

Methyl propiolate coupling at the $\text{Fe}(\text{CO})_2(\text{PEt}_3)_2$ fragment¹

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Received 27 January 1997

Abstract

The in situ solution mixture of $\text{Fe}(\text{CO})_2(\text{PEt}_3)_2(\text{N}_2)$ **3a** and $(\mu\text{-N}_2)[\text{Fe}(\text{CO})_2(\text{PEt}_3)_2]_2$ **3b** reacts with $\text{HC}\equiv\text{CCOOMe}$ to afford an acetylene $\text{Fe}(\text{CO})_2(\text{PEt}_3)_2(\eta^2\text{-HC}\equiv\text{CCOOMe})$ **4a** and an acetylido hydrido complex $\text{Fe}(\text{CO})_2(\text{PEt}_3)_2(\text{H})(\text{C}\equiv\text{CCOOMe})$ **4b** as primary products. Compounds **4a** and **4b** are in equilibrium. The equilibrium mixture is irreversibly converted to a vinylidene species $\text{Fe}(\text{CO})_2(\text{PEt}_3)_2(\text{C}=\text{CHCOOMe})$ **5** in the presence of silylated silica. Addition of further equivalents of $\text{HC}\equiv\text{CCOOMe}$ to **5** leads to the isolation of carbonyl[2,4,6-tris(methoxycarbonyl)-hexa-1,3,5-trien-1,5-diy]bis(triethylphosphane)iron **9** and dicarbonyl[methoxycarbonyl(1,4-di-methoxycarbonyl-but-1,3-dien-2-yl)vinylidene]bis(triethylphosphane)iron **10** as iron-bound trimerization products of $\text{HC}\equiv\text{CCOOMe}$. **10** was characterized by a single crystal X-ray diffraction study. © 1997 Elsevier Science S.A.

Keywords: Methyl propiolate; Single crystal X-ray diffraction study

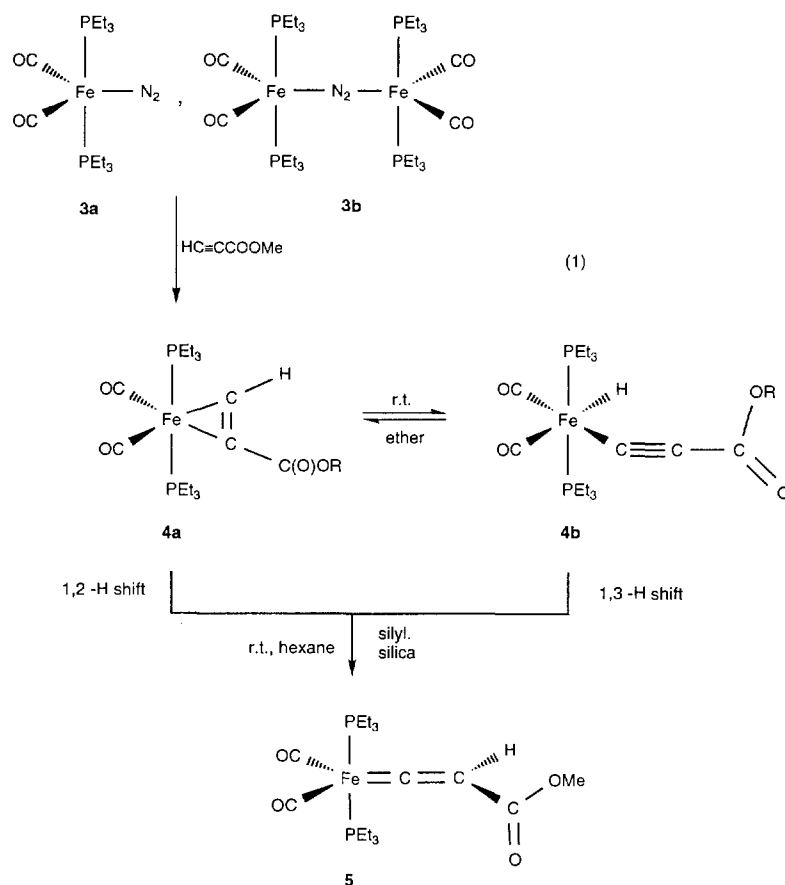
1. Introduction

Stoichiometric and catalytic acetylene coupling at transition metal centers leads in the majority of cases to benzene derivatives with trimerization of the acetylenic units [1,2]. The assembly of the acetylene building

blocks requires at least two free coordination sites [2]. We have recently shown that methyl propiolate as an electron deficient terminal acetylene may be involved in trimerization reactions at $\text{Fe}(\text{CO})_2(\text{phosphite})_2$ fragments, however demanding only one coordination site [3]. This deviating reaction behavior is based on the acetylene/vinylidene rearrangement of the terminal acetylene as the initiating reaction step (for selected references see Refs. [4–8]; see also Ref. [9]). The highly unsaturated alkoxy carbonyl vinylidene products [9] formed in this way can act as reactive intermediates allowing further addition and insertion of methyl propiolate without opening of additional coordination sites. Thus, the complexes **1a,b** and **2** became available [3].

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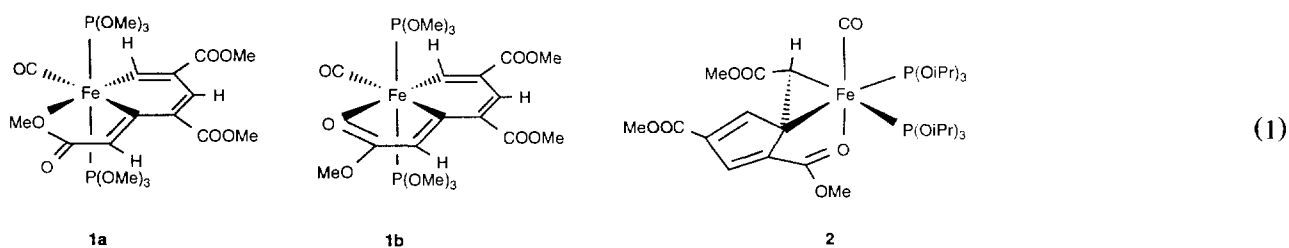
¹ Dedicated to Professor Wolfgang Beck, Institut für Anorganische Chemie, Universität München, on the occasion of his 65th birthday.



The investigations of this paper are sought to extend the scope of this type of unusual acetylene reactivity by probing the reactions of methyl propiolate at electron richer $\text{Fe}(\text{CO})_2(\text{PEt}_3)_2$ centers.

2. Results and discussions

The reaction of a mixture of the dinitrogen complexes **3a** and **3b** in ether [10] with methyl propiolate affords an approximate 1:1 mixture of the expected π acetylene species **4a** and of the hydrido acetylide complex **4b** (Eq. (1)).



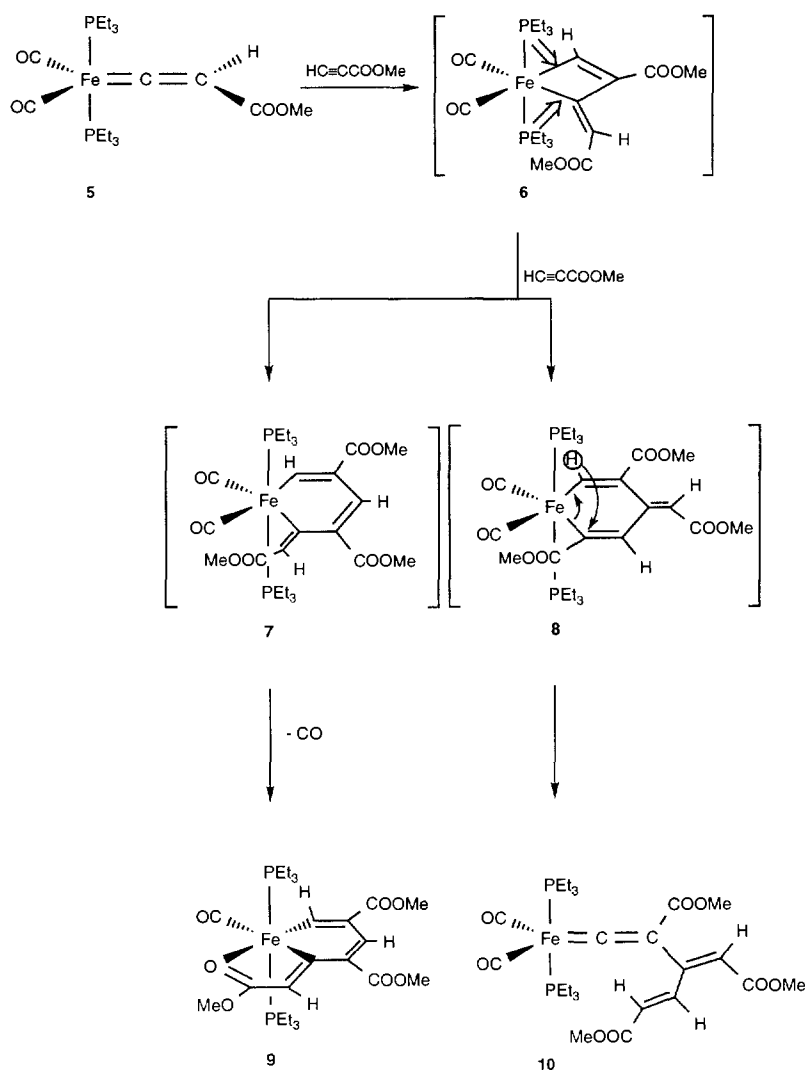
Compounds **4a** and **4b** were stable at room temperature (r.t.); however, their separation could not be achieved. Attempts at a separation by crystallization were not successful; neither was column chromatography on silylated silica, silica or alumina, which partially caused conversion to the vinylidene derivative **5**. **4a** and **4b** were therefore characterized spectroscopically from the mixture. Typical features of **4a** are the $\nu(\text{C}\equiv\text{C})$

band at 1739 cm^{-1} in the IR and the resonance of the acetylenic proton in the ^1H NMR spectrum. **4b** shows a characteristic $\nu(\text{C}=\text{C})$ band at 2100 cm^{-1} and a ^1H NMR signal for the iron-bound proton at -8.74 ppm . For both complexes the structural assignment was additionally based on the ^{13}C NMR spectra including P–C and C–H couplings.

The subsequent reaction of the **4a,b** mixture to the

vinylidene complex **5** was accomplished in the presence of silylated silica. Concerning the necessity of the oxide support for this transformation, it should be mentioned that similar observations were made in other acetylene/vinylidene rearrangement steps in relative electron-rich complexes [11]. In terms of a more detailed mechanistic interpretation of Eq. (1) it remains unclear from our data, whether the conversion to **5** passes through the acetylene compound **4a** or the hydrido acetylido complex **4b**. A 1,2- or a 1,3-H shift reaction would be required, respectively [7,8,11]. The vinylidene complex **5** possesses $\nu(\text{C}=\text{O})$ IR absorptions distinguished from those of **4a** and **4b**, which allows its facile identification in mixtures of even all three components. Furthermore, **5** shows a unique $\nu(\text{C}=\text{C})$ band at 1561 cm^{-1} . Its ^1H NMR spectrum reveals a $\text{H}_{\text{vinylidene}}$ triplet resonance at 5.40 ppm ($J_{\text{PH}} = 10\text{ Hz}$) and in the ^{13}C NMR a signal at 317.6 ppm ($J_{\text{PH}} = 48\text{ Hz}$), the latter emphasizing the presence of an iron-bound carbenoid center. The chemical shift of this

resonance falls into the typical range of other $\text{Fe}(\text{CO})_2(\text{PEt}_3)_2(\text{vinylidene})$ complexes [11]. Its position does not, however, reflect a supposed electron deficiency at this carbon atom, which could be anticipated by conjugative electron withdrawal of the ester group. In terms of reactivity, **5** nevertheless appears to be quite electron deficient at the vinylidene α carbon, since it is capable of reacting further with methyl propiolate under quite mild conditions. In such consecutive steps even two molecules of $\text{HC}\equiv\text{CCOOMe}$ can be added and, as shown in Scheme 1, a methylene ferracyclobutene compound **6** is formed as the primary intermediate. Such an addition reaction to an $\text{M}=\text{C}$ bond is given precedence by various other literature reports [12]. The ferracyclobutene complex then offers two regio-orientations for the insertion of a second $\text{HC}\equiv\text{CCOOMe}$ molecule; both of these are apparently realized, leading to **7** as the 'unsymmetric' and **8** as the 'symmetric' insertion products (Scheme 1). While **7** stabilizes itself by loss of a CO group and oxygen coordination of the vinylidene



Scheme 1.

ester functionality, the divinyl species **8** is suggested to undergo a 1,5-H shift with reductive elimination of the iron-attached carbon atom. Similar rearrangements are known from early transition metal metallocene divinyl derivatives [13]. It is maybe interesting to note that the conceivable but not observed reductive C/C elimination from **8**, can indeed be accessed in the related chemistry of $\text{Fe}(\text{CO})_2[\text{P}(\text{O}i\text{Pr})_3]_2$ fragments and leads to the fulvene complex **2** [5]. The mentioned 1,5-H shift expectedly produces the vinyl vinylidene complex **10** with an *E*-configuration at the terminal olefinic bond. The structures of **9** and **10** are consistent with the observed spectroscopic data, but could not be derived fully from these alone. For **10** the ^{13}C NMR signal of the vinylidene β carbon (C(2)), which is essential to structural discussions, could not be detected. While the structure of **10** has finally been established by an X-ray diffraction study, the elucidation of the structure of **9** has been accomplished on the basis of a detailed spectroscopic comparison with the data of **1a** and **1b** [3]. This way $\text{O}_{\text{carbonyl}}$ coordination of the ester group as in **1b** was assured. Somewhat surprising, and yet unexplained, is that despite the similarity of **5** and **10**, and despite a thorough search for these, we were not able to detect any subsequent 2 + 2 addition products of $\text{HC}\equiv\text{CCOOME}$ to **10**.

3. X-ray diffraction study of **10**

The crystal structure of **10** (Fig. 1) was determined by an X-ray diffraction study [14]. The iron center possesses a pseudo-trigonal bipyramidal coordination and the $\text{Fe}(\text{CO})_2(\text{PET}_3)_2$ framework appears to be very similar with regard to related $\text{Fe}(\text{CO})_2\text{L}_2$ complexes [4,11,15].

The interchain distances of the vinyl vinylidene unit alternate (see Table 1). However, some delocalization of the π system is indicated by the C(4)–C(7) distance shortened with respect to a C–C single bond length. The Fe(1)–C(1) distance is in the range of the Fe–CO

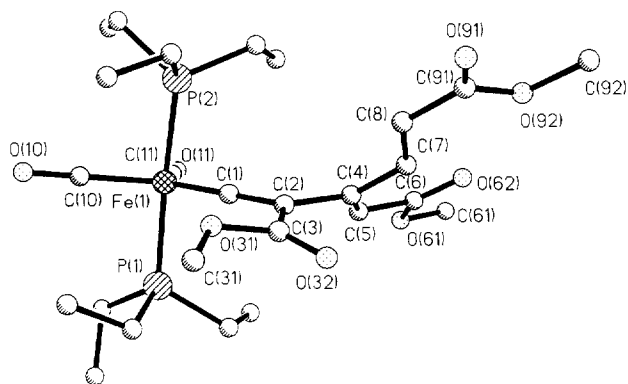


Fig. 1. Structure of complex **10**.

Table 1

Selected bond lengths (Å) and angles (deg) of complex **10**

Fe(1)–P(1)	2.226(3)	C(1)–Fe(1)–C(10)	135.6(3)
Fe(1)–P(2)	2.235(3)	C(1)–Fe(1)–C(11)	125.0(3)
Fe(1)–C(1)	1.730(8)	C(10)–Fe(1)–C(11)	99.4(4)
Fe(1)–C(10)	1.779(8)	C(1)–Fe(1)–P(1)	86.5(2)
Fe(1)–C(11)	1.771(10)	C(1)–Fe(1)–P(2)	83.3(3)
C(1)–C(2)	1.370(9)	P(1)–Fe(1)–P(2)	167.1(1)
C(2)–C(3)	1.462(9)	Fe(1)–C(1)–C(2)	178.8(6)
C(2)–C(4)	1.494(9)	C(1)–C(2)–C(3)	121.1(6)
C(4)–C(5)	1.356(9)	C(1)–C(2)–C(4)	119.5(6)
C(4)–C(7)	1.464(9)	C(3)–C(2)–C(4)	119.3(6)
C(5)–C(6)	1.478(9)	C(4)–C(7)–C(8)	126.9(7)
C(7)–C(8)	1.314(9)	C(7)–C(8)–C(9)	124.4(7)
C(8)–C(9)	1.460(10)	Fe(1)–C(10)–O(10)	179.7(8)
C(10)–O(10)	1.148(9)	Fe(1)–C(11)–O(11)	178.1(9)
C(11)–O(11)	1.165(9)	C(2)–C(4)–C(5)	119.7(6)
		C(2)–C(4)–C(7)	119.3(6)
		C(5)–C(4)–C(7)	120.9(6)
		C(4)–C(5)–C(6)	126.3(6)

Table 2

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for **10**

	x	y	z	U_{eq}^a
Fe(1)	7955(1)	1830(1)	6241(1)	52(1)
C(1)	6926(5)	2382(6)	6463(3)	47(2)
C(2)	6110(4)	2834(6)	6627(3)	43(2)
C(3)	5986(5)	3250(7)	7330(3)	47(2)
O(31)	6655(3)	2858(5)	7796(2)	67(2)
C(31)	6652(6)	3320(9)	8493(3)	84(3)
O(32)	5382(4)	3870(5)	7494(3)	65(2)
C(4)	5355(4)	2983(6)	6068(3)	41(2)
C(5)	5542(4)	3315(6)	5423(3)	47(2)
C(6)	4885(5)	3402(6)	4803(3)	48(2)
O(61)	5332(3)	3749(5)	4260(2)	66(2)
C(61)	4792(6)	3832(8)	3602(4)	73(3)
O(62)	4091(4)	3205(6)	4755(3)	78(2)
C(7)	4427(5)	2692(7)	6216(4)	48(2)
C(8)	4180(5)	1975(7)	6705(4)	53(2)
C(9)	3240(5)	1716(8)	6827(5)	61(2)
O(91)	2650(3)	2020(6)	6300(3)	76(2)
C(91)	1715(5)	1813(10)	6379(5)	107(4)
O(92)	3008(4)	1293(6)	7357(3)	97(2)
C(10)	8973(6)	1314(8)	6704(5)	73(3)
O(10)	9633(4)	984(6)	7002(4)	110(3)
C(11)	8259(6)	1655(9)	5380(5)	75(3)
O(11)	8456(5)	1574(8)	4810(4)	118(3)
P(1)	8453(1)	3714(2)	6328(1)	55(1)
C(12)	8505(5)	4304(8)	7206(4)	71(2)
C(13)	9002(6)	3555(8)	7774(5)	92(3)
C(14)	9605(5)	3920(9)	6080(4)	77(3)
C(15)	10003(6)	5149(10)	6107(5)	108(4)
C(16)	7803(5)	4864(8)	5836(5)	77(3)
C(17)	7784(6)	4778(10)	5057(5)	105(4)
P(2)	7286(2)	53(2)	6359(1)	74(1)
C(18)	7972(8)	–1300(11)	6292(6)	138(4)
C(19)	8477(5)	–1409(7)	5698(4)	183(6)
C(20)	6247(5)	–209(7)	5801(4)	88(3)
C(21)	6302(7)	18(10)	5049(5)	108(3)
C(22)	6855(7)	–226(9)	7217(5)	91(3)
C(23)	7507(8)	–46(10)	7834(5)	119(4)

^a U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 3
Data collection and processing parameters for **10**

Formula	C ₂₆ H ₄₂ FeO ₈ P ₂	Scan speed (deg min ⁻¹)	1.50–14.65
Crystal system	monoclinic	2θ range (deg)	3.5–46.0
Space group	P2 ₁ /c	No. of unique data	4448
a (Å)	14.794(12)	No. of refl. obsd.	2502
b (Å)	11.144(8)	(F ≥ nσ(F))	4
c (Å)	119.313(13)	Weighting scheme	w ⁻¹ = s ² (F) + 0.0001 F ²
β (deg)	95.05(6)	R	0.0901
V (Å ³)	3172(4)	R _w	0.1509
Z	4	Residual extrema in final diff. map (e ⁻ Å ⁻³)	0.51
ρ _{calcd} (g cm ⁻³)	1.257		
Absorption coeff. (cm ⁻¹)	6.13	Goodness of fit	1.81
F ₀₀₀	1272	No. of variables	311
T (K)	293	Absorption correction	none
Scan type	2θ-θ		

separations, in accord with observations of structure determinations of other vinylidene complexes [4,10,15,16].

Finally, it should be noted that the vinylidene plane at C(2) is coplanar with the equatorial plane of the iron unit, which represents the electronically preferred orientation. The π bonding capabilities of C_{2v} d⁸ ML₄ and vinylidene fragments are anisotropic [17]. While the metal fragment possesses a higher propensity for π donation in the equatorial plane, the higher π-accepting capacity of a vinylidene is located in the C(H)R plane. Thus, π interaction is optimized between the metal fragment and the ligands in the given rotameric conformation.

The atomic coordinates of **10** are given in Table 2 and details of the X-ray crystal structure analyses are provided in Table 3. Further details of the X-ray structure determinations may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein Leopoldshafen, Germany. Requests should contain the deposition number CSD-406607, names of the authors and citation of this article.

4. Experimental part

All manipulations were performed by standard

NMR spectra were measured on Varian Gemini 200 or 300 instruments (frequencies: ¹H 200 or 300 MHz; ¹³C 50.3 or 75.4 MHz; ³¹P 121.5 MHz). Standards: ¹H and ¹³C, δ rel. TMS; ³¹P, δ rel. H₃PO₄.

Methyl propiolate was purchased from Fluka. Fe(CO)₂(PEt₃)₂I₂ was obtained as reported earlier [18]. Ether solutions of the mixture of [(OC)₂(Et₃P)₂Fe]₂N₂ **3a** and Fe(CO)₂(PEt₃)₂N₂ **3b** were prepared in situ according to Ref. [10].

4.1. Dicarbonyl(methylpropynoate)bis(triethylphosphane)iron **4a** and dicarbonylhydrido(methylpropynoate-1-yl)bis(triethylphosphane)iron **4b**

At -30 °C 126 mg (1.5 mmol) HC≡CCOOMe was added to an ether solution of **1a,b** prepared from 1 mmol of Fe(CO)₂(PEt₃)₂I₂. After warming to r.t. the solvent was removed. The oily residue was dissolved in hexane and filtered over Celite. Removal of the hexane afforded 360 mg (86%) of the mixture of **4a** and **4b**.

4a. IR (hexane): ν (cm⁻¹) 1960, 1892 (s, C=O), 1739 (w, C≡C), 1689 (m, C=O). ¹H NMR (C₆D₆, 200 MHz): δ = 0.94 (m_c, CH₂CH₃), 1.30 (m_c, CH₂CH₃), 3.40 (s, OCH₃), 7.00 (s, ≡CH). ¹³C NMR (C₆D₆, 50 MHz): δ = 87.6 (s, CH₂CH₃), 17.6 (pseudo-t, J_{PC} = 11.4 Hz, CH₂CH₃), 51.2 (s, OCH₃), 94.4 (t, ³J_{PC} = 9 Hz, C(H)COOMe), 114.1 (t, ²J_{PC} = 12 Hz, ≡CH), 169.0 (s, COOMe), 221.1 (t, ²J_{PC} = 26 Hz,

4.2. Dicarbonyl(methoxycarbonylvinylidene)bis(triethylphosphane)iron **5**

360 mg of the above mixture of **4a** and **4b** was dissolved in 100 ml of hexane and stirred at r.t. together with ca. 100 mg of silylated silica for 24 h. After removal of the solvent in vacuo the residue was subjected to column chromatography on silica. Elution with hexane–ether 10:1 yields a yellow band, from which after concentration of the solution and crystallization at -30°C a yellow precipitate of **5** was formed. **5** melts when it is warmed to r.t. Yield 210 mg (58%).

IR (hexane): ν (cm^{-1}) = 1967, 1905 (s, $\text{C}\equiv\text{O}$), 1702 (m, $\text{C}=\text{O}$), 1561 (m, $\text{C}=\text{C}$). ^1H NMR (C_6D_6 , 200 MHz): δ = 1.00 (m, CH_2CH_3), 1.65 (m, CH_2CH_3), 3.54 (s, OCH_3), 5.40 (t, $^4J_{\text{PH}} = 10.0$ Hz, $=\text{CH}$). ^{13}C NMR (C_6D_6 , 50.3 MHz): δ = 8.2 (s, CH_2CH_3), 21.4 (pseudo-t, $J_{\text{PC}} = 15$ Hz, CH_2CH_3), 50.1 (s, OCH_3), 113.3 (t, $^3J_{\text{PC}} = 7$ Hz, $=\text{C}(\text{H})\text{COOMe}$), 168.6 (t, $^4J_{\text{PC}} = 7$ Hz, COOMe), 215.1 (t, $^2J_{\text{PC}} = 19$ Hz, $\text{C}\equiv\text{O}$), 317.6 (t, $^2J_{\text{PC}} = 48$ Hz, $\text{Fe}=\text{C}$). ^{31}P NMR (C_6D_6): δ = 61.0. MS (70 eV): m/e (%) = 432 (5) $[\text{M}]^+$, 404 (10) $[\text{M} - \text{CO}]^+$, 376 (40) $[\text{M} - 2\text{CO}]^+$, 348 (30) $[\text{M} - 3\text{CO}]^+$, 292 (100) $[\text{M} - 2\text{CO}, \text{C}_4\text{H}_4\text{O}_2]^+$, 264 (30) $[\text{M} - 2\text{CO}, \text{C}_4\text{H}_4\text{O}_2, \text{C}_2\text{H}_5]^+$, 230 (70) $[\text{M} - 3\text{CO}, \text{PEt}_3]^+$, 200 (60) $[\text{M} - 3\text{CO}, \text{OCH}_3, \text{PEt}_3]^+$, 182 (5) $[\text{M} - 3\text{CO}, \text{C}(\text{O})\text{OCH}_3, \text{PEt}_3]^+$, 174 (30) $[\text{Fe}(\text{PEt}_3)]^+$, 154, 146 (40) $[\text{Fe}(\text{PEt}_2)]^+$, 118 (50) $[\text{PEt}_3]^+$, 106, 90 (45) $[\text{PEt}_2]^+$, 77, 62, 57, 49. $\text{C}_{18}\text{H}_{34}\text{FeO}_4\text{P}_2$ (432.66) Calcd: C 50.02 H 7.93 Fe 12.92 Found: C 49.79 H 7.93 Fe 12.95

4.3. Carbonyl[2,4,6-tris(methoxycarbonyl)-hexa-1,3,5-trien-1,5-diyl]bis(triethylphosphane)iron **9** and dicarbonyl[methoxycarbonyl(1,4-dimethoxycarbonyl-but-1,3-dien-2-yl)vinylidene]bis(triethylphosphane)iron **10**

210 mg (0.49 mmol) of **5** and 101 mg (1.2 mmol) of $\text{HC}\equiv\text{CCOOMe}$ were dissolved in ether and stirred at r.t. for 3 h. The solvent was removed in vacuo. Column chromatography on silica and elution with hexane–ether 2:1 revealed a green zone, which was collected and concentrated in vacuo. At -30°C **9** precipitated from this solution. Elution with ether afforded a red zone, from which **10** also crystallized upon standing at -30°C .

9. Yield 25 mg (9%). IR (hexane): ν (cm^{-1}) = 1922 (s, $\text{C}\equiv\text{O}$), 1737, 1691, 1572 (w, $\text{C}=\text{O}$). ^1H NMR (C_6D_6 , 200 MHz): δ = 0.77 (dt, $^3J_{\text{HH}} = 7.3$ Hz, $^3J_{\text{PH}} = 14.3$ Hz, 18 H, CH_2CH_3), 1.34–1.44 (m, 12 H, CH_2CH_3), 3.30, 3.56, 3.58 [$3 \times$ s, $\text{C}(\text{O})\text{OCH}_3$], 7.56 (t, $^3J_{\text{PH}} = 4.8$ Hz, 1 H, $\text{Fe}-\text{CH}=\text{CR}'$), 8.94 (d, $^5J_{\text{HH}} = 2.0$ Hz), 12.66 (d, $^5J_{\text{HH}} = 2.0$ Hz). ^{31}P NMR (C_6D_6): δ = 40.2. MS (70 eV): m/e (%) = 572 (8) $[\text{M}]^+$, 544 $[\text{M}^+ - \text{CO}]$, 426 (100) $[\text{M}^+ - \text{CO}, \text{PEt}_3]^+$, 398, 368,

342, 292 $[\text{Fe}(\text{PEt}_3)]^+$, 280, 221, 205, 175, 118 $[\text{PEt}_3]^+$, 90, 62.

$\text{C}_{25}\text{H}_{42}\text{O}_7\text{P}_2$ (572.40) Calcd: C 52.46 H 7.40
Found: C 52.29 H 7.31

10. Yield 193 mg (66%). IR (hexane): ν (cm^{-1}) 1970, 1910 (s, $\text{C}\equiv\text{O}$), 1737, 1717, 1695, (w, $\text{C}=\text{O}$). ^1H NMR (C_6D_6 , 200 MHz): δ = 0.96 (dt, $^3J_{\text{HH}} = 7.8$ Hz, $^3J_{\text{PH}} = 16.0$ Hz, 18 H, CH_2CH_3), 1.53–1.67 (m, 12 H, CH_2CH_3), 3.36, 3.38, 3.43 [$3 \times$ s, $\text{C}(\text{O})\text{OCH}_3$], 6.36 (dd, $^3J_{\text{HH}} = 16.0$ Hz, $^4J_{\text{HH}} = 0.5$ Hz, 1 H, $\text{C}(4)\text{H}$), 6.48 (m, 1 H, $\text{C}(\text{exo methylene})$), 9.04 (dd, $^3J_{\text{HH}} = 16.0$ Hz, $^4J_{\text{HH}} = 0.8$ Hz, 1 H, $\text{C}(5)\text{H}$). ^{13}C NMR (C_6D_6 , 50.3 MHz): δ = 7.7 (s, CH_2CH_3), 21.3 (pseudo-t, $J_{\text{PC}} = 15$ Hz, CH_2CH_3), 50.4, 50.6, 50.9 [$3 \times$ s, $\text{C}(\text{O})\text{OCH}_3$], 117.5 (t, $^5J_{\text{PC}} = 2$ Hz, $=\text{C}$ (exo methylene)), 123.3, 143.2 ($2 \times$ s, $\text{C}(4)$, $\text{C}(5)$), 148.7 (t, $^4J_{\text{PC}} = 6$ Hz, $\text{C}(3)$), 166.6, 166.8 ($2 \times$ s, $\text{C}=\text{O}$ (exo methylene), $\text{C}=\text{O}$ (vinyl)), 167.9 (t, $^4J_{\text{PC}} = 6$ Hz, $\text{C}=\text{O}$ (vinylidene)), 214.6 (t, $^2J_{\text{PC}} = 21$ Hz, $\text{C}=\text{O}$), 214.8 (t, $^2J_{\text{PC}} = 18$ Hz, $\text{C}\equiv\text{O}$), 315.1 (t, $^2J_{\text{PC}} = 47$ Hz, $\text{Fe}=\text{C}$). ^{31}P NMR (C_6D_6): δ = 61.5. MS (70 eV): m/e (%) 600(4) $[\text{M}]^+$, 544 $[\text{M}^+ - 2\text{CO}]$, 482 $[\text{M}^+ - \text{PEt}_3]^+$, 454 $[\text{M}^+ - \text{CO}, \text{PEt}_3]$, 426 $[\text{M}^+ - 2\text{CO}, \text{PEt}_3]$, 398, 368, 292 (100) $[\text{Fe}(\text{PEt}_3)_2]^+$, 280, 221, 205, 175, 149, 118 $[\text{PEt}_3]^+$, 90, 62.

$\text{C}_{26}\text{H}_{42}\text{FeO}_8\text{P}_2$ (600.41) Calcd: C 52.01 H 7.05 Fe 9.30
Found: C 52.15 H 6.93 Fe 9.06

Acknowledgements

Financial support from the Swiss National Science Foundation is gratefully acknowledged.

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