Acetylene/Vinylidene Rearrangements of $Fe(CO)_2L_2$(silylacetylene) Complexes (L = Phosphorus Donor)

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The reaction of a mixture of $Fe(CO)_2(PEt_3)_2N_2$ (**1a**) and $[Fe(CO)_2(PEt_3)_2]_2N_2$ (**1b**) with acetylene leads to three complexes: $Fe(CO)_2(PEt_3)_2(\pi\text{-}HC{\equiv}CH)$ (**2a**), $Fe(CO)_2(PEt_3)_2(H)(C{\equiv}CH)$ (**2b**), and $Fe(CO)_2(PEt_3)_2{=}C{=}CH_2$ (**2c**). Upon chromatography on silylated silica gel the mixture of **2a–c** is completely transformed into **2c**. The analogous reaction of **1a**, **b** or of $Fe(CO)_2[P(OiPr)_3]_2N_2$ (**1d**) with $HC{\equiv}CSiMe_3$ affords the primary oxidative addition products $Fe(CO)_2L_2(H)(C{\equiv}CSiMe_3)$ [L = PEt_3, **3a**; L = $P(OiPr)_3$, **3c**]. The presence of a small amount of Al_2O_3 in hexane irreversibly converts **3a** and **3c** into the vinylidene compounds $Fe(CO)_2L_2{=}C{=}C(H)SiMe_3$[L = PEt_3, **4a**; L = $P(OiPr)_3$, **4c**]. The chromatographic work-up of **4c** additionally leads to the hydrolysis product $Fe(CO)_2[P(OiPr_3)_2]_2{=}C{=}CH_2$ (**2d**). The reaction of the phosphite-substituted derivative $Fe(CO)_2[P(OMe)_3]_2I^-$ (**1c**) with silylacetylene allows detection of the acetylene species $Fe(CO)_2[P(OMe)_3]_2(HC{\equiv}CSiMe_3)$ (**3b**), as well as the acetylido hydrido derivative $Fe(CO)_2[P(OMe)_3]_2(H)(C{\equiv}CSiMe_3)$ (**4b**). In a slow subsequent process, or with promotion by Al_2O_3 in hexane, the vinylidene compound $Fe(CO)_2[P(OMe)_3]_2{=}C{=}C(H)SiMe_3$ is formed. **3b** or **4b** are hydrolyzed to $Fe(CO)_2[P(OMe)_3]_2{=}C{=}CH_2$ (**5c**) in the presence of SiO_2. The reaction of disilylacetylene with **1a–d** results in the formation of disilylvinylidene complexes $Fe(CO)_2L_2{=}C{=}C(SiMe_3)_2$ (L = PMe_3, **7a**; L = PEt_3, **7b**; L = $PiPr_3$, **7c**). An intermediate acetylene derivative could be isolated for L = PEt_3 (**6a**) and spectroscopically detected for L = $P(OMe)_3$ (**6b**), but could not be traced for L = $P(OiPr)_3$. Further studies were devoted to the reactions of silyl diynes ($Me_3SiC{\equiv}CR$, R = $C{\equiv}CSiMe_3$, $p\text{-}C_6H_4{-}C{\equiv}CSiMe_3$) with **1a–c**. In all cases the acetylene compounds $Fe(CO)_2L_2(Me_3SiC{\equiv}CR)$ [L = PEt_3, R = $C{\equiv}CSiMe_3$, **8a**; R = $p\text{-}C_6H_4{-}C{\equiv}CSiMe_3$, **9a**; L = $P(OMe)_3$, R = $CSiMe_3$, **8b**; R = $p\text{-}C_6H_4{-}C{\equiv}CSiMe_3$, **9b**] were isolated, but only for **8b** was an equilibrium process observed to form the corresponding vinylidene derivative $Fe(CO)_2[P(OMe)_3]_2{=}C{=}C(SiMe_3)C{-}C\text{-}SiMe_3$ (**10b**). **10b** hydrolyzes upon chromatography on silica gel to give $Fe(CO)_2[P(OMe)_3]_2{=}C{=}CH{-}C{\equiv}CSiMe_3$ (**11b**): Finally, the reaction of *p*-diethynylbenzene with **1a–c** was explored. The acetylido hydrido species $Fe(CO)_2L_2(H)C{\equiv}C{-}p\text{-}C_6H_4{-}C{\equiv}CH$ was isolated in the case of L = PEt_3 (**12a**) and spectroscopically detected for L = $P(OMe)_3$ (**12b**). **12b** and **12a** transform spontaneously and in the presence of Al_2O_3 in hexane, respectively, to the vinylidene complexes $Fe(CO)_2L_2{=}C{=}C(H)R$ [R = $C_6H_4{-}C{\equiv}CH$, L = PEt_3, **13a**; L = $P(OMe)_3$, **13b**]. **6a**, **7a**, and **8a** have been characterized by single-crystal X-ray diffraction studies.

Complexes of terminal acetylenes display high propensity to rearrange into isomeric vinylidene species[1,2]. In many cases the latter appear to be the thermodynamically more stable isomeric forms. Such behaviour has also been observed for silyl-1-alkynes, albeit only in a few instances[2f,3]. This prompted us to further explore the synthetic scope of this rearrangement. In particular, it was interesting to see whether silylvinylidene complexes could be obtained, since silyl substitution would in principal allow further derivatization of such compounds, especially with regard to carbon–carbon coupling reactions.

Our group has previously demonstrated, that $Fe(CO)_2L_2$ fragments (L = phosphorus donor) are electronically quite flexible units, which can not only bind acetylenes, but also induce their rearrangements to vinylidene species. This latter reaction step presumably takes a course via the intermediacy of acetylido hydrido complexes[4]. In these investigations, synthetic access to $Fe(CO)_2L_2$ units was achieved via the photochemically generated dinitrogen compounds $[Fe(CO)_2L_2]_2N_2$ or $Fe(CO)_2L_2(N_2)$. Recently, we established a reductive synthetic pathway to iron(0) compounds starting from readily accessible $Fe(CO)_2L_2X_2$ species (X = halogen)[5]. Depending on the ligand L, either the dinitrogen compounds or anionic halogeno complexes $[Fe(CO)_2L_2X]^-$ were obtained, which allow facile exchange of the N_2 or the X^- ligand, even with weakly coordinating groups.

Results and Discussion

The investigations presented in this paper refer to complexes with $Fe(CO)_2L_2$ moieties predominantly with L = PEt_3 or $P(OMe)_3$ ligands, although in some cases chemistry of the $Fe(CO)_2[P(OiPr)_3]_2$ unit is also included. The starting compounds for ligand exchange reactions at these fragments were variously $[Fe(CO)_2(PEt_3)_2]_2N_2$ (**1a**) and $Fe(CO)_2(PEt_3)_2(N_2)$ (**1b**), $Na[Fe(CO)_2\{P(OMe)_3\}_2I]$ (**1c**) or $Na[Fe(CO)_2\{P(OiPr)_3\}_2I]$ (**1d**) all of which were prepared in situ in THF solutions[5].

It is well-known that the silyl groups of silylacetylenes are labilized upon coordination and can easily be protolyzed under mild conditions to afford to the parent acetylene compounds[6]. In order to facilitate the analyses of the expected reaction mixtures we decided to attempt the inves-

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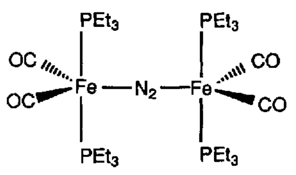
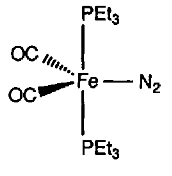
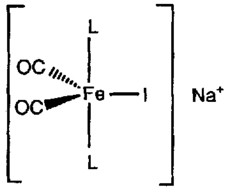


1a



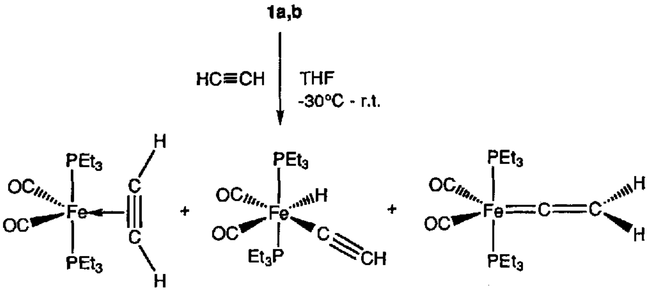
1b



L = P(OMe)$_3$ **1c**
L = P(OiPr)3 **1d**

tigation of the parent acetylene chemistry first, despite the anticipated instability of the products.

The reaction of a THF solution of a mixture of **1a** and **1b** with 1 bar of acetylene leads to 3 complexes **2a**–**c** (1:2:2 ratio) identified in the reaction mixture by the presence of 6 ν(CO)- and two ν(CC)-IR bands (eq. 1). In an attempt to establish the reaction sequence of eq. 1 we carried out ^{1}H-NMR studies. However, all three products appeared in the solution, even at an early stage of the reaction and it was not possible to achieve clear evidence on the nature of the initial product. Under the reaction conditions the mixture of **2a**–**2c** appeared to be quite labile, which prevented prolonged spectroscopic pursuit of the reaction course at room temp. However, it became quite apparent that **2c** accumulated with respect to **2a** and **2b** as a function of time. From this it can be concluded that **2c** is formed irreversibly from **2a** or **2b**.

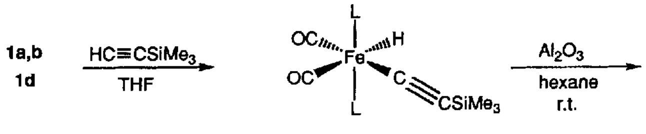


(1)

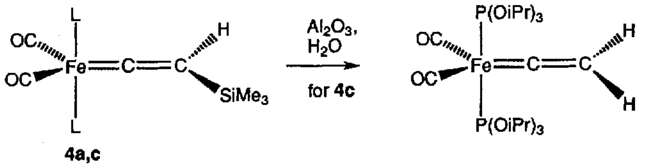
2a–**c** could not be separated by chromatography on silica gel due to complete decomposition on this stationary phase. However, after column chromatography of the 1:2:2 reaction mixture on silylated silica gel only the IR bands of **2c** remained, which allowed the isolation of this compound as a brown oil in 76% yield. Apparently, the contact of **2a** and **2b** with silylated silica leads to an acceleration of the conversion to **2c**. The IR [ν(CO): 1941, 1875; ν(C=C): 1598 cm^{-1}] and the ^{1}H-, ^{13}C-, and ^{31}P-NMR data of **2c** are in agreement with the vinylidene structure. Quite diagnostic is a unique ^{1}H-NMR resonance at $\delta = 4.15$ ($J_{PH} = 12$ Hz) which is attributed to the H_{vinyl} nuclei. **2a** and **2b**, which could not be separated, were identified from the reaction mixture by their IR and ^{1}H-, ^{13}C-, and ^{31}P-NMR spectra. **2b** shows characteristic ^{1}H-NMR resonances at $\delta = -8.67$ for the iron hydride ($^2J_{PH} = 50.5$ Hz) and at $\delta = 2.20$ for the $H_{acetylene}$ nucleus. **2a** displays a typical ν(C≡C)-IR absorption at 1658 cm^{-1} and an $H_{acetylene}$ resonance at $\delta = 5.55$ ($^4J_{HP} = 4.6$ Hz) in the ^{1}H-NMR spectrum. Quite characteristically, **2a**–**c** are easily distinguished in the ^{13}C-NMR spectra, since the signals for the iron-attached atom(s) of the C_2 units appear with large separation at $\delta = 85.1$, 108.0, and 317.2, respectively.

Starting from the phosphite compound $Na[Fe(CO)_2\{P(OMe)_3\}_2I]$ (**1c**), the analogous reaction to eq. 1 did not afford detectable amounts of an acetylene-derived organometallic product. Instead, $Fe(CO)_2[P(OMe)_3]_3$, $Fe(CO)_3[P(OMe)_3]_2$, and $Fe(CO)_2[P(OMe)_3]_2I_2$ were identified by comparison with literature IR data[7] and a considerable amount of intractable, insoluble material was noticed after evaporation of the solvent and extraction of the iron components. The appearance of iron(0) and iron(II) ligand-disproportionation products may be interpreted in terms of a reaction course involving one-electron transfer as an initiation step, and the intermediacy of the 17e$^-$ species $Fe(CO)_2[P(OMe)_3]_2I$[5].

In order to gain further insight into the acetylene transformations at iron centers, we then turned to the investigation of silyl-substituted acetylenes. The conversion of **1a**, **b** or **1d** with HC≡CSiMe$_3$ leads to the C–H oxidative addition products $Fe(CO)_2L_2(H)(C{\equiv}CSiMe_3)$ (**3a** or **3c**) as the only detectable species, which has been ascertained by ^{31}P-NMR spectroscopy in the temperature range from −60 to +50°C (eq. 2). In both cases there is no evidence for the existence of an intermediate acetylene complex.



L = PEt$_3$ **a**; L = P(OiPr)$_3$ **c** (2)



4a,c

2d

3a and **3c** were isolated as a brown oil and as a yellow solid in 90% and 82% yield, respectively. Their structures were established by IR [1 ν(C≡C) and 2 ν(CO) bands], ^{1}H-, ^{13}C-, ^{31}P-NMR spectroscopy, and mass spectrometry. The ^{1}H-NMR spectra exhibited two characteristic signals at $\delta = -9.6$ and 0.09 (**3a**) and at $\delta = -8.21$ and 0.22 (**3c**) which were attributed to the H_{Fe} and the Me$_3$Si protons.

The ^{13}C-NMR spectra displayed two resonances at $\delta = 114.8$ ($^2J_{PC} = 39$ Hz) and 116.6 (**3a**) and at $\delta = 130.3$ ($^2J_{PC} = 49$ Hz) and 121.1 (**3c**) which were assigned to the carbon nuclei of the acetylide units.

The stability of **3a** and **3c** is presumably of kinetic origin, since in the presence of Al_2O_3 at room temp. in hexane solution, they are readily transformed into the vinylidene compounds **4a** and **4c** (eq. 2). **4a** was isolated as a yellow oil (m.p. ca. −30 °C) after a reaction time of 30 min, while for **4c** the reaction was completed in 12 h. Upon chromatographic work-up of **4c** on silica gel, **4c** and its hydrolysis product **2d** were obtained in a 1:2 ratio.

4c and **2d** can be separated by repeated chromatography on silica gel. The spectroscopic properties of **4a** and **4c** differ remarkably from those of the isomeric omplexes **3a** and **3c**. In the IR spectrum the ν(CC) vibrations of the C_2 unit in **4a** and **4c** are shifted to distinctly lower wave numbers, while in the ^{1}H-NMR spectrum both complexes display a H_{vinyl} signal which appears instead of an iron hydride resonance [$\delta = 4.15$, $^4J_{PH} = 12$ Hz (**4a**); $\delta = 4.47$, $^4J_{PH} = 13.7$ Hz (**4c**)]. Furthermore, an extremely low-field shift is seen in the ^{13}C-NMR spectrum for the triplet of the iron-bound carbon atoms. The spectroscopic data of **2d** resemble those of **2c**, which emphasizes their structural relationship. Most noteworthy are the similar chemical shifts and couplings of the H_{vinyl} and $C_{vinylidene}$ resonances in the ^{1}H- and ^{13}C-NMR spectra [^{1}H NMR: $\delta = 4.15$, $^4J_{PH} = 12$ Hz (**2c**), $\delta = 4.55$, $^4J_{PH} = 12$ Hz (**2d**); ^{13}C NMR: $\delta C_a = 317.2$, $^2J_{PC} = 51$ Hz (**2c**); $\delta = 318.7$, $^2J_{PH} = 63$ Hz (**2d**). $\delta C_\beta = 99.7$, $^3J_{PH} = 8$ Hz (**2c**); $\delta = 103.9$, $^3J_{PC} = 10$ Hz (**2d**)].

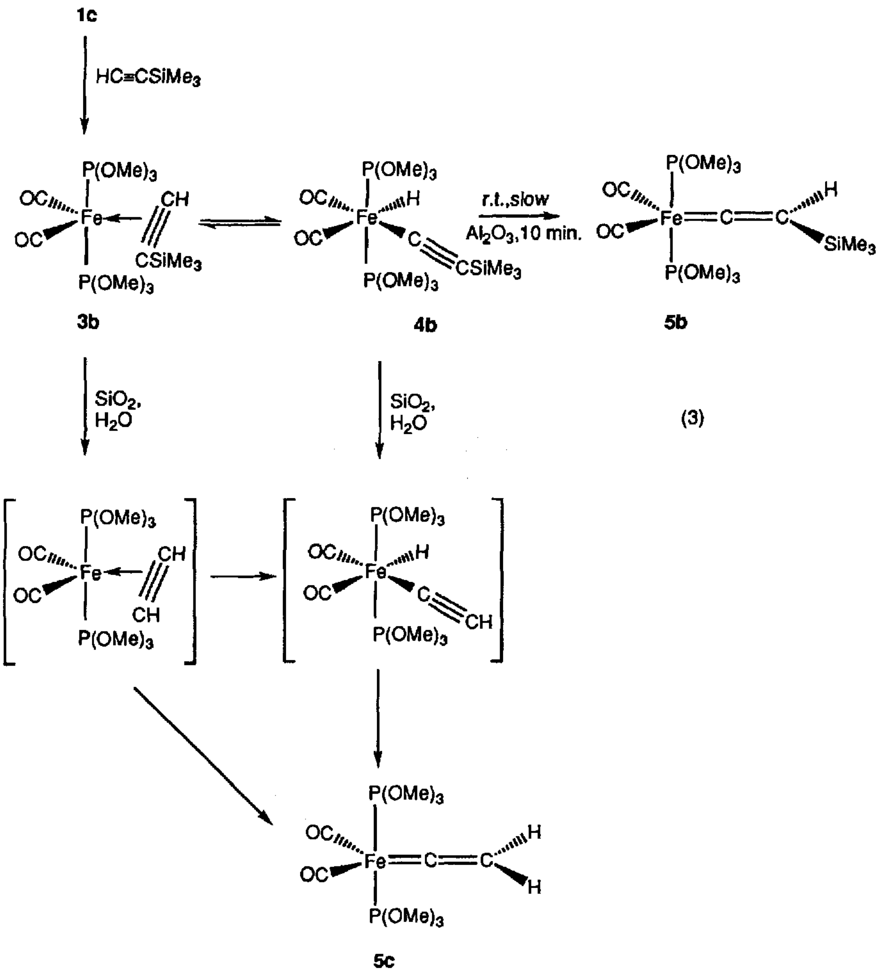
At 0 °C, the analogous reaction of the phosphite complex **1c** with $HC{\equiv}CSiMe_3$ takes a course similar to that of eq. 2. It leads to a single detectable species, the C−H insertion product $Fe(CO)_2[P(OMe)_3]_2(H)(C{\equiv}CSiMe_3)$ (**4b**) (eq. 3). At room temp., however, different reaction behaviour is observed and three products are found: besides **4b**, the π-acetylene system $Fe(CO)_2[P(OMe)_3]_2(HC{\equiv}CSiMe_3)$ (**3b**) and the vinylidene compound $Fe(CO)_2[P(OMe)_3]_2(HC{\equiv}CSiMe_3)$ (**3b**) and the vinylidene compound $Fe(CO)_2[P(OMe)_3]_2{=}C{=}C(H)SiMe_3$ (**5b**) are present (eq. 3). It is envisaged that **3b** and **4b** are in equilibrium with each other (2:3 ratio), while, akin to the conversions of eq. 2, the formation of **5b** is the result of a slow but irreversible rearrangement reaction starting from **4b**. The involvement of **3b** as a direct precursor to **5b** cannot be ruled out, but seems less likely. **3b** and **4b** were identified from the room-temperature reaction mixture. Attempts to separate these compounds by column chromatography were unsuccessful; on silylated silica gel insufficient separation could be achieved, while on silica gel conversion to the silylvinylidene complex **5b** and the parent vinylidene compound **5c** occurred. **5b** withstands further chromatography on silica gel, thus it is reasonable to assume that this latter hydrolysis reaction takes place at the stage of the silyl-substituted acetylenic derivatives **3b** or **4b**.

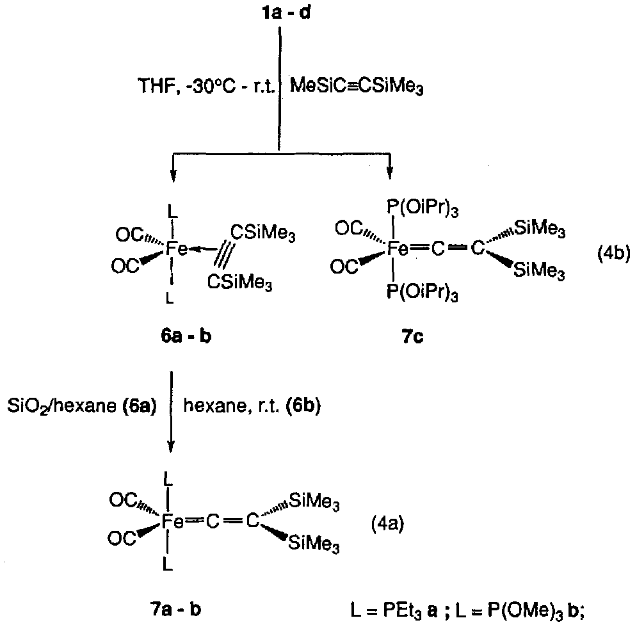
Stirring of the mixture of all three compounds **3b**, **4b**, and **5b** with Al_2O_3 for 10 min in hexane results in the complete and irreversible conversion of **3b** and **4b** to **5b**, without formation of **5c**. From this observation it can be concluded that **5b** is thermodynamically more stable than **3b** and **4b**; the reaction path leading to it has the highest kinetic barrier of all transformations of eq. 3. In fact, stirring a solution of **5b** for a longer period of time at room temp. does not reverse its formation and leads to **3b** or **4b**. Eq. 3 is consistent with a report by Bianchini et al.[2f] on $[(HC{\equiv}CR)/(PP_3)Co]^+$ systems, in which $[(PP_3)Co(H)(C{\equiv}CR)]^+$ species have been identified as the kinetic and $[(PP_3)Co{=}C{=}C(H)R]^+$ complexes as the thermodynamic products. In this paper π-$HC{\equiv}CR$ derivatives have been observed as short-lived intermediates on the way to acetylido hydrido compounds, which indicates a low barrier for this C−H oxidative addition process. Similarity, the findings of other related earlier work[2c] suggest that **4b** is the direct precursor of **5b**.

The route to **5c** described would seem to be unique, since its synthesis could not be accomplished by the substitution reaction of **1c** with acetylene (vide supra). Complexes **5b** and **5c** are structurally similar to compounds **2c**, **2d**, **4a**, and **4c**. They indeed show spectroscopic similarities, notably in the position of the ν(CC)-IR bands attributed to the vinylidene group, and in the ^{1}H- and ^{13}C-NMR chemical shifts and couplings of the vinylidene protons, as well as in the shifts of the C_α nuclei of the vinylidene unit [IR. ν(CC): 1614 (**5b**), 1616 cm^{-1} (**5c**); ^{1}H NMR: $\delta = 4.47$ (**5b**), 4.52 (**5c**); ^{13}C NMR: $\delta = 313.9$ (t, $^2J_{PC} = 62$ Hz) (**5b**), 318.5 (t, $^2J_{PC} = 66$ Hz) (**5c**)].

The experiments according to eqs. 2 and 3 have indicated that there is a greater aptitude of the H group than of the Me_3Si residue to undergo 1,3-shifts, since the competitive migratory transformations involving Me_3Si were not observed. In order to test the migrating capability of $SiMe_3$ moieties in our systems, we sought to investigate the reaction behaviour of $Me_3SiC{\equiv}CSiMe_3$ coordinated to $Fe(CO)_2L_2$ fragments. According to eq. 4a the reaction of **1a−d** with $Me_3SiC{\equiv}CSiMe_3$ was expected to result in formation of acetylene complexes $Fe(CO)_2L_2(Me_3SiC{\equiv}CSiMe_3)$ [L = PEt_3, **6a**; $P(OMe)_3$, **6b**; $P(O\mathit{i}Pr)_3$, **6c**].

Indeed, in the case of the reaction of **1a**, **b**, the acetylene complex **6a** could be isolated and fully characterized. In the transformation of **1c**, compound **6b** was detected by IR spectroscopy [ν(CO): 1931, 1872 cm^{-1}], but the existence of an analogous triisopropyl phosphite substituted acetylene derivative **6c** could not be proven. Under the reaction conditions of eq. 4, **6b** slowly, and **6c** rapidly (if formed at all), transform into the vinylidene complexes **7b** and **7c**, even in the absence of a promoting oxide compound. **6a** is apparently more reluctant to undergo the 1,2-silyl shift and to generate the vinylidene isomer. Its rearrangement could not be induced in THF or ether in the absence or presence of Al_2O_3 or SiO_2 or at elevated temperatures (50 °C). Surprisingly however, in hexane solution, in the presence of SiO_2, it cleanly converts to **7a**. This solvent dependence is unprecedented and is as yet unexplained[3b]. It is nevertheless corroborated by the observation that the transformation of **6b** to **7b** is also greatly enhanced in hexane. Some other ex-



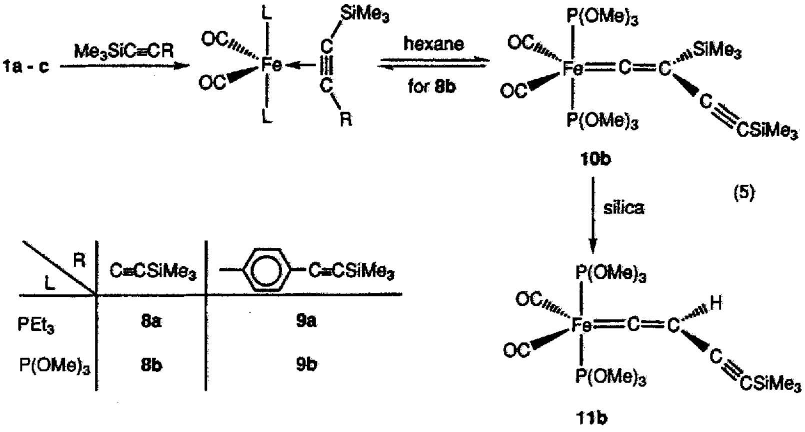


amples of conversions of disilylacetylene complexes into disilylvinylidene compounds have been reported[2g,3], and in some cases they have been accelerated by SiO_2 or Al_2O_3. Mechanistically, for all such silyl migrations, there is no evidence that reaction paths other than the 1,2-silyl shift are operative. An alternative route involving initial oxidative addition of the C–Si bond to the metal center and subsequent 1,3-silyl shift, in analogy to the H chemistry of terminal acetylenes, has never been indicated.

The structures of **6a** and **7a** have been established by exemplary X-ray diffraction studies. Since the spectroscopic properties of these compounds in solution are similar to those of **6b** and of **7b**, **c**, it is envisaged that all these complexes are closely related structurally. The IR spectrum of **6a** displays two ν(CO) bands and a band at 1750 cm^{-1}. The latter is attributed to the ν(CC) vibration of the acetylene moiety. In contrast, isomer **7a** shows ν(CO) absorptions at higher wavenumbers [this apparently is a general trend for vinylidene complexes with respect to their acetylene congeners; compare also ν(CO) of **6b**: 1931, 1872 cm^{-1}; and of **7b**: 1967, 1906 cm^{-1}] and expectedly a ν(CC) band for the vinylidene unit at significantly lower wavenumber (1560 cm^{-1}). The ^{13}C-NMR data of the carbon atoms of the C_2 unit are also worthy of note. While **6a** gives rise to a single phosphorus-coupled resonance at $\delta = 117.2$ for these nuclei, **7a–c** display two signals with the C_α resonances between $\delta = 300$ and 311 ($^2J_{PC} = 40-60$ Hz) and the C_β chemical shifts between $\delta = 103$ and 107 ($^3J_{PC} = 4-5$ Hz).

Further studies were devoted to the coordination and reaction behaviour of silyl diyne moieties bound to $Fe(CO)_2L_2$ centers. In particular, we were interested to see whether two iron units could be attached to such potentially bifunctional ligand systems and also to study the propensity to undergo acetylene/vinylidene rearrangements. 1,4-Bis(trimethylsilyl)butadiyne and the arene-spaced system *p*-bis(trimethylsilylethynyl)benzene were selected for use in these investigations.

When **1a**, **b** are treated in THF with $Me_3Si-C{\equiv}C-C{\equiv}CSiMe_3$ an almost quantitative transformation to the $Fe(CO)_2(PEt_3)_2$-monosubstituted complex **8a** is observed (eq. 5). The comparable reaction of **1c** with this dialkyne system leads to an equilibrium mixture of the corresponding π-alkyne compound **8b** and the vinylidene derivative **10b** (ca. 2:1 ratio). It was possible to separate **8b** and **10b** manually after crystallization of the reaction mixture from hexane at −30°C (ca. 1:1 solid-state ratio), since **8b** forms orange prisms and **10b** yellow needles. Both compounds turned out to be quite light- and temperature-sensitive, so that they had to be stored in the dark below 0°C.



An attempt to separate **8b** and **10b** by column chromatography on silica gel or silylated silica gel produced, in addition to a band of the unseparated mixture, a red band of the hydrolysis product **11b**. **11b** represents a vinylidene complex in which the vinylic silyl group of **10b** is replaced by a proton. The overall yield for all three products was ca. 50% and the components were obtained in an approximate 2:1:1 ratio (**8b**/**10b**/**11b**).

According to eq. 5, the reaction of **1a**−**c** with *p*-bis(trimethylsilylethynyl)benzene affords the $Fe(CO)_2L_2$-monosubstituted complexes **9a** (L = PEt_3) and **9b** (L = $P(OMe)_3$). Even if an excess of **1a**−**c** is used, the formation of disubstituted complexes is not observed. This behaviour parallels the findings of the disilylbutadiyne coordination and is furthermore in accord with reports on the diacetylene coordination capability of $[RhCl(P\textit{i}Pr_3)_2]$ fragments[1b,2d]. Presumably, the attachment of one $Fe(CO)_2L_2$ group deactivates the free alkyne moiety for further coordination, even with the strongly donating ligand, L = PEt_3. Upon metal binding, the overall withdrawal of electron density from the acetylenic system is too great to allow coordination of the other alkyne terminus. Quite surprisingly, **9a** and **9b** were reluctant to rearrange to vinylidene compounds, regardless of the presence of SiO_2 or Al_2O_3 as accelerating supports.

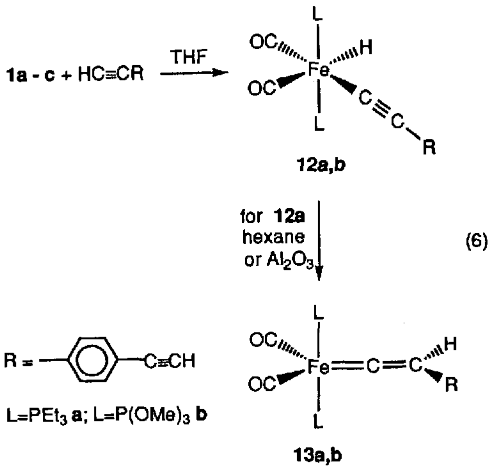
The structure of **8a** was determined by an X-ray diffraction study. It is consistent with the spectroscopic data in solution. For **8b** and **9a**, **b** the pentacoordinate geometries around the iron center were established by spectroscopic means and by comparison with the data of **8a**. While **8b** and **9a**, **b** show two bands for the acetylenic groups in the IR spectrum (presumably attributable to only weakly coupled vibrations of the coordinated and non-coordinated moieties), the spectrum of **8a** does not reveal such absorptions. Quite diagnostic for the given structures of **8a**, **b** and **9a**, **b** are the ^1H- and ^{13}C-NMR spectra, which display two separate signals for the silyl and the carbonyl groups. In addition, the ^{13}C-NMR spectra of all four compounds display four signals for the carbon atoms of the diyne chain or the two separate acetylenic units of the diethynylbenzene moieties.

The vinylidene structures of **10b** and **11b** were confirmed by the appearance of $\nu(C{=}C)$-IR bands at 1591 and 1583 cm^{-1} respectively, and by typical phosphorus-coupled low-field signals for the metal-bound $C_{vinylidene}$ atoms in the ^{13}C-NMR spectra. Since the acetylene/vinylidene rearrangement could not be accomplished in the silyl-substituted complexes **9a**, **b**, it was interesting to see how the parent H-substituted compounds would behave.

When *p*-diethynylbenzene was treated with **1a**−**c**, initial formation of the acetylido hydrido systems **12a**, **b** could be observed (eq. 6). The phosphite-substituted derivative **12b** could, however, only be detected in situ by IR spectroscopy [ν(CO): 1931, 1872 cm^{-1}], because it rapidly transformed intot he vinylidene complex **13b**.

The conversion of **12a** to the more stable vinylidene complex **13a** was accomplished by the addition of Al_2O_3 or by changing the solvent to hexane (vide supra). It should be mentioned that, as in the reactions of the silyl-substituted diacetylenes, double complexation of the acetylenic substrate could not be achieved. However, the H derivatives **12a**, **b** showed a greater propensity to undergo the acetylene/vinylidene rearrangement, as compared to **9a**, **b**.

The structures of **12a** and **13a**, **b** were derived from their spectroscopic properties and by comparison with the related species of type **3** and **4** [characteristic spectroscopic features: IR: $\nu(C{=}C)$; ^1H NMR: chemical shift of $H_{vinylidene}$; ^{13}C NMR: chemical shift of $Fe-C_{\alpha}$]. However,



(6)

12a could not be fully characterized (IR, ^1H NMR), because it tended to decompose even at low temperatures.

X-ray Diffraction Studies of 6a, 7a, and 8a

The complexes **6a**, **7a**, and **8a** show trigonal bipyramidal coordination geometry around the iron centers (see Figures 1 and 2). The $Fe(CO)_2(PEt_3)_2$ frameworks of these complexes are very similar in terms of their bond lengths and bond angles and furthermore, their C–Si distances are very close. The Fe(C≡C) geometries of the two acetylene complexes **6a** and **8a** differ only slightly. While the C–C distances are identical within the standard deviations, the Fe–C bond lengths appear to be somewhat shorter in **8a** than in **6a**, and, as would be expected, are asymmetric in the latter case.

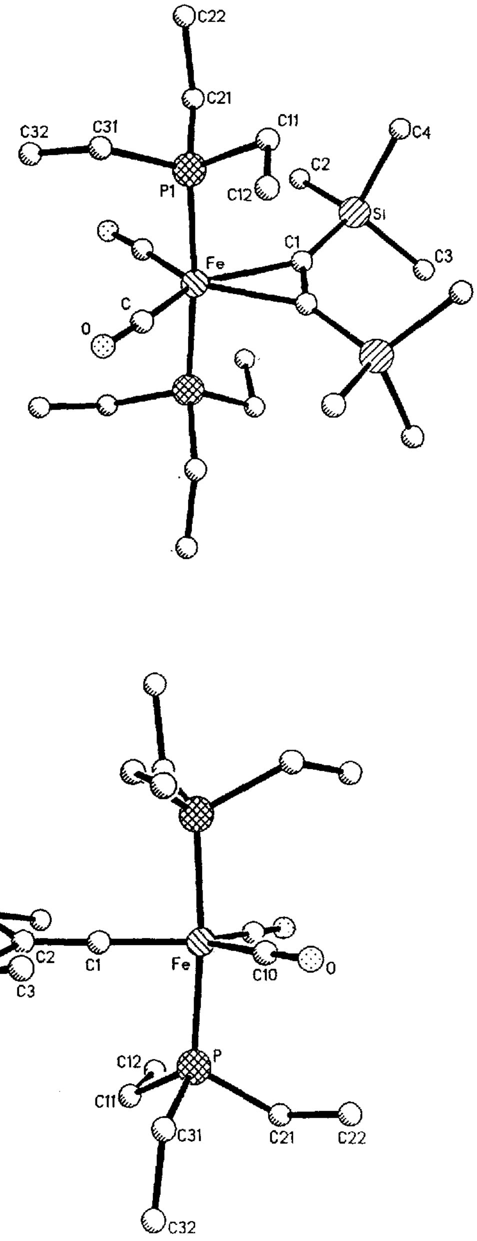
Nevertheless, all the Fe–C distances fall into the range determined for related compounds[8]. In either complex the R residues (R = $SiMe_3$ or $C{\equiv}CSiMe_3$) are bent back with angles between 140° and 150°, indicating a strong electronic back-donation from the iron atom to the acetylenic unit, thereby approaching the geometry of metallacyclopropene structures[2d,9]. The non-coordinated acetylene of **8a** is practically linear and its C≡C bond length compares well with standard values for such moieties. The structural parameters of the iron-bound vinylidene unit in **7a**, in particular the Fe1–C1 and the C1–C2 distances, are also very close to those found for other vinylidene complexes containing 3d transition metals[1,4b,8,10–12].

The Si–C–Si plane is coplanar with the equatorial plane of the $Fe(CO)_2(PEt_3)_2$ fragment[13], which is expected on the basis of the anisotropies of the π-bonding capabilities of C_{2v}-d^8-ML_4[13] and vinylidene fragments. While the metal units possess a higher propensity for π donation in the equatorial plane, the π-accepting capacity of vinylidenes is located in the vinylidene plane[14]. Thus, π interaction is optimized between the ligand and the metal fragment in the given rotameric conformation, which is also found in other trigonal-bipyramidal vinylidene complexes[10,12].

Conclusions

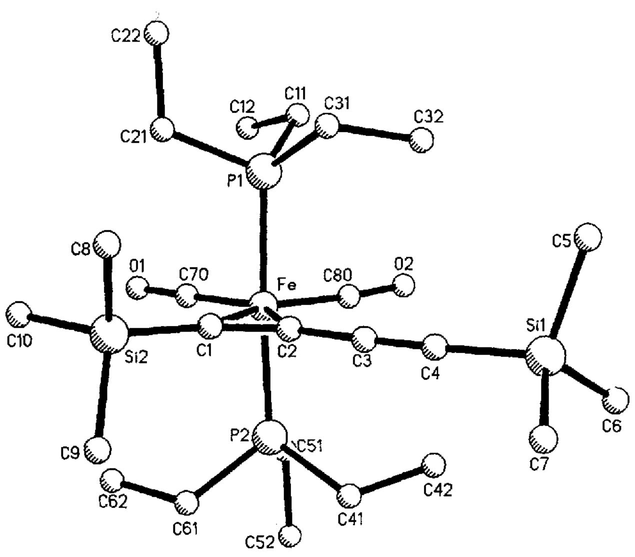
Our investigations of the reactions of $Fe(CO)_2L_2$ units with silyl-substituted acetylenes have demonstrated that terminal acetylenes are transformed to acetylido hydrido and vinylidene compounds upon complexation. In analogy to the observed H mobility in these systems, complexes of disilyl-substituted acetylenes show silyl migration to form silylvinylidene compounds. In addition, it was observed that acetylene/vinylidene rearrangements at $Fe(CO)_2L_2$ centers are more facile for the more electron-deficient systems (L = phosphite). Moreover, our investigations have shown that in the case of difunctionalized acetylenes, only one $Fe(CO)_2L_2$ fragment binds to the acetylenic unit.

Figure 1. Structures of **6a** (top)[a] and **7a** (bottom)[b]



[a] Selected bond lengths [Å] and angles [°]: Fe–P1 2.243(2), Fe–C 1.722(13), Fe–C1 2.123(9), C–O 1.164(17), C1–Si 1.828(18), C1–C1A 1.287(45); P1–Fe–P1A 175.0(1), C–Fe–CA 112.2(7), C1A–C1–Si 141.9(5). – [b] Selected bond lengths [Å] and angles [°]: Fe–P 2.211(1), Fe–C10 1.767(5), Fe–C1 1.777(5), C1–C2 1.320(6), C2–Si 1.875(3), C10–O 1.161(6); P–Fe–PA 174.6(1), C10–Fe–C10A 110.7(3), C1–C2–Si 119.5(1).

Figure 2. Structure of **8a**[a]



[a] Selected bond lengths [Å] and angles [°]: Fe−P1 2.245(3), Fe−P2 2.254(3), Fe−C1 2.083(8), Fe−C2 2.043(8), Fe−C70 1.772(8), Fe−C80 1.714(11), C70−O1 1.153(10), C80−O2 1.184(13), C1−C2 1.253(10), C2−C3 1.418(10), C3−C4 1.213(10), C1−Si2 1.837(8), C4−Si1 1.828(8); P1−Fe−P2 176.8(1), C70−Fe−C80 109.6(4), C2−C1−Si2 143.5(6), C1−C2−C3 150.0(8), C2−C3−C4 176.8(9), C3−C4−Si1 177.6(8).

We thank the *Swiss National Science Foundation* for financial support.

Experimental Section

All manipulations were performed by standard Schlenk techniques under dry N_2. Solvents were dried by conventional procedures and freshly distilled before use. – Column chromatography was performed with jacket-cooled columns at −10°C. Stationary phases were Kieselgel 60 (40−63 μm, Merck), silylated silica gel (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 with a Finnigan MAT 8230 spectrometer. – ^{1}H-, ^{13}C-, and ^{31}P-NMR spectra were measured on Varian Gemini 200 or 300 instruments (frequencies: ^{1}H: 200 or 300 MHz; ^{13}C: 50.3 or 75.4 MHz; ^{31}P: 121.5 MHz). Standards: ^{1}H and ^{13}C: δ rel. to TMS; ^{31}P: δ rel. to H_3PO_4.

$Me_3SiC{\equiv}CH$ was purchased from Fluka. $Me_3SiC{\equiv}CSiMe_3$[15], $Me_3Si(C{\equiv}C)_2SiMe_3$[15], *p*-bis(trimethylsilyl)ethynylbenzene[16] and *p*-diethylbenzene[17] were prepared according to literature procedures. $Fe(CO)_2L_2I_2$ (L = PEt_3[18−21], $P(OMe)_3$[7], $P(OiPr)_3$[7b]) were obtained as reported earlier. THF solutions of $[(OC)_2(Et_3P)_2Fe]_2N_2$ (**1a**) and $Fe(CO)_2(PEt_3)_2N_2$ (**1b**), $[Fe(CO)_2\{P(OMe)_3\}_2I]Na$ (**1c**) and $[Fe(CO)_2\{P(OiPr)_3\}_2I]Na$ (**1d**) were prepared in situ according to ref.[5]; their syntheses are repeated here.

$[(OC)_2(Et_3P)_2Fe]_2N_2$ (**1a**), *$Fe(CO)_2(PEt_3)_2N_2$* (**1b**) *and $[Fe(CO)_2L_2I]Na$, L = $P(OMe)_3$* (**1c**), *$P(OiPr)_3$* (**1d**): At −30°C, freshly prepared sodium amalgam (<1%, ca. 12 mmol Na) and solutions of 1 mmol of $Fe(CO)_2L_2I_2$ [L = PEt_3 (0.6 g), $P(OMe)_3$ (0.6 g), $P(OiPr)_3$ (0.78 g)] in 150 ml THF were stirred vigorously under N_2. After 3 h, the reaction mixture was cooled to −70°C and the supernatant solutions were transferred via a cannula to a frit covered with Celite. After filtration, these solutions were ready for use in further reactions.

Acetylenedicarbonylbis(triethylphosphane)iron(0) (**2a**), *Acetylidodicarbonylhydridobis(triethylphosphane)iron(II)* (**2b**), *and Dicarbonylbis(triethylphosphane)vinylideneiron(0)* (**2c**): A solution of **1a**, **b** in THF was warmed from −30°C to room temp., while a steady stream of acetylene was bubbled through it. – IR monitoring revealed the presence of **2a**−**c** in a 1:2:2 ratio. After removal of the solvent, 0.31 g of an oily mixture of the complexes **2a**−**c** remained (crude yield 83%). Subsequent column chromatography on silylated silica gel, elution with hexane/ether (100:1) and removal of the solvent afforded 0.29 g of **2c** as a brown oil (yield 76%). **2c**, as well as the mixture of **2a**−**c**, was unstable at room temp. preventing their characterization by elemental analysis.

2a: IR (hexane): $\tilde{\nu}$ = 1955, 1890 cm^{-1} (s, C≡O). – ^{1}H NMR (C_6D_6, 200 MHz): δ = 1.19 (m_c, CH_2CH_3), 1.80 (m_c, CH_2CH_3), 5.55 (t, $^{3}J_{PH}$ = 4.6 Hz, ≡CH). – ^{13}C NMR (C_6D_6, 50.3 MHz): δ = 7.7 (s, CH_2CH_3), 17.5 (pseudo-t, J_{PC} = 11 Hz, CH_2CH_3), 85.1 (t, $^{2}J_{PC}$ = 8 Hz, ≡CH), 223.6 (t, $^{2}J_{PC}$ = 28 Hz, C≡O). – ^{31}P NMR (C_6D_6): δ = 56.8.

2b: IR (hexane): $\tilde{\nu}$ = 1998, 1941 cm^{-1} (s, C≡O). – ^{1}H NMR (C_6D_6, 200 MHz): δ = −8.67 (t, $^{2}J_{PH}$ = 50.5 Hz, FeH), 1.10 (m_c, CH_2CH_3), 1.70 (m_c, CH_2CH_3), 2.21 (s, ≡CH). – ^{13}C NMR (C_6D_6, 50.3 MHz): δ = 7.9 (s, CH_2CH_3), 20.5 (pseudo-t, J_{PC} = 13 Hz, CH_2CH_3), 97.8 (s, ≡CH), 108.0 (t, $^{2}J_{PC}$ = 39 Hz, FeC≡), 213.7 (t, $^{2}J_{PC}$ = 13 Hz, C≡O), 215.4 (t, $^{2}J_{PC}$ = 20 Hz, C≡O). – ^{31}P NMR (C_6D_6): δ = 57.0.

2c: IR (hexane): $\tilde{\nu}$ = 1941, 1875 (s, C≡O), 1598 cm^{-1} (m, C=C). – ^{1}H NMR (C_6D_6, 200 MHz): δ = 1.00 (m_c, CH_2CH_3), 1.60 (m_c, CH_2CH_3), 4.15 (t, $^{4}J_{PH}$ = 12.0 Hz, CH_2). – ^{13}C NMR (C_6D_6, 50.3 MHz): δ = 8.3 (s, CH_2CH_3), 21.2 (pseudo-t, J_{PC} = 15 Hz, CH_2CH_3), 99.7 (t, $^{3}J_{PC}$ = 8 Hz, $=CH_2$), 216.6 (t, $^{2}J_{PC}$ = 19 Hz, C≡O), 317.2 (t, $^{2}J_{PC}$ = 51 Hz, Fe=C). – ^{31}P NMR (C_6D_6): δ = 61.3. – MS (70 eV): *m/z* (%) = 374 (20) $[M]^+$, 346 (20) $[M - CO]^+$, 318 (70) $[M - 2\,CO]^+$, 293 (25) $[M - 2\,CO, C_2H]^+$, 292 (90) $[M - 2\,CO, C_2H_2]^+$, 264 (25) $[M - 2\,CO, C_2H, C_2H_5]^+$, 200 (30) $[M - 2\,CO, PEt_3]^+$, 174 (30) $[Fe(PEt_3)]^+$, 146 (40) $[Fe(PEt_2)]^+$, 118 (80) $[PEt_3]^+$, 106, 90, 78, 77, 62, 57, 49.

Dicarbonylhydridobis(triethylphosphane)(trimethylsilylethynyl)iron(II) (**3a**): At −30°C, 2.1 ml (1.5 mmol) $Me_3SiC{\equiv}CH$ was added to the THF solution of **1a**, **b**. After warming to room temp., THF was removed in vacuo, the residue was extracted with 50 ml of hexane and filtered through Celite. The solvent was removed in vacuo, leaving analytically pure **3a** as a brown oil [yield 0.41 g (90%)]. – IR (hexane): $\tilde{\nu}$ = 2035 (w, C≡C), 1989, 1948 cm^{-1} (s, C≡O). – ^{1}H NMR (CD_2Cl_2, 300 MHz, −60°C): δ = −9.60 (t, $^{2}J_{PH}$ = 50.0 Hz, FeH), 0.09 [s, $Si(CH_3)_3$], 1.03 (m_c, CH_2CH_3), 1.77 (m_c, CH_2CH_3). – ^{13}C NMR (CD_2Cl_2, 75.4 MHz, −60°C): δ = 0.6 [s, $Si(CH_3)_3$], 7.4 (s, CH_2CH_3), 19.3 (pseudo-t, J_{PC} = 14 Hz, CH_2CH_3), 114.8 (t, $^{2}J_{PC}$ = 39 Hz, FeC≡), 116.6 (s, ≡CSi), 213.1 (t, $^{2}J_{PC}$ = 14.0 Hz, C≡O), 214.7 (t, $^{2}J_{PC}$ = 20 Hz, C≡O). – ^{31}P NMR (C_6D_6): δ = 56.3. – MS (70 eV): *m/z* (%) = 446 (5) $[M]^+$, 418 (1) $[M - CO]^+$, 389 (5) $[M - 2\,CO]^+$, 348 (10) $[M - C_5H_{10}Si]^+$, 320 (20) $[M - CO, C_5H_{10}Si]^+$, 292 (100) $[M - 2\,CO, C_5H_{10}Si]^+$, 272 (20) $[M - 2\,CO, PEt_3]^+$, 200 (<10) $[M - 2\,CO, C_5H_{10}Si, 3\,Et]^+$, 175, 174 (<10) $[Fe(PEt_3)]^+$, 146 (10) $[Fe(PEt_2)]^+$, 118 (<10) $[PEt_3]^+$, 106. – $C_{19}H_{40}FeO_2P_2Si$: calcd. C 51.12, H 9.03, Fe 12.51; found C 51.13, H 9.33, Fe 12.51.

Dicarbonylhydridobis(triisopropyl phosphite)(trimethylsilylethynyl)iron(II) (**3c**): A THF solution of **1d** was treated with 2.1 ml (1.5 mmol) of $Me_3SiC{\equiv}CH$ at −30°C. After warming to room temp., the solvent was removed and replaced by 5 ml of hexane. Upon column chromatography on silylated silica gel with hexane as eluent a yellow band with **3c** was collected. The mixture was concentrated to a few ml. Crystallization at −30°C afforded 0.52

g (83%) **3c** with spectroscopically detectable slight impurities of **4c** and of Fe(CO)$_2$[P(O*i*Pr)$_3$]$_3$. – IR (hexane): ṽ = 2048 (w, C≡C), 2013, 1990 cm^{-1} (s, C≡O). – ^{1}H NMR (C$_6$D$_6$, 300 MHz): δ = −8.21 (t, $^2J_{PH}$ = 57.4 Hz, FeH), 0.22 [s, Si(CH$_3$)$_3$], 1.28, 1.35 [2 × d, $^3J_{CH}$ = 5.9 Hz, OCH(C*H*$_3$)$_2$], 5.14 [m, OC*H*(CH$_3$)$_2$]. – ^{13}C NMR (C$_6$D$_6$, 75.4 MHz): δ = 1.6 [s, Si(CH$_3$)$_3$], 24.3 [br., OCH(*C*H$_3$)$_2$], 70.2 [s, O*C*H(CH$_3$)$_2$], 121.1 (s, ≡CSi), 130.3 (t, $^2J_{PC}$ = 49 Hz, Fe≡C), 210.4 (t, $^2J_{PC}$ = 19 Hz, C≡O), 210.6 (t, $^2J_{PC}$ = 28 Hz, C≡O). – ^{31}P NMR (C$_6$D$_6$): δ = 161.6. – MS (70 eV): *m/z* (%) = 626 (1) [M]$^+$, 599 (1) [M – CO]$^+$, 570 (5) [M – 2 CO]$^+$, 528 (35) [M – C$_5$H$_{10}$Si]$^+$, 500 (30) [M – CO, C$_5$H$_{10}$Si]$^+$, 473 (100) [M – 2 CO, C$_5$H$_{10}$Si]$^+$, 429 (20) [M – 2 CO, C$_5$H$_{10}$Si, CH(CH$_3$)$_2$]$^+$, 362 (60) [M – 2 CO, P{OCH(CH$_3$)$_2$}$_3$]$^+$, 323, 265 (5) [FeP{OCH(CH$_3$)$_2$}$_3$]$^+$, 221 (30) [FeP{OCH(CH$_3$)$_2$}$_3$ – CH(CH$_3$)$_2$]$^+$, 179 (35) [FeP{OCH(CH$_3$)$_2$}$_3$ – 2 CH(CH$_3$)$_2$]$^+$, 137, 124, 107, 81, 65, 42. – C$_{25}$H$_{52}$FeO$_8$P$_2$Si: calcd. C 47.92, H 8.37, Fe 8.91; found C 47.64, H 8.10, Fe 8.85.

Dicarbonylbis(triethylphosphane)(trimethylsilylvinylidene)iron(0) (**4a**): According to the reaction of **1a**, **b** with Me$_3$SiC≡CH as described in the preparation of **3a**, THF was removed in vacuo. The brown oily residue was redissolved in 50 ml of hexane and then ca. 100 mg of Al$_2$O$_3$ was added. Stirring was continued for 30 min at room temp. Filtration through Celite and removal of the solvent afforded **4a** as a yellow oil (m.p. ca. −30 °C). Yield 0.37 g (83%). – IR (hexane): ṽ = 1950, 1887 (s, C≡O), 1585 cm^{-1} (m, C=C). – ^{1}H NMR (C$_6$D$_6$, 200 MHz): δ = 0.19 [s, Si(CH$_3$)$_3$], 1.08 (m$_c$, CH$_2$C*H*$_3$), 1.76 (m$_c$, C*H*$_2$CH$_3$), 4.15 (t, $^4J_{PH}$ = 12.0 Hz, ^{1}C*H*). – ^{13}C NMR (C$_6$D$_6$, 75.4 MHz): δ = 0.5 (s, Si(CH$_3$)$_3$), 8.3 (s, CH$_2$*C*H$_3$), 21.0 (pseudo-t, J_{PC} = 14 Hz, *C*H$_2$CH$_3$), 103.4 (t, $^3J_{PC}$ = 5 Hz, =CH), 216.8 (t, $^2J_{PC}$ = 21 Hz, C≡O), 314.0 (t, $^2J_{PC}$ = 47 Hz, FeC=). – ^{31}P NMR (C$_6$D$_6$): δ = 62.4. – MS (70 eV): *m/z* (%) = 446 (<5) [M]$^+$, 418 (5) [M – CO]$^+$, 389 (30) [M – 2 CO]$^+$, 348 (40) [M – C$_5$H$_{10}$Si]$^+$, 320 (60) [M – CO, C$_5$H$_{10}$Si]$^+$, 292 (100) [M – 2 CO, C$_5$H$_{10}$Si]$^+$, 272 (50) [M – 2 CO, PEt$_3$]$^+$, 175, 174 (10) [Fe(PEt$_3$)]$^+$, 146 (20) [Fe(PEt$_2$)]$^+$, 119, 118 (10) [PEt$_3$]$^+$, 103, 90, 62. – C$_{15}$H$_{40}$FeO$_2$P$_2$Si: calcd. C 51.12, H 9.03, Fe 12.51; found C 50.89, H 9.15, Fe 12.49.

Dicarbonylbis(triisopropyl phosphite)(trimethylsilylvinylidene)iron(0) (**4c**) *and Dicarbonylbis(triisopropyl phosphite)(vinylidene)iron(0)* (**2d**): The reaction was carried out according to the conversion of **1d** with Me$_3$SiC≡CH (preparation of **3c**). The solid residue was dissolved in 20 ml of hexane and subsequent addition of ca. 100 mg of Al$_2$O$_3$ was followed by stirring for 12 h at room temp. The solvent was removed in vacuo and work-up by column chromatography [eluent hexane/ether (10:1)] on silica gel afforded **4c** and **2d** as a solid 1:2 mixture enriched in **2d**. Repeated chromatography and elution with hexane/ether (100:1) gave first **4c** and then **2d** in analytically pure form.

4c: Yield 0.11 g (17%). – IR (hexane): ṽ = 1978, 1915, 1900 (s, C≡O), 1607 cm^{-1} (m, C=C). – ^{1}H NMR (C$_6$D$_6$, 200 MHz): δ = 0.17 [s, Si(CH$_3$)$_3$], 1.32 [d, $^3J_{CH}$ = 6.1 Hz, OCH(C*H*$_3$)$_2$], 4.47 (t, $^4J_{PH}$ = 13.7 Hz, ^{2}CH), 4.92 [m, OC*H*(CH$_3$)$_2$]. – ^{13}C NMR (C$_6$D$_6$, 50.3 MHz): δ = 0.7 [s, Si(CH$_3$)$_3$], 24.2 [s, OCH(*C*H$_3$)$_2$], 69.4 [s, O*C*H(CH$_3$)$_2$], 106.4 (t, $^3J_{PC}$ = 7 Hz, =CH), 213.8 (t, $^2J_{PC}$ = 32 Hz, C≡O), 316.8 (t, $^2J_{PC}$ = 58 Hz, Fe=C). – ^{31}P NMR (C$_6$D$_6$): δ = 173.8. – MS (70 eV): *m/z* (%) = 626 (1) [M]$^+$, 599 (1) [M – CO]$^+$, 570 (5) [M – 2 CO]$^+$, 528 (35) [M – C$_5$H$_{10}$Si]$^+$, 500 (30) [M – CO, C$_5$H$_{10}$Si]$^+$, 472 (100) [M – 2 CO, C$_5$H$_{10}$Si]$^+$, 429 (20) [M – 2 CO, C$_5$H$_{10}$Si, CH(CH$_3$)$_2$]$^+$, 362 (60) [M – 2 CO, P{OCH(CH$_3$)$_2$}$_3$]$^+$, 323, 290, 265 (5) [FeP{OCH(CH$_3$)$_2$}$_3$]$^+$, 221 (30) [FeP{OCH(CH$_3$)$_2$}$_3$ – CH(CH$_3$)$_2$]$^+$, 179 (35) [FeP{OCH(CH$_3$)$_2$}$_3$ – 2 CH(CH$_3$)$_2$]$^+$, 137, 124, 107, 81, 65, 42. C$_{25}$H$_{52}$FeO$_8$P$_2$Si: calcd. C 47.92, H 8.37; found C 47.30, H 8.64.

2d: Yield 0.38 g (68%). – IR (hexane): ṽ = 1995, 1933 (s, C≡O), 1610 (m, C=C) cm^{-1}. – ^{1}H NMR (C$_6$D$_6$, 200 MHz): δ = 1.29 [d, $^3J_{CH}$ = 6.1 Hz, OCH(C*H*$_3$)$_2$], 4.55 (t, $^4J_{PH}$ = 14.5 Hz, CH$_2$), 4.92 [m, OC*H*(CH$_3$)$_2$]. – ^{13}C NMR (C$_6$D$_6$, 50.3 MHz): δ = 24.0 [s, OCH(*C*H$_3$)$_2$], 69.7 [s, O*C*H(CH$_3$)$_2$], 103.9 (t, $^3J_{PC}$ = 10 Hz, =CH), 213.1 (t, $^2J_{PC}$ = 29 Hz, C≡O), 318.7 (t, $^2J_{PC}$ = 63 Hz, Fe=C). – ^{31}P NMR (C$_6$D$_6$): δ = 170.4. – MS (70 eV): *m/z* (%) = 554 (10) [M]$^+$, 526 (5) [M – CO]$^+$, 498 (10) [M – 2 CO]$^+$, 472 (100) [M – 2 CO, C$_2$H$_2$]$^+$, 429 (20) [M – 2 CO, C$_2$H$_2$, CH(CH$_3$)$_2$]$^+$, 362 (70) [M – 2 CO, P{OCH(CH$_3$)$_2$}$_3$]$^+$, 323, 290, 265 (10) [FeP{OCH(CH$_3$)$_2$}$_3$]$^+$, 221 (20) [FeP{OCH(CH$_3$)$_2$}$_3$ – CH(CH$_3$)$_2$]$^+$, 179 (30) [FeP{OCH(CH$_3$)$_2$}$_3$ – 2 CH(CH$_3$)$_2$]$^+$, 107, 65. C$_{22}$H$_{44}$FeO$_8$P$_2$: calcd. C 47.66, H 8.00; found C 47.83, H 8.14.

Dicarbonylbis(trimethyl phosphite)(trimethylsilylacetylene)iron(0) (**3b**), *Dicarbonylhydridobis(trimethyl phosphite)(trimethylsilylacetylido)iron(II)* (**4b**), *Dicarbonylbis(trimethyl phosphite)(trimethylsilylvinylidene)iron(0)* (**5b**) *and Dicarbonylbis(trimethyl phosphite)vinylideneiron(0)* (**5c**): A THF solution of **1d**, prepared as described above, was treated with 2.1 ml (1.5 mmol) of Me$_3$SiC≡CH at −30 °C. After warming to room temp., the solvent was removed. A ^{1}H-NMR spectrum of the residual brown oil showed the presence of **3b**, **4b**, and **5b** in a 4:6:1 ratio. Column chromatography on silylated silica gel with hexane/ether (100:1) afforded a yellow band, removal of the solvent from which left a brown oil, consisting of a mixture of all three compounds [yield 0.38 g (81%)].

3b: IR (hexane): ṽ = 1961, 1894 cm^{-1} (s, C≡O). – ^{1}H NMR (C$_6$D$_6$, 200 MHz): δ = 0.44 [s, Si(CH$_3$)$_3$], 3.37 (pseudo-t, J_{PH} = 5.5 Hz, OCH$_3$), 5.28 (t, $^3J_{PH}$ = 3.7 Hz, CH). – ^{13}C NMR (C$_6$D$_6$, 50.3 MHz): δ = 1.30 [s, Si(CH$_3$)$_3$], 51.3 (s, OCH$_3$), 77.6 (br., ≡CSi), 96.0 (t, $^2J_{PC}$ = 10 Hz, ≡CH), 221.1 (t, $^2J_{PC}$ = 40 Hz, C≡O). – ^{31}P NMR (C$_6$D$_6$): δ = 171.7.

4b: IR (hexane): ṽ = 2055 (w, C≡C), 2023, 1982 cm^{-1} (s, C≡O). – ^{1}H NMR (C$_6$D$_6$, 200 MHz): δ = −8.64 (t, $^2J_{PH}$ = 57.4 Hz, FeH), 0.13 [s, Si(CH$_3$)$_3$], 3.61 (pseudo-t, J_{PH} = 5.8 Hz, OCH$_3$). – ^{13}C NMR (C$_6$D$_6$, 50.3 MHz): δ = 1.3 [s, Si(CH$_3$)$_3$], 52.9 (s, OCH$_3$), 121.8 (s, ≡CSi), 125.2 (t, $^2J_{PC}$ = 51 Hz, FeC≡), 209.5 (t, $^2J_{PC}$ = 28 Hz, C≡O), 209.6 (t, $^2J_{PC}$ = 18 Hz, C≡O). – ^{31}P NMR (C$_6$D$_6$): δ = 176.2.

5b: The brown oil obtained initially was redissolved in 20 ml of hexane and stirred together with ca. 100 mg of Al$_2$O$_3$ for 10 min at room temp. The solvent was removed in vacuo and the residue was subjected to column chromatography on silica gel [eluent hexane/ether (100:1)], which resulted in the elution of a brown band of **5b**. The solvent was stripped off and **5b** remained as an analytically pure brown oil. Yield 0.37 g (76%). – IR (hexane): ṽ = 1985, 1925, 1917 (s, C≡O), 1614 cm^{-1} (m, C=C). – ^{1}H NMR (C$_6$D$_6$, 200 MHz): δ = 0.17 [s, Si(CH$_3$)$_3$], 3.5 (pseudo-t, J_{PH} = 5.9 Hz, OCH$_3$), 4.47 (t, $^4J_{PH}$ = 14.2 Hz, CH). – ^{13}C NMR (C$_6$D$_6$, 50.3 MHz): δ = 0.4 [s, Si(CH$_3$)$_3$], 52.2 (s, OCH$_3$), 106.1 (t, $^3J_{PC}$ = 7 Hz, =CH), 213.0 (t, $^2J_{PC}$ = 29 Hz, C≡O), 313.9 (t, $^2J_{PC}$ = 62 Hz, Fe=C). – ^{31}P NMR (C$_6$D$_6$): δ = 182.2. – MS (70 eV): *m/z* (%) = 458 (10) [M]$^+$, 430 (5) [M – CO]$^+$, 427 (5) [M – OCH$_3$]$^+$, 401 (20) [M – 2 CO]$^+$, 360 (35) [M – C$_5$H$_{10}$Si]$^+$, 332 (45) [M – CO, C$_5$H$_{10}$Si]$^+$, 304 (90) [M – 2 CO, C$_5$H$_{10}$Si]$^+$, 278 (75) [M – 2 CO, P(OCH$_3$)$_3$]$^+$, 211 (55) [M – 2 CO, 3 OCH$_3$, C$_5$H$_{10}$Si]$^+$, 180 (20) [FeP(OCH$_3$)$_3$]$^+$, 165 (40) [FeP(OCH$_3$)$_3$ – CH$_3$]$^+$, 140 (55) [FeP(OCH$_3$)$_3$, – 2 CH$_3$]$^+$, 135 (10) [FeP(OCH$_3$)$_2$ – CH$_3$]$^+$, 110 (100) [P(OCH$_3$)$_3$ – CH$_3$]$^+$, 93 (70) [P(OCH$_3$)$_2$]$^+$, 78, 75, 63. – C$_{13}$H$_{28}$FeO$_8$P$_2$Si: calcd. C 34.07, H 6.16, Fe 12.19; found C 34.53, H 6.48, Fe 12.00.

5c: Continuing the procedure described above, after elution of **5b**, hexane/ether (10:1) eluted an orange-brown band containing

5c. The solvent was removed in vacuo leaving behind a brown oil, which did not give correct elemental analyses. – IR (hexane): ṽ = 2000, 1993, 1941, 1932 (s, C≡O), 1616 cm^{-1} (m, C=C). – ^{1}H NMR (C_6D_6, 100 MHz): δ = 3.51 (pseudo-t, $^{2}J_{PH}$ = 6.1 Hz, OCH_3), 4.52 (t, $^{4}J_{PH}$ = 14.2 Hz, CH_2). – ^{13}C NMR (C_6D_6, 50.3 MHz): δ = 52.5 (s, OCH_3), 103.7 (t, $^{3}J_{PC}$ = 9 Hz, CH_2), 212.3 (t, $^{2}J_{PC}$ = 29 Hz, C≡O), 318.5 (t, $^{2}J_{PC}$ = 66 Hz, Fe=C). – ^{31}P NMR (C_6D_6): δ = 179.3.

[Bis(trimethylsilylacetylene)]dicarbonylbis(triethylphopshane)-iron(0) (**6a**): A solution of **1a**, **b** as prepared above was treated with 0.26 g (1.5 mmol) of bis(trimethylsilyl)acetylene at –30°C. After warming to room temp., the solvent was removed in vacuo. The oily orange residue was dissolved in 10 ml of hexane. Upon column chromatography on silylated silica gel with hexane an orange band was eluted, the solution of which was concentrated and left to crystallize at –30°C. Yield 0.38 g (73%) of orange needles of **6a**. – IR (hexane): ṽ = 1925, 1861 (s, C≡O), 1750 cm^{-1} (w, C=C). – ^{1}H NMR (CD_2Cl_2, 300 MHz, –60°C): δ = 0.20 [s, $Si(CH_3)_3$], 0.94 (m_c, CH_2CH_3), 1.29 (m_c, CH_2CH_3). – ^{13}C NMR (CD_2Cl_2, 75.4 MHz, –60°C): δ = 1.5 [s, $Si(CH_3)_3$], 7.3 (s, CH_2CH_3), 16.7 (pseudo-t, J_{PC} = 11 Hz, CH_2CH_3), 117.2 (br., ≡C), 225.3 (t, $^{2}J_{PC}$ = 32 Hz, C≡O). – ^{31}P NMR (CD_2Cl_2): δ = 54.6. – MS (70 eV): *m/z* (%) = 518 (<1) [M]$^+$, 490 (<1) [M – CO]$^+$, 462 (5) [M – 2 CO]$^+$, 348 (5) [M – Me_3SiC –$CSiMe_3$]$^+$, 372 (10) [M – CO – PEt_3]$^+$, 344 (95) [M – 2 CO – PEt_3]$^+$, 320 (10) [M – CO, $Me_3SiC{\equiv}CSiMe_3$]$^+$, 292 (70) [M – 2 CO, $Me_3SiC{\equiv}CSiMe_3$]$^+$, 226 (20) [M – 2 CO, 2 PEt_3]$^+$, 174 (5) [$Fe(PEt_3)$]$^+$, 170 (30) [$Me_3SiC{\equiv}CSiMe_3$]$^+$, 155 (100) [$(CH_3)_2SiC{\equiv}CSiMe_3$]$^+$, 146 (20) [$Fe(PEt_2)$]$^+$, 118 (20) [$PEt_3$]$^+$, 90, 73 (20) [$SiMe_3$]$^+$, 57. – $C_{22}H_{48}FeO_2P_2Si_2$: calcd. C 50.95, H 9.33, Fe 10.77; found C 51.81, H 9.24, Fe 10.76.

[Bis(trimethylsilyl)vinylidene]dicarbonylbis(triethylphosphane)-iron(0) (**7a**), *[Bis(trimethylsilyl)vinylidene]dicarbonylbis(trimethyl phosphite)iron(0)* (**7b**), *and [Bis(trimethylsilyl)vinylidene]dicarbonylbis(triisopropyl phosphite)iron(0)* (**7c**): A solution of **1a**, **b**, **1c**, or **1d**, prepared as described above, was treated with 0.26 g (1.5 mol) of bis(trimethylsilyl)acetylene at –30°C. After warming to room temp., the solvent was removed in vacuo. The residue was dissolved in 5 ml of hexane and subjected to column chromatography on silica gel. Hexane/ether (10:1) (**7a**) or (100:1) (**7b**, **c**) eluted a yellow (**7a**, **7b**) or an orange-yellow (**7c**) band. After concentration of the solutions, light-yellow (**7a**), bright-yellow (**7b**) or orange crystals (**7c**) precipitated at –30°C.

7a: Yield: 0.42 g (81%). – IR (hexane): ṽ = 1940, 1879 (s, C–O), 1560 cm^{-1} (m, C=C). – ^{1}H NMR (C_6D_6, 300 MHz): δ = 0.28 [s, $Si(CH_3)_3$], 1.05 (m_c, CH_2CH_3), 1.73 (m_c, CH_2CH_3). – ^{13}C NMR (CD_2Cl_2, 75.4 MHz, –60°C): δ = 1.1 [s, $Si(CH_3)_3$], 7.6 (s, CH_2CH_3), 19.6 (pseudo-t, J_{PC} = 13 Hz, CH_2CH_3), 103.2 (t, $^{3}J_{PC}$ = 5 Hz, CH_2), 217.3 (t, $^{2}J_{PC}$ = 22 Hz, C≡O), 307.4 (t, $^{2}J_{PC}$ = 43 Hz, Fe=C). – ^{31}P NMR (CD_2Cl_2): δ = 64.3. – MS (70 eV): *m/z* (%) = 518 (10) [M]$^+$, 490 (<1) [M – CO]$^+$, 462 (5) [M – 2 CO]$^+$, 348 (30) [M – $(CH_3)_3SiC{\equiv}CSi(CH_3)_3$]$^+$, 344 (55) [M – 2 CO – PEt_3]$^+$, 320 (50) [M – CO, $(CH_3)_3SiC{\equiv}CSi(CH_3)_3$]$^+$, 292 (100) [M – 2 CO, $(CH_3)_3SiC{\equiv}CSi(CH_3)_3$]$^+$, 226 (20) [M – 2 CO, 2 PEt_3]$^+$, 174 (5) [$Fe(PEt_3)$]$^+$, 155 (30) [$(CH_3)_2SiC{\equiv}CSi(CH_3)_3$]$^+$, 146 (10) [$Fe(PEt_2)$]$^+$, 118 (10) [$PEt_3$]$^+$, 90, 73 (10) [$Si(CH_3)_3$]$^+$, 62. – $C_{22}H_{48}FeO_2P_2Si_2$: calcd. C 50.95, H 9.33, Fe 10.77; found C 51.12, H 9.59, Fe 10.76.

7b: Yield: 0.45 g (84%). – IR (hexane): ṽ = 1967, 1906 (s, C≡O), 1605 cm^{-1} (m, C=C). – ^{1}H NMR (CD_2Cl_2, 300 MHz, –60°C): δ = 0.06 [s, $Si(CH_3)_3$], 3.60 (pseudo-t, J_{PH} = 5.8 Hz, OCH_3). – ^{13}C NMR (CD_2Cl_2, 75.4 MHz, –60°C): δ = 0.5 [s, $Si(CH_3)_3$], 52.0 (s, OCH_3), 106.5 (t, $^{3}J_{PC}$ = 4 Hz, CH_2), 213.9 (t, $^{2}J_{PC}$ = 29 Hz, C≡O), 302.7 (t, $^{2}J_{PC}$ = 58 Hz, Fe=C). – ^{31}P NMR (C_6D_6): δ = 185.0. – MS (70 eV): *m/z* (%) = 530 (15) [M]$^+$, 502 (1) [M – CO]$^+$, 474 (5) [M – 2 CO]$^+$, 350 (100) [M – 2 CO, $P(OCH_3)_3$]$^+$, 360 (50) [M – $C_8H_{18}Si_2$]$^+$, 332 (55) [M – CO, $C_8H_{18}Si_2$]$^+$, 304 (80) [M – 2 CO, $C_8H_{18}Si_2$]$^+$, 180 (5) [$FeP(OCH_3)_3$]$^+$, 93. – $C_{16}H_{36}FeO_8P_2Si_2$: calcd. C 36.23, H 6.84, Fe 10.53; found C 36.12, H 7.09, Fe 10.36.

7c: Yield: 0.56 g (80%). – IR (hexane): ṽ = 1957, 1891 (s, C≡O), 1589 cm^{-1} (m, C=C). – ^{1}H NMR (C_6D_6, 200 MHz): δ = 0.44 [s, $Si(CH_3)_3$], 1.34 [d, $^{3}J_{CH}$ = 6.2 Hz, $OCH(CH_3)_2$], 4.94 [m, $OCH(CH_3)_2$]. – ^{13}C NMR (C_6D_6, 50.3 MHz): δ = 2.2 [s, $Si(CH_3)_3$], 24.4 [s, $OCH(CH_3)_2$], 69.2 [s, $OCH(CH_3)_2$], 105.4 (t, $^{3}J_{PC}$ = 5 Hz, CH_2), 214.7 (t, $^{2}J_{PC}$ = 37 Hz, C≡O), 310.9 (t, $^{2}J_{PC}$ = 49 Hz, Fe=C). – ^{31}P NMR (C_6D_6): δ = 175.6. – MS (70 eV): *m/z* (%) = 698 (5) [M]$^+$, 639 (5) [M – $OCH(CH_3)_2$]$^+$, 528 (20) [M – $C_8H_{18}Si_2$]$^+$, 500 (25) [M – CO, $C_8H_{18}Si_2$]$^+$, 472 (100) [M – 2 CO, $C_8H_{18}Si_2$]$^+$, 434 (90) [M – 2 CO, $P\{OCH(CH_3)_2\}_3$]$^+$, 323, 265 (10) [$FeP\{OCH(CH_3)_2\}_3$]$^+$, 221, 179, 155, 107, 43. – $C_{28}H_{60}FeO_8P_2Si_2$: calcd. C 48.13, H 8.70, Fe 7.99; found C 47.96, H 8.40, Fe 7.97.

[Bis(trimethylsilyl)butadiyne]dicarbonylbis(triethylphosphane)-iron(0) (**8a**): A THF solution of **1a**, **b** prepared as described above was treated with 0.29 g (1.5 mmol) of $Me_3Si(C{\equiv}C)_2SiMe_3$ at –30°C. After warming to room temp. and evaporation of the solvent, the residue was extracted with 50 ml of hexane and filtered through Celite. Concentration of this solution and crystallization at –30°C afforded 0.46 g (85%) of orange crystals of **8a**. – IR (hexane): ṽ = 2109 (w, C≡C), 1946, 1882 (s, C≡O), 1750 cm^{-1} (w, C≡C). – ^{1}H NMR (C_6D_6, 200 MHz): δ = 0.27 [s, $Si(CH_3)_3$], 0.38 [s, $Si(CH_3)_3$], 1.03 (m_c, CH_2CH_3), 1.31 (m_c, CH_2CH_3). – ^{13}C NMR (C_6D_6, 75.4 MHz): δ = 0.5 [s, $Si(CH_3)_3$], 1.4 [s, $Si(CH_3)_3$], 8.0 (s, CH_2CH_3), 17.9 (pseudo-t, J_{PC} = 11 Hz, CH_2CH_3), 103.6 (t, $^{4}J_{PC}$ = 3 Hz, C^4), 105.3 (s, C^3), 112.0 (t, $^{2}J_{PC}$ = 9 Hz, FeC^2), 113.1 (t, $^{2}J_{PC}$ = 6 Hz, FeC^1), 221.5 (t, $^{2}J_{PC}$ = 24 Hz, C≡O), 224.0 (t, $^{2}J_{PC}$ = 31 Hz, C≡O). – ^{31}P NMR (C_6D_6): δ = 55.1. – MS (70 eV): *m/z* (%) = 542.61 (<1) [M]$^+$, 487 (<1) [M – 2 CO]$^+$, 368 (100) [M – 2 CO – PEt_3]$^+$, 320 (10) [M – CO, $(CH_3)_3Si(C{\equiv}C)_2Si(CH_3)_3$]$^+$, 292 (30) [M – 2 CO, $(CH_3)_3Si(C{\equiv}C)_2Si(CH_3)_3$]$^+$, 250 (10) [M – 2 CO, 2 PEt_3]$^+$, 194 (20) [$(CH_3)_3Si(C{\equiv}C)_2Si(CH_3)_3$]$^+$, 179 (70) [$(CH_3)_2Si(C{\equiv}C)_2Si(CH_3)_3$]$^+$, 174 (5) [$Fe(PEt_3)$]$^+$, 146 (20) [$Fe(PEt_2)$]$^+$, 118 (20) [$PEt_3$]$^+$, 90, 73 (20) [$Si(CH_3)_3$]$^+$, 62. – $C_{24}H_{48}FeO_2P_2Si_2$: calcd. C 53.12, H 8.92, Fe 10.30; found C 53.65, H 8.96, Fe 10.19.

[Bis(trimethylsilyl)butadiyne]dicarbonylbis(trimethyl phosphite)iron(0) (**8b**), *Dicarbonylbis(trimethyl phosphite)[trimethylsilyl(trimethylsilylethynyl)vinylidene]iron(0)* (**10b**), *and Dicarbonylbis(trimethyl phosphite)[(trimethylsilylethynyl)vinylidene]iron(0)* (**11b**): A THF solution of **1c** prepared as described above was treated with 0.29 g (1.5 mmol) of $Me_3Si(C{\equiv}C)_2SiMe_3$ at –30°C. After warming to room temp. and evaporation of the THF in vacuo, the yellow oily residue was extracted with 10 ml of hexane and then subjected to column chromatography on silica gel. Hexane/ether (100:1) eluted a light-yellow band, which contained a mixture of **8b** and **10b**. Crystallization at –30°C gave a crystalline mixture of both complexes **8b** (orange prisms) and **10b** (light-yellow needles) were separated manually. Hexane/ether (75:1) eluted an orange band of **11b**. After concentration of the solution, crystalization at –80°C afforded a red, microcrystalline powder of **11b**.

8b: Yield: 0.15 g (27%). – IR (hexane): ṽ = 2047 (w, C≡C), 1966, 1905 (s, C≡O), 1815 cm^{-1} (w, C=C). – ^{1}H NMR (C_6D_6, 200 MHz): δ = 0.12, 0.46 [2 × s, $Si(CH_3)_3$], 3.50 (pseudo-t, J_{PH} = 5.6 Hz, OCH_3). – ^{13}C NMR ([D_6]acetone, 75.4 MHz, –60°C):

$\delta = 0.1, 0.6$ [2 × s, $Si(CH_3)_3$], 51.9 (pseudo-t, $J_{PC} = 2$ Hz, OCH_3), 91.7 (t, $^2J_{PC} = 9$ Hz, FeC^2), 97.5 (t, $^2J_{PC} = 7$ Hz, FeC^1), 101.1 (s, C^3), 101.5 (t, $^4J_{PC} = 3$ Hz, C^4), 218.2 (t, $^2J_{PC} = 42$ Hz, C≡O), 221.0 (t, $^2J_{PC} = 36$ Hz, C≡O). – ^{31}P NMR (C_6D_6): $\delta = 171.9$. – MS (70 eV): *m/z* (%) = 555 (2) $[M]^+$, 526 (1) $[M - CO]^+$, 498 (5) $[M - 2\ CO]^+$, 374 (100) $[M - 2\ CO, P(OCH_3)_3]^+$, 360 (20) $[M - C_{10}H_{18}Si_2]^+$, 332 (30) $[M - CO, C_{10}H_{18}Si_2]^+$, 304 (70) $[M - 2\ CO, C_{10}H_{18}Si_2]^+$, 250 (20) $[M - 2\ CO, 2\ P(OCH_3)_3]^+$, 180 (20) $[FeP(OCH_3)_3]^+$, 179 (50) $[C_{10}H_{18}Si_2]^+$, 165 (15) $[FeP(OCH_3)_3 - CH_3]^+$, 124 (10) $[P(OCH_3)_3]^+$, 93, 73. – $C_{18}H_{36}FeO_8P_2Si_2$: calcd. C 38.99, H 6.54, Fe 10.07; found C 39.19, H 6.32, Fe 10.21.

10b: Yield: 0.08 g (14%). – IR (hexane): $\tilde{\nu} = 2107$ (w, C≡C), 1994, 1936, 1927 (s, C≡O), 1591 cm^{-1} (w, C=C). – ^1H NMR (C_6D_6, 200 MHz): $\delta = 0.14, 0.34$ [2 × s, $Si(CH_3)_3$], 3.58 (pseudo-t, $J_{PH} = 6.0$ Hz, OCH_3). – ^{13}C NMR (C_6D_6, 50.3 MHz): $\delta = 0.3$, 1.0 [2 × s, $Si(CH_3)_3$], 52.6 (s, OCH_3), 98.3 (br, C^4), 99.0 (t, $^4J_{PC} = 12$ Hz, C^3), 104.7 (t, $^3J_{PC} = 8$ Hz, $=C^2$), 211.8 (t, $^2J_{PC} = 30$ Hz, C≡O), 319.5 (t, $^2J_{PC} = 65$ Hz, $Fe=C^1$). – ^{31}P NMR (C_6D_6): $\delta = 177.0$. – MS (70 eV): *m/z* (%) = 554 (20) $[M]^+$, 526 (1) $[M - CO]^+$, 498 (5) $[M - 2\ CO]^+$, 374 (85) $[M - 2\ CO, P(OCH_3)_3]^+$, 360 (40) $[M - C_{10}H_{18}Si_2]^+$, 332 (50) $[M - CO, C_{10}H_{18}Si_2]^+$, 304 (100) $[M - 2\ CO, C_{10}H_{18}Si_2]^+$, 250 (20) $[M - 2\ CO, 2\ P(OCH_3)_3]^+$, 211 $[Fe\{P(OCH_3)_3\}_2 - 3\ OCH_3]^+$, 180 (10) $[FeP(OCH_3)_3]^+$, 179 (20) $[C_{10}H_{18}Si_2]^+$, 165 (20) $[FeP(OCH_3)_3 - CH_3]^+$, 124 (5) $[P(OCH_3)_3]^+$, 93, 73. – $C_{18}H_{36}FeO_8P_2Si_2$: calcd. C 38.99, H 6.54, Fe 10.07; found C 39.31, H 6.28, Fe 10.21.

11b: Yield: 0.06 g (10%). – IR (hexane): $\tilde{\nu} = 2009$, 2001, 1951, 1942 (s, C≡O), 1583 cm^{-1} (w, C=C). – ^1H NMR (C_6D_6, 300 MHz): $\delta = 0.13$ [s, $Si(CH_3)_3$], 3.54 (pseudo-t, $J_{PH} = 5.8$ Hz, OCH_3), 5.26 (t, $^4J_{PH} = 13.3$ Hz, C^2H). – ^{13}C NMR (C_6D_6, 75.4 MHz): $\delta = 0.3$ [s, $Si(CH_3)_3$], 52.8 (s, OCH_3), 98.0 (t, $^4J_{PC} = 12$ Hz, C^3), 101.3 (br, C^4), 104.2 (t, $^3J_{PC} = 9$ Hz, $=C^2$), 211.0 (t, $^2J_{PC} = 29.0$ Hz, C≡O), 323.8 (t, $^2J_{PC} = 68$ Hz, $Fe=C^1$). – ^{31}P NMR (C_6D_6): $\delta = 174.6$. – MS (70 eV): *m/z* (%) = 482 (1) $[M]^+$, 454 (1) $[M - CO]^+$, 426 (5) $[M - 2\ CO]^+$, 360 (10) $[M - C_7H_{10}Si]^+$, 332 (10) $[M - CO, C_7H_{10}Si]^+$, 304 (50) $[M - 2\ CO, C_7H_{10}Si]^+$, 302 (10) $[M - 2\ CO, P(OCH_3)_3]^+$, 250 (20) $[M - 2\ CO, 2\ P(OCH_3)_3]^+$, 211 (30) $[Fe\{P(OCH_3)_3\}_2 - 3\ OCH_3]^+$, 180 (10) $[FeP(OCH_3)_3]^+$, 165 (5) $[FeP(OCH_3)_3 - CH_3]^+$, 124 (5) $[P(OCH_3)_3]^+$, 110, 109 (100) $[P(OCH_3)_3 - CH_3]^+$, 93, 73. – $C_{15}H_{36}FeO_8P_2Si_2$: calcd. C 37.36, H 5.85, Fe 11.58; found C 37.72, H 6.01, Fe 11.72.

Dicarbonyl[p-bis(trimethylsilylethynyl)benzene]bis(triethylphosphane)iron(0) (**9a**) *and Dicarbonyl[p-bis(trimethylsilylethynyl)benzene]bis(trimethyl phosphite)iron(0)* (**9b**): A THF solution of **1a**, **b** or **1c** prepared as described above was treated with 0.41 g (1.5 mmol) of *p*-bis(trimethylsilylethynyl)benzene at −30 °C. After warming to room temp., the solvent was removed in vacuo. The residue was dissolved in hexane and then subjected to column chromatography on silica gel. Hexane/ether (20:1) eluted an orange-red (**9a**) or a yellow (**9b**) band. Repeated crystallization from hexane (**9a**) or single crystallization from the concentrated solution (**9b**) at −30 °C gave crystalline solids of both complexes.

9a: Yield: 0.15 g (24%). – IR (hexane): $\tilde{\nu} = 2094$ (w, C≡C), 1936, 1872 (s, C≡O), 1770 cm^{-1} (w, C=C). – ^1H NMR ([D_6]acetone, 300 MHz): $\delta = 0.23$ [s, $Si(CH_3)_3$], 0.37 [s, $Si(CH_3)_3$], 0.98 (m_c, CH_2CH_3), 1.37 (m_c, CH_2CH_3), 7.44 (m_c, 2H, H_{Ar}), 7.80 (m_c, 2H, H_{Ar}). – ^{13}C NMR ([D_6]acetone, 75.4 MHz): $\delta = -0.1$ [s, $Si(CH_3)_3$], 1.7 [s, $Si(CH_3)_3$], 8.0 (s, CH_2CH_3), 18.6 (pseudo-t, $J_{PC} = 11$ Hz, CH_2CH_3), 95 (s, ≡CSi), 96.8 (s, −C≡), 100.6 (t, $^2J_{PC} = 5$ Hz, FeCSi), 121.2 (s, C_{ipso}), 131.7 (t, $^2J_{PC} = 9$ Hz, FeC_{Ar}), 132.1 (s, C≡, 132.8 (s, C_{Ar}), 136.5 (br., ^3C), 224.6 (t, $^2J_{PC} = 30$ Hz, C≡O), 224.8 (t, $^2J_{PC} = 27$ Hz, C≡O). – ^{31}P NMR ([D_6]acetone): $\delta = 53.9$. – MS (70 eV): *m/z* (%) = 618 (<1) $[M]^+$, 444 (2) $[M - 2\ CO, 2\ Si(CH_3)_3]^+$, 270 (50) $[TMSC{\equiv}CC_6H_4C{\equiv}CTMS]^+$, 255 (100) $[TMSC{\equiv}CC_6H_4C{\equiv}CTMS]^+$, 174 (5) $[Fe(PEt_3)]^+$, 146 (5) $[Fe(PEt_2)]^+$, 118 (10) $[PEt_3]^+$, 90, 73 (50) $[Si(CH_3)_3]^+$, 62. – $C_{30}H_{52}FeO_2P_2Si_2$: calcd. C 58.24, H 8.47, Fe 9.03; found C 58.78, H 8.58, Fe 8.77.

9b: Yield: 0.52 g (83%). – IR (hexane): $\tilde{\nu} = 2100$ (w, C≡C), 1961, 1898 (s, C≡O), 1814 cm^{-1} (w, C=C). – ^1H NMR ([D_6]acetone, 200 MHz): $\delta = 0.23$ [s, $Si(CH_3)_3$], 0.32 [s, $Si(CH_3)_3$], 3.44 (pseudo-t, $J_{PH} = 5.4$ Hz, OCH_3), 7.40 (m, 2H, H_{Ar}), 7.80 (m, 2H, H_{Ar}). – ^{13}C NMR ([D_6]acetone, 50.3 MHz): $\delta = -0.02$ [s, $Si(CH_3)_3$], 0.9 [s, $Si(CH_3)_3$], 52.3 (pseudo-t, $J_{PC} = 3$ Hz, OCH_3), 89.9 (t, $^2J_{PC} = 6$ Hz, FeCSi), 94.9 (s, ≡CSi), 106.6 (s, −C≡), 115.1 (t, $^2J_{PC} = 11$ Hz, FeC≡), 121.3 (s, C_{ipso}), 132.0 (s, C_{Ar}), 133.0 (s, C_{Ar}), 135.8 (br., C_{ipso}), 221.8 (t, $^2J_{PC} = 40$ Hz, C≡O). – ^{31}P NMR ([D_6]acetone): $\delta = 170.3$. – MS (70 eV): *m/z* (%) = 630 (<1) $[M]^+$, 574 (5) $[M - 2\ CO]^+$, 450 (40) $[M - 2\ CO, P(OCH_3)_3]^+$, 304 (15) $[M - 2\ CO, (CH_3)_3SiC{\equiv}CC_6H_4C{\equiv}CSi(CH_3)_3]^+$, 270 (60) $[(CH_3)_3SiC{\equiv}CC_6H_4C{\equiv}CSi(CH_3)_3]^+$, 255 (100) $[(CH_3)_2SiC{\equiv}CC_6H_4C{\equiv}CSi(CH_3)_3]^+$. – $C_{24}H_{40}FeO_2P_2Si_2$: C 45.72, H 6.40, Fe 8.86; found C 47.07, H 6.64, Fe 8.82.

Dicarbonyl[(p-ethynylphenyl)acetylido]bis(triethylphosphane)iron(II) (**12a**), *Dicarbonyl[(p-ethynylphenyl)vinylidene]bis(triethylphosphane)iron(0)* (**13a**), *and Dicarbonyl[(p-ethynylphenyl)vinylidene]bis(trimethyl phosphite)iron(0)* (**13b**): THF solutions of **1a**, **b** and **1c** were treated with 0.19 g (1.5 mmol) of *p*-diethynylbenzene at −30 °C. **12b** was detected in low concentration in this solution by IR spectroscopy. After warming to room temp., the solvents were removed in vacuo. The conversion of **1a**, **b** to **12a** was demonstrated by IR and ^1H-NMR spectroscopy. Due to relatively rapid decomposition of **12a**, it was impossible to record a ^{13}C-NMR spectrum. **12a** was then stirred at room temp. with ca. 100 mg of Al_2O_3 in 50 ml of hexane. Filtration through Celite gave a bright-red solution, which was concentrated in vacuo. Crytallization at −30 °C afforded a dark-red powder of **13a**. **13b** was isolated by column chromatography on silica gel upon elution with hexane/ether (50:1). Concentration of the solution and crystallization at −30 °C gave crystalline **13b**.

12a: IR (hexane): $\tilde{\nu} = 2095$ (w, C≡C), 1993, 1945 cm^{-1} (s, C≡O). – ^1H NMR (CD_2Cl_2, 300 MHz): $\delta = -8.71$ (t, $^2J_{PH} = 50.0$ Hz, FeH), 1.30 (m, CH_2CH_3), 1.80 (m, CH_2CH_3), 3.20 (br. s, ≡CH).

13a: Yield: 0.33 g (70%). – IR (hexane): $\tilde{\nu} = 2107$ (w, C≡C), 1960, 1899 (s, C≡O), 1585 cm^{-1} (m, C=C). – ^1H NMR (CD_2Cl_2, 300 MHz): $\delta = 1.13$ (m_c, CH_2CH_3), 1.84 (m_c, CH_2CH_3), 3.04 (s, ≡CH), 5.66 (t, $^4J_{PH} = 11.2$ Hz,H), 7.00 (m_c, 2H, H_{Ar}), 7.24 (m_c, 2H, H_{Ar}). – ^{13}C NMR (CD_2Cl_2, 75.4 MHz, −60 °C): $\delta = 7.8$ (s, CH_2CH_3), 20.3 (pseudo-t, $J_{PC} = 15$ Hz, CH_2CH_3), 76.2 (s, ≡CH), 84.6 (s, −C≡), 115.5 (s, C_{ipso}), 120.0 (t, $^3J_{PC} = 8$ Hz, =C), 122.9 (s, C_{Ar}), 132.2 (s, C_{Ar}), 139.7 (t, $^4J_{PC} = 8$ Hz, C_{ipso}), 215.1 (t, $^2J_{PC} = 20$ Hz, C≡O), 215.9 (t, $^2J_{PC} = 18$ Hz, C≡O), 315.0 (t, $^2J_{PC} = 51$ Hz, Fe=C). – ^{31}P NMR (CD_2Cl_2): $\delta = 61.0$. – MS (70 eV): *m/z* (%) = 474 (10) $[M]^+$, 446 (5) $[M - CO]^+$, 418 (60) $[M - 2\ CO]^+$, 348 (30) $[M - HC{\equiv}CC_6H_4C{\equiv}CH]^+$, 320 (50) $[M - CO, HC{\equiv}CC_6H_4C{\equiv}CH]^+$, 300 (30) $[M - 2\ CO, PEt_3]^+$, 292 (100) $[M - 2\ CO, HC{\equiv}CC_6H_4C{\equiv}CH]^+$, 174 (15) $[Fe(PEt_3)]^+$, 146 (40) $[Fe(PEt_2)]^+$, 118 (20) $[PEt_3]^+$, 90, 62. – $C_{24}H_{36}FeO_2P_2$: calcd. C 60.77, H 7.65, Fe 11.77; found C 60.76, H 7.88, Fe 11.71.

13b: Yield: 0.10 g (20%). – IR (hexane): $\tilde{\nu} = 2107$ (w, C≡C), 1997, 1945, 1938, 1929 (s, C≡O), 1595 cm^{-1} (m, C=C). – ^1H NMR (CD_2Cl_2, 200 MHz): $\delta = 3.09$ (s, ≡CH), 3.68 (pseudo-t, $J_{PH} = 6.0$ Hz, OCH_3), 6.06 (t, $^4J_{PH} = 13.4$ Hz, =CH), 7.09 (m, 2H, H_{Ar}), 7.30 (m, 2H, H_{Ar}). – ^{13}C NMR (CD_2Cl_2, 50.3 MHz): $\delta = 53.0$ (br., OCH_3), 76.5 (s, ≡CH), 84.6 (s, −C≡), 117.7 (s, C_{ipso}), 124.2 (t, $^3J_{PC} = 10$ Hz, =CH), 124.5 (s, C_{Ar}), 132.3 (s, C_{Ar}), 136.7

(t, $^4J_{PC}$ = 9 Hz, C_{ipso}), 211.5 (t, $^2J_{PC}$ = 29 Hz, C≡O), 321.0 (t, $^2J_{PC}$ = 67 Hz, FeC=). – ^{31}P NMR (CD_2Cl_2): δ = 174.3. – MS (70 eV): *m/z* (%) = 486 (10) $[M]^+$, 458 (1) $[M - CO]^+$, 455 (2) $[M - OCH_3]^+$, 430 (10) $[M - 2\ CO]^+$, 360 (30) $[M - HC{\equiv}CC_6H_4C{\equiv}CH]^+$, 332 (20) $[M - CO, HC{\equiv}CC_6H_4C{\equiv}CH]^+$, 306 (40) $[M - 2\ CO, P(OCH_3)_3]^+$, 304 (100) $[M - 2\ CO, HC{\equiv}CC_6H_4C{\equiv}CH]^+$, 211 (30) $[Fe\{P(OCH_3)_3\}_2 - 3\ OCH_3]^+$, 180 (25) $[FeP(OCH_3)_3]^+$, 165 (40) $[FeP(OCH_3)_3 - CH_3]^+$, 126 (25) $[HC{\equiv}CC_6H_4C{\equiv}CH]^+$, 124 (10) $[P(OCH_3)_3]^+$, 93 (40) $[P(OCH_3)_2]^+$, 62. – $C_{18}H_{24}FeO_8P_2$: calcd. C 44.47, H 4.98, Fe 11.49; found C 44.46, H 5.24, Fe 11.50.

Crystal-Structure Determinations of **6a**, **7a**, *and* **8a**: Crystals of **6a**, **7a**, and **8a** suitable for X-ray diffraction studies were obtained by slow cooling of hexane solutions to −30 °C (**6a**, **7a**) or −80 °C (**8a**). The crystals were mounted in air on glass fibres using 5-min epoxy resin. The unit cells were determined and refined from 24 equivalent reflections with $2\Theta \geq 26-28°$ obtained with a Siemens R3/m four-circle diffractometer. Intensity data were collected at room temp. (**6a**), −40 °C (**7a**) and −60 °C (**8a**) and corrected for Lorentz and polarization effects. Three check reflections, monitored periodically for crystal decomposition or movement, showed no significant variations in these standards, and therefore no corrections were applied.

The H atoms of all compounds were generated geometrically (C–H bond fixed at 0.96 Å), and a temperature factor of U = 0.08 Å was assigned to all H atoms. The DIFABS method[22] was used for the absorption correction at the stage of the isotropic approximation. Computations were performed witht the SHELXTL PLUS program package[23] on a VAX station 3100. Details of the crystal parameters, data collections and structure refinements are given in Table 1. Tables of structure determination summaries, lists of anisotropic displacement parameters, lists of atom coordinates and full lists of bond lengths and angles were deposited[24].

Table 1. Data-collection and processing parameters for complexes **6a**, **7a**, and **8a**

	6a	**7a**	**8a**
Formula	$C_{22}H_{48}FeO_2P_2Si_2$	$C_{22}H_{48}FeO_2P_2Si_2$	$C_{24}H_{48}FeO_2P_2Si_2$
Cryst. system	monoclinic	monoclinic	monoclinic
Space group	*C2/c*	*C2/c*	$P2_1/c$
a [Å]	18.631(6)	22.011(6)	10.589(7)
b [Å]	10.528(2)	10.813(3)	12.469(5)
c [Å]	16.947(5)	16.000(6)	24.200(2)
β [°]	115.31(2)	129.03(2)	87.10(6)
V [Å^3]	3005.0(14)	2958.4(16)	3191.0(4)
Z	4	4	4
ρ(calcd.) [g/cm^3]	1.146	1.164	1.129
Abs. coeff [cm^{-1}]	7.03	7.14	6.60
F_{000}	1120	1120	1168
T[K]	293	233	213
Scan type	ω	2Θ–Θ	2Θ–Θ
Scan speed [°/min]	1.50–14.65	2.39–14.65	2.49–14.65
2θ range [°]	4.0–48.0	5.0–50.0	4.0–46.0
No of unique data	1213	2584	2150
No of refl. absd.	955	2263	2149
$[F - n\sigma(F)]$	$n = 6$	$n = 4$	$n = 6$
No of variables	132	133	280
Weighting scheme	$w^{-1}=\sigma^2(F)+0.01F^2$	$w^{-1}=\sigma^2(F)+0.01F^2$	$w^{-1}=\sigma^2(F)+0.01F^2$
R	0.0485	0.0423	0.0464
R_w	0.0489	0.0480	0.0547
resid. extr. in fin. diff. map [e Å^{-3}]	0.28 to –0.22	0.36 to –0.37	0.43 to –0.40

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[24] 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, on quoting the depository number CSD-59370.

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