of type **6** is fully consistent with the known behaviour of unsubstituted *endo*-oriented allylic iron carbonyl complexes [4].

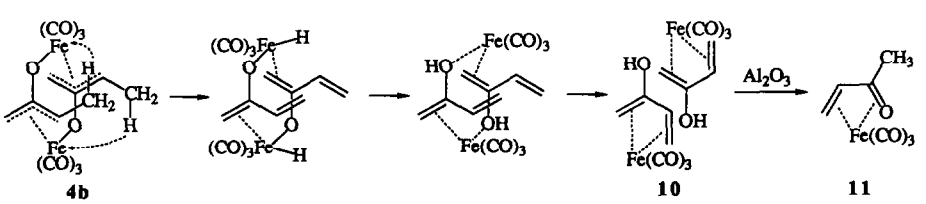
Dehydrohalogenation of **6b** yielded two complexes, the expected dimeric oxyallyliron complex **4b** and tricarbonyl(η^3-2-hydroxybutadiene)iron (**10**) [5], in varying ratios. In the experiment giving the best yield of **4b**, products **4b** and **10** were formed in a ratio of 3/2, as indicated by ^{1}H NMR spectroscopy.

There is no rigorous proof of the dimeric nature of compound **4b** because its instability precludes any further analytical investigations, especially by mass spectrometry, but there are very similar highfield shifts in the ^{1}H NMR spectrum for 1-H_{syn} and 1-H_{anti} on going from **6b** to **4b** (0.44 and 1.66 ppm) as on going from **6a** to **4a** (0.52 and 1.40 ppm). The configuration of the methyl substituent in complex **4b** remains *Z*, as shown again by the absence of a ^4J(HH) *W*-coupling. Of the two possible structures **A** and **B** for a dimeric complex **4b** only one is obtained. Neither of these could be assigned unambiguously, although isomer **B** is expected to be formed preferentially because of the smaller steric interactions in the folded dimeric structure, assumed to be similar to that of the unsubstituted complex **4a**, which possesses a folded, dynamic C_2 structure [1].



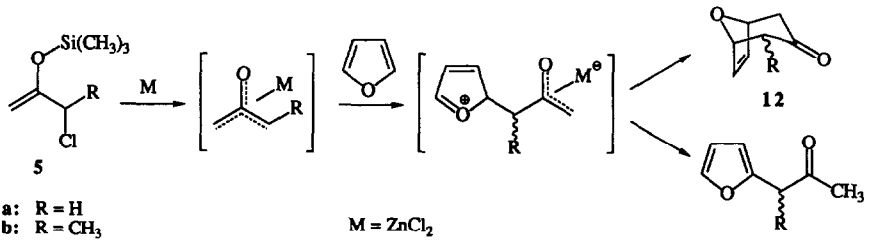
4b

In solution, even at low temperatures (−78 °C), **4b** gradually decomposes, and is partly converted into **10**, the only isolable product (yield up to 70%). In a typical run, the decrease in the amount of **4b** in dichloromethane at room temperature had a first-order rate constant of $k = 8 \times 10^{-3}$ s^{-1} and **10** was formed in a relative yield of 20%, as shown by ^{1}H NMR spectroscopy by using an internal standard. It is difficult to define the mechanism of this facile transformation, since intermolecular deprotonation or protonation steps are probably not involved: such steps would immediately transform the dienol complex **10** into the known heterodienic complex **11** [6], a reaction which even occurs during chromatography of **10** on neutral alumina. One possible mechanism (Scheme 2) would start from a dimeric complex with a double hydrogen shift from carbon to iron together with a release of the carbon atoms C(3) of the allylic ligands from the coordination sphere of iron and formation of freely rotating vinyl groups. Such hydrogen shifts could be facilitated by the short trajectory distance in the high energy conformer of isomer



4b **10** **11**

Scheme 2.



Scheme 3.

B of **4b**. This distance is about 2 Å as estimated from a molecular model based on the structural data for **4a**, i.e. only slightly above the distance between iron and an agostic [7] hydrogen. Transfer of the hydrogen atoms from iron to the oxygen atoms of the organic ligands is favored thermodynamically. Complexation of the rotated free vinyl groups and release of the hydroxyl group ligands would finally lead to two molecules of **10**.

Evidence for the existence of the monomeric complex **7b**, at least in the gas phase, was provided by the mass spectra of the complexes investigated so far. On *EI* ionization, both complex **6b** and **4b** yield typical mass spectra showing fragments from consecutive losses of CO ligands. In addition, further fragments from either a loss of the halogen atom X or of both H and X, are noted. The loss of both H and X can be clearly seen to take place in a thermal process prior to ionization from the pronounced increase in the relative intensity of the peaks (tentatively) assigned to **7b** with increase in the source temperature. This assignment is based on both the isotopic pattern and the exact mass of the pertinent mass fragments.

Nevertheless, preparative flash vacuum pyrolysis of complex **6b** in the presence of furan gave no trace of the expected cycloaddition product **12**, but instead yielded 2-butanone (27%). In an attempt to trap the proposed intermediate **7b** in a cycloaddition reaction, the dehydrohalogenation of **6b** was carried out in furan as solvent, but again no cycloaddition product **12** was isolated (Scheme 3).

An alternative to a concerted [4 + 3]-cycloaddition would be a stepwise mechanism (Scheme 3) involving electrophilic addition of oxyallyl to furan followed by an intramolecular attack on the enolic double bond by the intermediate carbocation. This route may perhaps be followed to some extent (6% yield) in the reaction of silyl enol ether **5a** (X = Cl) with furan in the presence of $ZnCl_2$ [1]. The replacement of the halide ligand in complexes of type **6** by CO should lead to increased electrophilicity and thereby enhance the reactivity towards furan by virtue of the resulting net positive charge on the tetracarbonyl complexes of type **8**.

8

Complexes **8a** and **8b** were readily prepared from the bromo complexes **6a** and **6b** by dehalogenation with $AgBF_4$ under an atmosphere of CO in CH_2Cl_2 [8] followed by extraction of the sparingly soluble precipitate with trifluoroacetic acid.

It is noteworthy that the ^2J coupling constants between the *syn* and *anti* protons in complexes **8a** and **8b** are 5.9 and 6.1 Hz, respectively, unprecedentedly large values for *geminal* coupling constants for π-complexed allylic ligands. This points to an important contribution by limiting metallacyclobutanone structures [1] in these complexes, a conclusion which is corroborated by the changes in the ^{13}C NMR chemical shifts of complexes of type **6** compared with those for type **4** or **8**.

The *EI* mass spectra of complexes **8a** and **8b** show only fragments from a loss of both HBF_4 and one CO ligand as the ions of highest mass. The mass spectra therefore indicate a facile thermal fragmentation to yield exclusively the still elusive monomeric complexes **7a** and **7b**.

Surprisingly, complexes of type **8** proved to be stable in trifluoroacetic acid for several hours at room temperature, although small amounts of the trifluoroacetato complexes **9a** and **9b** were formed (yield up to 10%). **9a** was also made independently from **5a** and CF_3CO_2Ag. In acetonitrile and acetone, however, both **8a** and **8b** decompose with a half-life time in the region of 1 h, presumably via exchange of one CO ligand by a solvent molecule. These observations point to a very labile CO ligand. Decomposition in the presence of furan, however, afforded no adduct, either in the presence or absence of base (pyridine).

Experimental

All ^1H and ^{13}C NMR spectra were recorded on a Bruker AM360 spectrometer operating at 360.13 and 90.56 MHz, respectively, and the *EI* MS spectra were obtained with a VG Instrument 70/70E instrument. The elemental analyses were carried out in the Analytical Laboratory of CIBA–GEIGY in Marly (Switzerland).

The silyl enol ethers **5a** and **5b** were prepared by published procedures [9]. All experiments were carried out under pure dry nitrogen using dried and oxygen-free solvents and reagents.

*Preparation of **6b***

2-Trimethylsiloxy-3-bromobutene (**5b**) (12 g, 53.8 mmol) and $Fe_2(CO)_9$ (40 g, 110 mmol) were stirred in 40 ml of benzene at 35 °C for 4 d. The dark solution was filtered and evaporated to dryness. The residue was dissolved in diethyl ether and the solution filtered through a plug of glass wool. The ^1H NMR spectrum of the solution showed it to contain a mixture of silylated (**6b**-Si$(CH_3)_3$) and desilylated **6b**. Complete conversion into **6b** occurred during subsequent chromatography on silica gel with diethyl ether as eluent. The orange fraction was evaporated and the residue crystallized from CH_2Cl_2 at −78 °C to yield 6.8 g (43%) of pure **6b**. Small scale preparations consistently gave much lower yields. Found: C, 28.97; H, 2.45. $C_7H_7FeBrO_4$ (290.75) calc.: C, 28.89; H, 2.41%.

6b: MS: *m/e* (rel. intensity) 264/262 (4), 236/234 (13), 211 (5), 210 (8), 208/206 (10), 183 (10), 182 (49), 155 (10), 154 (35), 127 (15), 126 (43), 109 (20), 108 (100), 86 (33), 84 (52), 73 (30), 56 (60), 49 (90), 43 (100).

*Preparation of **4b***

To a solution of 694 mg (3.57 mmol) $AgBF_4$ in 50 ml of dry diethyl ether was added 25 ml of diethyl ether containing 282 mg (3.57 mmol) of pyridine. A white precipitate was formed. To the mixture was added 500 mg (1.72 mmol) of **6b** in 25

ml of diethyl ether. The mixture was stirred at room temperature for 15 min, then filtered through a small amount of silica and glasswool. The solvent was evaporated in vacuo at room temperature, and the yellow residue (204 mg, 57%) was purified by column chromatography on silica with CH_2Cl_2 as eluent. The main fraction (93.1 mg) consisted of an inseparable mixture of **4b** and tricarbonyl(η^4-2-hydroxy-1,3-butadiene)iron (**10**) in a 3/1 ratio.

Preparation of 8b and 8a

A suspension of 106.7 mg (0.55 mmol) $AgBF_4$ in 10 ml dichloromethane was saturated with carbon monoxide by passing a slow stream of CO through it for 2 min. A solution of 150 mg (0.52 mmol) **6b** in 5 ml of dichloromethane was added in portions during 3 min. The colour of the solution changed from orange to yellow and a yellow precipitate separated. The passage of CO was continued for 10 min and the mixture was then filtered. The precipitate was washed twice with cold CH_2Cl_2 and dried *in vacuo* at room temperature (215.3 mg). The filtrate and washings were combined and evaporated *in vacuo* at room temperature to yield 44.4 mg of yellow crystals, which were shown by NMR spectroscopy to consist of a mixture of starting material and **4b**. The original precipitate was extracted with trifluoroacetic acid to yield **8b** (72.6 mg, 43%). A satisfactory elemental analysis could not be obtained owing to partial exchange of the counter ion during extraction.

Complex **8a** was synthesized by the same procedure starting from **6a** (yield 58%).

8a: MS: *m/e* (rel. intensity) 196 (30), 168 (65), 140 (40), 112 (20), 84 (60), 69 (80), 56 (95), 45 (100).

8b: MS: *m/e* (rel. intensity) 210 (10), 182 (40), 154 (40), 126 (95), 84 (30), 72 (90), 56 (100).

Reactions of 8a and 8b with CF_3CO_2H, and preparation of 9a and 9b

Solutions of **8a** or **8b** in trifluoroacetic acid slowly lost a CO ligand to form the unstable complexes **9a** and **9b**, respectively. Attempts to isolate these complexes by evaporation of the solvent *in vacuo* were frustrated by rapid decomposition of the compounds under these conditions. Solutions of **9a** in trifluoroacetic acid were obtained independently by reaction of **6a** with 1 equivalent of CF_3CO_2Ag.

Conclusion

Although the reactivity of the complexed oxyallyl system towards [4 + 3]-cycloaddition, e.g. with furan, could not be increased by introduction of an alkyl substituent or a positive charge, their possible participation in the Noyori cycloaddition reaction cannot be ruled out, since the corresponding α,α'-dibromoketones also fail to react under the conditions of the Noyori reaction [10].

Acknowledgements

F. Nydegger is thanked for obtaining the mass spectra. The CIBA-GEIGY company is thanked for carrying out the elemental analyses. This work was supported by the Swiss National Science Foundation (Grant Nos. 20-5112.86 and

20-26458.89), which is gratefully acknowledged. M.F. wishes to thank the "Stipendienfonds der Basler Chemischen Industrie" for a fellowship.

References

1 M. Frey, T.A. Jenny and H. Stoeckli-Evans, Organometallics, 9 (1990) 1806.
2 R. Noyori, Y. Hayakawa, M. Funakura, H. Takaya, S. Murai, R. Kobayashi and S. Tsutsumi, J. Am. Chem. Soc., 94 (1972) 7202.
3 B. Czauderna, K.H. Jogun, J.J. Stezowski and B. Föhlisch, J. Am. Chem. Soc., 98 (1976) 6696.
4 A.N. Nesmeyanov, Y.A. Ustynyuk, I.I. Kritskaya and G.A. Shchembelov, J. Organomet. Chem., 14 (1968) 395.
5 C.H. De Puy, R.N. Greene and T.E. Schroer, J. Chem. Soc., Chem. Commun., (1968) 1225.
6 A.N. Nesmeyanov, L.V. Rybin, N.T. Gubenko, M.I. Rybinskaya and P.V. Petrovskii, J. Organomet. Chem., 71 (1974) 271.
7 M. Brookhart and M.L.H. Green, J. Organomet. Chem., 250 (1983) 395.
8 T.H. Whitesides, R.W. Arhart and R.W. Slaven, J. Am. Chem. Soc., 95 (1973) 5792.
9 A. Hosomi, A. Shirahata, Y. Araki and H. Sakurai, J. Org. Chem., 46 (1981) 4631.
10 Y. Hayakawa, H. Takaya, S. Makino, N. Hayakawa and R. Noyori, Bull. Chem. Soc. Jpn., 50 (1977) 1990; H. Takaya, S. Makino, Y. Hayakawa and R. Noyori, J. Am. Chem. Soc., 100 (1978) 1765.