Novel Synthesis of (Butatriene)hexacarbonyldiiron Complexes. Stereochemical Aspects and an X-ray Crystal Structure Determination

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Summary: (Butatriene)hexacarbonyldiiron complexes with various substituents at either end of the triene ligand were prepared in good yields from 2-butyne-1,4-diols and enneacarbonyldiiron. For (2,5-dimethyl-2,3,4-hexatriene)-hexacarbonyldiiron an X-ray crystal structure was obtained.

Introduction

Butatrienes could in principle be valuable building blocks for organic synthesis, but due to their limited stability, they are difficult to prepare and store.[1] In contrast to this, the corresponding (butatriene)hexacarbonyldiiron complexes **3** are very stable compounds. (2,5-Dimethyl-2,3,4-hexatriene)hexacarbonyldiiron (**3a**), for instance, can be stored as a solid or in solution for months, and it even sublimes without decomposition.

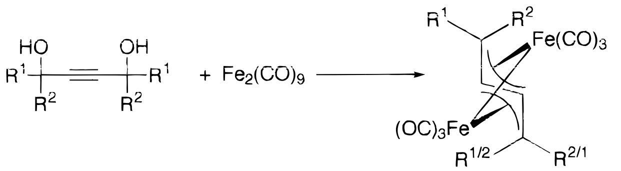
Hitherto, (butatriene)hexacarbonyldiiron complexes **3** had been prepared in two different ways: (a) from 1,4-dihalo-2-butynes and dodecacarbonyltriiron (for better yields in the presence of zinc)[2] and (b) from the butatrienes themselves and iron carbonyls (pentacarbonyliron,[2] enneacarbonyldiiron, or dodecacarbonyltriion[3]). Both methods are unsatisfactory, due to either their low yields or the restricted accessibility of the starting materials. In the present paper we report a novel synthesis of (butatriene)hexacarbonyldiiron complexes **3** from readily accessible materials as well as an X-ray structure analysis of **3a**. Stereochemical aspects of the reaction are discussed.

Results and Discussion

When 2-butyne-1,4-diols (**1**) and enneacarbonyldiiron (**2**) are stirred in THF, the corresponding (butatriene)-hexacarbonyldiiron complexes (**3**) are obtained in good yields (Scheme 1, Table 1).

2-Butyne-1,4-diols (**1**) were either purchased or prepared by published methods. For butynediols **1** bearing four identical substituents ($R^1 = R^2$), method A[4] might be used instead of method B.[5] As the latter one turned out to give higher yields throughout, it is to be preferred even when $R^1 \neq R^2$ (Scheme 2). (It is worth noting that 2-butene-1,4-diols furnish ferralactones once treated with **2**, thus following quite a different reaction pathway.[6])

Scheme 1



1 **2** **3**

1a $R^1 = R^2 = CH_3$
1b $R^1 = R^2 = Ph$
1c $R^1 = H$, $R^2 = CH_3$
1d $R^1 = H$, $R^2 = CH_3$
(*meso*-form)

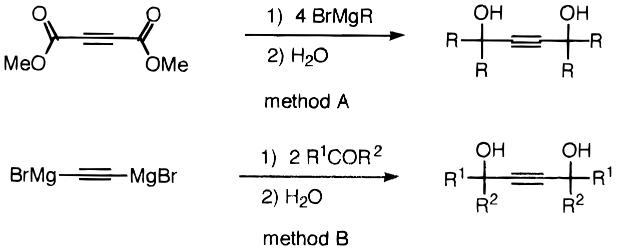
3a $R^1 = R^2 = CH_3$
3b $R^1 = R^2 = Ph$
3c $R^1 = H$, $R^2 = CH_3$
(*Z*-form)
3d $R^1 = H$, $R^2 = CH_3$
(*E*-form)

Table 1. Reaction Parameters for the Synthesis of 3 from 1

butynediol	product	period	temp	yield (%)
1a	**3a**	2 days	room temp	79.6
1b	**3b**	5 h	reflux	82.4
1c	**3c,d**[a]	1 day	room temp	65.4
1d	**3c,d**[a]	1 day	room temp	65.4

[a] 1:1 mixture of **3c** and **3d**.

Scheme 2



As butatrienes are planar, *cis*−*trans* isomerism is possible, but since the barrier of rotation is very low, separation of the isomers is rather difficult.[7] Therefore, a stereoselective synthesis of *cis*- or *trans*-(1,4-disubstituted-1,2,3-butatriene)hexacarbonyldiiron complexes **3** would be highly welcome.

To investigate the stereochemistry of the reaction of **1** with **2**, we considered the following: if the first step of the reaction were the fixation of the triple bond at the diiron moiety, an orientation of both hydroxy groups either toward the iron atoms or away from them should

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Scheme 3

$$\begin{array}{lll} \mathrm{Me_4C_4(OH)_2} + 2\,e^- & \longrightarrow \mathrm{Me_4C_4} + 2\,\mathrm{OH^-} & \times 3 \\ \mathrm{Fe_2(CO)_9} + 6\,\mathrm{OH^-} & \longrightarrow 2\,\mathrm{Fe(OH)O} + 9\,\mathrm{CO} + 2\,\mathrm{H_2O} + 6\,e^- & \\ \hline 3\,\mathrm{Me_4C_4(OH)_2} + 4\,\mathrm{Fe_2(CO)_9} & \rightarrow 3\,\mathrm{Me_4C_4} + 2\,\mathrm{Fe(OH)O} + 2\,\mathrm{H_2O} + 9\,\mathrm{CO} & \end{array}$$

result. The (simultaneous) abstraction of the hydroxy groups from one side of this intermediate complex (either from the diiron-shielded side or the opposite side) would be consistent, as any rotation of the alcoholic C atoms is very unlikely to ensue the initial complexation. Therefore, the reaction of *meso*-3-hexyne-2,5-diol (**1d**)[8] with **2** would lead to *cis*-(2,3,4-hexatriene)hexacarbonyldiiron (**3c**) stereoselectively. However, what we found eventually was a 1:1 mixture of **3c** and *trans*-(2,3,4-hexatriene)hexacarbonyldiiron (**3d**), regardless of which diastereomers were used; thus, the mechanistic rationale outlined above needs revision. The reaction of the butynediol **1** to give a butatriene corresponds to a reduction, with **2** serving as the reducing as well as the complexing agent (Scheme 3).

This explains why an excess of **2** is needed for maximum yields of **3**. To check for side reactions or intermediates, the synthesis of **3b** was carefully monitored by TLC (silica; hexane). Besides the continuous formation of **3b** (R_f 0.85) a second yellow spot emerged (R_f 0.72). Though obviously stable to air, this spot corresponded to a transient species which had completely disappeared before workup by column chromatography. We postulate this intermediate compound to be the monoiron complex ((2,3-η^2)-1,1,4,4-tetraphenyl-1,2,3-butatriene)tetracarbonyliron (**4**), which had been prepared from 1,1,4,4-tetraphenylbutatriene and **2** by Joshi.[9] This strongly suggests that the formation of **3b** proceeds via **4**, but more profound investigations into this mechanism have yet to be done.

Structure. Crystals of **3a** appropriate for X-ray diffraction recording were obtained.[10] Its structure shows great resemblance to the one established earlier by Bright and Mills for the bis(biphenylidene)butatriene derivative.[11] Within the bounds of accuracy, **3a** has C_2 symmetry. The C_2 axis is defined as going through the centers of the iron–iron bond and of the C2–C3 bond of the butatriene ligand, which is almost planar. Two of the three carbonyl groups at each iron atom are mutually eclipsed; the third one lies nearly on the Fe–Fe axis. A view from C1 down to C4 of the butatriene shows that the terminal CMe$_2$ groups are distorted by approximately 90°.

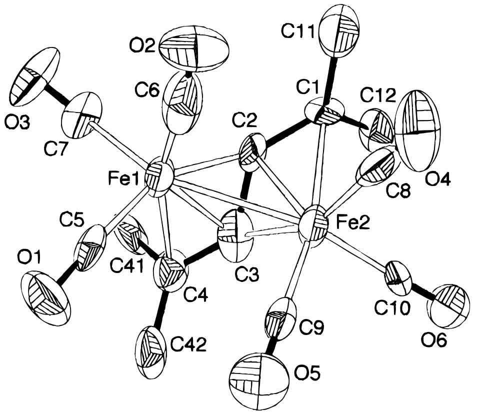

Figure 1. Molecular structure of **3a** (ORTEP, 50% probability ellipsoids). Selected bond lengths (Å), bond angles (deg), and dihedral angles (deg): Fe1–Fe2, 2.593; Fe2–C1, 2.401; Fe2–C2, 2.074; Fe2–C3, 1.977; C1–C2, 1.371; C2–C3, 1.459; Fe2–Fe1–C1, 79.0; Fe2–Fe1–C2, 48.6; Fe2–Fe1–C3, 51.9; C1–C2–C3, 130.7; C11–C1–C2, 118.6; C12–C1–C2, 122.4; C11–C1–C2–C12, 162.0; C11–C1–C4–C42, 106.6; C12–C1–C4–C41, 78.0.

These X-ray analytical data were taken as an input for semiempirical calculations to get an idea of their reliability in dealing with highly unsaturated π-complexes. We employed SINDO,[12] which has proven quite useful in prior investigations concerning iron–allyl complexes,[13] as well as AMPAC[14] with its new SAM1 method.[15] Only the latter method found a minimum close to the X-ray results on the energy surface. The results of these and other calculations will be published in more detail soon.

Experimental Section

All reactions were carried out under an atmosphere of dry argon. Solvents were dried by standard methods and freshly distilled prior to use.

Safety Note. Most reactions of **2** lead to small amounts of other iron carbonyls, especially pentacarbonyliron. These compounds are volatile and presumably strongly toxic and must be handled with the utmost care. They can be decomposed with an aqueous solution of KOH and H$_2$O$_2$.

General Method for the Preparation of (Butatriene)hexacarbonyldiiron Complexes 3. In a 100 mL round-bottomed flask equipped with a magnetic stirrer **2** (3.4 g, 9.4 mmol) and the appropriate butynediol **1** (6.0 mmol) were dissolved in 50 mL of THF (for particular reaction conditions refer to Table 1). After the solvent and all volatile were removed under high vacuum (see Safety Note), the residue was submitted to column chromatography on silica gel. Eluting with hexane and subsequent drying under high vacuum furnished **3** as deep red crystals (for yields see Table 1).

3a: mp 108 °C; IR (KBr) 2910 (w), 2875 (w), 2830 (w), 2060 (vs), 2005 (vs), 1975 (vs), 1900 (vs), 1360 (w), 1055 (m), 820 (w), 790 (m), 670 (w), 630 (s) cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 1.99 (s, 6H, CH$_3$), 2.16 (s, 6H, CH$_3$); ^{13}C NMR (CDCl$_3$, 100.5 MHz) δ 27.2 (CH$_3$), 34.9 (CH$_3$), 119.7 (C1, C4), 120.1 (C2, C3) 211.3 (C═O); MS (70 eV) m/z (%) 388 (43) [M$^+$], 360 (28) [M$^+$ – CO], 332 (7) [M$^+$ – 2 CO], 304 (16) [M$^+$ – 3 CO], 276 (67) [M$^+$ – 4 CO], 248 (100) [M$^+$ – 5 CO], 220 (51) [M$^+$ – 6 CO], 162 (31), 112 (36) [Fe$_2^+$, Fe(CO)$_2^+$], 56 (8) [Fe$^+$], 28 (13) [CO$^+$]. Anal. Calcd for C$_{14}$H$_{12}$Fe$_2$O$_6$: C, 43.35; H, 3.12. Found: C, 43.34; H, 3.01.

3b: mp 176 °C dec; IR (KBr) 3080 (m), 3040 (m), 2980 (m), 2065 (vs), 2015 (vs), 1990 (vs), 1660 (m), 1600 (m), 1490 (s), 1450 (s), 1070 (m), 1035 (m), 985 (s), 910 (m), 880 (w), 845

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[8] The 1:1 mixture of the racemic and the *meso*-3-hexyne-2,5-diol proved inseparable. Esterification with acetic anhydride led to the 2,5-diacetoxy-3-hexynes, which were separated by column chromatography (silica gel 60, Et$_2$O/hexane 1:1, R_f 0.65 (meso form), R_f 0.54 (racemate)). Subsequent saponification yielded the *meso*-3-hexyne-2,5-diol.

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[10] Crystal data (recrystallized from hexane): triclinic red blocks; space group $P1$; unit cell dimensions a = 7.558(14) Å, b = 8.416(7) Å, c = 12.92(2) Å, α = 89.20(7)°, β = 98.11(12)°, γ = 104.25(12)°; R_{int} = 8.98%.

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[12] (a) Version 3.1 performed on a Silicon Graphics Indigo R4000 computer. (b) Li, J.; Correa de Mello, P.; Jug, K. *J. Comput. Chem.* **1992**, *13*, 85. (c) Li, J.; Jug, K. *J. Comput. Chem.* **1992**, *13*, 93.

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[15] Holder, A. J. Personal communication.

(w), 775 (m), 740 (m), 690 (s), 630 (m) cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.4 (m, 20H); ^{13}C NMR (CDCl$_3$, 100.5 MHz) δ 120.2 (C1, C4), 120.7 (C2, C3), 134.4, 134.6, 134.9, 135.8, 139.3, 139.5, 139.8, 140.1, 211.3 (C=O); MS (70 eV) m/z (%) 636 (7) [M$^+$], 608 (5) [M$^+$ − CO], 580 (16) [M$^+$ − 2 CO], 552 (8) [M$^+$ − 3 CO], 524 (78) [M$^+$ − 4 CO], 496 (22) [M$^+$ − 5 CO], 468 (100) [M$^+$ − 6 CO], 412 (36) [FeC$_4$(C$_6$H$_5$)$_4$$^+$], 356 (54) [C$_4$(C$_6H_5$)$_4$$^+$], 278 (34), 234 (29), 167 (31), 105 (32) [C$_6$H$_5$CO$^+$], 84 (26), 56 (14) [Fe$^+$], 28 (85) [CO$^+$]. Anal. Calcd for $C_{34}H_{20}Fe_2O_6$: C, 64.19; H, 3.17. Found: C, 64.11; H, 3.02.

1:1 Mixture of 3c and 3d: mp 86 °C; IR (KBr) 2930 (m), 2870 (m), 2050 (vs), 1970 (vs), 1940 (vs), 1480 (w), 1430 (m), 1370 (m), 1320 (w), 1255 (w), 1030 (w), 920 (m), 855 (m), 630 (s) cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 1.86 (m, 9H), 2.00 (m, 3H), 5.16 (q, $^3J = 6.5$ Hz, 1H), 5.86 (m, 3H); ^{13}C NMR (CDCl$_3$, 100.5 MHz) δ 19.5 (C1, C6), 19.6 (C1, C6), 26.9 (C1, C6), 92.2 (C2, C5), 92.7 (C2, C5), 94.5 (C2, C5), 121.4 (C3, C4), 122.4 (C3, C4), 123.2 (C3, C4), 210.2 (C=O); MS (70 eV) m/z (%) 360 (45) [M$^+$], 332 (43) [M$^+$ − CO], 304 (13) [M$^+$ − 2 CO], 276 (21) [M$^+$ − 3 CO], 248 (75) [M$^+$ − 4 CO], 220 (100) [M$^+$ − 5 CO], 192 (76) [M$^+$ − 6 CO], 134 (20), 112 (58) [Fe$_2$$^+$, Fe(CO)$_2$$^+$], 56 (32) [Fe$^+$]. Anal. Calcd for $C_{12}H_8Fe_2O_6$: C, 40.05; H, 2.24. Found: C, 39.99; H, 2.08.

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Supporting Information Available: Tables giving a structure determination summary, atomic coordinates, bond distances and bond angles, and anisotropic diplacement coefficients for complex **3a** (9 pages). Ordering information is given on any current masthead page.

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