The reactions of dicarbonylbis(phosphorus donor)iron fragments with tertiary propargyl alcohols

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Abstract

The reaction of the mixture of $Fe(CO)_2(PEt_3)_2N_2$ (**1a**) and $[Fe(CO)_2(PEt_3)_2]_2N_2$ (**1b**) with propargyl alcohols $HC{\equiv}C-CR_1R_2OH$ ($R_1 = R_2 = Me$; $R_1 = Me$, $R_2 = Et$; $R_1 = Me$, $R_2 = iPr$; $R_1 = Me$; $R_2 = tBu$; $R_1 = R_2 = tBu$; $R_1 = R_2 = Ph$) in THF affords isolable $Fe(CO)_2(PEt_3)_2(H)(C{\equiv}C-CR_1R_2OH)$ complexes ($R_1 = R_2 = Me$ **2a**; $R_1 = Me$, $R_2 = Et$ **2b**; $R_1 = Me$, $R_2 = iPr$ **2c**; $R_1 = Me$, $R_2 = tBu$ **2d**; $R_1 = R_2 = tBu$ **2e**; $R_1 = R_2 = Ph$ **2f**). Complexes **2a–d** underwent dehydration in hexane in the presence of silylated silica to yield vinylvinylidene complexes $Fe(CO)_2(PEt_3)_2{=}C{=}C(H)R'C-CR''R'''$ ($R' = Me$, R'', $R''' = H$ **3a**; $R' = R'' = Me$, $R''' = H$ **3b**; $R' = R''' = Me$, $R'' = H$ **3c**; $R' = R'' = R''' = Me$ **3d**; $R' = tBu$, $R'' = R''' = H$ **3e**). **2e** and **2f** did not eliminate water. However, double deprotonation with *n*-BuLi and deoxygenation with acetyl chloride ultimately produced then their formal products of dehydration: di(t-butyl) or diphenylallenylidene(dicarbonyl)bis(triethylphosphine)iron compounds **4a** or **4b**. The reactions of dicarbonylbis(trimethylphosphite)iodoferrate **1b** with the same propargyl alcohol derivatives $HC{\equiv}C-CR_1R_2OH$ as mentioned above resulted in the formation of dicarbonylbistrimethylphosphite(vinylidene)iron derivatives $Fe(CO)_2[P(OMe)_3]_2{=}C{=}C(H)CR_1R_2OH$ ($R_1 = R_2 = Me$) **7a**; $R_1 = Me$; $R_2 = Et$ **7b**; $R_1 = Me$, $R_2 = iPr$; **7c**; $R_1 = Me$, $R_2 = tBu$ **7d**; $R_1 = R_2 = tBu$ **7e**; $R_1 = R_2 = Ph$ **7f**). Dehydration processes of **7a–f** in the presence of Al_2O_3 or SiO_2 led to allenylidene or vinylvinylidene complexes $Fe(CO)_2[P(OMe)_3]_2{=}C{=}C{=}CR_1R_2$ ($R_1 = Me$, $R_2 = tBu$ **8a**; $R_1R_2 = tBu$ **8b**; $R_1 = R_2 = Ph$ **8c**) or $Fe(CO)_2[P(OMe)_3]_2{=}C{=}C(H)CR'{=}CR''R'''$ ($R' = Me$, $R'' = R''' = H$ **9a**; $R' = Et$, $R'' = R''' = H$ **9b**; $R' = R'' = Me$, $R''' = H$ **9c**; $R' = R''' = Me$, $R'' = H$ **9d**; $R' = iPr$, $R'' = R''' = H$ **9e**; $R' = R'' = R''' = Me$ **9f**; $R' = tBu$, $R'' = R''' = H$ **9g**). **8c** was also prepared by an alternative route starting from **1c** and $HC{\equiv}C-CPh_2OAc$ which provided a higher yield. **7e** and **8b** were characterized by single crystal X-ray diffraction studies. © 1997 Elsevier Science S.A.

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1. Introduction

Earlier, we and others have shown that metal-bound propargyl units can be transformed into a variety of compounds [1,2]: for example vinylidene complexes have been found as products of hydrogen shift reactions (for

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selected references see Refs. [3,4]), and quite often in subsequent dehydration steps highly unsaturated vinyl vinylidene [5–8] and allenylidene species [5–15]. In some cases also C–C coupling occurred with multiple involvement of the acetylenic derivatives [13,16,17]. For all this versatile reactivity the initial acetylene transformations were as mentioned the acetylene/vinylidene rearrangement or the oxidative addition of the acetylene terminal C–H bond to the metal centre.
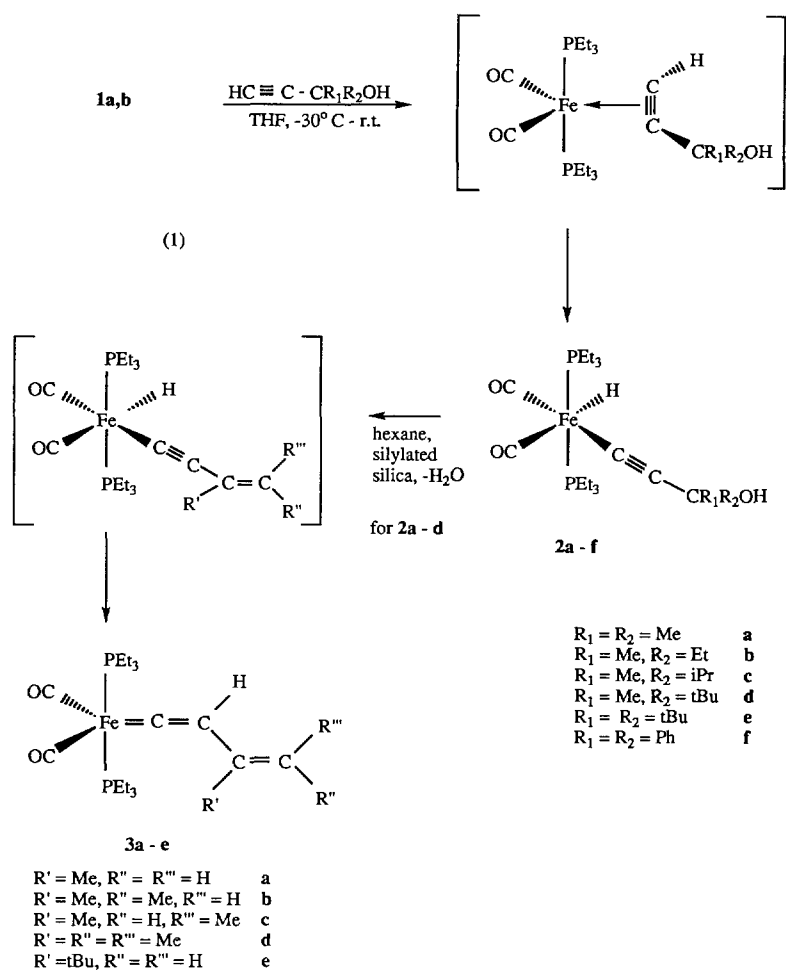
It is the goal of this paper to further explore the scope of propargylic conversions by probing the reactive behaviour of appropriate organic derivatives at carbenoid $Fe(CO)_2L_2$ centres (L = phosphorus donor). These iron units seemed to be especially suited for such explorations, since the mentioned fundamental reaction modes were already reported to be accessible [3,16,18].

2. Results and discussions

Some years ago we discovered that dinitrogen complexes of the type $[Fe(CO)_2L_2]_2(\mu\text{-}N_2)$ or $Fe(CO)_2L_2(N_2)$ provide a convenient source for $[Fe(CO)_2L_2]$ units, since at room temperature in solution they undergo facile loss of the N_2 ligand [18,19]. More recently we could then demonstrate that the in situ preparation of the above dinitrogen complexes with $L = PEt_3$, $P(OiPr)_3$ can be achieved by reductive routes [20], which afford these compounds starting from $Fe(CO)_2L_2X_2$ species in practically quantitative yield. For $L = P(OMe)_3$ it was not possible to obtain the dinitrogen complex by this method. However, the thus generated iron(0) species $\{Fe(CO)_2[P(OMe)_3]_2X\}^-$ readily lose an X^- substituent and therefore can serve as convenient $Fe(CO)_2[P(OMe)_3]_2$ sources, as well. We have chosen to investigate in this paper the propargyl reactions of two kinds of $[Fe(CO)_2L_2]$ fragments $L = PEt_3$, $P(OMe)_3$, among other aspects in order to trace any influence of the electronic properties of the iron moiety. THF solutions of **1a,b** (ca. 20:1 under 1 bar N_2) and of **1c** were used as the iron-containing starting materials [20].

1a   1b

1c
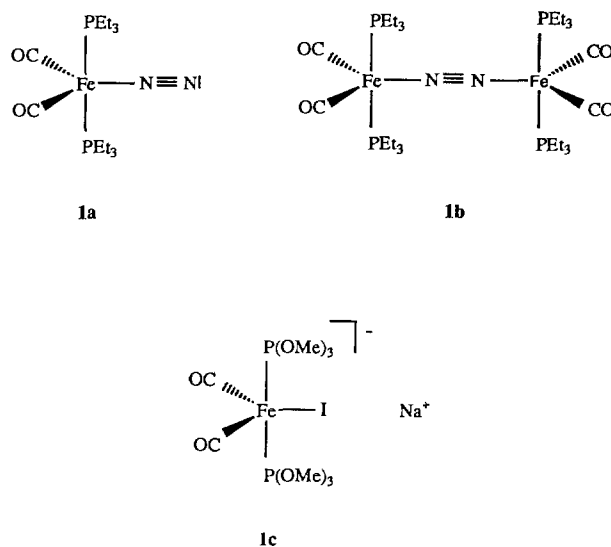
The reactions of **1a,b** with a variety of tertiary propargyl alcohols ($-30\,°C$ to room temperature (r.t.)) revealed in all cases hydrido acetylido iron products (**2a–f**), which were presumably formed via the intermediacy of π acetylene species (Eq. (1)). **2a–f** were isolated as oils stable at r.t. They were fully characterized spectroscopically and by elemental analyses.

$R_1 = R_2 = Me$ **a**
$R_1 = Me, R_2 = Et$ **b**
$R_1 = Me, R_2 = iPr$ **c**
$R_1 = Me, R_2 = tBu$ **d**
$R_1 = R_2 = tBu$ **e**
$R_1 = R_2 = Ph$ **f**

3a - e

R' = Me, R" = R''' = H   a
R' = Me, R" = Me, R''' = H   b
R' = Me, R" = H, R''' = Me   c
R' = R" = R''' = Me   d
R' = tBu, R" = R''' = H   e

(1)

Their structural assignment follows from typical spectroscopic features. The IR spectra reveal an acetylide band and two $\nu(CO)$ absorptions, which appear for all derivatives at remarkably constant positions indicating that the stereoelectronic properties of the iron centres are very similar. In the ^{1}H NMR spectra of **2a–f** resonances at around -8.7 ppm with J_{P-H} couplings between 48 and 52 Hz are attributed to hydride ligands. Furthermore, the ^{13}C NMR spectra show two sets of $C_{acetylide}$ signals, from which the low field ones are P coupled and therefore originate from the iron-bound carbon atoms. Each of the complexes **2a–f** gives rise to two $^{13}C_{CO}$ resonances confirming the chemical inequivalence of the carbonyl groups.

Earlier work in this field demonstrated that tertiary propargyl alcohol complexes or their vinylidene congeners can be dehydrated to give allenylidene compounds [9–15]. However, for compounds **2a–f** this kind of reactivity was not available in a spontaneous fashion. An alternative type of water elimination became accessible with formation of the vinyl vinylidene complexes **3a–e** [5–8]. These reactions required the presence of an oxidic promoter and were quite surprisingly found to be greatly facilitated in hexane solution [5]. For **3a–e** the best yields were obtained with silylated SiO_2. As shown in Eq. (1) it is suggested that these processes proceed via vinyl acetylide species as primary intermediates and not via hydroxy vinylidene complexes, which could be envisaged as products of initial 1,3-H migrations in **2a–d**. If this latter type of step were available, it would be expected, that subsequent 1,2-elimination of H_2O would then directly lead to allenylidene complexes, as is actually seen in the chemistry of phosphite-substituted derivatives (vide infra). The apparent inaccessibility of the 1,3-H shift in **2a–d** indicates the preference of the $Fe(CO)_2 L_2(acetylene)$ system for the iron(II) hydride state. The vinyl acetylide species formed as subsequent products can obviously overcome the hydride 'sink'. This can be explained based on the availability of enhanced π stabilization in the final vinyl vinylidene frameworks of **3a–e**.

Within the acetylenic moieties of **2b** and **2c** two principally possible directions of H_2O elimination can be

anticipated. However, only Saytzeff products are found. This supports the idea, that these reactions follow an E_1 mechanism, which is presumably H^+ or Lewis acid catalysed. The Saytzeff process of **2b** leads to the two E, Z isomers **3b** and **3c**, which could not be separated. The formation of vinyl vinylidene complexes via the elimination of small molecules like H_2O, NH_3 or HCl is a common feature in propargyl-derived vinylidene chemistry [6].

The conceivable direct formation of allenylidene complexes by 1,4-eliminations of H_2O from **2a–d** involving the iron-bound H atom can apparently not be accessed. This also mirrors the great stabilization effect of the iron hydrogen bond and is especially reflected in the reaction behaviour of **2e** and **2f**. Both compounds bear no protons β to the OH group and are reluctant to undergo the necessary spontaneous or SiO_2- or Al_2O_3-induced dehydration reactions.

The unsaturated species **3a–e** are isolated in analytically pure form. Their structural assignment was mainly based on IR and NMR spectroscopy. The IR spectra ($2000–1500\,cm^{-1}$) reveal two $\nu(CO)$ bands and weak absorptions varying in their positions between 1604 and $1568\,cm^{-1}$. These latter bands are attributed to $\nu(C=C)_{vinylidene}$ vibrations. They are all shifted to lower wavenumbers in comparison with unconjugated vinylidene congeners. The ^1H NMR spectra show characteristic resonances for the $H_{vinylidene}$ protons, which are found in the typical region between 5 and 6 ppm and are phosphorus coupled. In the ^{13}C NMR spectra it was possible to assign signals for all C_{vinyl} nuclei and for the iron-bound $C_{vinylidene}$ atoms, which typically appear at very low field (> 310 ppm) possessing a strong P coupling of around 52 Hz.

In further investigations we then attempted the conversion of **2e** and **2f** into allenylidene compounds. Since this could not even be induced with SiO_2 or Al_2O_3 under mild conditions (vide supra), more forcing conditions were considered applying n-BuLi as a strong base to allow abstraction of both the OH and the hydride protons. Indeed, after subsequent addition of acetyl chloride deoxygenation occurred [12–14] with formation of the desired allenylidene complexes **4a** (56%) and **4b** (57% yield) (Eq. (2)).

$$R = tBu\ \mathbf{4a}$$
$$R = Ph\ \mathbf{4b}$$

(2)
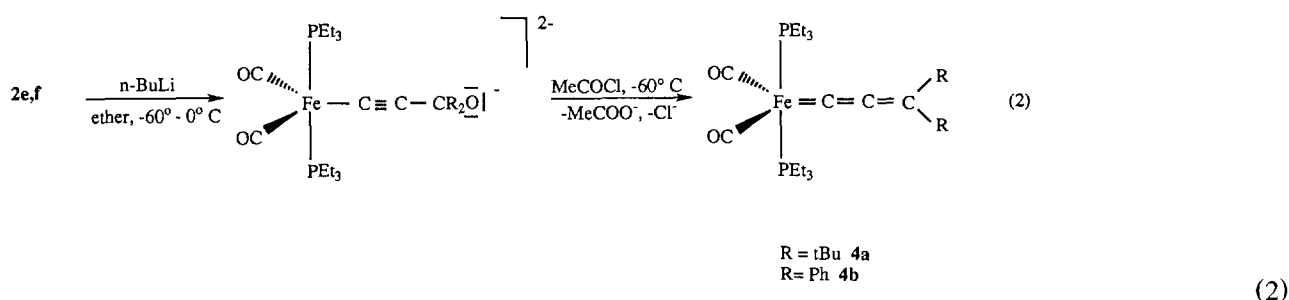
4a and **4b** were isolated as brown and dark green oils respectively. They were characterized by elemental analyses and by spectroscopy, the latter also based on comparisons with data of related complexes reported earlier [11–14]. In the region of $2100–1800\,cm^{-1}$ the IR spectra show two $\nu(CO)$ bands. The expected $\nu(C_3)$ vibrations of the allenylidene residues were, however, not observable. Presumably they are hidden by the $\nu(CO)$ absorptions at lower wavelengths. Nevertheless, the allenylidene ligand could be identified by three typical ^{13}C NMR resonances (C_α: 242.6 ppm (**4a**), 224.5 ppm (**4b**); C_β: 200.2 ppm (**4a**), 208.1 ppm (**4b**), C_γ: 139.3 ppm (**4a**), 118.7 ppm (**4b**)), which all display coupling to the ^{31}P nuclei. This suggests their embedment in a π system connected to the iron centre.

When the phosphite derivative **1c** is reacted with the same series of tertiary propynols as the mixture of **1a,b**, a somewhat different chemistry with respect to that of the phosphine-substituted complexes (Eq. (1)) evolves. While the PEt_3 derivatives characteristically demonstrated the preferential formation of hydrido acetylido compounds, the initial IR analysis of the $\nu(CO)$ region of the reaction mixtures of **1c** at room temperature in THF immediately reveals the presence of the π acetylene complexes **5a–d** and **5f**. Additional pairs of $\nu(CO)$ bands of low intensity suggest the existence of minor equilibrium amounts of the corresponding $Fe(H)(C\equiv CR)$ species **6a–d** and **6f** (Eq. (3)). Apparently the $Fe(CO)_3[P(OMe)_3]_2$ fragment lacks sufficient electron density to enforce conversion to products of oxidative addition. The only exception in this series is the equilibrium of the t-butyl derivative, for which the hydrido acetylido isomer **6e** strongly dominates over the π acetylene complex **5e**, which can only be detected IR and NMR spectroscopically in low concentration (**6e**: IR (THF): $\nu(C\equiv O)$ 2028, $1985\,cm^{-1}$, ^1H NMR (C_6D_6, 200 MHz): $\delta = -8.71$ ppm (t, $^2J_{PH} = 58.4\,Hz$, FeH)). It is assumed, that the major factor which determines this specific

behaviour is sterics rather than electronics. The bulky t-butyl groups effect greater steric congestion and therefore relative destabilization of the π acetylene form.
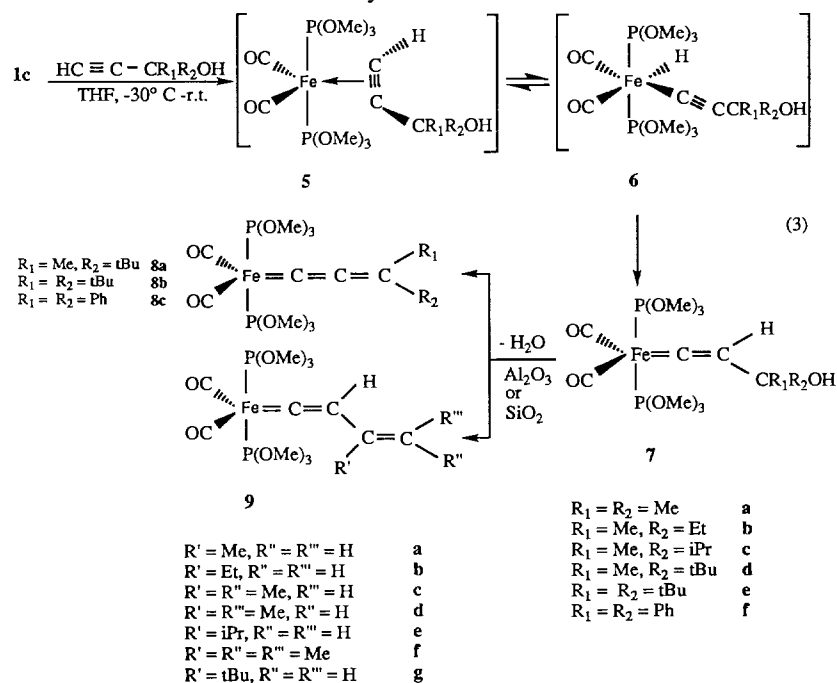

(3)

The analyses of the π acetylene/hydrido acetylido equilibria and the structural description of the major equilibrium component were somewhat complicated by their slow and irreversible conversion to vinylidene complexes, which were therefore already present in small amounts in the initial reaction mixtures. Attempts at chromatographic separations of **5a–d**, **5f** and **6e** from the other equilibrium constituents were further obscured by the fact that the contact with a stationary phase, like silylated silica, silica or alumina, caused enhancement of the transformations to vinylidene species and partly also of the still slower subsequent dehydration reactions (Eq. (3)). For this reason most of the π acetylene species or **6e** could not be isolated; except for **5a**, **5b** and **5f**, which were obtained together with the vinylidene compounds by low temperature column chromatography on silylated silica and characterized from such mixtures by spectroscopic methods.

When after the initial reaction the solvent was changed from THF to hexane, the π acetylene and the hydrido acetylide components were found to be immediately converted to the thermodynamically favoured vinylidene species **7a–f**. Their prevailing presence now allowed their purification by low temperature column chromatography. In the formation of **7c** and **7d** minor side reactions have been encountered, which were also observed in other related investigations [3], but not with any of the PEt₃ derivatives. The propargyl residues were in these cases degraded with extrusion of methyl-i-propyl or methyl-t-butyl ketone to afford the known parent vinylidene complex **10** [3,21].
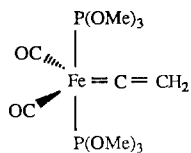
10

The isolation of P(OMe)₃-substituted vinylidene complexes contrasts our observations in the Fe(CO)₂(PEt₃)₂ realm, where the primary isolable products of the reactions with the propargyl alcohols were hydrido acetylide species and the vinylidene complexes were not traceable at all. Compounds **7a–f** were isolated in moderate to good yields and characterized by elemental analyses and through their spectroscopic properties. In addition to this, it was possible to obtain suitable crystals from **7e**, which allowed its prototypical X-ray structural analysis.
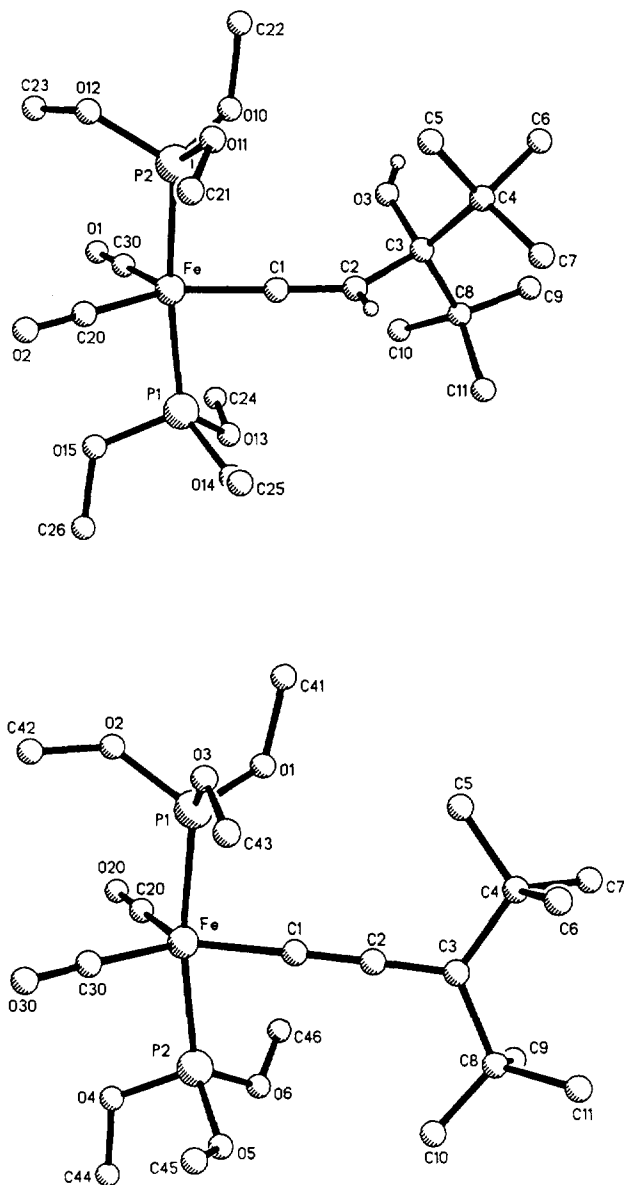
Fig. 1. Molecular structures of **7e** (above) and **8b** (below).

The IR spectra of complexes **7a–f** show two distinct ν(CO) bands around 1990 and 1930 cm^{-1} and a shoulder at the low energy absorption. This observation is presumably due to the presence of another Fe=C=C axis rotamer. In addition to these bands, an absorption for the ν(C=C) vibration of the vinylidene moiety is identified. The given structural assignments of **7a–f** are supported further by the NMR spectra. Like the PEt$_3$-substituted complexes **3a–e**, **7a–f** display typical ^{1}H NMR resonances for the vinylidene protons and in the ^{13}C NMR spectra these complexes show two phosphorus-coupled signals for the carbon atoms of the metallacumulenic chain.

Table 1
Bond lengths (Å) and angles (deg) for **7e**

Fe–P1	2.162(2)	P1–Fe–P2	170.6(1)
Fe–P2	2.155(1)	C1–Fe–C20	128.2(1)
Fe–C20	1.789(3)	C20–Fe–C30	103.3(1)
Fe–C30	1.777(2)	Fe–C1–C2	174.5(2)
C20–O2	1.148(3)	C1–C2–C3	128.4(2)
C30–O1	1.147(4)	C1–Fe–C30	128.5(1)
Fe–C1	1.778(3)		
C1–C2	1.321(4)		

Table 2
Bond lengths (Å) and angles (deg) for **8b**

Fe–P1	2.159(1)	P1–Fe–P2	170.8(1)
Fe–P2	2.154(1)	C20–Fe–C30	102.3(2)
Fe–C1	1.833(4)	Fe–C1–C2	179.1(2)
Fe–C20	1.780(4)	C1–C2–C3	177.8(3)
Fe–C30	1.778(3)	C1–Fe–C20	130.3(1)
C20–O20	1.160(5)	C1–Fe–C30	127.4(2)
C30–O30	1.149(4)		
C1–C2	1.266(5)		
C2–C3	1.344(6)		

As mentioned above, the dehydration reactions of complexes **7a–d** (Eq. (3)) can be accelerated in hexane [5] or in the presence of silica or alumina. The type of solvent and the type of adsorbent or the combination of both is however decisive for the regioselectivity of the water elimination. For instance, the use of Al_2O_3 and THF establishes **9b–d** and **9e,f** as products of the reactions of **7b** and **7c** respectively. With SiO_2 and hexane only the E,Z mixture **9c,d** and **9f** are observed. Apparently this latter condition leads to the exclusive generation of the Saytzeff products comparable to the transformations of the PEt_3 derivatives (vide supra).

The vinyl vinylidene complexes **9** show similar spectroscopic features as their PEt_3 congeners. Even rotational isomerism around the $Fe=C=C$ axis seems to be operative for most of them (**9b–d**), since their IR spectra display a third $\nu(CO)$ band appearing as a shoulder. Also, the $^1H_{vinylidene}$ resonances are detected in the same chemical shift region as those of **3a–e**. The ^{13}C resonances of the iron-bound $C_{vinylidene}$ atoms of **9a–d** are shifted only slightly upfield with regard to the PEt_3 series possessing also a somewhat higher J_{PC} coupling.

In contrast to the $Fe(CO)_2(PEt_3)_2$ chemistry, the oxide-promoted conversions of tertiary propargyl derivatives at

Table 3
Atomic coordinates and equivalent isotropic temperature factors of **7e**

Atom	x	y	z	U_{eq}
Fe	2093(1)	8507(1)	2525(1)	24(1)
P(1)	1488(1)	10057(1)	3115(1)	38(1)
P(2)	2565(1)	6793(1)	2120(1)	24(1)
O(1)	2033(3)	9281(3)	555(2)	63(1)
O(2)	5178(2)	10406(2)	3917(2)	50(1)
O(3)	−1875(2)	4584(2)	1330(2)	45(1)
O(10)	1261(2)	5468(2)	1149(2)	32(1)
O(11)	2793(2)	5952(2)	2949(2)	32(1)
O(12)	4052(2)	7162(2)	1850(2)	33(1)
O(13)	−52(3)	9967(3)	2540(2)	65(1)
O(14)	1038(3)	10062(3)	4134(3)	26(1)
O(15)	2716(3)	11638(2)	3183(2)	52(1)
C(1)	610(3)	7166(2)	2809(2)	27(1)
C(2)	−393(3)	6161(3)	3088(2)	30(1)
C(3)	−1885(3)	4858(3)	2390(2)	31(1)
C(4)	−2033(3)	3488(3)	2757(2)	40(1)
C(5)	−594(3)	3451(3)	2913(3)	68(1)
C(6)	−3292(4)	2045(3)	1972(3)	66(1)
C(7)	−2279(4)	3525(3)	3827(3)	65(1)
C(8)	−3168(3)	5237(3)	2330(3)	49(1)
C(9)	−4724(3)	3992(4)	1776(3)	74(1)
C(10)	−2964(3)	6307(4)	1670(4)	96(1)
C(30)	2070(3)	8974(3)	1323(2)	37(1)
C(11)	−3075(4)	5946(4)	3411(3)	86(1)
C(20)	3971(3)	9680(2)	3360(2)	30(1)
C(21)	3673(3)	6724(3)	4030(2)	45(1)
C(22)	1376(3)	4224(3)	736(2)	42(1)
C(23)	4375(3)	7873(3)	1056(3)	47(1)
C(25)	1776(3)	9812(3)	5045(2)	53(1)
C(26)	2669(4)	12915(3)	3618(3)	70(1)
C(24)	−509(4)	9866(4)	1455(3)	84(1)
O(14D)	1962(4)	10675(4)	4442(4)	72(1)

Table 4
Atomic coordinates and equivalent isotropic temperature factores of **8b**

Atom	x	y	z	U_{eq}
Fe	1411(1)	6445(1)	7236(1)	27(1)
P(1)	−708(1)	7748(1)	6877(1)	30(1)
P(2)	3596(1)	5436(1)	7540(1)	36(1)
O(1)	−729(2)	9035(3)	5901(2)	50(1)
O(2)	−1557(3)	7253(3)	6302(3)	59(1)
O(2D)	−1971(5)	7176(5)	7083(5)	56(1)
O(3)	−1881(3)	8274(3)	7817(2)	84(1)
O(4)	4175(3)	3937(2)	7453(3)	56(1)
O(5)	4065(3)	5309(3)	8678(2)	53(1)
O(6)	4807(3)	6002(3)	6781(2)	55(1)
O(20)	1991(3)	5628(3)	5175(2)	67(1)
O(30)	472(3)	4365(3)	8938(2)	60(1)
C(1)	1600(3)	7884(3)	7448(3)	30(1)
C(2)	1747(3)	8878(3)	7582(3)	34(1)
C(3)	1956(3)	9916(3)	7706(3)	35(1)
C(4)	741(3)	11294(3)	7511(3)	44(1)
C(5)	−429(4)	11237(3)	7010(4)	66(1)
C(6)	56(4)	11644(4)	8613(3)	78(1)
C(7)	1254(4)	1?412(3)	6684(4)	71(1)
C(8)	3417(3)	9669(3)	8010(3)	49(1)
C(9)	4444(5)	9811(5)	6944(5)	105(1)
C(9D)	4600(6)	8665(6)	7488(6)	60(1)
C(10)	4049(5)	8262(4)	8659(4)	70(1)
C(10D)	3316(6)	8843(6)	9301(6)	55(1)
C(11)	3380(5)	10511(5)	8717(4)	80(1)
C(11D)	3899(6)	10805(6)	7897(6)	48(1)
C(20)	1763(3)	5929(3)	5999(3)	41(1)
C(30)	843(3)	5176(3)	8264(3)	37(1)
C(41)	−2027(3)	10075(3)	5529(3)	55(1)
C(42)	−1882(4)	6088(4)	6798(4)	78(1)
C(43)	−1728(4)	8182(4)	8886(3)	62(1)
C(44)	5620(4)	3079(4)	7589(4)	81(1)
C(45)	3163(4)	5144(4)	9705(3)	70(1)
C(46)	4767(4)	6666(4)	5627(3)	66(1)

$Fe(CO)_2[P(OMe)_3]_2$ centres revealed also access to those H_2O eliminations, by which under mild conditions allenylidene compounds are formed. Stirring of **7d–f** with Al_2O_3 in hexane for 12 h at room temperature converts **7d,f** partially to **8a,c** and **7e** almost quantitatively into **8b** (Eq. (3)). **8a** was separated from **9g** by column chromatography. Comparable to the reactions to **7c** and **7d**, the conversion to **8c** was accompanied by the formation of a considerable amount of **10** and benzophenone. Unfortunately, **8c** could not be separated from these side products. Therefore, in order to obtain **8c** in pure form, we attempted a modified reaction involving 1,1-diphenyl-2-propyne-1-acetate and **1c**. Indeed, subsequent spontaneous acetic acid elimination afforded analytically pure **8c** (Eq. (4)) passing presumably through a vinylidene intermediate.
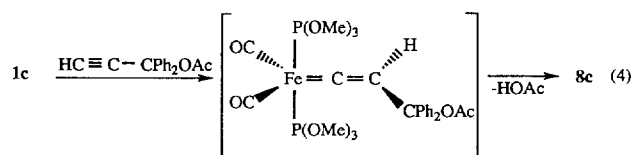
The highly coloured allenylidene complexes **8a–c** (dark-red, dark-brown, black-green) were identified spectroscopically and they gave correct elemental analyses. In an exemplary way the structure of **8b** was confirmed by single crystal X-ray diffraction. The $\nu(CO)$ bands of **8a–c** are found at somewhat lower wavenumbers with respect to those of **7a–f**, which stresses the fact that allenylidene units are weaker π acceptors than vinylidene moieties. Remarkably, just **8b** shows doubling of the $\nu(CO)$ absorptions indicating rotational isomerism around the ferra cumulene bond. A

Table 5
Data collection and processing parameters for complexes **7e** and **8b**

	7e	8b
Formula	$C_{19}H_{38}FeO_9P_2$	$C_{19}H_{36}FeO_8P_2$
Crystal system	triclinic	triclinic
Space group	$P1$	$P1$
a (Å)	10.664(5)	10.317(5)
b (Å)	10.801(4)	11.348(6)
c (Å)	10.691(6)	12.855(6)
α (deg)	98.61(4))	70.34(4)
β (deg)	103.46(3)	75.30(4)
ν (deg)	116.50(3)	66.49(3)
V	2	2
V (Å³)	1313.0(9)	1288(11)
Z	2	2
ρ_{calcd} (g cm^{-3})	1.336	1.316
Absorption coefficient (cm^{-1})	7.33	7.42
F_{000}	560	540
T (K)	213	243
Scan type	$2\Theta-\Theta$	$2\Theta-\Theta$
Scan speed (deg min^{-1})	2.49–14.65	2.40–14.50
2θ range (deg)	4.0–52.0	4.0–54.0
No. of unique data	5137	5542
No. of refl obsd	4413	4455
$(F \geq n\alpha(F))$	10.0	6.0
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0016F^2$	$w^{-1} = \sigma^2(F) + 0.0007F^2$
R	4.77	5.59
R_w	7.40	8.16
Residual extrema in final diff. map (e$^-$ Å^{-3})	0.98	1.05
Goodness of fit	1.59	2.47
No. of variables	291	307
Absorption correction	DIFABS [26]	DIFABS [26]

$\nu(C_3)$ absorption was detected only for **8b** (1865 cm^{-1}) and like in the cases of the phosphane-substituted complexes **4a** and **4b**, the ^{13}C NMR spectra of **8a–c** revealed typical resonances for the C_3 backbone.

3. X-ray diffraction studies on 7e and 8b

Both complexes **7e** and **8b** display approximate trigonal bipyramidal coordination around the d^8 iron centres (Fig. 1) and their Fe(CO)$_2$[P(OMe)$_3$]$_2$ frameworks are very similar in bond lengths and angles (see Tables 1 and 2). The IR spectroscopically derived conclusion, that vinylidene units bind more strongly to metal centres than allenylidene ligands, is corroborated by the observation of a shorter Fe–C1 distance for **7e** than for **8b** (1.778(3) vs. 1.833(4) Å) [21,22].

The interchain C–C distances of the unsaturated units resemble values of earlier structure determinations of related complexes [1,21–23]. The C–C distances of **8b** alternate, which is a general feature of allenylidene complexes [5,8,10,14,15]. Finally, it should be noted that the 'vinylidene plane' of **7e** and the 'allenylidene plane' of **8b** are approximately perpendicular to each other. They are found in the electronically preferred orientation with respect to the equatorial plane of the trigonal bipyramid. The π bonding capabilities of C_{2v} d^8 ML$_4$, vinylidene and allenylidene fragments are anisotropic [24]. While the metal possesses a higher propensity for π donation in the equatorial plane, the higher π accepting capacities of vinylidenes and allenylidenes are located in or perpendicular to the C(H)R or CR$_2$ planes respectively. Thus, π interaction is optimized between the metal fragment and the ligands in the given rotameric conformations of **7e** and **8b**. They are found in many other trigonal bipyramidal vinylidene and allenylidene complexes, as well.

The atomic coordinates of **7e** and **8b** are given in Tables 3 and 4 and details of the X-ray crystal structure analyses (SHELXTL PLUS program package [25]) are provided in Table 5. [2]

4. Conclusions

Our investigations of the reactions of $Fe(CO)_2L_2$ units with tertiary propargyl alcohols have demonstrated that, dependent on the type of L, the initially formed terminal acetylene complexes can be transformed into hydrido acetylido (L = PEt_3) or vinylidene species (L = $P(OMe)_3$) as isolable primary products. This difference in chemical behaviour reflects the different electronic properties of the iron centres, since oxidative additions preferably take place in electron-rich coordination environment and the H mobility following either a 1,2- or a 1,3-shift apparently is more facile at iron centres with lower electron density. The observed mainly oxide-induced dehydration processes of these two types of derivative could principally lead to the same type of product, but the course of these reactions was again found to be dependent on the type of phosphorus ligand. For L = PEt_3, they exclusively led to formation of vinyl vinylidene complexes, while for L = $P(OMe)_3$ the H_2O elimination reaction took also the direction to allenylidene complexes.

5. Experimental part

All manipulations were performed by standard Schlenk techniques under an atmosphere of dry N_2. Solvents were dried by conventional procedures and freshly distilled before use. All column chromatographic separations were carried out with jacket-cooled columns at $-10\,^\circ C$. Stationary phases were silica (Kieselgel 60, 40–63 μm, Merck), silylated silica (63–200 μm, Merck) and alumina (Aluminiumoxid 90, neutral, Merck).

IR spectra were recorded on a Biorad FTS 45 instrument, and EI mass spectra (70 eV) were obtained on a Finnigan MAT 8230 spectrometer. ^1H, ^{13}C and ^{31}P NMR spectra were measured on Varian Gemini 200 or 300 instruments (frequencies: ^1H 200 or 300 MHz; ^{13}C 50.3 or 75.4 MHz; ^{31}P 121.5 MHz); standards: ^1H and ^{13}C, δ rel. TMS; ^{31}P, δ rel. H_3PO_4. 2-Methyl-3-methyl-4-pentyn-3-ol, 2,2-dimethyl-3-methyl-4-pentyn-3-ol, 3-ethinyl-2,2,4,4-tetramethyl-3-pentynol, 1,1-diphenyl-2-propyn-1-ol and 1,1-diphenyl-2-propyne-1-acetate [27,28] were prepared according to literature procedures. $Fe(CO)_2L_2I_2$ (L = PEt_3 [29], $P(OMe)_3$ [30]) were obtained as reported earlier. THF solutions, the mixture of $[Fe(CO)_2(PEt_3)_2]_2N_2$ 1a and $Fe(CO)_2(PEt_3)_2N_2$ 1b and $\{Fe(CO)_2[P(OMe)_3]_2I\}Na$ 1c were prepared in situ according to Ref. [20].

5.1. Dicarbonylhydrido(3-hydroxy-3-methyl-butyn-1-yl)-bis(triethylphosphane)iron 2a

At $-30\,^\circ C$ 126 mg (1.5 mmol) HC≡CCMe$_2$OH was added to a THF solution of 1a,b prepared from 1 mmol of $Fe(CO)_2(PEt_3)_2I_2$. After warming to r.t. the solvent was removed. The oily residue was dissolved in hexane and filtered over Celite. Column chromatography on silylated silica eluting with hexane affords an orange band of 2a. Removal of the solvent in vacuo gives 2a as a brown oil. Yield 0.37 g (86%).

IR (hexane): $\nu(cm^{-1})$ = 2106 (w, C≡C), 1993, 1942 (s, C≡O). ^1H NMR (C_6D_6, 200 MHz): δ = -8.75 (t, $^2J_{PH}$ = 50.6 Hz, FeH), 1.01 (m_c, CH_2CH_3), 1.54 (s, $^4CH_3$), 1.75 (m_c, CH_2CH_3), 2.60 (s(br), OH). ^{13}C NMR (C_6D_6, 50 MHz): δ = 8.0 (s, CH_2CH_3), 20.9 (pseudo-t, J_{PC} = 14 Hz, CH_2CH_3), 33.0 (s, $^4CH_3$), 69.9 (s, ^3C), 101.1 (t, $^2J_{PC}$ = 40 Hz, ^1C), 117.1 (s, ^2C), 213.7 (t, $^2J_{PC}$ = 13 Hz, C≡O), 215.5 (t, $^2J_{PC}$ = 20 Hz, C≡O). ^{31}P NMR (C_6D_6): δ = 56.9. MS (70 eV): $m/e(\%)$ = 432 (1) $[M]^+$, 376 (5) $[M - 2CO]^+$, 348 (1) $[M - C_5H_7OH]^+$, 320 (5) $[M - 2CO, C_5H_7OH]^+$, 240 (15) $[M - 2CO, PEt_3, H_2O]^+$, 174 (5) $[Fe(PEt_3)]^+$, 146 (5) $[Fe(PEt_2)]^+$, 118 (90) $[PEt_3]^+$, 103, 90, 62, 57, 42.

$C_{19}H_{38}FeO_3P_2$ (432.30)				
	Calcd.	C 52.79	H 8.86	Fe 42.92
	Found	C 51.41	H 8.94	Fe 12.68

5.2. Dicarbonylhydrido(3-hydroxy-3-methyl-pentyn-1-yl)-bis(triethylphosphane)iron 2b

The same procedure as for 2a was followed (147 mg (1.5 mmol) HC≡CMe(Et)OH and 1 mmol $Fe(CO)_2(PEt_3)_2I_2$); however, column chromatography was not necessary. After removal of the solvent 2b remained as a brown oil. Yield 0.37 g (83%).

IR (hexane): $\nu(cm^{-1})$ = 2106 (w, C≡C), 1993, 1942 (s, C≡O). ^1H NMR (C_6D_6, 300 MHz): δ = -8.73 (t, $^2J_{PH}$ = 50.8 Hz, FeH), 1.01 (m_c, CH_2CH_3), 1.16 (t, $^3J_{CH}$ = 7.4 Hz, $^5CH_3$), 1.51 (s, CCH_3), 1.62 (q, $^3J_{CH}$ = 7.4 Hz, $^4CH_2$), 1.76 (m_c, CH_2CH_3), 2.40 (s(br), OH). ^{13}C NMR (C_6D_6, 50.3 MHz): δ = 8.0 (s, CH_2CH_3), 9.9 (s, ^5C), 20.8

(pseudo-t, J_{PC} = 14.1 Hz, CH_2CH_3), 30.9 (s, CCH_3), 38.1 (s, $^4CH_3$), 69.8 (s, ^3C), 102.2 (t, $^2J_{PC}$ = 40 Hz, ^1C), 115.8 (s, ^2C), 213.7 (t, $^2J_{PC}$ = 13 Hz, C≡O), 215.5 (t, $^2J_{PC}$ = 20 Hz, C≡O). ^{31}P NMR (C_6D_6): δ = 57.13. MS (70 eV): $m/e(\%)$ = 390 (1) $[M - 2CO]^+$, 348 (5) $[M - C_6H_9OH]^+$, 320 (5) $[M - CO, C_6H_9OH]^+$, 292 (50) $[M - 2CO, C_6H_9OH]^+$, 254 (40) $[M - 2CO, PEt_3 \cdot H_2O]^+$, 174 (5) $[Fe(PEt_3)]^+$, 146 (10) $[Fe(PEt_2)]^+$, 134, 118 (40) $[PEt_3]^+$, 106, 90, 78, 77, 69, 62, 49, 42.

$C_{20}H_{40}FeO_3P_2$ (446.33)	Calcd.	C 53.82	H 9.03	Fe 12.51
	Found	C 53.74	H 9.23	Fe 12.23

5.3. Dicarbonylhydrido(3-hydroxy-3,4-dimethyl-pentyn-1-yl)-bis(triethylphosphane)iron 2c

The same procedure as for **2a** was followed. The eluent of the column chromatography was hexane–ether 10:1. After evaporation of the solvent **2c** remains as an orange-red oil. Yield 0.38 g (83%).

IR (hexane): $\nu(cm^{-1})$ = 2102 (w, C≡C), 1993, 1943 (s, C≡O). ^1H NMR (C_6D_6, 300 MHz): δ = −8.72 (t, $^2J_{PH}$ = 51.0 Hz, FeH), 1.01 (m_c, CH_2CH_3), 1.12, 1.20 (2 × d, $^3J_{CH}$ = 6.7 Hz, $^5CH_3$), 1.49 (s, CCH_3), 1.62 (m_c, CH_2CH_3), 2.40 (br, OH), 1.80 (m_c, $^3J_{CH}$ = 6.7 Hz, CH). ^{13}C NMR (C_6D_6, 75.4 MHz): δ = 7.9 (s, CH_2CH_3), 18.5, 18.7 (2 × s, ^5C), 20.8 (pseudo-t, J_{PC} = 14 Hz, CH_2CH_3), 28.8 (s, CCH_3), 40.2 (s, CH_3), 72.7 (br, ^3C), 103.0 (t, $^2J_{PC}$ = 40 Hz, ^1C), 114.8 (s, ^2C), 213.7 (t, $^2J_{PC}$ = 13 Hz, C≡O), 215.5 (t, $^2J_{PC}$ = 20 Hz, C≡O). ^{31}P NMR (C_6D_6): δ = 57.3. MS (70 eV): $m/e(\%)$ = $[M - 2CO]^+$, 348 (5) $[M - C_7H_{11}OH]^+$, 320 (15) $[M - CO, C_7H_{11}OH]^+$, 292 (100) $[M - 2CO, C_7H_{11}OH]^+$, 268 (35) $[M - 2CO, PEt_3, H_2O]^+$, 191, 174 (15) $[Fe(PEt_3)]^+$, 146 (250) $[Fe(PEt_2)]^+$, 118 (80) $[PEt_3]^+$, 106, 90, 77, 69, 62, 42.

$C_{21}H_{42}FeO_3P_2$ (460.36)	Calcd.	C 54.79	H 9.20	Fe 12.13
	Found	C 55.03	H 9.08	Fe 11.87

5.4. Dicarbonyl(3-hydroxy-3,4,4-trimethyl-pentyn-1-yl)-hydrido-bis(triethylphosphane)iron 2d

The same procedure as for **2a** was followed, which afforded **2d** as a brown oil. Yield 0.41 g (86%).

IR (hexane): $\nu(cm^{-1})$ = 2098 (w, C≡C), 1994, 1943 (s, C≡O). ^1H NMR (C_6D_6, 200 MHz): δ = −8.71 (t, $^2J_{PH}$ = 51.0 Hz, FeH), 1.00 (m_c, CH_2CH_3), 1.23 (s, $^5CH_3$), 1.53 (s, CCH_3), 1.61 (m_c, CH_2CH_3), 2.00 (s(br), OH). ^{13}C NMR (C_6D_6, 50.3 MHz): δ = 7.9 (s, CH_2CH_3), 20.8 (pseudo-t, J_{PC} = 14 Hz, CH_2CH_3), 26.1 (s, $^5CH_3$), 26.6 (s, CCH_3), 38.9 (s, ^4C), 75.0 (br, ^3C), 102.8 (t, $^2J_{PC}$ = 40 Hz, ^1C), 115.5 (s, ^2C), 213.7 (t, $^2J_{PC}$ = 13 Hz, C≡O), 215.5 (t, $^2J_{PC}$ = 21 Hz, C≡O). ^{31}P NMR (C_6D_6): δ = 57.5. MS (70 eV): $m/e(\%)$ = 474 (20) $[M]^+$, 446 (1) $[M - CO]^+$, 418 (5) $[M - 2CO]^+$, 348 (10) $[M - C_8H_{13}OH]^+$, 320 (40) $[M - CO, C_8H_{13}OH]^+$, 292 (100) $[M - 2CO, C_8H_{13}OH]^+$, 282 (60) $[M - 2CO, H_2O, PEt_3]^+$, 202, 191, 174 (50) $[Fe(PEt_3)]^+$, 146 (30) $[Fe(PEt_2)]^+$, 118 (20) $[PEt_3]^-$, 90, 62.

$C_{22}H_{44}FeO_3P_2$ (479.39)	Calcd.	C 55.70	H 9.35	Fe 11.77
	Found	C 53.62	H 9.52	Fe 11.31

5.5. Dicarbonylhydrido(3-hydroxy-3-t-butyl-4-dimethylpentyn-1-yl)-hydrido-bis(triethylphosphane)iron 2e

The same procedure as for **2a** was followed. Recrystallization from hexane at −30 °C afforded an orange-yellow powder of **2e**. Yield 0.46 g (90%).

IR (hexane): $\nu(cm^{-1})$ = 2094 (w, C≡C), 1993, 1942 (s, C≡O). ^1H NMR (C_6D_6, 200 MHz): δ = −8.69 (t, $^2J_{PH}$ = 52.0 Hz, FeH), 1.00 (m_c, CH_2CH_3), 1.40 (s, $^5CH_3$), 1.64, 1.74 (2 × m_c, CH_2CH_3), 2.10 (s(br), OH). ^{13}C NMR (C_6D_6, 50.3 MHz): δ = 7.9 (s, CH_2CH_3), 20.7 (pseudo-t, J_{PC} = 14 Hz, CH_2CH_3), 29.8 (s, $^5CH_3$), 42.3 (s, ^4C), 82.6 (br, ^3C), 103.1 (t, $^2J_{PC}$ = 39 Hz, ^1C), 114.8 (s, ^2C), 213.6 (t, $^2J_{PC}$ = 16 Hz, C≡O), 215.5 (t, $^2J_{PC}$ = 21 Hz, C≡O). ^{31}P NMR (C_6D_6): δ = 57.7. MS (70 eV): $m/e(\%)$ = 515 (<1) $[M]^+$, 487 (<1) $[M - CO]^+$, 459, 469 (10)

[M − 2CO]$^+$, 342 (20) [M − 2CO, PEt$_3$]$^+$, 348 (10) [M − C$_{11}$H$_{20}$O]$^+$, 292 (100) [M − 2CO, C$_{11}$H$_{20}$O]$^+$, 191, 174 (5) [Fe(PEt$_3$)]$^+$, 146 (< 10) [Fe(PEt2)]$^+$, 118 (10) [PEt$_3$]$^+$, 106, 90, 57, 49.

| C$_{25}$H$_{49}$FeO$_3$P$_2$ (515.46) | Calcd. | C 58.25 | H 9.58 | Fe 10.83 |
| | Found | C 58.49 | H 9.80 | Fe 11.13 |

5.6. Dicarbonylhydrido(3-hydroxy-3,3-diphenyl-propyn-1-yl)-bis(triethylphosphane)iron 2f

The same procedure as for **2a** was followed. Recrystallization from hexane afforded a yellow-green powder of **2f**. Yield 0.48 g (86%).

IR (hexane): ν(cm^{-1}) = 2106 (w, C≡C), 1993, 1944 (s, C≡O). ^{1}H NMR (acetone-d_6, 300 MHz): δ = −8.71 (t, $^2J_{PH}$ = 48.7 Hz, FeH), 1.03 (m$_c$, CH$_2$CH_3), 2.04 (s(br), OH), 7.24, 7.52 (m$_c$, Ph). ^{13}C NMR (acetone-d_6, 75.4 MHz, −60 °C): δ = 7.7 (s, CH$_2$CH$_3$), 19.5 (pseudo-t, J_{PC} = 14 Hz, CH$_2$CH$_3$), 74.6 (br, ^{3}C), 109.3 (t, $^2J_{PC}$ = 39 Hz, ^{1}C), 113.6 (s, ^{2}C), 126.7, 126.9, 127.9 (s, Ph), 149.4 (br, C$_{ipso}$), 214.0 (t, $^2J_{PC}$ = 13 Hz, C≡O). ^{31}P NMR (acetone-d_6): δ = 59.2. MS (70 eV): m/e(%) = 556 (1) [M]$^+$, 538 (5) [M − H$_2$O]$^+$, 510 (< 1) [M − CO, H$_2$O]$^+$, 500 (5) [M − 2CO], 482 (35) [M − 2CO, H$_2$O]$^+$, 382 (50) [M − 2CO, PEt$_3$]$^+$, 364 (365) [M − 2CO, H$_2$O, PEt$_3$]$^+$, 305 (20) [M − 2CO, H$_2$O, PEt$_3$, C$_6$H$_5$]$^+$, 320 (20) [M − CO, C$_{15}$H$_{12}$O]$^+$, 292 (100) [M − 2CO, C$_{15}$H$_{12}$O]$^+$, 191 (80) [C$_{15}$H$_{10}$]$^+$, 174 (10) [Fe(PEt$_3$)]$^+$, 146 (20) [Fe(PEt$_2$)]$^+$, 118 (60) [PEt$_3$]$^+$, 106, 90, 57, 49.

| C$_{29}$H$_{42}$FeO$_3$P$_2$ (556.45) | Calcd. | C 62.30 | H 7.61 | Fe 10.04 |
| | Found | C 62.75 | H 7.92 | Fe 10.03 |

5.7. Dicarbonyl(3-methyl-butadien-1,1-diyl)bis(triethylphosphane)iron(0) 3a

0.37 g (0.86 mmol) of **2a** was dissolved in 50 ml of hexane and stirred with silylated silica at room temperature for 24 h. Evaporation of the solvent is followed by column chromatography over silylated silica. Elution with hexane–ether (50:1) yields a yellow band of **3a**, which remains as a red-brown oil after removal of the solvent. Yield 0.23 g (65%).

IR (hexane): ν(cm^{-1}) = 1959, 1894 (s, C≡O), 1603, 1583 (w, C=C). ^{1}H NMR (C$_6$D$_6$, 200 MHz): δ = 0.99 (m$_c$, CH$_2$CH_3), 1.61 (m$_c$, CH_2CH$_3$), 1.88 (s, CCH$_3$), 4.31, 4.68 (2 × m$_c$, CH$_2$), 5.68 (t, J_{PC} = 11.6 Hz, CH). ^{13}C NMR (C$_6$D$_6$, 50.3 MHz): δ = 8.0 (s, CCH_3), 8.3 (s, CH$_2$CH_3), 21.2 (pseudo-t, J_{PC} = 13.8 Hz, CH$_2$CH$_3$), 102.6 (t, $^5J_{PC}$ = 3.6 Hz, ^{4}C), 125.9 (t, $^3J_{PC}$ = 8.5 Hz, ^{2}C), 139.7 (t, $^4J_{PC}$ = 8.0 Hz, ^{3}C), 216.7 (t, $^2J_{PC}$ = 18.0 Hz, C≡O), 317.9 (t, $^2J_{PC}$ = 51.9 Hz, ^{1}C). ^{31}P NMR (C$_6$D$_6$): δ = 60.4. MS (70 eV): m/e(%) = 414 [M]$^+$, 386 [M − CO]$^+$, 358 [M − 2CO]$^+$, 292 (90) [Fe(PEt$_3$)$_2$]$^+$, 174 (30) [Fe(PEt$_3$)]$^+$, 146 (40) [Fe(PEt$_2$)]$^+$, 118 (80) [PEt$_3$]$^+$, 106, 90, 78, 77, 62, 57, 49.

| C$_{19}$H$_{36}$FeO$_2$P$_2$ (414.29) | Calcd. | C 55.08 | H 8.76 | Fe 13.48 |
| | Found | C 55.43 | H 9.02 | Fe 13.12 |

5.8. Dicarbonyl(3-methyl-E/Z-pentadien-1,1-diyl)bis(triethylphosphane)iron(0) 3b/3c

The same procedure as for **3a** was followed starting from 0.37 g (0.83 mmol) **2b**. Yield of the nearly 1:1 **3b/3c** mixture 0.28 g (78%).

3b/3c: IR (hexane): ν(cm^{-1}) = 1955, 1899 (s, C≡O), 1594 (w, C=C). MS (70 eV): m/e(%) = 428 (20) [M]$^+$, 400 (5) [M − CO]$^+$, 372 (30) [M − 2CO]$^+$, 292 (90) [M − 2CO, C$_6$H$_8$]$^+$, 174 (30) [Fe(PEt$_3$)]$^+$, 146 (40) [Fe(PEt$_2$)]$^+$, 118 (80) [PEt$_3$]$^+$, 106, 90, 78, 77, 62, 57, 49.

| C$_{20}$H$_{38}$FeO$_2$P$_2$ (428.32) | Calcd. | C 56.08 | H 8.94 | Fe 13.04 |
| | Found | C 54.61 | H 8.76 | Fe 12.88 |

3b: ^{1}H NMR (CD$_2$Cl$_2$, 300 MHz): δ = 1.10 (m$_c$, CH$_2$CH_3), 1.60 (s(br), ^{5}CH$_3$), 1.80 (s(br), CCH$_3$), 1.85 (m$_c$, CH_2CH$_3$), 4.68 (m$_c$, ^{4}CH), 5.45 (t, J_{PC} = 11.6 Hz, ^{2}CH). ^{13}C NMR (C$_6$D$_6$, 50.3 MHz): δ = 8.3 (s, CH$_2$CH_3), 13.5 (s, ^{5}C), 14.8 (s, CCH$_3$), 21.2 (pseudo-t, J_{PC} = 14 Hz, CH$_2$CH$_3$), 110.7 (t, $^5J_{PC}$ = 4 Hz, ^{4}C), 124.9 (t, $^3J_{PC}$ = 9 Hz,

^{2}C), 130.6 (t, $^4J_{PC} = 8$ Hz, ^{3}C), 216.4 (t, $^2J_{PC} = 19$ Hz, C≡O), 318.2 (t, $^2J_{PC} = 53$ Hz, ^{1}C). ^{31}P NMR (C$_6$D$_6$): δ = 60.1.

3c: ^{1}H NMR (CD$_2$Cl$_2$, 300 MHz): δ = 1.10 (m$_c$, CH$_2$CH_3), 1.53 (s(br), ^{5}CH$_3$), 1.84 (m$_c$, CH_2CH$_3$), 1.95 (s(br), CCH$_3$), 4.45 (m$_c$, ^{4}CH), 5.70 (t, $^3J_{PH} = 11.6$ Hz, ^{2}CH). ^{13}C NMR (C$_6$D$_6$, 50.3 MHz): δ = 8.2 (s, CH$_2$CH_3), 14.3 (s, ^{5}C), 21.2 (pseudo-t, $J_{PC} = 18$ Hz, CH$_2$CH$_3$), 23.0 (s, CCH$_3$), 111.9 (t, $^5J_{PC} = 4.2$ Hz, ^{4}C), 119.2 (t, $^3J_{PC} = 9$ Hz, ^{2}C), 130.0 (t, $^4J_{PC} = 9$ Hz, ^{3}C), 216.8 (t, $^2J_{PC} = 19$ Hz, C≡O), 319.9 (t, $^2J_{PC} = 52$ Hz, ^{1}C). ^{31}P NMR (C$_6$D$_6$): δ = 60.1.

5.9. Dicarbonyl(3,4-dimethylpentadien-1,2-diyl)bis(triethylphosphane)iron(0) 3d

A similar procedure as for **3a** was used; however, the reaction time was 24 h and alumina was applied instead of silylated silica. Starting compound 0.38 g (0.83 mmol) **2c**. Yield 0.29 g (78%).

IR (hexane): ν(cm^{-1}) = 1953, 1893 (s, C≡O), 1603, 1586 (w, C=C). ^{1}H NMR (C$_6$D$_6$, 200 MHz): δ = 1.02 (m$_c$, CH$_2$CH_3), 1.65 (m$_c$, CH_2CH$_3$), 1.69 (s, ^{5}CH$_3$), 1.90 (s, CCH$_3$), 6.1 (t, $J_{PC} = 11.6$ Hz, ^{2}CH). ^{13}C NMR (C$_6$D$_6$, 50.3 MHz): δ = 8.3 (s, CH$_2$CH_3), 16.9 (s, ^{5}CH$_3$), 20.4, 20.9 (2 × s, CCH$_3$, ^{5}CH$_3$), 21.4 (pseudo-t, $J_{PC} = 15$ Hz, CH$_2$CH$_3$), 116.2 (t, $^5J_{PC} = 4$ Hz, ^{4}C), 121.8 (t, $^3J_{PC} = 8$ Hz, ^{2}C), 121.9 (t, $^4J_{PC} = 7$ Hz, ^{3}C), 216.9 (t, $^2J_{PC} = 18$ Hz, C≡O), 320.8 (t, $^2J_{PC} = 52$ Hz, ^{1}C). ^{31}P NMR (C$_6$D$_6$): δ = 59.9. MS (70 eV): m/e(%) = 442 (10) [M]$^-$, 414 (1) [M − CO]$^+$, 386 (15) [M − 2CO]$^+$, 292 (100) [M − 2CO, C$_7$H$_{10}$]$^+$, 268 (40) [M − 2CO, PEt$_3$]$^+$, 264 (40), 174 (20) [Fe(PEt$_3$)]$^+$, 146 (50) [Fe(PEt2)]$^+$, 118 (50) [PEt$_3$]$^+$, 90, 77, 62.

C$_{21}$H$_{40}$FeO$_2$P$_2$ (442.34)	Calcd.	C 57.02	H 9.12	Fe 12.63
	Found	C 56.89	H 9.47	Fe 12.13

5.10. Dicarbonyl(3-t-butylpentadien-1,1-diyl)bis(triethylphosphane)iron(0) 3e

The same procedure as for **3a** was followed starting from 0.41 g (0.86 mmol) **2d**. Yield 0.23 g (58%).

IR (hexane): ν(cm^{-1}) = 1956, 1894 (s, C≡O), 1604 (w, C=C). ^{1}H NMR (C$_6$D$_6$, 200 MHz): δ = 1.01 (m$_c$, CH$_2$CH_3), 1.06 (s, t-Bu), 1.71 (m$_c$, CH_2CH$_3$), 4.90, 5.29 (2 × m$_c$, =CH$_2$), 5.40 (t, $J_{PH} = 11.6$ Hz, CH). ^{13}C NMR (C$_6$D$_6$, 50.3 MHz): δ = 8.4 (s, CH$_3$), 8.3 (s, CH$_2$CH_3), 21.6 (pseudo-t, $J_{PC} = 13.9$ Hz, CH$_2$CH$_3$), 29.4 (s, C$_{t-Bu}$), 101.2 (t, $J_{PC} = 3.5$ Hz, ^{4}C), 117.9 (t, $^3J_{PC} = 8.5$ Hz, ^{2}C), 152.1 (t, $^4J_{PC} = 7.4$ Hz, ^{3}C), 216.2 (t, $^2J_{PC} = 18.4$ Hz, C≡O), 318.7 (t, $^2J_{PC} = 52.4$ Hz, ^{1}C). ^{31}P NMR (C$_6$D$_6$): and 62.5. MS (70 eV): m/e(%) [M]$^+$, 414 (1) (M − CO)$^+$, [M − 2CO]$^+$, 292 (100) [M − 2CO, C$_7$H$_{10}$]$^+$, [M − 2CO, PEt$_3$]$^+$, [M − 2CO, C$_7$H$_{10}$, Et$_3$]$^+$, 174 (20) [Fe(PEt$_3$)]$^+$, 146 (50) [Fe(PEt$_2$)]$^+$, 118 (50) [PEt$_3$]$^+$, 90, 77, 62.

C$_{22}$H$_{42}$FeO$_2$P$_2$ (456.37)	Calcd.	C 57.90	H 9.27	Fe 12.24
	Found	C 57.48	H 9.41	Fe 11.98

5.11. Dicarbonyl(di-t-butylallenylidene)bis(triethylphosphane)iron(0) 4a

To an ether solution of 0.46 g (0.89 mmol) **2e** 2 ml of a 1.2 M solution of BuLi in hexane was added. After warming to 0 °C and recooling to −60 °C 70 μl (1 mmol) of acetyl chloride was added. Warming to room temperature afforded a brown solution. After removal of the solvent in vacuo the residue was dissolved in hexane and filtered over a short column (3 cm) of alumina. After evaporation of the hexane a brown oil of **4a** remained. Yield 0.29 g (65%).

IR (hexane): ν(cm^{-1}) = 1946, 1884 (s, C≡O). ^{1}H NMR (CD$_2$Cl$_2$, 300 MHz): δ = 1.12 (m$_c$, CH$_2$CH_3), 1.27 (s, t-Bu), 1.97 (m$_c$, CH_2CH$_3$). ^{13}C NMR (CD$_2$Cl$_2$, 75.4 MHz, −60 °C): δ = 7.7 (s, CH$_2$CH_3), 20.1 (pseudo-t, $J_{PC} = 13$ Hz, CH_2CH$_3$), 31.4 (s, CH$_3$), 43.0 (t, $^5J_{PC} = 6$ Hz, C$_{t-Bu}$), 139.3 t, $J_{PC} = 12$ Hz, ^{3}C), 200.2 (t, $^3J_{PC} = 9$ Hz, ^{2}C), 217.6 (t, $^2J_{PC} = 22$ Hz, C≡O), 242.6 (t, $^2J_{PC} = 50$ Hz, Fe=C). ^{31}P NMR (CD$_2$Cl$_2$): δ = 57.7. MS (70 eV): m/e(%) = 498 (10) [M]$^+$, 470 (1) [M − CO]$^+$, 442 (50) [M − 2CO]$^+$, 324 (35) [M − 2CO, PEt$_3$]$^+$, 292 (100) [M − 2CO, C$_{11}$H$_{18}$]$^+$, 264 (20) (M − 2CO, C$_{11}$H$_{18}$, Et$_3$]$^+$, 174 (10) [Fe(PEt$_3$)]$^+$, 146 (20) [Fe(PEt$_2$)]$^+$, 118 (20) [PEt$_3$]$^+$, 90, 62.

C$_{25}$H$_{48}$FeO$_2$P$_2$ (498.45)	Calcd.	C 60.24	H 9.70	Fe 11.20
	Found	C 59.79	H 9.26	Fe 10.97

5.12. Dicarbonyl(diphenylallenylidene)bis(triethylphosphane)iron(0) 4b

The same procedure as for **4a** was followed starting from 0.48 g (0.86 mmol) of **2d**. 0.31 g of a dark-green oil of **4b** remained (yield 67%).

IR (hexane): $\nu(\text{cm}^{-1})$ = 1954, 1894 (s, C=O). ^{1}H NMR (CD$_2$Cl$_2$, 200 MHz): δ = 1.13 (m$_c$, CH$_2$CH_3), 1.93 (m$_c$, CH_2CH$_3$), 7.28, 7.45 (m$_c$, H$_{Ph}$). ^{13}C NMR (CD$_2$Cl$_2$, 50.3 MHz): δ = 8.5 (s, CH$_2$CH_3), 21.5 (pseudo-t, J_{PC} = 14 Hz, CH_2CH$_3$), 118.7 (t, $^4J_{PC}$ = 11 Hz, ^{3}C), 126.2, 127.7, 128.7 (s, C$_{Ph}$), 145.0 (t, $^4J_{PC}$ = 7 Hz, C$_{ipso}$), 208.1 (t, $^3J_{PC}$ = 10 Hz, ^{2}C), 218.3 (t, $^2J_{PC}$ = 19 Hz, C=O), 224.5 (t, $^2J_{PC}$ = 56 Hz, Fe=C). ^{31}P NMR (CD$_2$Cl$_2$): δ = 59.8. MS (70 eV): $m/e(\%)$ = 538 (1) [M]$^+$, 482 (10) [M $-$ 2CO]$^+$, 364 (10) [M $-$ 2CO, PEt$_3$]$^+$, 292 (100) [M $-$ 2CO, C$_{15}$H$_{10}$]$^+$, 264 (10) [M $-$ 2CO, C$_{15}$H$_{10}$, Et]$^+$, 191 (10) [C$_{15}$H$_{10}$]$^+$, 174 (5) [Fe(PEt$_3$)]$^+$, 146 (10) [Fe(PEt$_2$)]$^+$, 118 (10) [PEt$_3$]$^+$, 90, 62.

C$_{29}$H$_{40}$FeO$_2$P$_2$ (538.07)	Calcd.	C 64.73	H 7.50	Fe 10.38
	Found	C 64.12	H 7.85	Fe 10.11

5.13. Dicarbonyl(3-hydroxy-3-methylbutyne)bis(trimethylphosphite)iron(0) 5a and dicarbonyl(3-hydroxy-3-methyl-buten-1,1-diyl)bis(trimethylphosphite)iron(0) 7a

At $-30\,^\circ$C 126 mg (1.5 mmol) HC≡CCMe$_2$OH was added to a THF solution of **1c** prepared from 1 mmol of Fe(CO)$_2$[P(OMe)$_3$]$_2$I$_2$. After warming to r.t. the solvent was removed. The oily residue was dissolved in hexane and subjected to column chromatography on silica. Elution with hexane–ether 1:10 and 1:1 afforded yellow bands of **5a** and **7a** respectively. The solvent of the zone of **5a** was removed. An orange-red oil of mainly **5a** remained, which showed **7a** as an impurity. **7a** remained as an orange-yellow oil after evaporation of the solvent.

5a: yield 80 mg (18%).

IR (hexane): $\nu(\text{cm}^{-1})$ = 1971, 1904 (s, C=O). ^{1}H NMR (C$_6$D$_6$, 200 MHz): and 1.77 (s, CH$_3$), 2.61 (br, OH), 3.35 (pseudo-t, J_{PH} = 5.5 Hz, OCH$_3$), 4.7 (t, $^3J_{PH}$ = 5.0 Hz, ≡CH). ^{13}C NMR (C$_6$D$_6$, 50.3 MHz): δ = 32.7 (s, CH$_3$), 51.3 (s, OCH$_3$), 64.0 (t, $^2J_{PC}$ = 11 Hz, ≡CH), 69.4 (br, COH), 98.0 (t, $^2J_{PC}$ = 11 Hz, ≡CC), 219.8 (t, $^2J_{PC}$ = 40 Hz, CO). ^{31}P NMR (C$_6$D$_6$): δ = 174.6.

7a: yield 150 mg (30%).

IR (hexane): $\nu(\text{cm}^{-1})$ = 1993, 1933 (s, C≡O), 1927 (sh, C≡O), 1639 (m, C=C). ^{1}H NMR (C$_6$D$_6$, 300 MHz): δ = 1.41 (s, CH$_3$), 2.63 (br, OH), 3.48 (pseudo-t, J_{PH} = 5.9 Hz, OCH$_3$), 5.26 (t, $^4J_{PH}$ = 13.7 Hz, CH). ^{13}C NMR (C$_6$D$_6$, 75.4 MHz): δ = 31.7 (t, $^5J_{PC}$ = 2 Hz, CH$_3$), 52.4 (s, OCH$_3$), 68.0 (t, $^4J_{PC}$ = 6.5 Hz, ^{3}C), 132.4 (t, $^3J_{PC}$ = 10 Hz, ^{2}C), 212.4 (t, $^2J_{PC}$ = 29 Hz, C≡O), 313.7 (t, $^2J_{PC}$ = 68 Hz, Fe=C). ^{31}P NMR (C$_6$D$_6$): δ = 177.2. MS (70 eV): $m/e(\%)$ = 444 (10) [M]$^+$, 304 (100) [M $-$ 2CO, C$_5$H$_7$OH]$^+$, 264 (70) [M $-$ 2CO, P(OCH$_3$)$_3$]$^+$, 246 (70) [M $-$ 2CO, H$_2$O, P(OCH$_3$)3]$^+$, 180 (10) [FeP(OCH$_3$)$_3$]$^+$, 165 (20) [FeP(OCH$_3$)$_3$ $-$ CH$_3$]$^+$, 124 ($<$10) [P(OCH$_3$)$_3$]$^+$, 93.

C$_{13}$H$_{26}$FeO$_9$P$_2$ (444.14)	Calcd.	C 35.16	H 5.90	Fe 12.57
	Found	C 34.98	H 6.13	Fe 12.31

5.14. Dicarbonyl(3-hydroxy-3-methylpentyne)bis(trimethylphosphite)iron(0) 5b and dicarbonyl(3-hydroxy-3-methyl-1-penten-1,1-diyl)bis(trimethylphosphite)iron(0) 7b

The same procedure as for the preparation of **7a** was followed starting from 1 mmol Fe(CO)$_2$[P(OMe)$_3$]$_2$I$_2$ and 147 mg (1.5 mmol) HC≡CCMe(Et)OH. However, column chromatography of **7b** was performed with hexane–ether 10:1 as eluent, which revealed two zones. The first one consisted of **5b**, which turned out to be quite unstable in solution and could only be characterized by spectroscopic methods after removal of the solvent. The second orange band of **7b** was collected and after evaporation of the solvent it was precipitated as an orange oil from hexane at $-30\,^\circ$C.

5b: yield 20 mg (4%).

IR (hexane): $\nu(\text{cm}^{-1})$ = 1973, 1903, (s, C≡O). ^{1}H NMR (C$_6$D$_6$, 300 MHz): δ = 1.14 (t, $^3J_{HH}$ = 7.0 Hz, CH$_2$CH_3), 1.64 (q, $^3J_{HH}$ = 7.0 Hz, CH$_2$), 1.70 (s, CH$_3$), 2.07 (br, OH), 3.35 (pseudo-t, J_{PH} = 5.5 Hz, OCH$_3$), 4.66 (t, $^3J_{PH}$ = 4.5 Hz, ≡CH). ^{13}C NMR (C$_6$D$_6$, 75.4 MHz): δ = 9.5 (s, CH$_2$CH_3), 29.5 (t, br, CH$_3$), 37.2 (br, CH$_2$), 51.5 (s, OCH$_3$), 64.9 (t, $^2J_{PC}$ = 11 Hz, CH), 72.4 (t, $^2J_{PC}$ = 2 Hz, COH), 95.9 (t, $^2J_{PC}$ = 12 Hz, ≡C), 219.8 (t, $^2J_{PC}$ = 40 Hz, C≡O). ^{31}P NMR (C$_6$D$_6$): δ = 174.7.

7b: yield 310 mg (68%).

IR (hexane): $\nu(\text{cm}^{-1})$ = 1993, 1933 (s, C≡O), 1926 (sh, C≡O), 1638 (m, C=C). ^{1}H NMR (C_6D_6, 300 MHz): δ = 1.06 (t, $^3J_{HH}$ = 7.4 Hz, CH_2CH_3), 1.42 (s, CH_3), 1.60 (q, $^3J_{HH}$ = 7.4 Hz, CH_2CH_3), 2.58 (br, OH), 3.48 (pseudo-t, J_{PH} = 6.0 Hz, OCH_3), 5.19 (t, $^4J_{PH}$ = 13.7 Hz, =CH). ^{13}C NMR (C_6D_6, 75.4 MHz): δ = 9.1 (s, CH_2CH_3), 29.0 (t, $^5J_{PC}$ = 3 Hz, CH_3), 37.3 (t, $^5J_{PC}$ = 2 Hz, CH_2), 52.4 (s, OCH_3), 70.6 (t, $^4J_{PC}$ = 7 Hz, COH), 131.2 (t, $^3J_{PC}$ = 10 Hz, =C), 212.4 (t, $^2J_{PC}$ = 29 Hz, C≡O), 314.0 (t, $^2J_{PC}$ = 67 Hz, Fe=C). ^{31}P NMR (C_6D_6): δ = 177.4. MS (70 eV): m/e(%) 458 (1) [M]$^+$, 430 (1) [M – CO]$^+$, 402 (5) [M – 2CO]$^+$, 360 (30) [M – CO, C_6H_9OH]$^-$, 332 (30) [M – CO, C_6H_9OH]$^+$, 304 (20) (M – 2CO, C_6H_9OH]$^+$, 278 (10) [M – 2CO, P(OCH$_3$)$_3$]$^+$, 260 [M – 2CO, H_2O, P(OCH$_3$)$_3$]$^+$, 211 (30) [Fe{P(OCH$_3$)$_3$}$_2$ – 3OCH$_3$]$^+$, 180 (5) [FeP(OCH$_3$)$_3$]$^+$, 165 (20) [FeP(OCH$_3$)$_3$ – CH$_3$]$^+$ 124 (< 10) [P(OCH$_3$)$_3$]$^+$, 93.

$C_{14}H_{28}FeO_9P_2$ (458.16)			
Calcd.	C 36.70	H 6.16	Fe 12.19
Found	C 36.47	H 5.92	Fe 12.04

5.15. Dicarbonyl-(3-hydroxy-3,5-dimethyl-1-penten-1,1-diyl)bis(trimethylphosphite)iron (0) 7c

The same procedure as for **7a** was followed starting from 1 mmol Fe(CO)$_2$[P(OMe)$_3$]$_2$I$_2$ and 168 mg (1.5 mmol) HC≡C–CMe(iPr)OH. Hexane–ether 25:1 was used as an eluent of the column chromatography. A zone of a small amount of complex **10** was obtained as a first band. Evaporation of the solvent gave **10** as a yellow-brown oil. Further elution afforded a second yellow zone of **7c**, which crystallized upon evaporation of the solvent.

7c: yield 220 mg (47%).

IR (hexane): $\nu(\text{cm}^{-1})$ = 1993, 1933, 1926 (s, C≡O). ^{1}H NMR (CD$_2$Cl$_2$, 300 MHz): δ = 0.87 (d, $^3J_{HH}$ = 6.8 Hz, CH(CH$_3$)$_2$), 1.53 (m, $^3J_{HH}$ = 6.8 Hz, CH(CH$_3$)$_2$), 1.67 (s, C(OH)CH$_3$), 2.20 (br, OH), 3.68 (pseudo-t, J_{PH} = 6.0 Hz, =OCH$_3$), 5.19 (t, $^4J_{PH}$ = 13.7 Hz, =CH). ^{13}C NMR (CD$_2$Cl$_2$, 75.4 MHz): δ = 17.7, 17.8 (2 × s, CH(CH$_3$)$_2$), 25.7 (t, $^5J_{PC}$ = 3 Hz, CH$_3$), 39.6 (t, $^5J_{PC}$ = 3 Hz, CH(CH$_3$)$_2$), 52.8 (s, OCH$_3$), 73.4 (t, $^4J_{PC}$ = 7 Hz, C(OH)), 129.7 (t, $^3J_{PC}$ = 10 Hz, =CH), 212.9 (t, $^2J_{PC}$ = 29 Hz, CO). ^{31}P NMR (C_6D_6): δ = 177.6. MS (70 eV): m/e(%) = 472 (1) [M]$^+$, 430 (1) [M – CO]$^+$, 402 (1) [M – 2CO]$^+$, 360 (30) [M – C$_7$H$_{11}$OH]$^+$, 332 (30) [M – CO, C$_7$H$_{11}$OH]$^+$, 304 (100) [M – 2CO, C$_7$H$_{11}$OH]$^+$, 274 (10) [M – 2CO, H$_2$O, P(OCH$_3$)$_3$]$^+$, 211 (30) [Fe{P(OCH$_3$)$_3$}$_2$ – 3OCH$_3$]$^+$, 180 (1) [FeP(OCH$_3$)$_3$]$^+$, 165 (20) [FeP(OCH$_3$)$_3$ – CH$_3$]$^+$, 124 (< 10) [P(OCH$_3$)$_3$]$^+$, 93.

$C_{15}H_{30}FeO_9P_2$ (472.20)			
Calcd.	C 38.16	H 6.40	Fe 11.83
Found	C 38.47	H 6.06	Fe 11.78

10: yield 25 mg (6%).

IR (hexane): $\nu(\text{cm}^{-1})$ = 2000, 1993, 1941, 1932 (s, C≡O), 1616 (m, C=C). ^{1}H NMR (C_6D_6, 200 MHz): δ = 3.51 (pseudo-t, J_{PH} = 6.1 Hz, OCH$_3$), 4.52 (t, $^4J_{PH}$ = 14 Hz, =CH$_2$). ^{13}C NMR (C_6D_6, 50.4 MHz): δ = 52.5 (s, OCH$_3$), 103.7 (t, $^3J_{PC}$ = 9 Hz, =CH$_2$), 212.3 (t, $^2J_{PC}$ = 29 Hz, CO), 318.5 (t, $^2J_{PC}$ = 66 Hz, Fe=C). ^{31}P NMR (C_6D_6): δ = 179.3. MS (70 eV): m/e(%) = 386 (60) [M]$^+$, 358 (55) [M – CO]$^+$, 330 (100) [M – 2CO]$^+$, 304 (60) [M – 2CO, C$_2$H$_2$]$^+$, 237 (70) [M – 2CO, 3OCH$_3$]$^+$, 211 (90) [M – 2CO, 3OCH$_3$, C$_2$H$_2$]$^+$, 206 (100) [M – 2CO, P(OCH$_3$)$_3$]$^+$, 180 (60) [Fe(P(OCH$_3$)$_3$)]$^+$, 165 (40) [FeP(OCH$_3$)$_3$ – CH$_3$]$^+$, 135 (20) [FeP(OCH$_3$)$_2$ – CH$_3$]$^+$, 93 (70) [P(OCH$_3$)$_2$]$^+$, 63.

5.16. Dicarbonyl(3-hydroxy-3,5,5-trimethyl-1-penten-1,1-diyl(bis(trimethylphosphite)iron(0) 7d

The same procedure as for **7a** was followed starting from 1 mmol Fe(CO)$_2$[P(OMe)$_3$]$_2$I$_2$ and 189 mg (1.5 mmol) HC≡C–CMe(tBu)OH. Column chromatography was performed on silylated silica. Elution with hexane–ether (50:1) yielded a small amount of **10** as a first zone, which was isolated and identified as in the case of the reaction of **7c**. **7d** was eluted as the second band, which remained as a brown oil after removal of the solvent. Yield: 380 mg (78%).

IR (hexane): $\nu(\text{cm}^{-1})$ = 1992, 1932 (s, C≡O), 1926 (sh, C≡O), 1641 (m, C=C). ^{1}H NMR (C_6D_6, 200 MHz): δ = 1.09 (s, tBu), 1.44 (s, CH$_3$), 2.42 (br, OH), 3.48 (pseudo-t, J_{PH} = 6.0 Hz, OCH$_3$), 5.47 (t, $^4J_{PH}$ = 13.7 Hz, =CH). ^{13}C NMR (C_6D_6, 50.3 MHz): δ = 24.9 (t, $^5J_{PC}$ = 3 Hz, CH$_3$). 25.8 (s, (CH$_3$)$_3$), 38.7 (br, C(CH$_3$)$_3$), 52.3 (s, OCH$_3$), 75.0 (t, $^4J_{PC}$ = 6 Hz, C(OH)), 128.9 (t, $^3J_{PC}$ = 10 Hz, =CH), 212.5 (t, $^2J_{PC}$ = 29 Hz, CO), 314.9 (t, $^2J_{PC}$ = 67 Hz, Fe=C). ^{31}P NMR (C_6D_6): δ = 177.6. MS (70 eV): m/e(%) = 486 (1) [M]$^+$, 458 (1) [M – CO]$^+$, 430 (1) [M – 2CO]$^+$, 360 (30) [M – C$_8$H$_{13}$OH]$^+$, 332 (30) [M – CO, C$_8$H$_{13}$OH]$^+$, 306 (80) [M – 2CO, P(OCH$_3$)$_3$]$^+$, 304

(100) $[M - 2CO, C_8H_{13}OH]^+$, 288 (10) $[M - 2CO, H_2O, P(OCH_3)_3]^+$, 211 (30) $[Fe\{P(OCH_3)_3\}_2 - 3OCH_3]^+$, 180 (1) $[FeP(OCH_3)_3]^+$, 165 (20) $[FeP(OCH_3)_3 - CH_3]^+$, 124 (< 10) $[P(OCH_3)_3]^+$, 93.

$C_{16}H_{32}FeO_9P_2$ (486.22)	Calcd.	C 39.52	H 6.63	Fe 11.49
	Found	C 39.54	H 6.91	Fe 11.32

5.17. Dicarbonyl(3-hydroxy-3-t-butyl-4-dimethyl-1-penten-1,1-diyl)bis(trimethylphosphite)iron(0) 7e

The same procedure as for **7a** was followed starting from 1 mmol $Fe(CO)_2[P(OMe)_3]_2I_2$ and 252 mg (1.5 mmol) $HC\equiv C-C(tBu)_2OH$. Elution with hexane–ether 50:1 afforded a first brown band, which was discarded and then a yellow-orange zone of **7e**. The solvent was partly removed in vacuo. At $-30\,^\circ C$ **7a** crystallized as orange prisms. Yield 280 mg (53%).

IR (hexane): $\nu(cm^{-1}) = 1988, 1938, 1923$ (s, $C\equiv O$), 1634 (m, $C=C$). ^1H NMR (C_6D_6, 300 MHz): $\delta = 1.33$ (s, tBu), 2.51 (br, OH), 3.44 (pseudo-t, $J_{PH} = 7.6\,Hz$, OCH_3), 5.44 (t, $^4J_{PH} = 14.0\,Hz$, $=CH$). ^{13}C NMR (C_6D_6, 75.4 MHz): $\delta = 29.6$ (s, CH_3), 42.4 (t, $^5J_{PC} = 2\,Hz$, $C(CH_3)_3$), 52.0 (s, OCH_3), 81.3 (t, $^4J_{PC} = 6\,Hz$, $C(OH)$), 127.7 (t, $^3J_{PC} = 10\,Hz$, $=CH$), 212.7 (t, $^2J_{PC} = 30\,Hz$, $C\equiv O$), 316.7 (t, $^2J_{PC} = 62\,Hz$, $Fe=C$). ^{31}P NMR (C_6D_6): $\delta = 178.4$. MS (70 eV): $m/e(\%) = 528$ (5) $[M]^+$, 500 (1) $[M - CO]^+$, 472 (1) $[M - 2CO]^+$, 454 (5) $[M - 2CO, H_2O]^+$, 360 (30) $[M - C_{11}H_{19}OH]^+$, 348 (20) $[M - 2CO, P(OCH_3)_3]^+$, 332 (30) $[M - CO, C_{11}H_{19}OH]^+$, 330 (10) $[M - 2CO, H_2O, P(OCH_3)_3]^+$, 304 (100) $[M - 2CO, C_{11}H_{19}OH]^+$, 211 (20) $[Fe\{P(OCH_3)_3\}_2 - 3OCH_3]^+$, 180 (5) $[FeP(OCH_3)_3]^+$, 165 (10) $[FeP(OCH_3)_3 - CH_3]^+$, 124 (< 10) $[P(OCH_3)_3]^+$, 93.

$C_{19}H_{38}FeO_9P_2$ (528.29)	Calcd.	C 43.19	H 7.25	Fe 10.57
	Found	C 43.45	H 7.20	Fe 10.88

5.18. Dicarbonyl(3-hydroxy-3,3-diphenyl-propyne)bis(trimethylphosphite)iron (0) 5f and dicarbonyl(3-hydroxy-3,3-diphenyl-propen-1,1-diyl)bis(trimethylphosphite)iron(0) 7f

The same procedure as for **7a** was followed starting from 1 mmol $Fe(CO)_2[P(OMe)_3]_2I_2$ and 312 mg (1.5 mmol) $HC\equiv CCPh_2OH$. **5f** was obtained and identified in a mixture with **7f** after chromatography over silylated silica and elution with hexane–ether 100:1. **7f** was obtained upon column chromatography on silica and elution with hexane–ether 10:1. Crystallization of the concentrated solution at $-30\,^\circ C$ yielded a yellow-green powder of **7f**.

5f: IR (hexane): $\nu(cm^{-1}) = 1977, 1908$ (s, $C\equiv O$), 1780 (m, $C=C$). ^1H NMR (d^6-acetone, 200 MHz): $\delta = 3.36$ (pseudo-t, $J_{PH} = 5.2\,Hz$, OCH_3), 4.22 (br, OH), 5.78 (t, $^3J_{PH} = 4.8\,Hz$, $\equiv CH$), 7.26, 7.47 (m, Ph). ^{13}C NMR (d^6-acetone, 75.4 MHz): $\delta = 51.9$ (s, OCH_3), 73.3 (t, $^2J_{PC} = 11\,Hz$, $\equiv CH$), 78.2 (br, COH), 98.2 (t, $^3J_{PC} = 10\,Hz$, $\equiv CC$), 126.9, 127.2, 128.3 (s, Ph), 150.1 (t, $^4J_{PC} = 3\,Hz$, C_{ipso}), 212.5 (t, $^2J_{PC} = 29\,Hz$, $C\equiv O$). ^{31}P NMR (d^6-acetone): $\delta = 173.7$.

7f: yield 260 mg (46%).

IR (hexane): $\nu(cm^{-1}) = 1996, 1937$ (s, $C\equiv O$), 1931 (sh, $C\equiv O$), 1634 (m, $C=C$). ^1H NMR (d^6-acetone, 200 MHz): $\delta = 3.77$ (br, OH), 3.60 (pseudo-t, $J_{PH} = 6.0\,Hz$, OCH_3), 6.03 (t, $^4J_{PH} = 13.7\,Hz$, $=CH$), 7.26, 7.47 (m, Ph). ^{13}C NMR (d^6-acetone, 75.4 MHz): $\delta = 53.0$ (s, OCH_3), 75.2 (t, $^5J_{PC} = 7\,Hz$, COH), 126.9, 127.2, 128.3 (s, Ph), 150.1 (t, $^4J_{PC} = 3\,Hz$, C_{ipso}), 132.1 (t, $^3J_{PC} = 10\,Hz$, $=CH$), 212.5 (t, $^2J_{PC} = 29\,Hz$, CO), 312.0 (t, $^3J_{PC} = 67\,Hz$, $Fe=C$). ^{31}P NMR (d^6-acetone): $\delta = 177.7$. MS (70 eV): $m/e(\%) = 568$ (30) $[M]^+$, 550 (20) $[M - H_2O]^+$, 522 (1) $[M - 2CO, H_2O]^+$, 512 (10) $[M - 2CO]^+$, 388 (20) $[M - 2CO, P(OCH_3)_3]^+$, 360 (30) $[M - C_{15}H_{11}OH]^+$, 332 (30) $[M - CO, C_{15}H_{11}OH]^+$, 304 (100) $[M - 2CO, C_{15}H_{11}OH]^+$, 246 (40) $[M - 2CO, 2P(OCH_3)_3]^+$, 211 (40) $[Fe\{P(OCH_3)_3\}_2 - 3OCH_3]^+$, 180 (5) $[FeP(OCH_3)_3]^+$, 165 (10) $[FeP(OCH_3)_3 - CH_3]^+$, 124 (20) $[P(OCH_3)_3]^+$, 93, 77, 63.

$C_{22}H_{30}FeO_9P_2$ (568.28)	Calcd.	C 48.61	H 5.32	Fe 9.83
	Found	C 48.74	H 5.60	Fe 9.78

5.19. Dicarbonyl(3-methylbutadien-1,1-diyl)bis(trimethylphosphite)iron(0) 9a

340 mg (0.76 mmol) **7a** and a small amount of Al_2O_3 were stirred in hexane at r.t. for 30 min. Column chromatography over silylated silica and elution with hexane–ether 200:1 afforded a yellow oil of spectroscopically pure **9a** after removal of the solvent. A satisfactory elemental analysis could not be obtained. Yield 210 mg (64%).

IR (hexane): $\nu(\mathrm{cm}^{-1})$ = 1994, 1933 (s, C≡O), 1613 (w, C=C). ^{1}H NMR (C_6D_6, 200 MHz): δ = 2.01 (br, CH_3), 3.47 (pseudo-t, J_{PH} = 6.0 Hz, OCH_3), 4.38, 4.70 (2 × m, CH_2), 6.03 (t, J_{PH} = 13.7 Hz, CH). ^{13}C NMR (C_6D_6, 50.3 MHz): δ = 21.4 (s, CH_3), 52.3 (s, OCH_3), 104.7 (t, $^5J_{PC}$ = 4 Hz, CH_2), 128.3 (t, $^3J_{PC}$ = 10 Hz, CH), 138.6 (t, $^4J_{PC}$ = 9 Hz, CCH_3), 212.3 (t, $^2J_{PC}$ = 29 Hz, C≡O), 323.0 (t, $^2J_{PC}$ = 67 Hz, Fe=C). ^{31}P NMR (C_6D_6): δ = 175.5. MS (70 eV): $m/e(\%)$ = 426 (5) [M]$^+$, 398 (< 5) [M − CO]$^+$, 370 (60) [M − 2CO]$^+$, 355 (40) [M − 2CO, CH_3]$^+$, 304 (100) [Fe{P(OCH$_3$)$_3$}$_2$]$^+$, 180 (60) [FeP(OCH$_3$)$_3$]$^+$, 165 (35) [FeP(OCH$_3$)$_2$]$^+$, 124 (80) [P(OCH$_3$)$_3$]$^+$.

$C_{13}H_{24}FeO_8P_2$ (426.12)	Calcd.	C 36.64	H 5.68	Fe 13.11
	Found	C 36.21	H 5.43	Fe 12.98

5.20. Dicarbonyl(3-ethylbutadien-1,1-diyl)bis(trimethylphosphite)iron(0) 9b and dicarbonyl(E,Z-3-methylpenta-1,3-dien-1,1-diyl)bis(trimethylphosphite)iron(0) 9c,d

The same procedure as for **9a** was followed starting from 480 mg (1.03 mmol) **7b**. Column chromatography on alumina and elution with hexane–ether 10:1 gave a yellow zone of **9b–d**. The volume of the solution was reduced and crystallization at −30 °C yielded the ca. 1:3 E/Z mixture of **9c,d**. **9b** remained in the mother liquor and was isolated by removal of the solvent. A correct elemental analysis was not obtained. **9c,d** could be obtained as the exclusive products of dehydration of **7b**, when the column chromatography was performed on silica as the stationary phase. Elution with hexane–ether 100:1 resulted in a yellow zone containing **9c** and **9d** in a 1:3 ratio. Separation of these isomers could not be achieved.

9b: Yield 90 mg (20%).

IR (hexane): $\nu(\mathrm{cm}^{-1})$ = 1993, 1932 (s, C≡O), 1925 (sh, C≡O), 1614 (w, C=C). ^{1}H NMR (C_6D_6, 300 MHz): δ = 1.19 (t, $^3J_{HH}$ = 7.4 Hz, CH_2CH_3), 2.31 (t, $^3J_{HH}$ = 7.4 Hz, CH_2CH_3), 3.47 (pseudo-t, J_{PH} = 5.6 Hz, OCH_3), 4.54, 4.86 (2 × m, =CH_2), 5.95 (t, $^4J_{PC}$ = 14 Hz, =CH_2). ^{13}C NMR (C_6D_6, 75.4 MHz): δ = 15.1 (s, CH_2CH_3), 30.1 (s, CH_2CH_3), 52.3 (s, OCH_3), 103.0 (t, $^5J_{PC}$ = 4 Hz, =CH_2), 130.4 (t, $^3J_{PC}$ = 9 Hz, =CH), 144.5 (t, $^4J_{PC}$ = 10 Hz, CEt), 212.3 (t, $^2J_{PC}$ = 30 Hz, C≡O), 322.6 (t, $^2J_{PC}$ = 65 Hz, Fe=C). ^{31}P NMR (C_6D_6): δ = 175.8. MS (70 eV): $m/e(\%)$ = 440 (10) [M]$^+$, 412 (1) [M − CO]$^+$, 409 (10) [M − OCH$_3$]$^+$, 384 (1) [M − 2CO]$^+$, 360 (40) [M − C_6H_8]$^-$, 332 (35) [M − CO, C_6H_8]$^+$, 304 (100) [M − 2CO, C_6H_8]$^+$, 260 (98) [M − 2CO − P(OCH$_3$)$_3$]$^+$, 211 (80) [Fe{P(OCH$_3$)$_3$}$_2$ − 3OCH$_3$]$^+$, 180 (30) [FeP(OCH$_3$)$_3$]$^+$, 165 (40) [FeP(OCH$_3$)$_2$]$^+$, 135, 124 (1) [P(OCH$_3$)$_3$]$^+$, 109, 93, 63.

9c,d: yield 160 mg (35%).

IR (hexane): $\nu(\mathrm{cm}^{-1})$ = 1992, 1931 (s, C≡O), 1925 (sh, C≡O), 1610 (w, C=C). MS (70 eV): $m/e(\%)$ = 440 (10) [M]$^+$, 412 (1) [M − CO]$^+$, 409 (10) [M − OCH$_3$]$^+$, 384 (1) [M − 2CO]$^+$, 360 (40) [M − C_6H_8]$^+$, 332 (35) [M − CO, C_6H_8]$^+$, 304 (100) [M − 2CO, C_6H_8]$^+$, 260 (98) [M − 2CO − P(OCH$_3$)$_3$]$^+$, 211 (80) [Fe{P(OCH$_3$)$_3$}$_2$ − 3OCH$_3$]$^+$, 180 (30) [FeP(OCH$_3$)$_3$]$^+$, 165 (40) [FeP(OCH$_3$)$_2$]$^+$, 135, 124 (1) [P(OCH$_3$)$_3$]$^+$, 109, 93, 63.

$C_{14}H_{26}FeO_8P_2$ (440.15)	Calcd.	C 38.20	H 6.00	Fe 12.69
	Found	C 37.99	H 5.85	Fe 13.08

9c: ^{1}H NMR (C_6D_6, 300 MHz): δ = 1.62 (m, CHC(CH_3)=), 2.08 (m, =CH(CH_3)), 3.48 (pseudo-t, J_{PH} = 6 Hz, OCH_3), 4.80 (m, =CH), 6.34 (td, $^4J_{PH}$ = 13.7 Hz, $^4J_{HH}$ = 1.3 Hz, =CH). ^{13}C NMR (C_6D_6, 75.4 MHz): δ = 13.8 (s, CH_3), 22.7 (s, CH_3), 52.3 (s, OCH_3), 113.9 (t, $^5J_{PC}$ = 4 Hz, =C(CH$_3$)), 122.3 (t, $^3J_{PC}$ = 9 Hz, =C=CH), 128.8 (t, $^4J_{PC}$ = 9 Hz, CCH_3), 212.5 (t, $^2J_{PC}$ = 29 Hz, C≡O), 325.4 (t, $^2J_{PC}$ = 67 Hz, Fe=C). ^{31}P NMR (C_6D_6): δ = 176.1.

9d: ^{1}H NMR (C_6D_6, 300 MHz): δ = 1.62 (m, CHC(CH_3)=), 2.08 (m, =CH(CH_3)), 3.48 (pseudo-t, J_{PH} = 6 Hz, OCH_3), 4.80 (m, =CH), 6.34 (td, $^4J_{PH}$ = 13.7 Hz, $^4J_{HH}$ = 1.3 Hz, =CH). ^{13}C NMR (C_6D_6, 75.4 MHz): δ = 13.8 (s, CH_3), 22.7 (s, CH_3), 52.3 (s, OCH_3), 113.9 (t, $^5J_{PC}$ = 4 Hz, =C(CH$_3$)), 122.3 (t, $^3J_{PC}$ = 9 Hz, =C=CH), 128.8 (t, $^4J_{PC}$ = 9 Hz, CCH_3), 212.5 (t, $^2J_{PC}$ = 29 Hz, C≡O), 325.4 (t, $^2J_{PC}$ = 67 Hz, Fe=C). ^{31}P NMR (C_6D_6): δ = 176.1.

5.21. Dicarbonyl(3-i-propylbutadien-1,1-diyl)bis(trimethylphosphite)iron(0) 9e and dicarbonyl(3,4-dimethylpentadien-1,1-diyl)bis(trimethyl-phosphite)iron(0) 9f

The same procedure as for the preparation of **9a** was followed starting from 220 mg (0.47 mmol) **7c**. Column chromatography was performed over alumina with elution of a ca. 1:1 mixture of **9e** and **9f** with CH_2Cl_2. Stirring of

7e with silica afforded after column chromatography over silylated silica and elution with hexane a yellow band. Partial evaporation of the solvent and crystallization at $-30\,^{\circ}\text{C}$ gave an orange-brown powder of **9f**. Yield 170 mg (80%).

9e: IR (hexane): $\nu(\text{cm}^{-1}) = 1991, 1930$ (s, C≡O), 1924 (sh, C≡O), 1605 (w, C=C). ^{1}H NMR (C_6D_6, 200 MHz): $\delta = 1.13$ (d, $^3J_{HH} = 6.8\,\text{Hz}$, CH_3), 2.42 (m, $^3J_{HH} = 6.8\,\text{Hz}$, $CH(CH_3)_2$), 3.48 (pseudo-t, $J_{PH} = 6.0\,\text{Hz}$, OCH_3), 4.64, 4.95 (2 × m, CH_2), 5.75 (t, $^4J_{PH} = 13.6\,\text{Hz}$, =CH). ^{13}C NMR ($C_6D_6$, 50.3 MHz): $\delta = 22.8$ (s, CH_3), 33.6 (s, $CH(CH_3)_2$), 51.4 (s, OCH_3), 102.7 (t, $^5J_{PC} = 4\,\text{Hz}$, =CH_2), 125.5 (t, $^3J_{PC} = 10\,\text{Hz}$, =CH), 149.3 (t, $^4J_{PC} = 9\,\text{Hz}$, $C(iPr)$), 212.3 (t, $^2J_{PC} = 29\,\text{Hz}$, C≡O), 322.6 (t, $^2J_{PC} = 67\,\text{Hz}$, Fe=C). ^{31}P NMR (C_6D_6): $\delta = 176.1$.

9f: IR (hexane): $\nu(\text{cm}^{-1}) = 1991, 1930$ (s, C≡O), 1924 (sh, C≡O), 1605 (w, C=C). ^{1}H NMR (C_6D_6, 200 MHz): $\delta = 1.65$ (br, CH_3), 1.71 (br, E-CH_3), 2.00 (m, Z-CH_3), 3.50 (pseudo-t, $J_{PH} = 6.0\,\text{Hz}$, OCH_3), 6.40 (t, $^4J_{PH} = 13.7\,\text{Hz}$, =CH). ^{13}C NMR ($C_6D_6$, 50.3 MHz): $\delta = 17.3$ (s, CH_3), 20.7 (s, $C(CH_3)_2$), 52.3 (s, OCH_3), 118.5 (t, $^5J_{PC} = 4\,\text{Hz}$, $C(CH_3)_2$), 120.7 (t, $^3J_{PC} = 9\,\text{Hz}$, CCH_3), 125.0 (t, $^4J_{PC} = 10\,\text{Hz}$, =CH), 212.7 (t, $^2J_{PC} = 29\,\text{Hz}$, C≡O), 326.3 (t, $^2J_{PC} = 68\,\text{Hz}$, Fe=C). ^{31}P NMR (C_6D_6): $\delta = 176.2$. MS (70 eV): $m/e(\%) = 454$ (5) $[\text{M}]^+$, 426 (1) $[\text{M}-\text{CO}]^+$, 423 (1) $[\text{M}-OCH_3]^+$, 398 (1) $[\text{M}-2\text{CO}]^+$, 360 (30) $[\text{M}-C_7H_{11}]^+$, 332 (30) $[\text{M}-\text{CO}, C_7H_{11}]^-$, 304 (100) $[\text{M}-2\text{CO}, C_7H_{11}]^+$, 274 (35) $[\text{M}-2\text{CO}-P(OCH_3)_3]^+$, 211 (70) $[\text{Fe}\{P(OCH_3)_3\}_2 - 3OCH_3]^+$, 180 (20) $[\text{Fe}P(OCH_3)_3]^+$, 165 (20) $[\text{Fe}P(OCH_3)_2]^+$, 135, 124 (5) $[P(OCH_3)_3]^+$, 109, 93, 63, 43.

$C_{15}H_{28}FeO_8P_2$ (454.17)	Calcd.	C 39.67	H 6.21	Fe 12.30
	Found	C 38.57	H 6.07	Fe 12.41

5.22. Dicarbonyl(3-t-butylbutadien-1,1-diyl)bis(trimethylphosphite)iron(0) 9g and dicarbonyl(t-butylmethylallenylidene)bis(trimethylphosphite)iron(0) 8a

The same procedure as for the preparation of **9a** was followed starting from 380 mg (0.78 mmol) of **7d**. Column chromatography was performed over silica. Elution with hexane–ether 100:1 produced a first yellow band of **9g**, from which **9g** remained as an orange oil after evaporation of the solvent. A second red zone contained **8a**, from which after partial evaporation of the solvent **8a** precipitated at $-30\,^{\circ}\text{C}$ as a dark red powder.

9g: yield 220 mg (60%).

IR (hexane): $\nu(\text{cm}^{-1}) = 1993, 1940$ (s, C≡O), 1932 (sh, C≡O), 1628, 1588 (w, C=C). ^{1}H NMR (C_6D_6, 300 MHz): $\delta = 1.08$ (s, CH_3), 3.50 (pseudo-t, $J_{PH} = 6.0\,\text{Hz}$, OCH_3), 5.02, 5.41 (2 × m, =CH_2), 5.80 (t, $^4J_{PH} = 13.6\,\text{Hz}$, =CH). ^{13}C NMR ($C_6D_6$, 75.4 MHz): $\delta = 29.4$ (s, CH_3), 35.6 (s, $C(CH_3)_2$), 52.4 (s, OCH_3), 105.7 (t, $^5J_{PC} = 4\,\text{Hz}$, =CH_2), 121.7 (t, $^3J_{PC} = 10\,\text{Hz}$, =CH), 150.3 (t, $^4J_{PC} = 8\,\text{Hz}$, $C(tBu)$), 212.4 (t, $^2J_{PC} = 29\,\text{Hz}$, C≡O), 322.6 (t, $^2J_{PC} = 67\,\text{Hz}$, Fe=C). ^{31}P NMR (C_6D_6): $\delta = 177.1$. MS (70 eV): $m/e(\%) = 469$ (5) $[\text{M}]^+$, 440 (1) $[\text{M}-\text{CO}]^+$, 437 (5) $[\text{M}-OCH_3]^+$, 412 (1) $[\text{M}-2\text{CO}]^+$, 360 (40) $[\text{M}-C_8H_{14}]^+$, 332 (50) $[\text{M}-\text{CO}, C_8H_{14}]^+$, 304 (100) $[\text{M}-2\text{CO}, C_8H_{14}]^+$, 288 (60) $[\text{M}-2\text{CO}-P(OCH_3)_3]^+$, 211 (55) $[\text{Fe}\{P(OCH_3)_3\}_2 - 3OCH_3]^+$, 180 (10) $[\text{Fe}P(OCH_3)_3]^+$, 165 (20) $[\text{Fe}P(OCH_3)_3 - CH_3]^+$, 124 (< 1) $[P(OCH_3)_3]^+$, 93.

$C_{16}H_{30}FeO_8P_2$ (468.20)	Calcd.	C 41.01	H 6.46	Fe 11.93
	Found	C 40.78	H 6.23	Fe 11.67

8a: yield 62 mg (17%).

IR (hexane): $\nu(\text{cm}^{-1}) = 1985, 1926$ (s, C≡O). ^{1}H NMR (C_6D_6, 300 MHz): $\delta = 1.17$ (s, tBu), 1.55 (t, $^6J_{PH} = 4.4\,\text{Hz}$, CH_3), 3.52 (pseudo-t, $J_{PH} = 6.0\,\text{Hz}$, OCH_3). ^{13}C NMR (C_6D_6, 75.4 MHz): $\delta = 24.2$ (t, $^5J_{PC} = 9\,\text{Hz}$, $C(CH_3)$), 28.8 (t, $^6J_{PC} = 2\,\text{Hz}$, $C(CH_3)_3$), 41.7 (t, $^5J_{PC} = 6\,\text{Hz}$, $C(CH_3)_3$), 52.3 (s, OCH_3), 138.4 (t, $^4J_{PC} = 11\,\text{Hz}$, ^3C), 201.4 (t, $^3J_{PC} = 11\,\text{Hz}$, ^2C), 213.8 (t, $^2J_{PC} = 28\,\text{Hz}$, C≡O), 248.9 (t, $^2J_{PC} = 67\,\text{Hz}$, Fe=C). ^{31}P NMR (C_6D_6): $\delta = 174.3$. MS (70 eV): $m/e(\%) = 469$ (10) $[\text{M}]^+$, 440 (1) $[\text{M}-\text{CO}]^+$, 437 (1) $[\text{M}-OCH_3]^+$, 412 (20) $[\text{M}-2\text{CO}]^+$, 360 (20) $[\text{M}-C_8H_{14}]^+$, 332 (20) $[\text{M}-\text{CO}, C_8H_{14}]^+$, 304 (100) $[\text{M}-2\text{CO}, C_8H_{14}]^+$, 288 (50) $[\text{M}-2\text{CO}, P(OCH_3)_3]^+$, 211 (35) $[\text{Fe}(P(OCH_3)_3)_2 - 3OCH_3]^+$, 180 (10) $[\text{Fe}P(OCH_3)_3]^+$, 165 (10) $[\text{Fe}P(OCH_3)_3 - CH_3]^+$, 124 (< 1) $[P(OCH_3)_3]^+$, 93.

$C_{16}H_{30}FeO_8P_2$ (468.20)	Calcd.	C 41.01	H 6.46	Fe 11.93
	Found	C 40.89	H 6.67	Fe 11.88

5.23. Dicarbonyl(di-t-butylallenylidene)bis(trimethylphosphite)iron(0) 8b

The same procedure as for the preparation of **9a** was followed starting from 280 mg (0.53 mmol) of **7e**. Column chromatography was performed over silica. Elution with hexane–ether 100:1. Partial removal of the solvent and crystallization at $-30\,^\circ$C yielded brown crystals of **8b**. Yield 197 mg (73%).

IR (hexane): $\nu(\text{cm}^{-1}) = 1984, 1980, 1930, 1921, 1914$ (s, C≡O), 1865 (w, C=C=C). ^{1}H NMR (C_6D_6, 200 MHz): $\delta = 1.40$ (s, tBu), 3.51 (pseudo-t, $J_{\text{PH}} = 6.2$ Hz, OCH$_3$). ^{13}C NMR (C_6D_6, 50.3 MHz): $\delta = 31.6$ (s, CH$_3$), 44.3 (t, $^5J_{\text{PC}} = 6$ Hz, C(CH$_3$)$_3$), 52.2 (s, OCH$_3$), 152.8 (t, $^4J_{\text{PC}} = 12$ Hz, ^{3}C), 202.9 (t, $^3J_{\text{PC}} = 11$ Hz, ^{2}C), 214.0 (t, $^2J_{\text{PC}} = 29$ Hz, C≡O), 253.9 (t, $^2J_{\text{PC}} = 70$ Hz, Fe=C). ^{31}P NMR (C_6D_6): $\delta = 178.4$. MS (70 eV): $m/e(\%) = 510$ (20) [M]$^+$, 482 (5) [M − CO]$^+$, 480 (1) [M − OCH$_3$]$^+$, 454 (80) [M − 2CO]$^+$, 330 (100) [M − 2CO, P(OCH$_3$)$_3$]$^+$, 273 (20) [M − 2CO, C(CH$_3$)$_3$, P(OCH$_3$)$_3$]$^+$, 211 (15) [Fe{P(OCH$_3$)$_3$}$_2$ − 3OCH$_3$]$^+$, 180 (5) [FeP(OCH$_3$)$_3$]$^+$, 165 (5) [FeP(OCH$_3$)$_3$ − CH$_3$]$^+$, 124 (< 1) [P(OCH$_3$)$_3$]$^+$, 93, 57.

$\text{C}_{19}\text{H}_{36}\text{FeO}_8\text{P}_2$ (510.28)	Calcd.	C 44.72	H 7.11	Fe 10.94
	Found	C 44.59	H 7.33	Fe 10.75

5.24. Dicarbonyl(diphenylallenylidene)bis(trimethylphosphite)iron(0) 8c

The same procedure as for the preparation of **7a** was followed starting from 375 mg (1.5 mmol) diphenylpropyneacetate and 1 mmol of Fe(CO)$_2$[P(OMe)$_3$]$_2$I$_2$. Column chromatography was performed over silica. Elution with hexane–ether 25:1 afforded a first yellow band which was discarded. The second olive-green zone contained **8c**. Crystallization at $-80\,^\circ$C gave a green-black powder of **8c**, which melted upon warming to r.t. Yield 210 mg (38%).

IR (hexane): $\nu(\text{cm}^{-1}) = 1994, 1989, 1940, 1928, 1922$ (s, C≡O), 1868 (w, C=C=C). ^{1}H NMR (CD$_3$COCD$_3$, 300 MHz): $\delta = 3.66$ (pseudo-t, $J_{\text{PH}} = 5.8$ Hz, OCH$_3$), 7.35, 7.69 (m, H$_{\text{Ar}}$). ^{13}C NMR (CD$_3$COCD$_3$, 75.4 MHz): $\delta = 52.2$ (s, OCH$_3$), 126.7 (t, $^4J_{\text{PC}} = 13$ Hz, ^{3}C), 127.9, 129.2, 129.3 (s, CAr), 143.8 (t, $^4J_{\text{PC}} = 8$ Hz, C$_{\text{ipso}}$), 209.5 (t, $^3J_{\text{PC}} = 12$ Hz, ^{2}C), 213.9 (t, $^2J_{\text{PC}} = 28$ Hz, C≡O), 230.3 (t, $^2J_{\text{PC}} = 74$ Hz, Fe=C). ^{31}P NMR (CD$_3$COCD$_3$): $\delta = 175.0$. MS (70 eV): $m/e(\%) = 550$ (15) [M]$^+$, 522 (1) [M − CO]$^+$, 519 (1) [M − OCH$_3$]$^+$, 494 (70) [M − 2CO]$^+$, 370 (100) [M − 2CO, P(OCH$_3$)$_3$]$^+$, 211 (15) [Fe{P(OCH$_3$)$_3$}$_2$ − 3OCH$_3$]$^+$, 180 (5) [FeP(OCH$_3$)$_3$]$^+$, 165 (5) [FeP(OCH$_3$)$_3$ − CH$_3$]$^+$, 124 (< 1) [P(OCH$_3$)$_3$]$^+$, 93, 57.

$\text{C}_{23}\text{H}_{28}\text{FeO}_8\text{P}_2$ (550.26)	Calcd.	C 50.20	H 5.13	Fe 10.15
	Found	C 49.78	H 5.43	Fe 9.97

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