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# FORMATION OF 1,3-DIENETRICARBONYLIRON COMPLEXES FROM THE REACTION OF DIPOTASSIUM TETRACARBONYLFERRATE WITH ALLYLIC COMPOUNDS

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## Summary

The reaction of dipotassium tetracarbonylferrate with various allylic phosphates and halides gives 1,3-dienetricarbonyliron complexes. The formation of the complexes is highly stereoselective depending on the geometry of the allylic compounds used.

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## Introduction

Tetracarbonylferrate $[Fe(CO)_4]^{2-}$ is a versatile anionic reagent widely used in synthetic organic chemistry. It is a useful reagent for the reduction of olefins [1], epoxides [2], allyl halides [3], nitro compounds [4], and enamines [5], and for converting alkyl halides and alkyl sulfonates into aldehydes [6], ketones [7], carboxylic acids [8], esters [8], and amides [8]. Collman described briefly in his review [9] that the reaction of tetracarbonylferrate with allylic compounds gave 1,3-dienetricarbonyliron complexes. However, the details have never been reported as far as we know. Here, we describe the results of the reaction of dipotassium tetracarbonylferrate with a variety of allylic phosphates and halides which yields 1,3-dienetricarbonyliron complexes besides the normal reduction products.

## Results and discussion

To a solution of dipotassium tetracarbonylferrate in ethanol was added prenyl diethyl phosphate (**1a**) and the mixture was stirred for 1 h. The reaction mixture was then distilled giving a pale yellow distillate and a brown residue. GLC analysis of the distillate showed that 2-methyl-2-butene (**2a**) was formed in 66% yield. The residue was purified by column chromatography on silica gel and subsequent vacuum distillation, a yellow oil was obtained, which was found to be isoprenetricarbonyliron (**3a**) by comparison with the sample prepared from isoprene and

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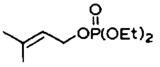
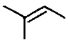
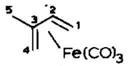
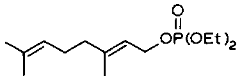
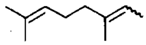
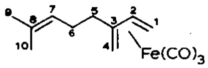
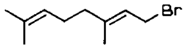
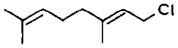
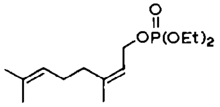
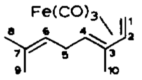
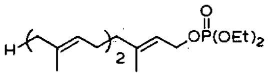
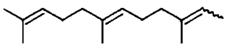
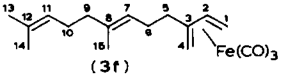
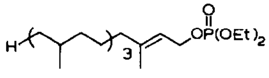
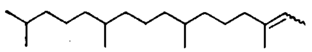
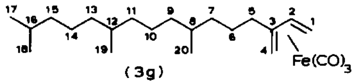
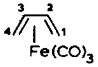
## TABLE 1

## REACTION OF DIPOTASSIUM TETRACARBONYLFERRATE WITH ALLYLIC PHOSPHATES AND HALIDES

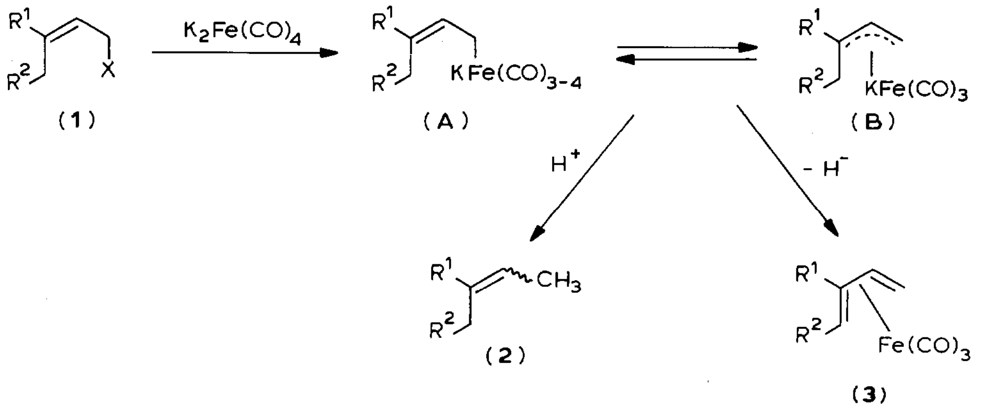
| Entry | Allylic phosphate or halide | Products | Yield (%) |
|---|---|---|---|
| a |  (1a) |  (2a) | 66 |
|  |  |  (3a) | 9 |
| b |  (1b) |  (2b) (*E*/*Z* = 83/17) | 26 |
|  |  |  (3b) | 15 |
| c |  (1c) | (2b) (*E*/*Z* = 91/9) | 32 |
|  |  | (3b) | 12 |
| d |  (1d) | (2b) (*E*/*Z* = 88/12) | 25 |
|  |  | (3b) | 13 |
| e |  (1e) | (2b) (*E*/*Z* = 82/18) | 43 |
|  |  |  (3e) | 10 |
| f |  (1f) |  (2f) (*E*/*Z* = 82/18) | 44 |
|  |  |  (3f) | 14 |
| g |  (1g) |  (2g) *E*/*Z* = 88/12 | 34 |
|  |  |  (3g) | 13 |
| h |  (1h) |  (3h) | 37 |

pentacarbonyliron according to the literature method [10]. The yield of **3a** was 9%. Takegami and co-workers reported [3] the reaction of dipotassium tetracarbonylferrate with prenyl chloride which yielded a mixture of the reduction products, predominantly 2-methyl-2-butene (**2a**), but formation of **3a** was not described.

Results for reactions of other allylic phosphates under similar conditions are summarized in Table 1. Geranyl diethyl phosphate (**1b**) gave 2,6-dimethyl-2,6-octadiene (*E*/*Z* 83/17) (**2b**) and myrcenetricarbonyliron (**3b**) in 26 and 15% yields, respectively. The iron complex **3b** was identical with an authentic sample prepared by the known method [11]. The use of geranyl bromide (**1c**) or chloride (**1d**) instead of the phosphate **1b** gave similar results. The reaction of neryl phosphate (**1e**), the *Z*-isomer of **1b**, yielded the same hydrocarbon (**2b**) and *E*-ocimenetricarbonyliron (**3e**). Banthorpe synthesized *Z*-ocimenetricarbonyliron from the reaction of *Z*-ocimene and pentacarbonyliron [11]. The $^1$H NMR data of **3e** are obviously different from those of the *Z*-ocimene complex. Therefore, the geometry of **3e** is confirmed to be *E*. It must be noted that the geranyl phosphate (**1b**) selectively gave myrcenetricarbonyliron (**3b**), and ocimenetricarbonyliron (**3e**) was not found in the reaction mixture. In turn, the formation of **3b** was not observed in the reaction of the neryl phosphate (**1e**). These two dienetricarbonyliron complexes are easily distinguishable by $^{13}$C NMR and GLC. On the contrary, the hydrocarbon **2b** produced in both the reactions had the almost coincident *E*/*Z* ratio. Higher analogs, (*E*,*E*)-farnesyl (**1f**) and phytyl diethyl phosphates (**1g**), also gave the respective dienetricarbonyliron complexes **3f** and **3g** along with the reduction products **2f** and **2g**. The allylic diphosphate **1h** gave a relatively higher yield (37%) of butadienetricarbonyliron (**3h**).

At present, the reaction mechanism is not completely clear, the following is the most likely. As described by Takegami et al. [3], the initially formed σ-allyl complex **A** is converted to π-allyl complex **B** which is protonated yielding the reduction product **2**, while the loss of a hydride ion (or a diethoxyphosphinyloxy anion in entry h (Table 1)) from **A** or **B** gives the dienetricarbonyliron complex **3**. The elimination process is highly regio- and stereo-selective. A hydrogen atom of the allylic methylene group *syn* to X (X = OP(O)(OEt)$_2$ or halogen) is abstracted and only the *E*-isomer is formed from *Z*-allylic phosphate. Thus, the geranyl compounds **1b**–**1d** regioselectively gave myrcenetricarbonyliron (**3b**), whereas the neryl phosphate **1e** gave *E*-ocimenetricarbonyliron (**3e**).

SCHEME 1



## Experimental

IR spectra were recorded on a JASCO IRA-1 spectrophotometer. $^{1}H$ and $^{13}C$ NMR spectra were measured with Hitachi R-24A (60 MHz) and Varian XL-200 (50 MHz) spectrometers, respectively. Mass spectra were run with a Hitachi M-52 instrument at 20 eV using a direct-inlet system. GLC analysis was performed on a Yanaco G 1800 gas chromatograph, equipped with columns (1 m × 3 mm) packed with Apiezon grease L on Uniport B (15%) and with Porapak Q. For Kugelrohr distillation, a Shibata GTO-250R apparatus was used. Dipotassium tetracarbonylferrate was prepared from pentacarbonyliron and potassium hydroxide in ethanol. Allylic diethyl phosphates **1a**, **1b**, and **1e–1h** were synthesized according to the method for the corresponding diphenyl phosphates [12].

*Reaction of dipotassium tetracarbonylferrate with allylic compounds 1a–1h*

The following reaction with prenyl diethyl phosphate (**1a**) is representative. To a solution of tetracarbonylferrate, prepared from pentacarbonyliron (1.61 ml, 12 mmol) and potassium hydroxide (3.17 g, 48 mmol) in 18 ml of ethanol, was added dropwise **1a** (2.22 g, 10 mmol) and the mixture was stirred at room temperature for 1 h. The reaction mixture was then distilled to dryness at atmospheric pressure giving a pale yellow distillate and a brown residue. GLC analysis of the distillate using the Porapak Q column (95°C) revealed that 2-methyl-2-butene (**2a**) was formed (confirmed by the co-injection with an authentic **2a** obtained commercially) in 66% yield. The residue was chromatographed on silica gel (light petroleum as eluant) giving an air-sensitive yellow oil (213 mg) which was finally distilled (b.p. 120°C/20 Torr) to afford pure isoprenetricarbonyliron (**3a**, 176 mg, 9%).

In entries b–h (Table 1), the reaction mixture was poured into water and the products were extracted with light petroleum. The extracts were dried ($Na_2SO_4$) and concentrated. The residue was chromatographed on silica gel (light petroleum) to give a mixture of the hydrocarbon **2** and the dienetricarbonyliron complex **3**. The separation of **2** and **3** was performed by careful Kugelrohr distillation. The *E/Z* ratios of **2** were determined by GLC using the Apiezon column. Dienetricarbonyliron complexes **3** are generally air-sensitive and gradually decompose in contact with atmospheric oxygen to form an insoluble brown precipitate. Satisfactory elemental analyses of **3e** and **3g**, therefore, could not be obtained.

*Isoprenetricarbonyliron (3a) [10].* B.p. 120°C/20 Torr; IR (neat) 3020, 2980, 2930, 2050, 1970, 1480, 1430, and 1380 $cm^{-1}$; Mass: $m/z$ (rel. intensity) 208 ($M^+$, 22), 180 ($M-$ CO, 86), 152 ($M-$ 2CO, 72), 124 ($M-$ 3CO, 100), and 68 (isoprene, 57); $^{1}H$ NMR ($CCl_4$): $\delta$ −0.06–0.34 (m, 2H, H(1) and H(4) (inner)), 1.54–1.82 (m, 2H, H(1) and H(4) (outer)), 2.20 (s, 3H, H(5)), 5.27 ppm (t, $J$ 8 Hz, 1H, H(2)); $^{13}C$ NMR ($CDCl_3$): 22.9 (C(5)), 38.0 (C(1)), 43.9 (C(4)), 84.7 (C(2)), 103.1 (C(3)), 211.5 ppm (CO).

*2,6-Dimethyl-2,6-octadiene (2b) [13].* B.p. 120°C/24 Torr; IR (neat): 2980, 2930, 2870, 1450, and 1380 $cm^{-1}$; Mass: $m/z$ (rel. intensity) 138 ($M^+$, 10) and 69 (100); $^{1}H$ NMR ($CCl_4$): $\delta$ 1.48–1.63 (m, 12H, $CH_3$), 1.94 (m, 4H, $CH_2$), 5.00 ppm (m, 2H, olefin).

*Myrcenetricarbonyliron (3b) [11].* B.p. 160°C/24 Torr; IR (neat): 2980, 2940, 2870, 2050, 1970, 1480, 1445, and 1380 $cm^{-1}$; Mass: $m/z$ (rel. intensity) 276 ($M^+$, 0.4), 248 ($M-$ CO, 4.3), 220 ($M-$ 2CO, 37), 192 ($M-$ 3CO, 80), and 93 (100); $^{1}H$

NMR ($CCl_4$): δ 0.00–0.25 (m, 2H, H(1) and H(4) (inner)), 1.62–1.71 (m, 8H, H(1) and H(4) (outer), H(9), and H(10)), 2.39 (m, 4H, H(5) and H(6)), 5.27 ppm (m, 2H, H(2) and H(7)); $^{13}C$ NMR ($CDCl_3$): 17.8 (C(10)), 25.7 (C(9)), 30.2 (C(6)), 37.7 (C(4) or C(5)), 38.3 (C(5) or C(4)), 43.1 (C(1)), 84.2 (C(2)), 106.8 (C(3)), 122.9 (C(7)), 132.8 (C(8)), 211.6 ppm (CO).

*E-Ocimenetricarbonyliron (3e).* B.p. 150°C/25 Torr; Found: C, 57.69; H, 6.38. $C_{13}H_{16}FeO_3$ calcd.: C, 56.55; H, 5.84%. IR (neat): 2980, 2930, 2880, 2050, 1960, 1440, 1380 cm$^{-1}$; Mass: $m/z$ (rel. intensity) 276 ($M^+$, 7), 248 (M − CO, 11), 220 ($M$ − 2CO, 56), 192 ($M$ − 3CO, 87), and 93 (100); $^1H$ NMR ($CCl_4$): δ 0.00–0.16 (m, 1H, H(1) (inner)), 0.65–0.90 (m, 1H, H(4)), 1.60–1.70 (m, 7H, H(1) (outer), H(8), and H(9)), 2.11 (s, 3H, H(10)), 2.35 (m, 2H, H(5)), 5.08 ppm (m, 2H, H(2) and H(6)); $^{13}C$ NMR ($CDCl_3$): 17.8 (C(9)), 18.5 (C(10)), 25.6 (C(8)), 29.5 (C(5)), 36.5 (C(1)), 64.9 (C(4)), 82.1 (C(2)), 102.5 (C(3)), 123.3 (C(6)), 132.1 (C(7)), 212.2 ppm (CO).

*2,6,10-Trimethyl-2,6,10-dodecatriene (2f) [14].* B.p. 110 °C/3 Torr; IR (neat): 2980, 2940, 2870, and 1380 cm$^{-1}$; Mass: $m/z$ (rel. intensity) 206 ($M^+$, 3) and 69 (100); $^1H$ NMR ($CCl_4$): δ 1.55 (m, 15H, $CH_3$), 1.94 (m, 8H, $CH_2$), 4.87–5.15 ppm (m, 3H, olefin).

*E-Farnesenetricarbonyliron (3f).* B.p. 150°C/3 Torr; Found: C, 62.76; H, 7.13. $C_{18}H_{24}FeO_3$ calcd.: C, 62.81; H, 7.03%. IR (neat): 2980, 2940, 2870, 2050, 1970, 1480, 1445, and 1380 cm$^{-1}$; Mass: $m/z$ (rel. intensity) 344 ($M^+$, 0.7), 316 ($M$ − CO, 1), 288 ($M$ − 2CO, 5), 260 ($M$ − 3CO, 100); $^1H$ NMR ($CCl_4$): δ 0.04–0.36 (m, 2H, H(1) and H(4) (inner)), 1.69–1.88 (m, 11H, H(1), H(4) (outer), H(13), H(14), and H(15)), 2.10 (m, 4H, H(9) and H(10)), 2.43 (m, 4H, H(5) and H(6)), 5.16–5.41 ppm (m, 3H, H(2), H(7), and H(11)); $^{13}C$ NMR ($CDCl_3$): 16.1 (C(15)), 17.7 (C(14)), 25.6 (C(13)), 26.7 (C(10)), 29.7 (C(6)), 37.7 (C(4) or C(5)), 38.2 (C(5) or C(4)), 39.7 (C(9)), 43.1 (C(1)), 84.3 (C(2)), 106.8 (C(3)), 122.8 (C(7)), 124.2 (C(11)), 131.4 (C(12)), 136.5 (C(8)), 211.4 ppm (CO).

*3,7,11,15-Tetramethyl-2-hexadecene (2g) [15].* B.p. 130°C/1 Torr; IR (neat): 2970, 2940, 2870, 1465, 1380, and 1370 cm$^{-1}$; Mass: $m/z$ (rel. intensity) 280 ($M^+$, 7) and 70 (100); $^1H$ NMR ($CCl_4$) δ 0.86 (d, $J$ 6 Hz, 12H, $CHCH_3$), 1.21 (m, 18H, $CH_2$), 1.47–1.56 (m, 9H, $CH_3$ and CH), 1.82–1.95 (m, 2H, allyl $CH_2$), 4.93–5.22 ppm (m, 1H, olefin).

*Phytadienetricarbonyliron (3g).* B.p. 185°C/1 Torr; Found: C, 67.53; H, 9.28. $C_{23}H_{38}FeO_3$ calcd.: C, 66.03; H, 9.15%: IR (neat): 2970, 2940, 2870, 2050, 1970, 1465, 1380, and 1370 cm$^{-1}$; Mass: $m/z$ (rel. intensity) 418 ($M^+$, 1), 390 ($M$ − CO, 5), 362 ($M$ − 2CO, 3), 334 ($M$ − 3CO, 100); $^1H$ NMR ($CCl_4$): δ − 0.03–0.27 (m, 2H, H(1) and H(4) (inner)), 0.89 (d, $J$ 6 Hz, 12H, H(17), H(18), H(19), and H(20)), 1.24 (m, 16H, H(6), H(7), H(9), H(10), H(11), H(13), H(14), and H(15)), 1.58–1.80 (m, 5H, H(1), H(4) (outer), H(8), H(12), and H(16)), 2.23–2.37 (m, 2H, H(5)), 5.24 ppm (t, $J$ 8 Hz, 1H, H(2)); $^{13}C$ NMR ($CDCl_3$): 19.7 (C(19) or C(20)), 19.8 (C(20) or C(19)), 22.7 (C(17) and C(18)), 24.5 (C(10) or (C(14)), 24.8 (C(14) or C(10)), 28.0 (C(16)), 29.5 (C(6)), 32.7 (C(8) or C(12)), 32.8 (C(12) or C(8)), 36.7 (C(4)), 37.3 (C(9) and C(11)), 37.5 (C(13)), 38.0, 38.2, 39.4 (C(5), C(7), or C(15)), 43.1 (C(1)), 84.1 (C(2)), 107.6 (C(3)), 211.6 ppm (CO).

*Butadienetricarbonyliron (3h) [16].* B.p. 100°C/16 Torr, IR (neat): 3080, 3020, 2070, 1970, 1480, 1440, and 1370 cm$^{-1}$; Mass: $m/z$ (rel. intensity) 194 ($M^+$, 20), 166 ($M$ − CO, 53), 138 ($M$ − 2CO, 44), and 110 ($M$ − 3CO, 100); $^1H$ NMR ($CCl_4$):

δ 0.23 (dd, *J* 8, 2 Hz, 2H, H(1)(inner)), 1.77 (dd, *J* 6, 2 Hz, 2H, H(1) (outer)), 5.35 (bt, *J* 8, 6 Hz, 2H, H(2)) ppm.

## References

1 Y. Takegami, Y. Watanabe, I. Kanaya, T. Mitsudo, T. Okajima, Y. Morishita and H. Masada, Bull. Chem. Soc. Jpn., 41 (1968) 2990.
2 Y. Takegami, Y. Watanabe, T. Mitsudo, I. Kanaya and H. Masada, Bull. Chem. Soc. Jpn., 41 (1968) 158.
3 Y. Takegami, Y. Watanabe, T. Mitsudo and T. Okajima, Bull. Chem. Soc. Jpn., 42 (1969) 1992.
4 German Patent, 4441179, 1925.
5 T. Mitsudo, Y. Watanabe, M. Tanaka, S. Atsuta, K. Yamamoto and Y. Takegami, Bull. Chem. Soc. Jpn., 48 (1975) 1506.
6 M.P. Cooke, J. Am. Chem. Soc., 92 (1970) 6080.
7 J.P. Collman, S.R. Winter and D.R. Clark, J. Am. Chem. Soc., 94 (1972) 1788.
8 J.P. Collman, S.R. Winter and R.G. Komoto, J. Am. Chem. Soc., 95 (1973) 249.
9 J.P. Collman, Acc. Chem. Res., 8 (1975) 342.
10 R.B. King, T.A. Manuel and F.G.A. Stone, J. Inorg. Nucl. Chem., 16 (1961) 233.
11 D.V. Banthorpe and H. Fitton, J. Chem. Soc., Perkin 1, (1973) 2051.
12 J.A. Miller and H.C.S. Wood, J. Chem. Soc. C, (1968) 1837.
13 F.J. McQuillin and D.G. Parker, J. Chem. Soc., Perkin 1, (1975) 2092.
14 J.E. McMurry and M. Silvestri, J. Org. Chem., 40 (1975) 2687.
15 F. Bohlmann and U. Fritz, Phytochemistry, 17 (1978) 1769.
16 M.L.H. Green, L. Pratt, and G. Wilkinson, J. Chem. Soc., (1959) 3753.