

# Functionalized Iron Ketene Complexes from Carbonyl Coupling Reactions

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The solution mixture of the dinitrogen complexes  $\text{Fe}(\text{CO})_2(\text{PET}_3)_2(\text{N}_2)$  (**1a**) and  $[\text{Fe}(\text{CO})_2(\text{PET}_3)_2]_2(\mu\text{-N}_2)$  (**1b**) reacts with methyl or ethyl haloacetates to yield the oxidative addition products  $\text{Fe}(\text{CO})_2(\text{PET}_3)_2(\text{X})\text{CH}_2\text{COOR}$  (X = Cl, R = Me, **2a**; X = Br, R = Me, **2b**; X = I, R = Et, **2c**). These complexes can be transformed in ether to carbonylhalo-bis(triethylphosphane)-[1-((trimethylsilyloxy)-2-(alkoxycarbonyl)ethenyl)]iron compounds (X = Cl, R = Me, **7a**; X = Br, R = Me, **7b**; X = I, R = Et, **7c**) in the presence of LDA and subsequent trapping of the formed anions with  $\text{Me}_3\text{SiCl}$ . When DBU is used as a base and 1 bar CO is applied with otherwise similar reaction conditions as before the transformations of **2a–c** take the course of the formation of ester-functionalized ketene compounds  $E,Z\text{-Fe}(\text{CO})_2(\text{PET}_3)_2[\eta^2\text{-}(C,O)\text{-}[\text{OCCH}(\text{COOR})]]$  (R = Me, **8a**; R = Et, **8b**) and of dicarbonyl(1-alkoxy-1,3-dioxopropen-3-yl)bis(triethylphosphane)iron derivatives (R = Me, **9a**, R = Et, **9b**). In the solid state only the Z form of complexes **8** is found. In a comparable manner as for the synthesis of compounds **2**, it is possible to obtain  $\text{Fe}(\text{CO})_2(\text{PET}_3)_2(\text{X})(\text{CH}_2\text{R})$  (R = OMe, **10a**; R = 1,3-dioxolan-2-yl, **10b**; R = 2,4,10-trioxoadamantan-3-yl, **10c**) species. While **10a** does not react, the derivatives **10b,c** are converted in the presence of DBU and CO to  $E,Z$  mixtures of ketene complexes  $\text{Fe}(\text{CO})_2(\text{PET}_3)_2[\eta^2\text{-}(C,O)\text{-}(\text{COCHR})]$  (R = 1,3-dioxolan-2-yl, **13b<sup>E,Z</sup>**; R = 2,4,10-trioxoadamantan-3-yl, **13c<sup>E,Z</sup>**). (**13b,c**)<sup>Z</sup> crystallize from solutions. In further attempts comparable to the reactions to **2** and **10**, haloorganyliron complexes  $\text{Fe}(\text{CO})_2(\text{PET}_3)_2(\text{X})(\text{CH}_2\text{Y})$  (X = Y = Cl, **14a**; X = Y = I, **14b**; X = I, Y =  $\text{CH}_2\text{CN}$ , **14c**) could be obtained. All derivatives **14** cannot be transformed to ketene complexes in the presence of DBU and CO. Finally the known complexes  $\text{Fe}(\text{CO})_2(\text{I})(\text{PET}_3)_2(\text{Me}, \text{Et})$  (**15a,b**) and the new species  $\text{Fe}(\text{CO})_2(\text{I})(\text{CH}_2\text{SiMe}_3)(\text{PET}_3)_2$  (**15c**) were attempted to be converted to ketene complexes. By IR spectroscopy it was possible to detect  $\text{Fe}(\text{CO})_2(\text{I})(\text{PET}_3)_2(\text{OCCHR})$  compounds (R = H, **17a**; R = Me, **17b**; R =  $\text{SiMe}_3$ , **17c**); however, these molecules could not be isolated from the reaction mixtures of the reaction of **15a–c** with DBU and CO. **17c** was then prepared by an independent route by reacting **1a,b** with  $\text{Me}_3\text{SiCH}=\text{C}=\text{O}$ . Under these conditions **17c** was much more stable. In an exemplary way it was shown that the ketene unit of **17c** can be cleanly replaced by CO to afford  $\text{Fe}(\text{CO})_3(\text{PET}_3)_2$  (**18**). The structures of **7a**, **8a<sup>Z</sup>**, **9b**, and **14a** have been determined by X-ray diffraction studies.

## Introduction

Transition metal ketene complexes have attracted considerable recent interest,<sup>1</sup> in particular in conjunction with the proposed role of CCO units as intermediates in homogeneous or heterogeneous Fischer–Tropsch type catalysis<sup>2</sup> and the fact that metal ketene compounds have great potential in organic synthesis. Their significance in organic synthesis is for instance nicely demonstrated by the reaction of alkynes with (alkoxyaryl)chromium carbene complexes involving a short-lived vinylketene complex as key intermediate to give 4-alkoxy-1-naphthol derivatives.<sup>3–8</sup>

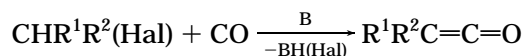
Synthetic access to transition metal attached ketene moieties can be achieved by direct addition of ketenes to unsaturated organometallic complexes,<sup>1,9–17</sup> the car-

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bonylation of carbenes,<sup>3-8,18-25</sup> or the deprotonation of acyl species.<sup>4,15b,26,27</sup> The latter two methods are of synthetic interest, because both could principally involve C-C coupling processes (note that metal-bound acyl units can be obtained by a CO insertion step) for the buildup of ketene moieties and thus circumvent the quite often tedious preparation of free ketene derivatives.

Our investigations in the realm of ketene complexes aimed at the utilization of Fe(CO)<sub>2</sub>(PET<sub>3</sub>)<sub>2</sub> fragments, since they were deemed to allow facile access to a versatile chemistry not only via known acyl compounds of the type Fe(CO)<sub>2</sub>(PET<sub>3</sub>)<sub>2</sub>(Hal)COR<sup>28</sup> but also via the "parent" alkyl carbonyl molecules Fe(CO)<sub>2</sub>(PET<sub>3</sub>)<sub>2</sub>(Hal)-(R). A metal-mediated buildup of ketene moieties could thus be envisaged by the following formal C-C coupling process involving a carbene unit and CO.



This quite desirable route is expected to allow the use of simple starting materials and moreover the access to a broad variety of substituted metal-bound ketene units independent of the restriction that the ketenes have to be stable in the free state.

## Results and Discussion

It has been demonstrated in our group that iron dinitrogen complexes of the type Fe(CO)<sub>2</sub>L<sub>2</sub>N<sub>2</sub> and [Fe-

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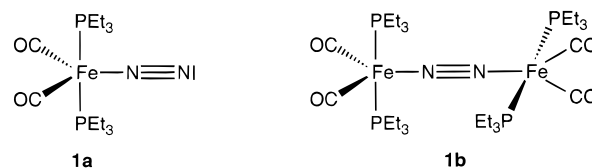
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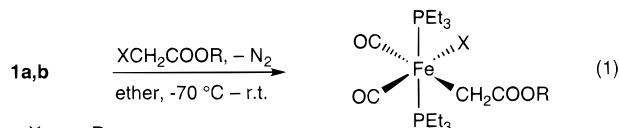
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(CO)<sub>2</sub>L<sub>2</sub>]<sub>2</sub>(μ-N<sub>2</sub>) (L = phosphorus donor) can be used as versatile starting materials for many types of reactions.<sup>28,29</sup> The N<sub>2</sub> ligand easily dissociates in solution generating the very reactive 16e<sup>-</sup> species [Fe(CO)<sub>2</sub>L<sub>2</sub>], which can add various types of ligands<sup>9</sup> or can undergo oxidative addition reactions of R-X derivatives.<sup>28</sup> The PET<sub>3</sub>-substituted dinitrogen compounds **1a,b** can be obtained by either photolysis of Fe(CO)<sub>3</sub>(PET<sub>3</sub>)<sub>2</sub><sup>28</sup> or by reduction of Fe(CO)<sub>2</sub>(PET<sub>3</sub>)<sub>2</sub>X<sub>2</sub> species (X = halogen) in the presence of N<sub>2</sub>.<sup>29</sup> Under N<sub>2</sub>, species **1a,b** are in



equilibrium, and both are satisfactory starting components in substitution and oxidative addition processes.

When ethereal solutions of the **1a,b** mixture are reacted with XCH<sub>2</sub>COOR compounds bearing electron-withdrawing ester functionalities, the oxidative addition products Fe(CO)<sub>2</sub>(PET<sub>3</sub>)<sub>2</sub>(X)(CH<sub>2</sub>COOR) (**2a-c**) (eq 1)



**1a,b**

X

Cl

Br

I

R

Me

Me

Et

**2a**

**2b**

**2c**

(1)

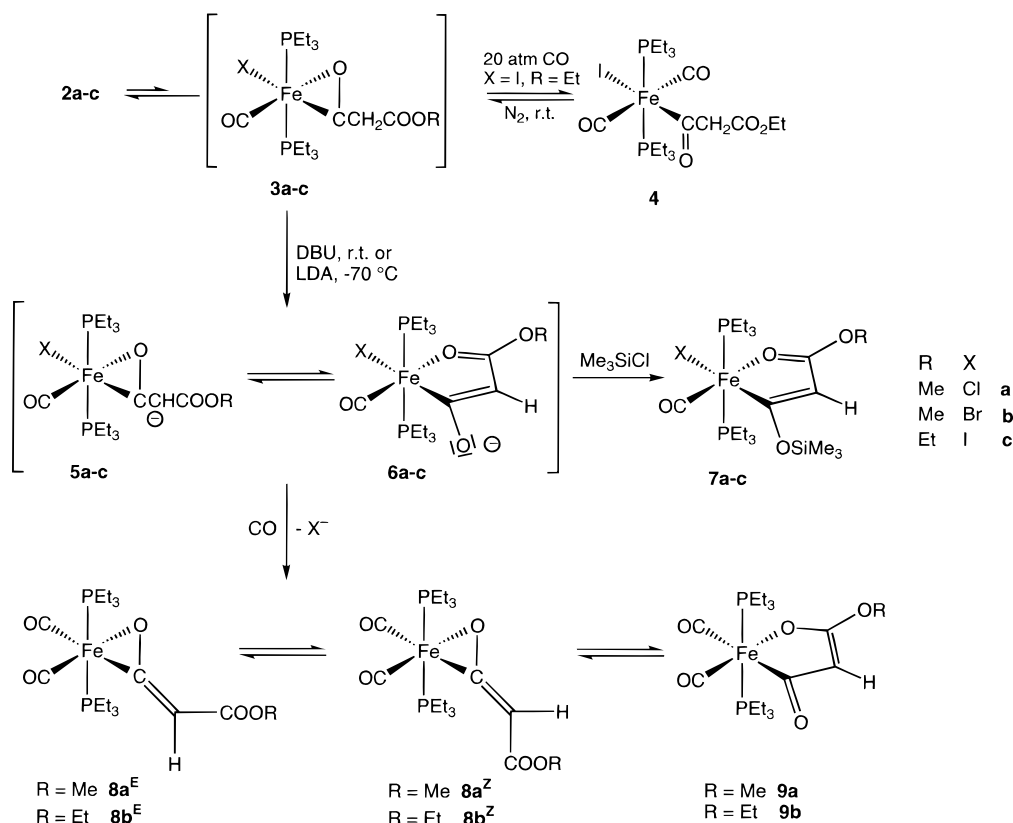
can be obtained after chromatographic workup in good to moderate yields. The spectroscopic data for **2a-c** are in accord with the presence of cis, trans Fe(CO)<sub>2</sub>(PET<sub>3</sub>)<sub>2</sub> units in these molecules. In the <sup>13</sup>C spectra two phosphorus-coupled triplets are assigned to the chemically inequivalent C<sub>CO</sub> nuclei. The low-field ones are attributed to the ligands trans to the alkyl substituents, while the high-field signals correspond to the CO groups trans to the halogen moiety. This assignment is mainly based on the magnitude of the J<sub>PC</sub> couplings, which have been related to the trans influence of the trans-disposed ligands in structurally similar complexes.<sup>30</sup> In addition to this the chemical shifts of the high-field CO signals vary significantly on going from **2a** to **2c** stressing their trans to halogen positions. The <sup>1</sup>H NMR spectra of **2a-c** show characteristic triplets for the metal-bound methylene groups, and the trans arrangement of the phosphorus donors is indicated by the observation of higher order splitting patterns of the CH<sub>2</sub> groups. Such virtual couplings are typical for trans phosphorus donor moieties. All complexes **2a-c** show correct elemental analyses.

In Scheme 1 it is suggested that compounds **2a-c** can react with bases. There is however strong indication that deprotonation does not occur from **2a-c** directly, rather than from their CO inserted η<sup>2</sup>-acyl isomers **3a-c**. It should be noted that spontaneous isomerizations

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Scheme 1



of iron alkyl carbonyl species into  $\eta^2$ -acyl compounds is a quite common phenomenon in the realm of  $\text{Fe}(\text{CO})_2\text{L}_2$  chemistry. Selected examples of such ( $\eta^2$ -acyl)iron complexes have been isolated and even been structurally characterized.<sup>9,28</sup>

In a separate exemplary experiment it has then been tested that **2c** can react with CO presumably via **3c** leading to a trans iodo malonyl compound **4**, however, requiring a 20 bar CO pressure. Under ambient conditions **4** is unstable and can only be traced IR spectroscopically, when samples are taken quickly from an autoclave. The IR spectrum shows a very weak and a strong  $\nu(\text{CO})$  band interpreted as a typical absorption pattern for a trans CO arrangement. In addition to these bands two  $\nu(\text{C}=\text{O})$  absorptions are observed. The apparent instability of **4** under ambient conditions may indicate that under an atmosphere of 1 bar CO, as applied for the reactions of Scheme 1, the  $\eta^2$ -acyl complexes of type **3** are probably present in a higher concentration than their  $\eta^1$ -congeners of type **4**. Nevertheless, **3a-c** and also potential intermediates such as **4** are all derivatives of  $\beta$ -keto esters and should therefore display an acidity much higher than that of the parent complexes **2a-c**.  $\text{MeCOCH}_2\text{COOEt}$ ,  $\text{CH}_2(\text{COOEt})_2$ , and  $[\text{DBUH}]^+$  have similar  $\text{p}K_a$  values of 25, 27, and 24 in acetonitrile,<sup>31</sup> so that their mutual deprotonation can be anticipated to a kinetically relevant extent by any of their conjugate bases. The  $\text{p}K_a$  effect of substituting the methyl or the ethoxy group in  $\text{MeCOCH}_2\text{COOEt}$  or  $\text{CH}_2(\text{COOEt})_2$  for the iron fragment in **3a-c** is not easily evaluated. However, it is reasonable to assume that these complexes have  $\text{p}K_a$

values in the vicinity of 24 and, hence, DBU could still effect deprotonation to give the isomeric mixture of **5a-c** and **6a-c** as indicated in Scheme 1.

As described for the DBU deprotonation process of **3a-c**, the stronger base LDA is expected to generate the equilibrium mixture of the isomeric anions **5a-c** and **6a-c**, as well. In the subsequent silylation with  $\text{Me}_3\text{SiCl}$  only the O-silylation products **7a-c** are isolated, which are related to **6a-c** and C-silyl derivatives of **5a-c** were not found. From this a predominance of **6a-c** may be concluded. In this context it should be noted that trapping of the  $\mathbf{5a-c} \rightleftharpoons \mathbf{6a-c}$  equilibrium positions requires that these equilibrium reactions are slow with respect to any of the silylation processes. Silylations of O-functionalized anions are presumably quite fast reactions and could perhaps satisfy this condition. However, assuming that they are also faster than C-silylations, the rates of the latter could be comparable to those of the above equilibria and then C-silylation products ought not to be found.

The structures of complexes **7a-c** were derived from an exemplary single-crystal X-ray diffraction study on **7a** and from their spectroscopic properties. The IR spectra are characterized by one  $\nu(\text{CO})$  band at  $1932 \text{ cm}^{-1}$  for all three derivatives and weak  $\nu(\text{C}=\text{O})$  absorptions in the range between  $1550$  and  $1570 \text{ cm}^{-1}$ . Their positions at relatively low wavenumbers are apparently due to the coordination of the oxygen atom. The  $^1\text{H}$  NMR spectra of these homologous complexes show singlets for the silyl protons between 0.1 and 0.3 ppm and resonances for the methoxy or ethoxy residues in **7a,b** and **7c**, respectively. The vinylic protons at the metallacyclic rings appear between 5 and 5.2 ppm with an expectedly small coupling to the phosphorus nuclei

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of 2 Hz. The most prominent characteristics of the  $^{13}\text{C}$  NMR spectra of **7a–c** consist of resonances at rather low field (270 ppm), which are attributed to the CO-SiMe<sub>3</sub> atoms. This low field position suggests contribution from a carbene type resonance structure (vide infra).

Another possibility for the trapping of the **5a–c** and **6a–c** species turned out to be the reaction with CO, which causes replacement of the X group by CO. Apparently, this step is fast with respect to the establishment of the **5a–c**  $\rightleftharpoons$  **6a–c** equilibria, since we were able to isolate two series of isomeric compounds: the ketene complexes (**8a,b**)<sup>Z</sup> and the (1-alkoxy-1,3-dioxopropan-3-yl) iron species **9a,b**. The ratios of the isolated complexes **8a**<sup>Z</sup>:**9a** and **8b**<sup>Z</sup>:**9b** were 1:39 and 1:13, respectively. These ratios could indeed reflect the respective **5:6** concentrations in solution. The assumption of slow interconversion rates for the **5**  $\rightleftharpoons$  **6** equilibria is supported further by the observation that the equilibria of the topologically related species **8a**<sup>Z</sup>  $\rightleftharpoons$  **9a** and **8b**<sup>Z</sup>  $\rightleftharpoons$  **9b** were found to be very slow, as well.

Indeed, the NMR spectroscopic pursuit of the equilibration reactions starting from either (**8a,b**)<sup>Z</sup> or **9a,b** takes a very long time. Nevertheless, these studies revealed additional resonances, which were assigned to the nonisolable *E* isomers (**8a,b**)<sup>E</sup>. As a quite puzzling phenomenon, it was found in our initial experiments that these processes were not always reproducible concerning the reaction rates. Apparently, if they were not conducted under very rigorous conditions, higher reaction rates were observed, and in these cases the transformations were also accompanied by the formation of decomposition products, like Fe(CO)<sub>3</sub>(PET<sub>3</sub>)<sub>2</sub>. <sup>1</sup>H and <sup>31</sup>P NMR spectra measured with rigorous exclusion of oxygen and with severely purified C<sub>6</sub>D<sub>6</sub> demonstrated that after 22 months a 50:5:1 ratio of **8a**<sup>Z</sup>:**8a**<sup>E</sup>:**9a** was reached starting from **8a**<sup>Z</sup> or **9a**. No other product was formed. A similar situation is observed for the equilibration of **8b**<sup>Z</sup> and **9b** in C<sub>6</sub>D<sub>6</sub> where a ratio of 11:1:2.5 (**8b**<sup>Z</sup>:**8b**<sup>E</sup>:**9b**) was obtained after the same period of time starting from both types of complexes.

Exemplary X-ray diffraction studies have been carried out on **8a**<sup>Z</sup> and **9b**. Their structures are in accord with their spectroscopic data, which are related to those of **8b**<sup>Z</sup> and **9b**, respectively. The IR spectra of all these complexes are characterized by two  $\nu(\text{CO})$  bands around 1990 and 1930 cm<sup>-1</sup>, which are typical of Fe(CO)<sub>2</sub>L<sub>2</sub> units with cis CO groups. In addition to this, both isomeric species show two bands of low intensity in the region of 1700–1500 cm<sup>-1</sup>. The <sup>1</sup>H NMR spectra of (**8a,b**)<sup>Z</sup> and **9a,b** display signals for the alkoxy residues and signals at about 6 ppm, which are assigned to the vinylic protons. For (**8a,b**)<sup>Z</sup> these show coupling to the P nuclei (<sup>4</sup>J<sub>PH</sub> = 3 Hz) and appear about 0.5 ppm low-field from those of **9a,b**, which allows facile distinction of these species.

The assignment of the low-field <sup>13</sup>C NMR resonances of the chemically inequivalent CO groups is mainly based on their <sup>2</sup>J<sub>PC</sub> values.<sup>30</sup> These couplings can again be correlated with the trans influence, which is smaller for the CO ligand located approximately trans to the O-donor atoms. The resonances of the iron-bound carbon nuclei of **9a,b** are found ca. 40 ppm down-field

of those of (**8a,b**)<sup>Z</sup>. The chemical shifts of these internal C<sub>ketene</sub> signals of (**8a,b**)<sup>Z</sup> compare however well with those of other  $\eta^2(\text{C},\text{O})$ -ketene complexes<sup>1</sup> and do not match with the expected chemical shifts for  $\eta^2(\text{C},\text{C})$  binding. It should finally be noted that the chemical shifts of the <sup>31</sup>P NMR resonances of both types of species **8**<sup>Z</sup> and **9** differ also significantly.

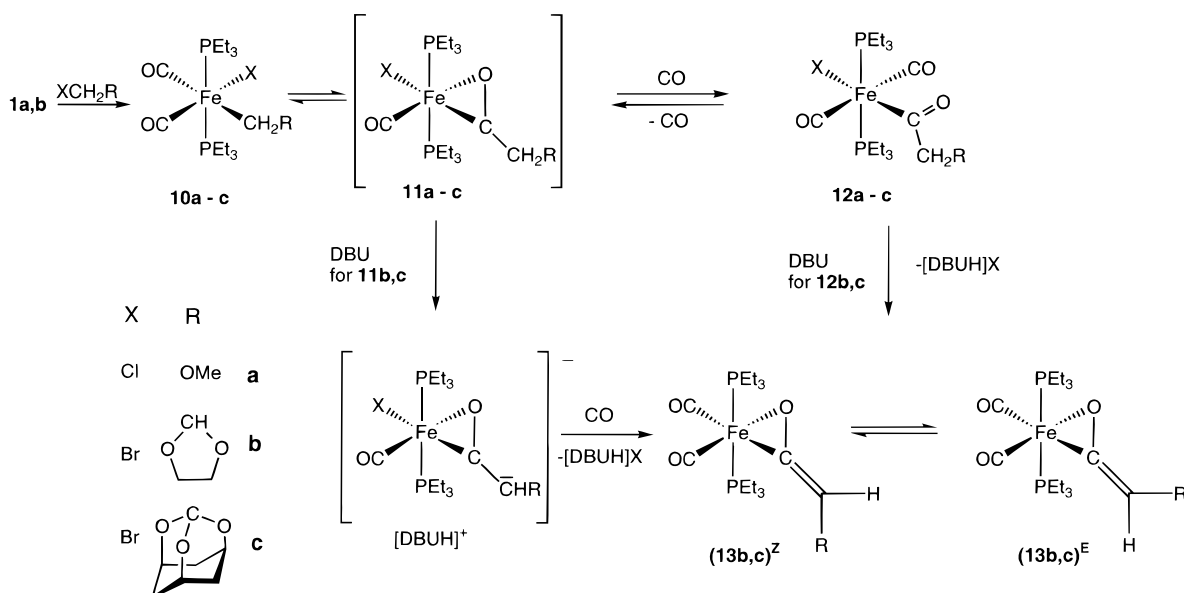
Due to their generally low equilibrium concentrations the (**8a,b**)<sup>E</sup> molecules could not be isolated and were characterized by NMR spectroscopy only. They show <sup>31</sup>P resonances at 53.5 (**8a**<sup>E</sup>) and 53.4 ppm (**8b**<sup>E</sup>) in a chemical shift region expected for Fe(CO)<sub>2</sub>(PET<sub>3</sub>)<sub>2</sub>-(ketene) complexes (cf. resonances of (**8a,b**)<sup>Z</sup>, **13a,b** and **17c**). In addition to this, the ketene protons of (**8a,b**)<sup>E</sup> appear downfield from those of (**8a,b**)<sup>Z</sup> with somewhat smaller <sup>4</sup>J<sub>PH</sub> couplings for (**8a,b**)<sup>E</sup> (<2 Hz for (**8a**)<sup>E</sup>; 1.5 Hz for **8b**<sup>E</sup>). Remarkably the resonances of the OMe or OCH<sub>2</sub> protons of (**8a,b**)<sup>E</sup> lie both downfield from those of (**8a,b**)<sup>Z</sup> and **9a,b** at 3.73 and 4.33 ppm, respectively.

Summarizing these isomerization reactions, it is suggested that they presumably involve kinetic barriers for the Fe–O<sub>ketene</sub> and Fe–O<sub>enolate</sub> bond making/breaking processes, then Fe–C bond rotations as additional motions in the Fe–O<sub>ketene</sub>/Fe–O<sub>enolate</sub> interconversions, and the C–C<sub>ketene</sub> bond rotation for the *E/Z* isomerizations. The latter could however also be accomplished by dissociation and readdition of the ketene. The foregoing equilibration studies suggest that the Fe–O<sub>enolate</sub> bond rupture is the slowest process and therefore has the highest activation barrier.

The observation of the **8**  $\rightleftharpoons$  **9** equilibria is specific to the presence of the ester functionality, which provides an extra ligating position. If the ester moiety were replaced by residues with only minor or no ligating properties, only ketene structures are expected to result from a combined dehydrohalogenation/ carbonylation process similar to Scheme 1. To prove this idea, we have investigated a sequence of transformations starting with the reaction of **1a,b** with other O-functionalized RCH<sub>2</sub>X compounds to yield in a first step oxidative addition products Fe(CO)<sub>2</sub>(PET<sub>3</sub>)<sub>2</sub>(Br)CH<sub>2</sub>R (R = methoxy (**10a**), 1,3-dioxolan-2-yl (**10b**), 2,4,10-trioxoadamantan-3-yl (**10c**)) comparable to compounds **2a–c** of eq 1 (Scheme 2).

The structures of the complexes **10a–c** were derived from their spectroscopic properties and from the exemplary X-ray diffraction study on **10c**. It is noteworthy that **10b,c** indicate at room temperature dynamic behavior on the NMR time scale. The <sup>13</sup>C NMR spectra of **10b,c** (toluene-*d*<sub>8</sub>) show significantly broadened signals for the metal-bound C<sub>methylene</sub> atoms and the carbonyl group cis to them. This suggests that a migratory insertion equilibrium involving the  $\eta^2$ -acyl species **11b,c** is operating at a rate comparable on the NMR time scale. These resonances become sharp by lowering the temperature; however, no resonances of a second species can be found. The <sup>31</sup>P NMR spectra give a comparable picture. **10b**, for instance, shows at room temperature in toluene-*d*<sub>8</sub> a single <sup>31</sup>P NMR resonance with a line width of 17.6 Hz. On lowering of the temperature, this signal broadens to 36.4 Hz (258 K) and becomes finally sharp again (4.4 Hz, 223 K). All these observations indicate a very low concentration of an acyl isomer and perhaps superimposed on this the

Scheme 2



effect that the equilibrium shifts to the side of the higher populated alkyl species at the lower temperature. The NMR spectra of compound **10a** do not change significantly with temperature and thus are not indicative of a similar alkyl migration equilibrium.

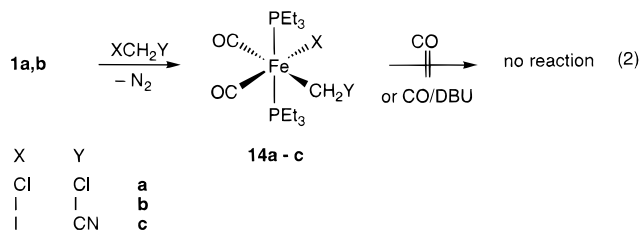
The carbonylation products **12a-c** turned out to be more stable than the analogous complex **4**. However, species **12a-c** were still too labile to be isolated. **12b,c** show typical  $\nu(\text{CO})$  bands at 2044 (w), 1960 (s), 1601 (w) and 2043 (w), 1958 (s), 1598 (w)  $\text{cm}^{-1}$ , which are persistent at room temperature over a long period of time. The IR spectrum of the reaction of **10a** with CO (1 bar) in hexane were interpreted in terms of the formation of *cis*- and *trans*-dicarbonylchloro(methoxyacetyl)bis(triethylphosphane)iron (2012, 1953 (*cis* isomer), and  $\nu(\text{CO})$  1972  $\text{cm}^{-1}$  (**12a**)), thus resembling the carbonylation of a dicarbonylchloro(hydroxyacetyl)bis(trimethyl phosphite)iron.<sup>32</sup>

Then, the reactions of **10a-c** with CO were attempted in the presence of DBU in etheral solution (Scheme 2). Even after prolonged reaction times the transformation of **10a** did not result in the formation of a ketene complex; only the mixture of carbonylation products **12a** and its *cis* isomer was detected. In contrast to this, **10b,c** can be converted in dehydrobromination processes in 24 h (**10b**) and 3 h (**10c**) producing mixtures of *E* and *Z* ketene complexes (**13b,c**)<sup>*E,Z*</sup> presumably via **11b,c** or **12b,c**. From these solution mixtures only (**13b,c**)<sup>*Z*</sup> crystallize, which were obtained in 45 and 55% yields, respectively. The IR spectra of **13b,c** in hexane or ether are not indicative of this equilibrium process, since apparently both isomers possess similar  $\nu(\text{CO})$  and  $\nu(\text{C}_2\text{O})$  absorptions. The <sup>1</sup>H NMR spectra (C<sub>6</sub>D<sub>6</sub>), however, change significantly evolving additional signals for (**13b,c**)<sup>*E*</sup>. In either case an equilibrium is reached after about 10 h and the *E:Z* ratios are approximately 1:6 for **13b** and 1:1 for **13c**. (**13b,c**)<sup>*Z*</sup> show low-field chemical shifts and higher <sup>4</sup>*J*<sub>PH</sub> of the H<sub>ketene</sub> proton with respect to the corresponding nuclei of (**13b,c**)<sup>*E*</sup>. It is not clear,

how the *E/Z* isomerizations occur. As for **8a,b** favorable alternatives are the C-C bond rotation or the elimination and readdition of the ketene ligand. The given ratios of the *E/Z* isomer could be explained in terms of a competition of destabilizing forces, as there are the steric hindrance of the ketene substituent in proximity to the metal center (*Z* form) and the lone pair repulsions between those of the ketene substituent and the O<sub>ketene</sub> atom (*E* form). Comparable *E/Z* isomerizations in solution have been reported by Bruno et al. for Cp'<sub>2</sub>Nb(Cl)(ketene) complexes.<sup>14</sup>

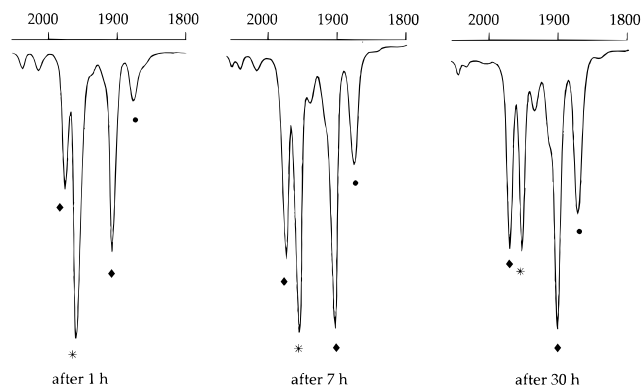
Otherwise, the IR spectroscopic data of **13b,c** are in good agreement with those of the ketene complexes **8a,b** and thus confirm the presence of the  $\eta^2(\text{C},\text{O})$ -ketene unit. The <sup>13</sup>C NMR data of the ketene moiety also reflect the  $\eta^2(\text{C},\text{O})$  coordination,<sup>1</sup> since the signals for the internal C<sub>ketene</sub> atom of (**13b,c**)<sup>*E,Z*</sup> appear in a typical absorption range at around 178 ppm with <sup>2</sup>*J*<sub>PC</sub> = 16 Hz.

In further experiments it was then sought to be tested whether ketene complexes substituted with CH<sub>2</sub>X groups (X = Cl, I, CN) could also be accessed by the CO/DBU method. According to eq 2, it was indeed possible to

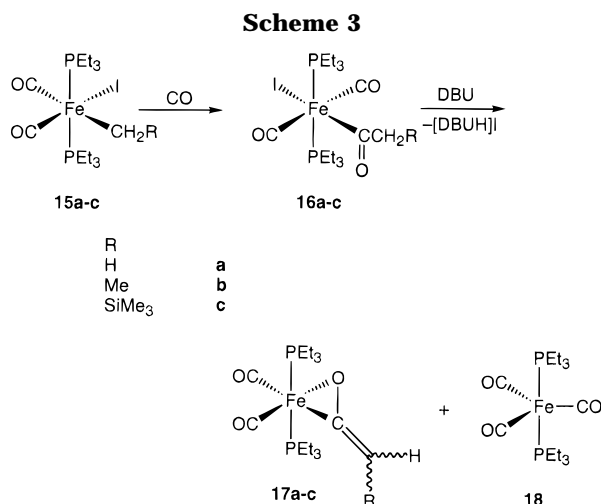


prepare the potential alkyl halo precursors to the ketene complexes (**14a-c**). They turned out to be isolable and stable compounds, but unfortunately all of them could not be transformed further with CO or CO in the presence of DBU (eq 2). All complexes **14a-c** were fully characterized, and the structure of **14a** was determined in an X-ray diffraction study. Supposedly, it is the reluctance of these complexes to undergo CO insertion that also prevents their further conversion in the presence of DBU.

(32) Berke, H.; Huttner, G.; Weiler, G.; Zsolnai, L. *J. Organomet. Chem.* **1981**, *219*, 353.



**Figure 1.** IR monitoring (2000–1800  $\text{cm}^{-1}$ ) of the reaction of **15b** with DBU/1 bar of CO at room temperature according to eq 3.  $\nu(\text{CO})$  bands: **15b**, ♦; **17b**, \*; **18**, ●.

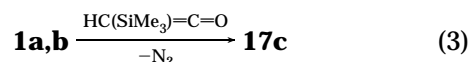


The successful CO/DBU experiments of Scheme 2 and the knowledge about the excellent migratory aptitude of alkyl groups at iron centers<sup>28</sup> encouraged us to finally approach the synthesis of alkyl-substituted ketene complexes using alkyl(iodo)dicarbonylbis(triethylphosphane)iron as starting components. In particular, the known compounds  $\text{Fe}(\text{CO})_2\text{I}(\text{Me}, \text{Et})(\text{PEt}_3)_2$  (**15a,b**) and a new species  $\text{Fe}(\text{CO})_2\text{I}(\text{CH}_2\text{SiMe}_3)(\text{PEt}_3)_2$  (**15c**) were chosen. The latter was generated in situ, since it could not be isolated from solution without considerable decomposition. According to Scheme 3 these complexes were then transformed with CO to the *trans*- $\text{Fe}(\text{CO})_2\text{I}(\text{OCMe}, \text{Et}, \text{CH}_2\text{SiMe}_3)(\text{PEt}_3)_2$  (**16a–c**) species.

The subsequent reaction of **16a–c** with DBU indeed afforded the desired ketene compounds **17a–c**; however, due to relatively fast decomposition and/or ketene substitution with CO, the complex **18** appeared during formation of the ketene complexes **17a–c**. The relative yields of these species in the mixture with **16a–c** and **18** did not exceed 10% for **17a**, 60% for **17b**, and 20% for **17c** as monitored by IR or <sup>31</sup>P NMR spectroscopy. Figure 1 demonstrates the described situation by an exemplary IR monitoring of the evolution of species **16b**, **17b**, and **18** with time. Besides the starting material **16b**, there is after 1 h a dominating amount of **17b**, while **18** is present in only minor quantities, and after 30 h one still finds unreacted **16b** but considerable amounts of **18** and a drastically decreased quantity of **17b**. Unfortunately, we were not able to separate these

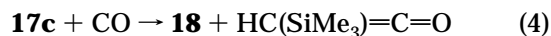
mixtures by chromatography or crystallization. The ketene complexes were too unstable under these conditions.

In an earlier publication we reported the preparation of an  $\text{Fe}(\text{CO})_2(\text{diphenylketene})(\text{PEt}_3)_2$  complex,<sup>9</sup> which was obtained by a substitutional route starting from the free ketene ligand. This ketene compound was quite stable at room temperature in solution and did not show decomposition over a prolonged period of time, a property that seemingly is in contrast to that of **17a–c** prepared according to Scheme 3. Since (trimethylsilyl)ketene is stable in the free state, an independent synthesis of **17c** was attempted by the same substitutional route as applied for the diphenylketene derivative. It was thus possible to obtain **17c** in 95% yield from the **1a,b** mixture and  $\text{HC}(\text{SiMe}_3)=\text{C}=\text{O}$  (eq 3).



However, more surprising than the successful access to **17c** was then the stability of this compound in solution at room temperature, which showed only a 20% decomposition after 2 h in hexane. Apparently a solution of pure **17c** was much more stable than when it was generated under the CO/DBU conditions of Scheme 3. In an attempt to simulate such reaction conditions for **17c**, we added  $\text{Fe}(\text{CO})_2(\text{PEt}_3)_2\text{I}_2$  to an ether solution of pure **17c** (1:5 ratio). In less than 1 h **17c** was completely decomposed with formation of free  $\text{HC}(\text{SiMe}_3)=\text{C}=\text{O}$ ,  $\text{Fe}(\text{CO})_3(\text{PEt}_3)_2$ , and other unidentified products. From this experiment we could conclude that the decomposition of **17c** may be accelerated by the presence of oxidative byproducts. It is not clear which component of the reaction mixture of Scheme 3 takes over the role of the decomposition promoter, but apparently there is one present.

Finally, since pure **17c** was stable enough for further investigations and also the ketene component was stable in the free state, the reaction of **17c** with CO (1 bar) was studied. By IR spectroscopy and GC, complete liberation of  $\text{HC}(\text{SiMe}_3)=\text{C}=\text{O}$  could thus be observed after 2 h (eq 4).



It seems worth mentioning that the solution spectra of **17c** reveal the notable feature that only one isomer is present. Furthermore, mainly on the basis of the relative highfield shift of the olefinic proton, an *E* configuration is assigned to the iron-bound ketene moiety. These findings are in marked contrast to the observations for the O-functionalized derivatives **8a,b** and **13b,c**, where overall the *Z* configuration prevailed.

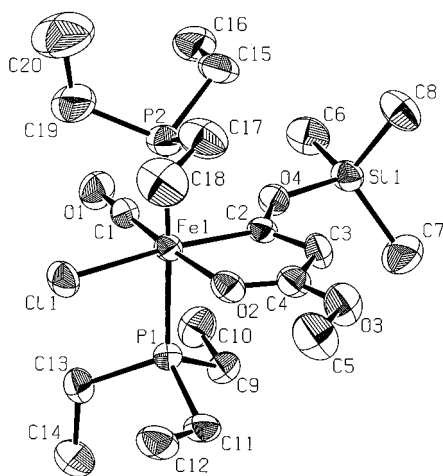
**X-ray Diffraction Studies on 7a, 8a<sup>Z</sup>, 9b, and 14a.** As derived from the spectroscopic data, the structural features of **7a** with the given special type of a conjugated ring system looked quite unique, and we therefore considered obtaining quantitative structural data from a single-crystal X-ray diffraction study. Suitable crystals were precipitated from an ether solution by cooling it to  $-30^\circ\text{C}$ .

The X-ray data collection and processing parameters of **7a** are given in Table 1. Figure 2 shows the

**Table 1. Summary of Crystallographic Data for 7a, 8a<sup>Z</sup>, 9b, and 14a**

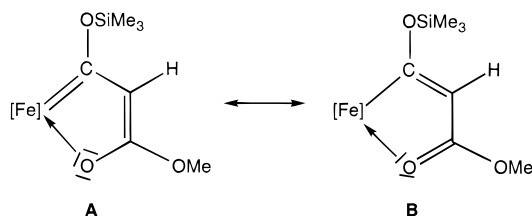
	<b>7a</b>	<b>8a<sup>Z</sup></b>	<b>9b</b>	<b>14a</b>
formula	C <sub>20</sub> H <sub>43</sub> ClFeO <sub>4</sub> P <sub>2</sub> Si	C <sub>18</sub> H <sub>34</sub> FeO <sub>5</sub> P <sub>2</sub>	C <sub>19</sub> H <sub>36</sub> FeO <sub>5</sub> P <sub>2</sub>	C <sub>15</sub> H <sub>32</sub> Cl <sub>2</sub> FeO <sub>2</sub> P <sub>2</sub>
color	yellow	yellow	yellow	yellow
cryst dimens (mm)	0.7 × 0.4 × 0.25	0.18 × 0.08 × 0.21	0.2 × 0.2 × 0.1	0.6 × 0.4 × 0.25
cryst syst	monoclinic	orthorhombic	monoclinic	monoclinic
space group	<i>Cc</i>	<i>Pna</i> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> (Å)	17.003(3)	24.392(5)	11.933(5)	7.772(4)
<i>b</i> (Å)	13.789(2)	11.509(4)	15.715(4)	30.671(12)
<i>c</i> (Å)	12.153(2)	8.149(2)	13.110(4)	9.152(2)
β (deg)	93.50(2)		93.01(3) <sup>o</sup>	104.68(3)
<i>V</i> (Å <sup>3</sup> )	2844.0(8)	2287.6(11)	2455.1(14)	2110.4(16)
<i>Z</i>	4	4	4	4
fw	528.87	448.2	462.27	433.1
<i>d</i> (calcd) (g/cm <sup>3</sup> )	1.235	1.301	1.251	1.363
abs coeff (mm <sup>-1</sup> )	0.800	0.822	0.768	1.123
<i>F</i> (000)	1128	952	984	912
temp (K)	237(5)	240(5)	245(5)	241(5)
2θ scan range (deg)	4.0 ≤ 2θ ≤ 58.0	4.0 ≤ 2θ ≤ 55.0	4.0 ≤ 2θ ≤ 55.0	5.0 ≤ 2θ ≤ 58.0
scan speed (deg min <sup>-1</sup> )	variable; 2.00–14.65	variable; 1.50–14.65	variable; 2.00–14.65	variable; 2.00–14.65
scan range (ω) (deg)	1.20	1.40	1.40	1.40
no. of unique data	3899	2808	5652	5591
no. of data obsd for <i>I</i> > 2σ( <i>I</i> )	3630	2297	3536	4502
abs corr	N/A	N/A	N/A	N/A
solution method	direct methods	direct methods	direct methods	direct methods
agreement factors: <sup>a</sup> <i>R</i> , <i>wR</i> 2 (%)	4.66, 9.77	9.04, 11.35	17.96, 18.84	9.18, 21.26
<i>R</i> 1 (obsd) (%)	4.19	6.67	11.27	7.18
goodness-of-fit	1.124	1.229	1.224	1.245

$$^a R = \sum(F_o - F_c)/\sum F_o; wR2 = [\sum\{w(F_o^2 - F_c^2)\}^2/\sum(wF_o^2)^2]^{1/2}.$$

**Figure 2.** Structure of **7a**. Thermal ellipsoids are drawn at the 50% probability level.

structural model of **7a**, which reveals pseudo-octahedral coordination of the iron center.

The iron atom is part of a nearly planar five-membered ring system forming an O<sub>2</sub>–Fe–C<sub>2</sub> angle of 81.2(2)° at iron (see Table 2). A striking property, unexpected to the determined extent, is the short Fe–C(2) distance of 1.880(5) Å, which confirms an Fe=C multiple bond character. This finding implies a carbenoid nature of the C(2) atom as given in **A** anticipated



also from the strong low-field position of this carbon atom in the <sup>13</sup>C NMR (267 ppm). The electronic

**Table 2. Selected Bond Distances (Å) and Angles (deg) of Complex 7a**

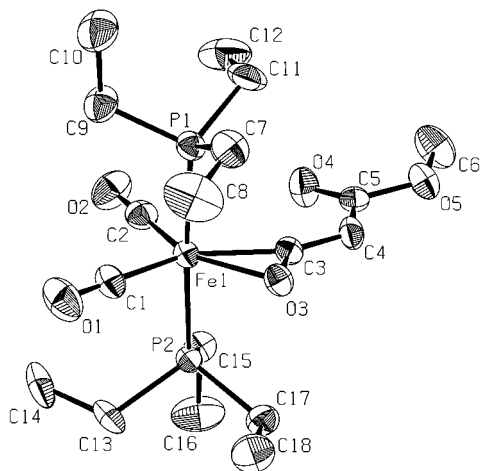
Fe(1)–Cl(1)	2.3774(12)	C(1)–O(1)	1.148(5)
Fe(1)–P(1)	2.2760(12)	C(2)–C(3)	1.380(6)
Fe(1)–P(2)	2.2719(13)	C(2)–O(4)	1.351(4)
Fe(1)–C(1)	1.728(4)	C(3)–C(4)	1.409(6)
Fe(1)–C(2)	1.899(4)	C(4)–O(2)	1.253(5)
Fe(1)–O(2)	2.040(3)	C(4)–O(3)	1.346(5)
Si(1)–O(4)	1.681(3)		
Cl(1)–Fe(1)–P(1)	89.16(4)	Fe(1)–C(1)–O(1)	178.8(4)
Cl(1)–Fe(1)–P(2)	88.35(5)	Fe(1)–C(2)–C(3)	115.9(3)
P(1)–Fe(1)–P(2)	177.50(5)	Fe(1)–C(2)–O(4)	123.1(3)
Cl(1)–Fe(1)–C(1)	95.91(13)	C(3)–C(2)–O(4)	121.0(3)
Cl(1)–Fe(1)–C(2)	169.73(13)	C(2)–C(3)–C(4)	111.1(4)
C(1)–Fe(1)–C(2)	94.35(18)	C(3)–C(4)–O(2)	121.2(4)
Cl(1)–Fe(1)–O(2)	88.59(9)	C(3)–C(4)–O(3)	118.0(4)
C(1)–Fe(1)–O(2)	175.50(16)	O(2)–C(4)–O(3)	120.9(4)
C(2)–Fe(1)–O(2)	81.15(15)	Fe(1)–O(2)–C(4)	110.7(3)

alternative for the binding of C(2) to the iron atom would be that of a C<sub>vinyl</sub> atom as represented by the resonance structure **B**. Vinyl substituents, however, have been seen to cause comparably long Fe–C bond separations.<sup>33</sup> The other bond lengths of the planar five-membered ring of **7a** confirm π conjugation with C–C bond distances between those of an isolated double bond and the bond lengths of aromatic systems.

For middle and late transition metal complexes the alternative binding mode of a ketene unit cannot easily be predicted, so that we sought to ensure the spectroscopically plausible η<sup>2</sup>(C,O) coordination of complexes **8** and **13** by an exemplary X-ray diffraction study on **8a<sup>Z</sup>**.

Crystals for the X-ray diffraction study of **8a<sup>Z</sup>** were obtained by slow cooling of an ether solution to –30 °C. The crystal, structure solution, and refinement data are given in Table 1. Figure 3 shows that **8a<sup>Z</sup>** is indeed a trigonal bipyramidal complex bearing a η<sup>2</sup>(C,O) ketene moiety in equatorial position with a *Z* configuration. The

(33) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans. II*, **1989**, S1.



**Figure 3.** Structure of **8a<sup>Z</sup>**. Thermal ellipsoids are drawn at the 50% probability level.

**Table 3. Selected Bond Distances (Å) and Angles (deg) of Complex 8a<sup>Z</sup>**

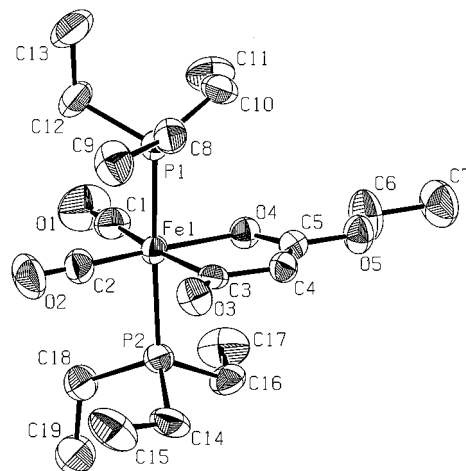
Fe(1)–C(1)	1.802(7)	C(2)–O(2)	1.142(9)
Fe(1)–C(2)	1.764(8)	O(3)–C(3)	1.277(8)
Fe(1)–O(3)	2.012(5)	C(3)–C(4)	1.358(9)
Fe(1)–C(3)	1.920(7)	C(4)–C(5)	1.425(10)
Fe(1)–P(1)	2.270(2)	C(5)–O(4)	1.225(9)
Fe(1)–P(2)	2.280(2)	C(5)–O(5)	1.365(8)
C(1)–O(1)	1.145(8)	O(5)–C(6)	1.431(9)
C(1)–Fe(1)–C(2)	101.5(4)	Fe(1)–C(2)–O(2)	179.1(7)
C(1)–Fe(1)–O(3)	108.9(3)	Fe(1)–O(3)–C(3)	67.2(4)
C(2)–Fe(1)–O(3)	149.6(3)	Fe(1)–C(3)–O(3)	75.0(4)
C(1)–Fe(1)–C(3)	146.7(3)	Fe(1)–C(3)–C(4)	153.8(6)
C(2)–Fe(1)–C(3)	111.8(3)	O(3)–C(3)–C(4)	131.2(7)
P(1)–Fe(1)–P(2)	175.12(7)	C(3)–C(4)–C(5)	124.4(7)
Fe(1)–C(1)–O(1)	179.6(6)		

general topology of **8a<sup>Z</sup>** is very similar to that of the Fe(CO)<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>(Ph<sub>2</sub>CCO) species<sup>9</sup> mentioned in the earlier context.

Expectedly, the C(3)–O(3) separation of 1.283(7) Å is longer than in free ketenes ( $d(C-O)$  in MeCH=C=O 1.171(2) Å<sup>34</sup>). In contrast to related  $\eta^2(C,O)$  ketene complexes of vanadium<sup>11,12</sup> and nickel,<sup>10</sup> the M–O distance of **8a<sup>Z</sup>** is longer than the M–C separation indicating a strengthened iron–carbon bond (Table 3). As discussed earlier, the *Z* configuration at the (C=C)<sub>ketene</sub> double bond is unexpected. On the basis of merely steric arguments, this coordination mode should not be preferred. A (cp)<sub>2</sub>V(Me(Ph)C=C=O) compound does indeed show *E* configuration,<sup>12</sup> as well as a unsymmetrically substituted niobium ketene system.<sup>14c</sup> Constructing the **8a<sup>E</sup>** molecule by a simple static approach from the structural parameters of **8a<sup>Z</sup>** results in a O<sub>Me</sub>...O<sub>ketene</sub> distance of about 2.54 Å. Since this value lies significantly below the sum of the van der Waals radii of the oxygens, the *E*-configured molecules are indeed expected to face steric O...O repulsions.

Suitable crystals for the X-ray diffraction study of **9b** were obtained by slow cooling of a hexane solution to –30 °C. The crystal, structure solution, and refinement data are given in Table 1. **9b** shows pseudo-octahedral coordination at the iron center (Figure 4), so that it seems plausible to attribute it a +II oxidation state.

By doing so, one has to assign the (methoxycarbonyl)ketene moiety a two minus charge. Thus, in comparison



**Figure 4.** Structure of **9b**. Thermal ellipsoids are drawn at the 50% probability level.

**Table 4. Selected Bond Distances (Å) and Angles (deg) of Complex 9b**

Fe(1)–C(1)	1.823(8)	C(1)–O(1)	1.145(9)
Fe(1)–C(2)	1.730(8)	C(2)–O(2)	1.154(8)
Fe(1)–C(3)	2.038(7)	C(3)–O(3)	1.214(8)
Fe(1)–O(4)	2.019(5)	C(3)–C(4)	1.445(9)
Fe(1)–P(1)	2.263(2)	C(4)–C(5)	1.343(10)
Fe(1)–P(2)	2.263(2)	C(5)–O(4)	1.284(8)
C(1)–Fe(1)–C(2)	94.4(4)	Fe(1)–C(2)–O(2)	178.9(8)
C(1)–Fe(1)–C(3)	172.0(3)	Fe(1)–C(3)–O(3)	127.3(5)
C(2)–Fe(1)–C(3)	93.6(3)	Fe(1)–C(3)–C(4)	107.8(5)
C(1)–Fe(1)–O(4)	89.1(3)	O(3)–C(3)–C(4)	124.8(6)
C(2)–Fe(1)–O(4)	176.4(3)	C(3)–C(4)–C(5)	115.3(6)
C(3)–Fe(1)–O(4)	82.9(2)	C(4)–C(5)–O(4)	123.7(7)
P(1)–Fe(1)–P(2)	172.94(9)	Fe(1)–O(4)–C(5)	110.2(4)
Fe(1)–C(1)–O(1)	177.7(8)		

to **8**, species **9** contain reduced organic residues. Like in the structure of **7a**, the iron atom of **9b** is part of a planar five-membered ring system. The  $\eta^2(C,O)$  coordination of the (methoxycarbonyl)ketene is accomplished via O(4) and C(3), which belong to the ester and the ketene group, respectively. The Fe–C distance of **9b** is however about 0.1 Å longer than in **8a<sup>Z</sup>** and lies in the range of M–C<sub>acyl</sub> distances<sup>33</sup> (Table 4). The C(3)–C(4) and C(4)–C(5) distances compare well with those of the structure of **7a** and other similar structural units reported in the literature.<sup>35</sup>

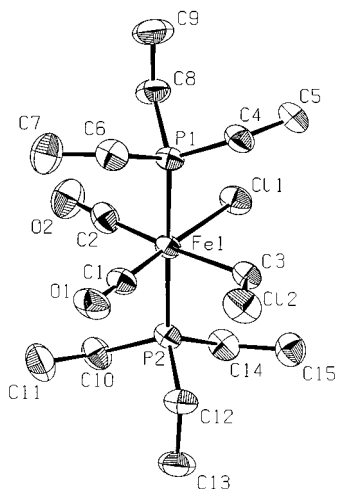
Halomethyl complexes such as **14a,b** have only rarely been structurally characterized due to the generally not too high stability of this class of compound.<sup>36</sup> However, **14a** appeared to be quite stable and could therefore be subjected to an X-ray diffraction study. The crystal, structure solution, and refinement data of **14a** are given in Table 1. Figure 5 shows a pseudo-octahedrally coordinated complex with the PEt<sub>3</sub> groups in trans position and the two cis CO, the Cl, and the CH<sub>2</sub>Cl ligands in an equatorial plane. The structural parameters around the iron center (Table 5) are found within the expected range.<sup>33</sup> The Fe(1)–C(3) and the C(3)–Cl(2) distances do not show unusual features. However, C(3) displays a significant deviation from tetrahedral geometry, since the Fe(1)–C(3)–Cl(2) angle is widened to almost 120°.

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**Figure 5.** Structure of **14a**. Thermal ellipsoids are drawn at the 50% probability level.

**Table 5.** Selected Bond Distances (Å) and Angles (deg) of Complex **14a**

Fe(1)–C(1)	1.744(6)	C(1)–O(1)	1.146(7)
Fe(1)–C(2)	1.811(7)	C(2)–O(2)	1.113(8)
Fe(1)–C(3)	2.048(6)	C(1)–Fe(1)–C(2)	95.1(3)
Fe(1)–P(1)	2.2913(17)	C(1)–Fe(1)–C(3)	91.8(3)
Fe(1)–P(2)	2.2919(17)	C(2)–Fe(1)–C(3)	173.1(2)
Fe(1)–Cl(1)	2.3447(17)	C(1)–Fe(1)–P(1)	90.5(2)
Cl(2)–C(3)	1.824(6)	C(2)–Fe(1)–P(1)	90.4(2)
C(3)–Fe(1)–P(1)	90.00(17)	C(3)–Fe(1)–Cl(1)	84.93(16)
C(1)–Fe(1)–P(2)	88.6(2)	P(1)–Fe(1)–Cl(1)	88.28(7)
C(2)–Fe(1)–P(2)	91.3(2)	P(2)–Fe(1)–Cl(1)	92.49(7)
C(3)–Fe(1)–P(2)	88.34(17)	O(1)–C(1)–Fe(1)	179.3(6)
P(1)–Fe(1)–P(2)	178.10(6)	O(2)–C(2)–Fe(1)	177.7(6)
C(1)–Fe(1)–Cl(1)	176.5(2)	Cl(2)–C(3)–Fe(1)	119.7(3)
C(2)–Fe(1)–Cl(1)	88.2(2)		

## Experimental Section

**General Data.** All preparations were carried out under an atmosphere of nitrogen by conventional Schlenk techniques.<sup>37</sup> Diethyl ether was dried with 4 Å molecular sieves.<sup>38</sup> All other solvents used in the preparations were dried by standard methods.<sup>39</sup> Chromatographic separations were performed on 2 × 20 cm columns of silica gel 60 (40–63 μm) cooled to –20 °C.

IR spectra were recorded on a Bio-Rad FTS-45 instrument. Mass spectra (EI) were run on a Finnigan MAT 8400 mass spectrometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were taken on a Varian Gemini-200 instrument operating at 200 and 50.3 MHz, respectively [ $\delta$  (ppm) relative to TMS,  $J$  (Hz)], and <sup>31</sup>P NMR spectra on a Varian-Gemini 300 at 121.5 MHz. The phosphorus chemical shifts [ $\delta$  (ppm)] are reported referenced to 85% H<sub>3</sub>PO<sub>4</sub> as an external standard.

**Materials.** A 1.5 mol/L cyclohexane solution of lithium diisopropylamide, methyl chloroacetate, methyl bromoacetate, ethyl iodoacetate, 2-(bromomethyl)-1,3-dioxalane, 3-(bromomethyl)-2,4,10-trioxadadamantane, and 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU) were used as received from commercial suppliers. Trimethylchlorosilane was distilled before use. Fe(CO)<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>Br<sub>2</sub> and I<sub>2</sub> were prepared by following a literature

procedure,<sup>40</sup> and HC(SiMe<sub>3</sub>)=C=O was obtained according to ref 41. **15a,b** were prepared according to ref 28.

**Preparation of Dicarboxylhalo((alkoxycarbonyl)methyl)bis(triethylphosphane)iron, Fe(CO)<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>(X)-(CH<sub>2</sub>COOR) (X = Cl, R = Me, **2a**; X = Br, R = Me, **2b**; X = I, R = Et, **2c**).** A mixture of 1.20 g (2.0 mmol) of Fe(CO)<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>I<sub>2</sub> in 250 mL of ether was stirred with sodium amalgam ( $\leq 1\%$ , ca. 15 mmol of Na) at –25 °C under 1 atm of N<sub>2</sub>. After 3 h the supernatant suspension was transferred to a frit via a canula. Cold filtration through Celite and reaction of the thus obtained yellow solution of the dinitrogen iron complexes **1a,b** with an excess of the corresponding haloacetic acid ester yielded the thermally stable complexes **2a–c**.

**2a:** 0.43 g (4.0 mmol) of methyl chloroacetate. Column chromatography and elution with hexane/ether from 8:1 to 2:1 (bright yellow fraction). Yield: 0.51 g (55%). Anal. Calcd for C<sub>17</sub>H<sub>35</sub>ClFeO<sub>4</sub>P<sub>2</sub>: C, 44.71; H, 7.72; Fe, 12.23. Found: C, 44.69; H, 8.00; Fe, 12.64. IR (hexane):  $\nu$  (cm<sup>-1</sup>) = 2004, 1944 (s, C≡O), 1703 (w, br, C=O). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 0.95 (dt, <sup>3</sup>J<sub>HH</sub> = 7.5, <sup>3</sup>J<sub>PH</sub> = 14.5, P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>), 1.88–2.03 (m, P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>), 2.51 (t, <sup>3</sup>J<sub>PH</sub> = 9.6, CH<sub>2</sub>COOCH<sub>3</sub>), 3.56 (s, OCH<sub>3</sub>). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 7.5 (s, P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>), 16.1 (t, <sup>2</sup>J<sub>PC</sub> = 15, CH<sub>2</sub>-COOCH<sub>3</sub>), 16.9 (pseudo-t,  $J_{\text{virt}}$  = 12, P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>), 49.5 (s, OCH<sub>3</sub>), 182.9 (s, COOCH<sub>3</sub>), 211.2 (t, <sup>2</sup>J<sub>PC</sub> = 21, C≡O), 216.8 (t, <sup>2</sup>J<sub>PC</sub> = 25, C≡O). <sup>31</sup>P NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 35.0. MS (EI, 70 eV):  $m/z$  (%) = 428 [M<sup>+</sup> – CO], 400 [M<sup>+</sup> – 2CO], 327 (100) [Fe(PEt<sub>3</sub>)<sub>2</sub>Cl]<sup>+</sup>, 292 [Fe(PEt<sub>3</sub>)<sub>2</sub>]<sup>+</sup>, 209 [Fe(PEt<sub>3</sub>)Cl]<sup>+</sup>, 146, 118 [PEt<sub>3</sub>]<sup>+</sup>, 103, 90, 62.

**2b:** 0.61 g (4.0 mmol) of methyl bromoacetate. Column chromatography and elution with hexane/ether from 10:1 to 4:1 (orange brown fraction). Yield: 0.69 g (69%). Anal. Calcd for C<sub>17</sub>H<sub>35</sub>BrFeO<sub>4</sub>P<sub>2</sub>: C, 40.74; H, 7.04; Fe, 11.14. Found: C, 40.63; H, 7.06; Fe, 11.13. IR (hexane):  $\nu$  (cm<sup>-1</sup>) = 2003, 1944 (s, C≡O), 1703 (w, br, C=O). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 0.96 (dt, <sup>3</sup>J<sub>HH</sub> = 7.6, <sup>3</sup>J<sub>PH</sub> = 14.4, P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>), 1.94–2.09 (m, P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>), 2.60 (t, <sup>3</sup>J<sub>PH</sub> = 9.8, CH<sub>2</sub>COOCH<sub>3</sub>), 3.58 (s, OCH<sub>3</sub>). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 8.1 (s, P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>), 13.6 (t, <sup>2</sup>J<sub>PC</sub> = 14, CH<sub>2</sub>-COOCH<sub>3</sub>), 18.0 (pseudo-t,  $J_{\text{virt}}$  = 12, P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>), 49.7 (s, OCH<sub>3</sub>), 182.9 (s, COOCH<sub>3</sub>), 211.1 (t, <sup>2</sup>J<sub>PC</sub> = 20, C≡O), 217.8 (t, <sup>2</sup>J<sub>PC</sub> = 25, C≡O). <sup>31</sup>P NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 32.8. MS (EI, 70 eV):  $m/z$  (%) = 474 [M<sup>+</sup> – CO], 446 [M<sup>+</sup> – 2CO], 373 (100) [Fe(PEt<sub>3</sub>)<sub>2</sub>Br]<sup>+</sup>, 292 [Fe(PEt<sub>3</sub>)<sub>2</sub>]<sup>+</sup>, 255 [Fe(PEt<sub>3</sub>)Br]<sup>+</sup>, 175, 146, 118 [PEt<sub>3</sub>]<sup>+</sup>, 103, 90, 75, 74, 62.

**2c:** 0.86 g (4.0 mmol) of ethyl iodoacetate. Column chromatography and elution with hexane/ether from 10:1 to 4:1 (dark red fraction). Yield: 0.86 g (76%). Anal. Calcd for C<sub>18</sub>H<sub>37</sub>FeIO<sub>4</sub>P<sub>2</sub>: C, 38.46; H, 6.63; Fe, 9.93. Found: C, 38.76; H, 6.54; Fe, 10.27. IR (hexane):  $\nu$  (cm<sup>-1</sup>) = 1999, 1943 (s, C≡O), 1689 (m, C=O). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 0.95 (dt, <sup>3</sup>J<sub>HH</sub> = 7.6, <sup>3</sup>J<sub>PH</sub> = 14.8, P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>), 1.08 (t, <sup>3</sup>J<sub>HH</sub> = 7.1, OCH<sub>2</sub>CH<sub>3</sub>), 1.97–2.18 (m, P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>), 2.61 (t, <sup>3</sup>J<sub>PH</sub> = 9.9, CH<sub>2</sub>COOEt), 4.16 (q, <sup>3</sup>J<sub>HH</sub> = 7.1, OCH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 8.2 (s, P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>), 8.4 (t, <sup>2</sup>J<sub>PC</sub> = 14, CH<sub>2</sub>COOEt), 14.4 (s, OCH<sub>2</sub>CH<sub>3</sub>), 19.1 (pseudo-t,  $J_{\text{virt}}$  = 12, P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>), 58.4 (s, OCH<sub>2</sub>CH<sub>3</sub>), 183.5 (s, COOEt), 212.6 (t, <sup>2</sup>J<sub>PC</sub> = 20, C≡O), 219.5 (t, <sup>2</sup>J<sub>PC</sub> = 25, C≡O). <sup>31</sup>P NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 29.8. MS (EI, 70 eV):  $m/z$  (%) = 562 (<1%) [M<sup>+</sup>], 534 [M<sup>+</sup> – CO], 506 [M<sup>+</sup> – 2CO], 419 (100) [Fe(PEt<sub>3</sub>)<sub>2</sub>I]<sup>+</sup>, 301 [Fe(PEt<sub>3</sub>)I]<sup>+</sup>, 292 [Fe(PEt<sub>3</sub>)<sub>2</sub>]<sup>+</sup>, 118 [PEt<sub>3</sub>]<sup>+</sup>, 90, 62.

**trans-Dicarbonyliodo((ethoxycarbonyl)acetyl)bis(triethylphosphane)iron(II) (4).** At room temperature 5.6 g (1.0 mmol) of **2c** dissolved in 100 mL hexane was stirred in an autoclave for 30 h under 20 bar CO. An IR spectrum of a sample was quickly taken through a siphon, which showed characteristic bands of **4**.

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IR (hexane):  $\nu$  ( $\text{cm}^{-1}$ ) = 2040 (w), 1960 (s,  $\text{C}=\text{O}$ ), 1746 (m,  $\text{C}(\text{O})\text{OEt}$ ), 1607 (m,  $\eta^1(\text{CO})$ ).

**Preparation of Carbonylhalobis(triethylphosphane)-[1-((trimethylsilyloxy)-2-(alkoxycarbonyl)ethenyl)]-iron,  $\text{Fe}(\text{CO})(\text{PETe}_3)_2(\text{X})[\text{C}(\text{OSiMe}_3)\text{CHCOOR}]$  (X = Cl, R = Me, **7a**; X = Br, R = Me, **7b**; X = I, R = Et, **7c**).** To an ether solution (35 mL) of 1.0 mmol **2a–c** was added dropwise 0.70 mL (1.05 mmol) of a 1.5 mL cyclohexane solution of lithium diisopropylamide in THF at  $-50^\circ\text{C}$ . After 10 min 0.63 mL (5.00 mmol) of trimethylchlorosilane was added and the reaction mixture was slowly warmed to room temperature. Evaporation of the solvent, extraction with hexane, filtration over Celite, and crystallization at  $-30^\circ\text{C}$  yielded the complexes **7a–c**.

**7a.** Yield: 0.29 g (55%). Anal. Calcd for  $\text{C}_{20}\text{H}_{43}\text{ClFeO}_4\text{P}_2$ -Si: C, 45.41; H, 8.20; Fe, 10.56. Found: C, 45.64; H, 8.02; Fe, 10.52. IR (hexane):  $\nu$  ( $\text{cm}^{-1}$ ) = 1932 (s,  $\text{C}=\text{O}$ ), 1562 (w,  $\text{C}=\text{O}$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 0.23 (s,  $\text{Si}(\text{CH}_3)_3$ ), 1.11 (dt,  $^3J_{\text{HH}} = 7.5$ ,  $^3J_{\text{PH}} = 14.5$ ,  $\text{P}(\text{CH}_2\text{CH}_3)_3$ ), 1.62–1.82 (m,  $\text{P}(\text{CH}_2\text{CH}_3)_3$ ), 3.81 (s,  $\text{OCH}_3$ ), 5.02 (t,  $^4J_{\text{PH}} = 2.0$ ,  $\text{CH-}$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  =  $-0.3$  (s,  $\text{Si}(\text{CH}_3)_3$ ), 7.5 (s,  $\text{P}(\text{CH}_2\text{CH}_3)_3$ ), 14.7 (pseudo-t,  $J_{\text{virt}} = 11$ ,  $\text{P}(\text{CH}_2\text{CH}_3)_3$ ), 52.4 (s,  $\text{OCH}_3$ ), 96.9 (s,  $=\text{CH-}$ ), 179.1 (s,  $\text{C}(\text{O})\text{Ome}$ ), 219.6 (t,  $^2J_{\text{PC}} = 32$ ,  $\text{C}=\text{O}$ ), 267.3 (t,  $^2J_{\text{PC}} = 24$ ,  $\text{Fe-C}=\text{CHR}$ ).  $^{31}\text{P}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  = 39.2. MS (EI, 70 eV):  $m/z$  (%) = 528 (<1%) [ $\text{M}^{+}$ ], 500 [ $\text{M}^{+} - \text{CO}$ ], 402, 382 (100) [ $\text{M}^{+} - \text{CO}$ ,  $\text{PETe}_3$ ], 209 [ $\text{Fe}(\text{PETe}_3)\text{Cl}$ ] $^{+}$ , 143, 118 [ $\text{PETe}_3$ ] $^{+}$ , 90, 73, 62.

**7b.** Yield: 0.37 g (65%). Anal. Calcd for  $\text{C}_{20}\text{H}_{43}\text{BrFeO}_4\text{P}_2$ -Si: C, 41.90; H, 7.56; Fe, 9.74. Found: C, 42.24; H, 7.38; Fe, 9.99. IR (hexane):  $\nu$  ( $\text{cm}^{-1}$ ) = 1933 (s,  $\text{C}=\text{O}$ ), 1563 (w,  $\text{C}=\text{O}$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 0.27 (s,  $\text{Si}(\text{CH}_3)_3$ ), 1.14 (dt,  $^3J_{\text{HH}} = 7.5$ ,  $^3J_{\text{PH}} = 14.1$ ,  $\text{P}(\text{CH}_2\text{CH}_3)_3$ ), 1.64–1.89 (m,  $\text{P}(\text{CH}_2\text{CH}_3)_3$ ), 3.83 (s,  $\text{OCH}_3$ ), 5.02 (t,  $^4J_{\text{PH}} = 2.0$ ,  $\text{CH-}$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  =  $-0.23$  (s,  $\text{Si}(\text{CH}_3)_3$ ), 8.1 (s,  $\text{P}(\text{CH}_2\text{CH}_3)_3$ ), 16.1 (pseudo-t,  $J_{\text{virt}} = 11$ ,  $\text{P}(\text{CH}_2\text{CH}_3)_3$ ), 52.2 (s,  $\text{OCH}_3$ ), 97.5 (s,  $=\text{CH-}$ ), 180.0 (s,  $\text{C}(\text{O})\text{Ome}$ ), 221.1 (t,  $^2J_{\text{PC}} = 32$ ,  $\text{C}=\text{O}$ ), 269.7 (t,  $^2J_{\text{PC}} = 24$ ,  $\text{Fe-C}=\text{CHR}$ ).  $^{31}\text{P}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  = 37.0. MS (EI, 70 eV):  $m/z$  (%) = 574 (<1%) [ $\text{M}^{+}$ ], 546 (17) [ $\text{M}^{+} - \text{CO}$ ], 428 [ $\text{M}^{+} - \text{CO}$ ,  $\text{PETe}_3$ ], 402 [ $\text{M}^{+} - 2\text{CO}$ ,  $\text{PETe}_3$ ], 373 (100) [ $\text{Fe}(\text{PETe}_3)_2\text{Br}$ ] $^{+}$ , 348 [ $\text{M}^{+} - \text{CO}$ ,  $\text{PETe}_3$ , Br], 292 [ $\text{Fe}(\text{PETe}_3)_2$ ] $^{+}$ , 255 [ $\text{Fe}(\text{PETe}_3)\text{Br}$ ] $^{+}$ , 118 [ $\text{PETe}_3$ ] $^{+}$ .

**7c.** Yield: 0.31 g (49%). Anal. Calcd for  $\text{C}_{21}\text{H}_{45}\text{FeIO}_4\text{P}_2$ -Si: C, 39.75; H, 7.15; Fe, 8.80. Found: C, 39.48; H, 6.92; Fe, 9.12. IR (hexane):  $\nu$  ( $\text{cm}^{-1}$ ) = 1932 (s,  $\text{C}=\text{O}$ ), 1557 (w,  $\text{C}=\text{O}$ ).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  = 0.14 (s,  $\text{Si}(\text{CH}_3)_3$ ), 1.04 (t,  $^3J_{\text{HH}} = 7.2$ ,  $\text{OCH}_2\text{CH}_3$ ), 1.11 (dt,  $^3J_{\text{HH}} = 7.4$ ,  $^3J_{\text{PH}} = 14.3$ ,  $\text{P}(\text{CH}_2\text{CH}_3)_3$ ), 1.76–1.93 (m,  $\text{P}(\text{CH}_2\text{CH}_3)_3$ ), 4.17 (q,  $^3J_{\text{HH}} = 7.2$ ,  $\text{OCH}_2\text{CH}_3$ ), 5.14 (t,  $^4J_{\text{PH}} = 2.0$ ,  $=\text{CH-}$ ).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  =  $-0.4$  (s,  $\text{Si}(\text{CH}_3)_3$ ), 8.3 (s,  $\text{P}(\text{CH}_2\text{CH}_3)_3$ ), 14.3 (s,  $\text{OCH}_2\text{CH}_3$ ), 17.5 (pseudo-t,  $J_{\text{virt}} = 11$ ,  $\text{P}(\text{CH}_2\text{CH}_3)_3$ ), 61.1 (s,  $\text{OCH}_2\text{CH}_3$ ), 97.6 (s,  $=\text{CH-}$ ), 180.8 (s,  $\text{C}(\text{O})\text{OEt}$ ), 222.8 (t,  $^2J_{\text{PC}} = 31$ ,  $\text{C}=\text{O}$ ), 270.3 (t,  $^2J_{\text{PC}} = 24$ ,  $\text{Fe-C}=\text{CHR}$ ).  $^{31}\text{P}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  = 34.1. MS (EI, 70 eV):  $m/z$  (%) = 606 [ $\text{M}^{+} - \text{CO}$ ], 548, 488 [ $\text{M}^{+} - \text{CO}$ ,  $\text{PETe}_3$ ], 430, 361, 301 [ $\text{Fe}(\text{PETe}_3)\text{I}$ ] $^{+}$ , 292 [ $\text{Fe}(\text{PETe}_3)_2$ ] $^{+}$ , 175, 147 (100), 118 [ $\text{PETe}_3$ ] $^{+}$ , 103, 90, 73, 62. MS (FAB, THF, NBOH matrix):  $m/z$  (%) = 506, 435, 419 (100) [ $\text{Fe}(\text{PETe}_3)_2\text{I}$ ] $^{+}$ , 338, 301 [ $\text{Fe}(\text{PETe}_3)\text{I}$ ] $^{+}$ , 219, 119.

**Preparation of Dicarbonyl[ $\eta^2$ -alkoxycarbonyl]ethenone-*C,O*]bis(triethylphosphane)iron,  $\text{Fe}(\text{CO})_2(\text{PETe}_3)_2[\text{OCCCH}(\text{COOR})]$  (R = Me, **8a** $^{\text{Z}}$ ; R = Et, **8b** $^{\text{Z}}$ ), and Dicarbonyl(1-alkoxy-1,3-dioxopropene-3-yl)bis(triethylphosphane)iron,  $\text{Fe}(\text{CO})_2(\text{PETe}_3)_2(\text{COCHCOOR})$  (R = Me, **9a**; R = Et, **9b**).** To a solution of 1.0 mmol of **2a** (50 mL of THF) or **2c** (50 mL of ether) was added 0.38 g (2.50 mmol) of DBU. The reaction mixture was stirred under 1 bar of CO for 3 h at room temperature and the solvent evaporated in vacuo. By column chromatography of the oily residues over silica and elution with 1:1 hexane/ether yellow zones of (**8a,b**) $^{\text{Z}}$  were collected. Elution with 9:1 ether/THF afforded orange fractions of **9a,b**. Evaporation of the solvent gave the pure complexes.

**8a** $^{\text{Z}}$ . Yield: 0.01 g (<2%). Anal. Calcd for  $\text{C}_{18}\text{H}_{34}\text{FeO}_5\text{P}_2$ : C, 48.24; H, 7.65; Fe, 12.46. Found: C, 48.44; H, 7.33; Fe, 13.17. IR (hexane):  $\nu$  ( $\text{cm}^{-1}$ ) = 1993, 1929 (s,  $\text{C}=\text{O}$ ), 1694 (w,  $\text{C}=\text{O}$ ), 1593 (w,  $\text{C}_2\text{O}$ ).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  = 0.83 (dt,  $^3J_{\text{HH}} = 7.6$ ,  $^3J_{\text{PH}} = 15.2$ ,  $\text{P}(\text{CH}_2\text{CH}_3)_3$ ), 1.32–1.51 (m,  $\text{P}(\text{CH}_2\text{CH}_3)_3$ ), 3.86 (s,  $\text{OCH}_3$ ), 5.81 (t,  $^3J_{\text{PH}} = 2.8$ ,  $=\text{CH}$ ).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  = 7.5 (s,  $\text{P}(\text{CH}_2\text{CH}_3)_3$ ), 16.8 (pseudo-t,  $J_{\text{virt}} = 12$ ,  $\text{P}(\text{CH}_2\text{CH}_3)_3$ ), 50.0 (s,  $\text{OCH}_3$ ), 74.3 (s,  $=\text{CH-}$ ), 172.0 (s,  $\text{C}(\text{O})\text{Ome}$ ), 196.0 (t,  $^2J_{\text{PC}} = 17$ ,  $\text{C}=\text{CHR}$ ), 213.8 (t,  $^2J_{\text{PC}} = 20$ ,  $\text{C}=\text{O}$ ), 218.8 (t,  $^2J_{\text{PC}} = 29$ ,  $\text{C}=\text{O}$ ).  $^{31}\text{P}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  = 53.0. MS (EI, 70 eV):  $m/z$  (%) = 448 (<1) [ $\text{M}^{+}$ ], 392 (<1) [ $\text{M}^{+} - 2\text{CO}$ ], 348 [ $\text{Fe}(\text{CO})_2(\text{PETe}_3)_2$ ] $^{+}$ , 320 [ $\text{Fe}(\text{CO})(\text{PETe}_3)_2$ ] $^{+}$ , 292 (100) [ $\text{Fe}(\text{PETe}_3)_2$ ] $^{+}$ , 264, 236, 175, 146, 118 [ $\text{PETe}_3$ ] $^{+}$ , 97, 71, 57.

**8b** $^{\text{Z}}$ . Yield: 0.03 g (5%). Anal. Calcd for  $\text{C}_{19}\text{H}_{36}\text{FeO}_5\text{P}_2$ : C, 49.37; H, 7.85; Fe, 12.08. Found: C, 48.83; H, 7.43; Fe, 12.07. IR (hexane):  $\nu$  ( $\text{cm}^{-1}$ ) = 1992, 1928 (s,  $\text{C}=\text{O}$ ), 1689 (w,  $\text{C}=\text{O}$ ), 1594 (w,  $\text{C}_2\text{O}$ ).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  = 0.84 [dt,  $^3J_{\text{HH}} = 7.5$ ,  $^3J_{\text{PH}} = 15.3$ ,  $\text{P}(\text{CH}_2\text{CH}_3)_3$ ], 1.29 (t,  $^3J_{\text{HH}} = 7.1$ ,  $\text{OCH}_2\text{CH}_3$ ), 1.33–1.49 (m,  $\text{P}(\text{CH}_2\text{CH}_3)_3$ ), 4.45 (q,  $^3J_{\text{HH}} = 7.1$ ,  $\text{OCH}_2\text{CH}_3$ ), 5.79 (t,  $^3J_{\text{PH}} = 2.7$ ,  $=\text{CH-}$ ).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  = 7.2 (s,  $\text{P}(\text{CH}_2\text{CH}_3)_3$ ), 15.1 (s,  $\text{OCH}_2\text{CH}_3$ ), 16.4 (pseudo-t,  $J_{\text{virt}} = 12$ ,  $\text{P}(\text{CH}_2\text{CH}_3)_3$ ), 57.7 (s,  $\text{OCH}_2\text{CH}_3$ ), 74.3 (s,  $=\text{CH-}$ ), 171.5 (s,  $\text{C}(\text{O})\text{OEt}$ ), 196.1 (t,  $^2J_{\text{PC}} = 17$ ,  $\text{C}=\text{CHR}$ ), 214.1 (t,  $^2J_{\text{PC}} = 20$ ,  $\text{C}=\text{O}$ ), 219.0 (t,  $^2J_{\text{PC}} = 29$ ,  $\text{C}=\text{O}$ ).  $^{31}\text{P}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  = 53.0. MS (EI, 70 eV):  $m/z$  (%) = 462 (<3) [ $\text{M}^{+}$ ], 406 [ $\text{M}^{+} - 2\text{CO}$ ], 348 [ $\text{Fe}(\text{CO})_2(\text{PETe}_3)_2$ ] $^{+}$ , 320 [ $\text{Fe}(\text{CO})(\text{PETe}_3)_2$ ] $^{+}$ , 292 (100) [ $\text{Fe}(\text{PETe}_3)_2$ ] $^{+}$ , 264, 236, 175, 174, 146, 118 [ $\text{PETe}_3$ ] $^{+}$ , 90, 62.

**9a.** Yield: 0.39 g (87%). Anal. Calcd for  $\text{C}_{18}\text{H}_{34}\text{FeO}_5\text{P}_2$ : C, 48.24; H, 7.65; Fe, 12.46. Found: C, 48.27; H, 7.40; Fe, 12.86. IR (hexane):  $\nu$  ( $\text{cm}^{-1}$ ) = 1995, 1933 (s,  $\text{C}=\text{O}$ ), 1601 (w,  $\text{C}=\text{O}$ ), 1543 (w,  $\text{C}_2\text{O}$ ).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  = 0.95 [dt,  $^3J_{\text{HH}} = 7.5$ ,  $^3J_{\text{PH}} = 14.9$ ,  $\text{P}(\text{CH}_2\text{CH}_3)_3$ ], 1.55–1.70 [m,  $\text{P}(\text{CH}_2\text{CH}_3)_3$ ], 3.40 (s,  $\text{OCH}_3$ ), 5.09 (s,  $=\text{CH-}$ ).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  = 7.5 (s,  $\text{P}(\text{CH}_2\text{CH}_3)_3$ ), 17.0 (pseudo-t,  $J_{\text{virt}} = 12$ ,  $\text{P}(\text{CH}_2\text{CH}_3)_3$ ), 51.9 (s,  $\text{OCH}_3$ ), 86.2 (s,  $=\text{CH-}$ ), 183.3 (s,  $\text{C}(\text{O})\text{Ome}$ ), 208.6 (t,  $^2J_{\text{PC}} = 10$ ,  $\text{C}=\text{O}$ ), 214.63 (t,  $^2J_{\text{PC}} = 28$ ,  $\text{C}=\text{O}$ ), 237.7 (t,  $^2J_{\text{PC}} = 18$ ,  $\text{Fe-C}(\text{O})\text{R}$ ).  $^{31}\text{P}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  = 45.3. MS (EI, 70 eV):  $m/z$  (%) = 448 (<2) [ $\text{M}^{+}$ ], 392 [ $\text{M}^{+} - 2\text{CO}$ ], 348 [ $\text{Fe}(\text{CO})_2(\text{PETe}_3)_2$ ] $^{+}$ , 320 [ $\text{Fe}(\text{CO})(\text{PETe}_3)_2$ ] $^{+}$ , 292 (100) [ $\text{Fe}(\text{PETe}_3)_2$ ] $^{+}$ , 264, 236, 205, 175, 146, 118 [ $\text{PETe}_3$ ] $^{+}$ , 103, 90, 62.

**9b.** Yield: 0.38 g (82%). Anal. Calcd for  $\text{C}_{19}\text{H}_{36}\text{FeO}_5\text{P}_2$ : C, 49.37; H, 7.85; Fe, 12.08. Found: C, 48.91; H, 7.40; Fe, 12.00. IR (hexane):  $\nu$  ( $\text{cm}^{-1}$ ) = 1994, 1932 (s,  $\text{C}=\text{O}$ ), 1599 (w,  $\text{C}=\text{O}$ ), 1537 (w,  $\text{C}_2\text{O}$ ).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  = 0.97 (dt,  $^3J_{\text{HH}} = 7.5$ ,  $^3J_{\text{PH}} = 14.9$ ,  $\text{P}(\text{CH}_2\text{CH}_3)_3$ ), 1.11 (t,  $^3J_{\text{HH}} = 7.1$ ,  $\text{OCH}_2\text{CH}_3$ ), 1.57–1.72 (m,  $\text{P}(\text{CH}_2\text{CH}_3)_3$ ), 3.90 (q,  $^3J_{\text{HH}} = 7.1$ ,  $\text{OCH}_2\text{CH}_3$ ), 5.08 (s,  $=\text{CH-}$ ).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  = 7.9 [s,  $\text{P}(\text{CH}_2\text{CH}_3)_3$ ], 15.2 (s,  $\text{OCH}_2\text{CH}_3$ ), 17.5 (pseudo-t,  $J_{\text{virt}} = 12$ ,  $\text{P}(\text{CH}_2\text{CH}_3)_3$ ), 60.7 (s,  $\text{OCH}_2\text{CH}_3$ ), 86.6 (s,  $=\text{CH-}$ ), 183.0 [s,  $\text{C}(\text{O})\text{Ome}$ ], 208.5 (t,  $^2J_{\text{PC}} = 10$ ,  $\text{C}=\text{O}$ ), 214.4 (t,  $^2J_{\text{PC}} = 28$ ,  $\text{C}=\text{O}$ ), 237.3 (s,  $^2J_{\text{PC}} = 18$ ,  $\text{Fe-C}(\text{O})\text{R}$ ).  $^{31}\text{P}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  = 45.4. MS (EI, 70 eV):  $m/z$  (%) = 462 (<1) [ $\text{M}^{+}$ ], 406 [ $\text{M}^{+} - 2\text{CO}$ ], 348 [ $\text{Fe}(\text{CO})_2(\text{PETe}_3)_2$ ] $^{+}$ , 320 [ $\text{Fe}(\text{CO})(\text{PETe}_3)_2$ ] $^{+}$ , 292 (100) [ $\text{Fe}(\text{PETe}_3)_2$ ] $^{+}$ , 264, 236, 175, 174, 146, 118 [ $\text{PETe}_3$ ] $^{+}$ , 103, 90, 62.

**Preparation of Bromodicarbonyl(alkoxyethyl)bis(triethylphosphane)iron,  $\text{Fe}(\text{CO})_2(\text{PETe}_3)_2(\text{X})(\text{CH}_2\text{R})$  (R = OMe, **10a**; R = 1,3-Dioxolan-2-yl, **10b**; R = 2,4,10-Trioxadamantan-3-yl, **10c**).** A 1.02 g (2.0 mmol) amount of  $\text{Fe}(\text{CO})_2(\text{PETe}_3)_2\text{Br}_2$  suspended in 150 mL of ether was stirred with sodium amalgam ( $\leq 1\%$ , ca. 15 mmol of Na) at  $-25^\circ\text{C}$  under a steady stream of  $\text{N}_2$ . After 3 h the supernatant suspension was transferred to a frit via a canula. Cold filtration through Celite and reaction of the yellow solution of the dinitrogen iron complexes **1a,b** with an excess of the corresponding halo organyl compound yielded the thermally stable complexes **10a–c**.

**10a:** 0.62 g (0.77 mmol) of chloromethyl methyl ether. (*Caution! This compound is a severe carcinogen.*) Column chromatography and elution with 20:1 hexane/ether (yellow zone). Yellow crystals from hexane at  $-80^\circ\text{C}$ . Yield: 0.38 g (45%). Anal. Calcd for  $\text{C}_{16}\text{H}_{35}\text{ClFeO}_3\text{P}_2$ : C, 44.83; H, 8.23;

Fe, 13.03. Found: C, 44.68; H, 8.34; Fe, 12.59. IR (hexane):  $\nu$  ( $\text{cm}^{-1}$ ) = 1999, 1940 (s, C=O).  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ , 200 MHz):  $\delta$  = 1.00 (dt,  $^3J_{\text{HH}} = 7.2$ ,  $^3J_{\text{PH}} = 15.0$  Hz, 18 H,  $(\text{CH}_2\text{CH}_3)$ ), 1.74–1.92 m, 12 Hz,  $\text{CH}_2\text{CH}_3$ ), 3.39 (s, 3 H,  $\text{CH}_2\text{OCH}_3$ ), 4.72 (t,  $^3J_{\text{PH}} = 7.1$  Hz, 2 H  $\text{CH}_2\text{OCH}_3$ ).  $^{13}\text{C NMR}$  ( $\text{C}_6\text{D}_6$ , 50.3 MHz):  $\delta$  = 8.1 (s,  $\text{CH}_2\text{CH}_3$ ), 17.2 (pseudo-t,  $J_{\text{PC}} = 12$  Hz,  $\text{CH}_2\text{CH}_3$ ), 63.4 (s,  $\text{CH}_2\text{CH}_3$ ), 82.5 (t,  $^2J_{\text{PC}} = 19$  Hz,  $\text{CH}_2\text{OCH}_3$ ), 210.5 t,  $^2J_{\text{PC}} = 17$  Hz, C=O), 218.7 (t,  $^2J_{\text{PC}} = 26$  Hz, C=O).  $^{31}\text{P NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  = 38.5. MS (70 eV):  $m/z$  (%) = 400 [ $\text{M}^+ - \text{CO}$ ], 327 [ $\text{Fe}(\text{PET}_3)_2\text{Cl}$ ] $^+$ , 292 (100) [ $\text{Fe}(\text{PET}_3)_2$ ] $^+$ , 209 [ $\text{Fe}(\text{PET}_3\text{Cl})$ ] $^+$ , 146, 118 [ $\text{PET}_3$ ] $^+$ , 90, 62.

**10b**: 0.66 g (4.0 mmol) of 2-(bromomethyl)-1,3-dioxalane. Evaporation of the reaction mixture, extraction of the oily residue with hexane, and crystallization at  $-80^\circ\text{C}$  yielded 0.60 g (58%) of **10b** as a brown orange powder.

Anal. Calcd for  $\text{C}_{18}\text{H}_{37}\text{BrFeO}_5\text{P}_2$ : C, 41.97; H, 7.24; Fe, 10.84. Found: C, 42.79; H, 7.33; Fe, 10.24. IR (hexane):  $\nu$  ( $\text{cm}^{-1}$ ) = 1994, 1934 (s, C=O).  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  = 0.98 (dt,  $^3J_{\text{HH}} = 7.2$ ,  $^3J_{\text{PH}} = 14.1$ ,  $\text{P}(\text{CH}_2\text{CH}_3)_3$ ), 1.80–2.05 (m,  $\text{P}(\text{CH}_2\text{CH}_3)_3$ ), 2.54 (dt,  $^3J_{\text{HH}} = 3.8$ ,  $^3J_{\text{PH}} = 8.1$ ,  $\text{FeCH}_2\text{CH}(\text{OR})_2$ ), 3.47, 3.66 (m,  $-\text{OCH}_2\text{CH}_2\text{O}-$ ), 5.36 (t,  $^3J_{\text{HH}} = 3.8$ ,  $\text{FeCH}_2\text{CH}(\text{OR})_2$ ).  $^{13}\text{C NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  = 7.9 (s,  $\text{P}(\text{CH}_2\text{CH}_3)_3$ ), 17.6 (pseudo-t,  $J_{\text{virt}} = 12$ ,  $\text{P}(\text{CH}_2\text{CH}_3)_3$ ), 24.5 (s (br),  $\text{FeCH}_2\text{CH}(\text{OR})_2$ ), 64.5 (s,  $\text{OCH}_2\text{CH}_2\text{O}$ ), 108.9 (s,  $\text{FeCH}_2\text{CH}(\text{OR})_2$ ), 211.9 (t,  $^2J_{\text{PC}} = 21$ , C=O (trans to  $\text{CH}_2\text{CH}(\text{OR})_2$ )), 226 (s (br), C=O (trans to Br)).  $^{31}\text{P NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  = 35.1.

**10c**: 0.47 g (2.00 mmol) of 3-(bromomethyl)-2,4,10-trioxadamantane. Column chromatography and elution with hexane/ethyl acetate from 4:1 to 2:1 (orange fraction). Yield: 0.46 g (40%). Anal. Calcd for  $\text{C}_{22}\text{H}_{41}\text{BrFeO}_5\text{P}_2$ : C, 45.30; H, 7.09; Fe, 9.57. Found: C, 45.61; H, 7.14; Fe, 9.56. IR (hexane):  $\nu$  ( $\text{cm}^{-1}$ ) = 1996, 1937 (s, C=O).  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  = 0.98–1.10 (m,  $\text{P}(\text{CH}_2\text{CH}_3)_3$  and  $H_{\text{eq}}$  (ortho ester)), 1.95–2.00 (m,  $\text{P}(\text{CH}_2\text{CH}_3)_3$ ), 2.38, 2.43 (m,  $H_{\text{ax}}$  (ortho ester)), 2.49 (t,  $^3J_{\text{PH}} = 10.7$ ,  $\text{FeCH}_2\text{C}(\text{OR})_3$ ), 4.05 (m,  $\text{OCHRR}'$ ).  $^{13}\text{C NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  = 7.8 (s,  $\text{P}(\text{CH}_2\text{CH}_3)_3$ ), 17.8 (pseudo-t,  $J_{\text{virt}} = 12$ ,  $\text{P}(\text{CH}_2\text{CH}_3)_3$ ), 26.0 (s (br),  $\text{FeCH}_2\text{R}$ ), 32.7 (s,  $-\text{CH}_2-$  (ortho ester)), 67.9 (s,  $\text{OCHRR}'$ ), 116.3 (s,  $\text{FeCH}_2\text{C}(\text{OR})_3$ ), 210.7 (t,  $^2J_{\text{PC}} = 19$ , C=O (trans to  $\text{CH}_2\text{R}$ )), 219 (s (br), C=O (trans to Br)).  $^{31}\text{P NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  = 34.7. MS (EI, 70 eV):  $m/z$  (%) = 556 (<1%) [ $\text{M}^+ - \text{CO}$ ], 410 [ $\text{M}^+ - 2\text{CO}$ ,  $\text{PET}_3$ ], 376 [ $\text{Fe}(\text{PET}_3)_2(\text{CO})_3$ ] $^+$ , 371 [ $\text{Fe}(\text{PET}_3)_2\text{Br}$ ] $^+$ , 320, 292 [ $\text{Fe}(\text{PET}_3)_2$ ] $^+$ , 264, 253 [ $\text{Fe}(\text{PET}_3\text{Br})$ ] $^+$ , 156, 146, 118 [ $\text{PET}_3$ ] $^+$ , 115, 103, 96, 90 (100), 75, 67, 62, 43.

**Reactions of 10a–c with 1 bar of CO.** A solution of 0.8 mmol of any of the derivatives **10a–c** in hexane was stirred at room temperature under 1 bar of CO. IR spectra were taken after 1 h and 1 d, which showed no change and indicated the presence of **12a** and its cis isomer or **12b,c**. Removal of the solvent resulted in oils, which could only partly redissolved in hexane. The IR spectra of these solutions showed the presence of **10a–c** and other unidentified products.

**12a and Cis Isomer.** IR (hexane):  $\nu$  ( $\text{cm}^{-1}$ ) = 2012, 1953 (s, C=O) (cis isomer), 1972 (s, C=O) (**12a**).

**12b.** IR (hexane):  $\nu$  ( $\text{cm}^{-1}$ ) = 2044 (w, C=O), 1960 (s, C=O), 1601 (w, C=O).

**12c.** IR (hexane):  $\nu$  ( $\text{cm}^{-1}$ ) = 2043 (w, C=O), 1958 (s, C=O), 1598 (w, C=O).

**Preparation of Dicarbonyl[ $\eta^2$ -(alkoxyalkyl)ethenone-C,O]bis(triethylphosphane)iron, *E/Z*- $\text{Fe}(\text{CO})_2(\text{PET}_3)_2$ -(COCHR) (**R** = 1,3-Dioxolan-2-yl, **13b<sup>E,Z</sup>**; **R** = 2,4,10-Trioxadamantan-3-yl, **13c<sup>E,Z</sup>**).** A 0.30 g (2.0 mmol) amount of DBU was added to a solution of 1.0 mmol of **10b** or **10c** in 80 mL of ether at room temperature. After being stirred for several hours under 1 bar of CO (IR monitoring: **10b**, 24 h; **10c**, 3 h), the reaction mixture was filtered over Celite. The solvent was evaporated *in vacuo*, and the residue was extracted with hexane. Crystallization at  $-80^\circ\text{C}$  yielded the yellow complexes **13b<sup>Z</sup>** and **13b<sup>Z</sup>**.

**13b<sup>Z</sup>.** Yield: 0.25 g (55%). Anal. Calcd for  $\text{C}_{19}\text{H}_{36}\text{FeO}_5\text{P}_2$ : C, 49.37; H, 7.85; Fe, 12.08. Found: C, 49.19; H, 7.68; Fe, 12.06. The spectroscopic data in solution refer to a mixture

of **13b<sup>E</sup>** and **13b<sup>Z</sup>**. IR (hexane):  $\nu$  ( $\text{cm}^{-1}$ ) = 1979, 1910 (s, C=O), 1660 (w,  $\text{C}_2\text{O}$ ).  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ ): **13b<sup>Z</sup>**,  $\delta$  = 5.25 (dt,  $^3J_{\text{HH}} = 8.3$ ,  $^4J_{\text{PH}} = 3.1$ ,  $\text{CHCH}(\text{OR})_2$ ), 6.29 (d,  $^3J_{\text{HH}} = 8.3$ ,  $\text{C}=\text{CHCH}(\text{OR})_2$ ); **13b<sup>E</sup>**,  $\delta$  = 4.65 (dt,  $^3J_{\text{HH}} = 7.7$  Hz,  $^4J_{\text{PH}} = 1.8$  Hz, 1H,  $\text{C}=\text{CHCH}(\text{OR})_2$ ), 6.16 (d,  $^3J_{\text{HH}} = 7.7$  Hz, 1H,  $\text{C}=\text{CHCH}(\text{OR})_2$ ). Data for both isomers:  $\delta$  = 0.91 (dt,  $^3J_{\text{HH}} = 7.6$ ,  $^3J_{\text{PH}} = 15.2$   $\text{P}(\text{CH}_2\text{CH}_3)_3$ ), 1.38–1.71 (m,  $\text{P}(\text{CH}_2\text{CH}_3)_3$ ), 3.65–3.86 (m,  $\text{OCH}_2\text{CH}_2\text{O}-$ ).  $^{13}\text{C NMR}$  ( $\text{C}_6\text{D}_6$ ): **13b<sup>Z</sup>**,  $\delta$  = 7.36 (s,  $\text{P}(\text{CH}_2\text{CH}_3)_3$ ), 16.5 (pt,  $J_{\text{virt}} = 12$ ,  $\text{P}(\text{CH}_2\text{CH}_3)_3$ ), 64.4 (s,  $-\text{OCH}_2\text{CH}_2\text{O}-$ ), 72.6 (s,  $\text{C}=\text{CHCH}(\text{OR})_2$ ), 110.6 (s,  $\text{C}=\text{CHCH}(\text{OR})_2$ ), 179.1 (t,  $^2J_{\text{PC}} = 16$ ,  $\eta^2\text{-O}=\text{C}$ ), 214.1 (t,  $^2J_{\text{PC}} = 20$ , C=O), 220.6 (t,  $^2J_{\text{PC}} = 29$ , C=O); **13b<sup>E</sup>**,  $\delta$  = 7.51 (s,  $\text{P}(\text{CH}_2\text{CH}_3)_3$ ), 16.6 (pt,  $J_{\text{virt}} = 12$ ,  $\text{P}(\text{CH}_2\text{CH}_3)_3$ ), 64.1 (s,  $-\text{OCH}_2\text{CH}_2\text{O}-$ ), 75.8 (s,  $\text{C}=\text{CHCH}(\text{OR})_2$ ), 105.2 (s,  $\text{C}=\text{CHCH}(\text{OR})_2$ ), 178.7 (t,  $^2J_{\text{PC}} = 17$ ,  $\eta^2\text{-O}=\text{C}$ ), 214.1 (t,  $^2J_{\text{PC}} = 19$ , C=O), 219.7 (t,  $^2J_{\text{PC}} = 29$ , C=O).  $^{31}\text{P NMR}$  ( $\text{C}_6\text{D}_6$ ): **13b<sup>Z</sup>**,  $\delta$  = 54.3; **13b<sup>E</sup>**,  $\delta$  = 54.4. MS (EI, 70 eV):  $m/z$  (%) = 462 (<1%) [ $\text{M}^+$ ], 348 [ $\text{M}^+ - \text{ketene}$ ], 320 [ $\text{Fe}(\text{PET}_3)_2\text{CO}$ ] $^+$ , 292 (100) [ $\text{Fe}(\text{PET}_3)_2$ ] $^+$ , 264, 236, 215, 175, 174, 146, 118 [ $\text{PET}_3$ ] $^+$ , 90, 62.

**13c<sup>Z</sup>.** Yield: 0.24 g (45%). Anal. Calcd for  $\text{C}_{23}\text{H}_{40}\text{FeO}_6\text{P}_2$ : C, 41.97; H, 7.24; Fe, 10.84. Found: C, 42.79; H, 7.33; Fe, 10.24. The spectroscopic data refer to a mixture of **13c<sup>E</sup>** and **13c<sup>Z</sup>**. IR (hexane):  $\nu$  ( $\text{cm}^{-1}$ ) = 1978, 1911 (s, C=O), 1653 (w,  $\text{C}_2\text{O}$ ).  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ ): **13c<sup>Z</sup>**,  $\delta$  = 4.31 (m, 1H,  $\text{OC}/\text{HRR}'$ ), 5.32 (t,  $^4J_{\text{PH}} = 3.1$ , 1H,  $\text{C}=\text{CHC}(\text{OR})_3$ ); **13c<sup>E</sup>**,  $\delta$  = 4.16 (m, 1H,  $\text{OCHRR}'$ ), 4.70 (t,  $^4J_{\text{PH}} = 2.0$ , 1H,  $\text{C}=\text{CHC}(\text{OR})_3$ ). Data for both isomers:  $\delta$  = 0.97 (dt,  $^3J_{\text{HH}} = 7.5$ ,  $^3J_{\text{PH}} = 14.9$ ,  $\text{P}(\text{CH}_2\text{CH}_3)_3$ ), 1.16, 1.22 (each m,  $H_{\text{eq}}$  ortho ester), 1.45–1.64, 1.67–1.86 (each m,  $\text{P}(\text{CH}_2\text{CH}_3)_3$ ), 2.51, 257 (each m,  $H_{\text{ax}}$  ortho ester).  $^{13}\text{C NMR}$  ( $\text{C}_6\text{D}_6$ ): **13c<sup>Z</sup>**,  $\delta$  = 7.5 (s,  $\text{P}(\text{CH}_2\text{CH}_3)_3$ ), 16.3 (pt,  $J_{\text{virt}} = 12$ ,  $\text{P}(\text{CH}_2\text{CH}_3)_3$ ), 33.3 (s,  $-\text{CH}_2-$  ortho ester), 67.8 (s,  $\text{OCHRR}'$ ), 77.9 (s,  $\text{C}=\text{CHC}(\text{OR})_3$ ), 112.3 (s,  $\text{C}=\text{CHC}(\text{OR})_3$ ), 175.8 (t,  $^2J_{\text{PC}} = 16.9$ ,  $\eta^2\text{-O}=\text{C}$ ), 214.3 (t,  $^2J_{\text{PC}} = 20$ , C=O), 221 (t,  $^2J_{\text{PC}} = 29$ , C=O); **13c<sup>E</sup>**,  $\delta$  = 7.6 (s,  $\text{P}(\text{CH}_2\text{CH}_3)_3$ ), 16.6 (pt,  $J_{\text{virt}} = 12$ ,  $\text{P}(\text{CH}_2\text{CH}_3)_3$ ), 33.1 (s,  $-\text{CH}_2-$  ortho ester), 68 (s,  $\text{OCHRR}'$ ), 79.4 (s,  $\text{C}=\text{CHC}(\text{OR})_3$ ), 110.7 (s,  $\text{C}=\text{CHC}(\text{OR})_3$ ), 173.9 (t,  $^2J_{\text{PC}} = 16$ ,  $\eta^2\text{-O}=\text{C}$ ), 214.3 (t,  $^2J_{\text{PC}} = 20$ , C=O), 220.2 (t,  $^2J_{\text{PC}} = 29$ , C=O).  $^{31}\text{P NMR}$  ( $\text{C}_6\text{D}_6$ ): **13c<sup>E</sup>** and **13c<sup>Z</sup>**,  $\delta$  = 55.4. MS (EI, 70 eV):  $m/z$  (%) = 530 (<1%) [ $\text{M}^+$ ], 502 (<1%) [ $\text{M}^+ - \text{CO}$ ], 474 (<1%) [ $\text{M}^+ - 2\text{CO}$ ], 348 [ $\text{M}^+ - \text{ketene}$ ], 320 [ $\text{Fe}(\text{PET}_3)_2\text{CO}$ ] $^+$ , 292 (100) [ $\text{Fe}(\text{PET}_3)_2$ ] $^+$ , 264, 236, 215, 175, 174, 146, 118 [ $\text{PET}_3$ ] $^+$ , 90, 62.

**Dicarbonylchloro(chloromethyl)bis(triethylphosphane)iron (14a), Dicarbonyliodo(iodomethyl)bis(triethylphosphane)iron (14b), and Dicarbonyl(cyano-methyl)iodobis(triethylphosphane)iron (14c).** A 1.12 g (2.0 mmol) amount of  $\text{Fe}(\text{CO})_2\text{PET}_3)_2\text{I}_2$  suspended in 150 mL of ether was stirred with sodium amalgam ( $\leq 1\%$ , ca. 15 mmol of Na) at  $-25^\circ\text{C}$  under a steady stream of  $\text{N}_2$ . After 3 h the supernatant suspension was transferred to a frit via a canula. Cold filtration through Celite was followed by the reaction of the yellow solution of the dinitrogen iron complexes **1a,b** with an excess of the corresponding dihalomethylene or iodocyanomethylene compound. After removal of the solvent *in vacuo*, the residues were subjected to individual workup.

**14a:** 0.2 mL (3.1 mmol) of  $\text{CH}_2\text{Cl}_2$ . Extraction with hexane, partial removal of the solvent *in vacuo*. Crystallization at  $-30^\circ\text{C}$ . Yield: 450 mg (52%). Anal. Calcd for  $\text{C}_{15}\text{H}_{32}\text{Cl}_2\text{FeO}_2\text{P}_2$ : C, 41.59; H, 7.44; Fe, 12.89. Found: C, 41.16; H, 7.49; Fe, 13.04. IR (hexane):  $\nu$  ( $\text{cm}^{-1}$ ) = 2007, 1949 (s, C=O).  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ , 200 Mz):  $\delta$  = 0.91 (dt,  $^3J_{\text{HH}} = 7.4$  Hz,  $^3J_{\text{PH}} = 14.3$  Hz, 18 H,  $\text{CH}_2\text{CH}_3$ ), 1.71–1.85 (m, 12 H,  $\text{CH}_2\text{CH}_3$ ), 4.45 (t,  $^3J_{\text{PH}} = 9.1$  Hz, 2 H,  $\text{CH}_2\text{Cl}$ ).  $^{13}\text{C NMR}$  ( $\text{C}_6\text{D}_6$ , 50.3 MHz):  $\delta$  = 7.5 (s,  $\text{CH}_2\text{CH}_3$ ), 16.5 (pt,  $J_{\text{PC}} = 12$  Hz,  $\text{CH}_2\text{CH}_3$ ), 46.3 (t,  $^2J_{\text{PC}} = 21$ ,  $\text{CH}_2\text{Cl}$ ), 210.3 (t,  $^2J_{\text{PC}} = 18$  Hz, C=O), 215.7 (t,  $^2J_{\text{PC}} = 26$  Hz, C=O).  $^{31}\text{P NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  = 36.3. MS (70 eV):  $m/z$  (%) = 404 [ $\text{M}^+ - \text{CO}$ ], 376 [ $\text{M}^+ - 2\text{CO}$ ], 327 (100) [ $\text{M}^+ - 2\text{CO}$ ,  $\text{CH}_2\text{Cl}$ ], 292 [ $\text{Fe}(\text{PET}_3)_2$ ] $^+$ , 209 [ $\text{Fe}(\text{PET}_3\text{Cl})$ ] $^+$ , 118 [ $\text{PET}_3$ ] $^+$ , 90, 62.

**14b:** 0.54 g (2.0 mmol) of  $\text{CH}_2\text{I}_2$ . Extraction with hexane, partial removal of the solvent *in vacuo*, and crystallization at  $-30^\circ\text{C}$ . Yield: 591 mg (48%). Anal. Calcd for  $\text{C}_{15}\text{H}_{32}\text{I}_2$

FeO<sub>2</sub>P<sub>2</sub>: C, 29.24; 5.23; Fe, 9.06. Found: C, 29.39; H, 5.34; Fe, 9.56. IR (hexane):  $\nu$  (cm<sup>-1</sup>) = 2003, 1949 (s, C=O). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 0.88 (dt, <sup>3</sup>J<sub>HH</sub> = 7.4 Hz, <sup>3</sup>J<sub>PH</sub> = 14.4 Hz, 18 H, CH<sub>2</sub>CH<sub>3</sub>), 1.83–1.99 (m, 12 H, CH<sub>2</sub>CH<sub>3</sub>), 3.57 (t, <sup>3</sup>J<sub>PH</sub> = 9.9 Hz, 2 H, CH<sub>2</sub>I). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 0 °C):  $\delta$  = 2.2 (t, <sup>2</sup>J<sub>PC</sub> = 22 Hz, CH<sub>2</sub>I), 8.0 (s, CH<sub>2</sub>CH<sub>3</sub>), 18.0 (pseudo-t, J<sub>PC</sub> = 12 Hz, CH<sub>2</sub>-CH<sub>3</sub>), 210.2 (t, <sup>2</sup>J<sub>PC</sub> = 19 Hz, C=O), 219.2 (t, <sup>2</sup>J<sub>PC</sub> = 26 Hz, C=O). MS (70 eV):  $m/z$  (%) = 602 [M<sup>+</sup> - CH<sub>2</sub>], 546 [M<sup>+</sup> - CH<sub>2</sub>, 2CO], 475 [M<sup>+</sup> - CH<sub>2</sub>I], 419 (100) [Fe(PET<sub>3</sub>)<sub>2</sub>I]<sup>+</sup>, 301 [Fe-(PET<sub>3</sub>)I]<sup>+</sup>, 292 [Fe(PET<sub>3</sub>)<sub>2</sub>]<sup>+</sup>, 174 [Fe(PET<sub>3</sub>)]<sup>+</sup>, 146, 118 [PET<sub>3</sub>]<sup>+</sup>, 90, 62.

**14c**: 0.67 g (4.0 mmol) of ICH<sub>2</sub>CN. Column chromatography; elution with 10:1 hexane/ether resulted in a first zone, which was discarded. Elution with 1:1 hexane/ethyl acetate yielded then an orange-red band of **14c**. After removal of the solvent red-brown analytically pure **14c** remained. Yield: 400 mg (39%). Anal. Calcd for C<sub>16</sub>H<sub>32</sub>FeINO<sub>2</sub>P<sub>2</sub>: C, 37.30; H, 6.26; Fe, 10.84. Found: C, 37.02; H, 6.07; Fe, 10.81. IR (ether):  $\nu$  (cm<sup>-1</sup>) = 2198 (w, C≡N), 2007, 1952 (s, C=O). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 200 MHz):  $\delta$  = 0.84 (dt, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, <sup>3</sup>J<sub>PH</sub> = 14.7 Hz, 18H, P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>), 1.72–2.00 (m, 14H, P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub> and CH<sub>2</sub>CN), <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 50.3 MHz):  $\delta$  = -14.3 (s, CH<sub>2</sub>CN), 8.1 (s, P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>), 18.9 (pseudo-t, J<sub>virt</sub> = 12 Hz, P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>), 212.8 (t, <sup>2</sup>J<sub>PC</sub> = 20 Hz, C=O (trans CH<sub>2</sub>CN)), 220.1 (t, <sup>2</sup>J<sub>PC</sub> = 25 Hz, C=O). <sup>31</sup>P NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 29.9. MS (EI, 70 eV):  $m/z$  (%) = 515 [M<sup>+</sup>], 475 [M<sup>+</sup> - CH<sub>2</sub>CN], 459 [M<sup>+</sup> - 2CO], 419 (100) [Fe(PET<sub>3</sub>)<sub>2</sub>I]<sup>+</sup>, 376 [Fe(PET<sub>3</sub>)<sub>2</sub>(CO)<sub>3</sub>]<sup>+</sup>, 320 [Fe(PET<sub>3</sub>)<sub>2</sub>CO]<sup>+</sup>, 292 [Fe(PET<sub>3</sub>)<sub>2</sub>]<sup>+</sup>, 118 [PET<sub>3</sub>]<sup>+</sup>, 90, 62.

**Preparation of Dicarbonyliodobis(triethylphosphane)-(trimethylsilyl)acetyliron (16c)**. A solution of the complexes **1a,b** was prepared in ether from 740 mg (1.23 mmol) of Fe(CO)<sub>2</sub>(PET<sub>3</sub>)<sub>2</sub>I<sub>2</sub> as described above and reacted with 396 mg (1.85 mmol) of (iodomethyl)trimethylsilane. Evaporation of the solvent, extraction with hexane, filtration over Celite, and stirring of the red filtrate under 1 bar of CO afforded 213 mg (30%) of the yellow complex **16c** after crystallization at -80 °C from a concentrated solution. The complex was spectroscopically pure; however, no satisfactory elemental analysis could be obtained.

IR (ether):  $\nu$  (cm<sup>-1</sup>) = 2036 (w), 1956 (s, C=O), 1589 (m, C=O). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  = 0.09 (s, 9H, CH<sub>2</sub>Si(CH<sub>3</sub>)<sub>3</sub>), 1.00 (dt, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, <sup>3</sup>J<sub>PH</sub> = 14.9 Hz, 18H, P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>), 1.86 (m, 12H, P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>), 2.81 (s, 2H, CH<sub>2</sub>Si(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  = -0.9 (s, 9H, CH<sub>2</sub>Si(CH<sub>3</sub>)<sub>3</sub>), 7.8 (s, P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>), 20.08 (pt, J<sub>virt</sub> = 13 Hz, P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>), 58.5 (t, <sup>3</sup>J<sub>PC</sub> = 2 Hz, CH<sub>2</sub>-Si(CH<sub>3</sub>)<sub>3</sub>), 215.8 (t, <sup>2</sup>J<sub>PC</sub> = 25 Hz, C=O), 273.4 (t, <sup>2</sup>J<sub>PC</sub> = 19 Hz, C(O)CH<sub>2</sub>Si(CH<sub>3</sub>)<sub>3</sub>). <sup>31</sup>P NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 32.0.

**Attempts of the Preparation of Dicarbonyl(ethenone)-bis(triethylphosphane)iron (17a) and Dicarbonyl(prop-1-en-1-one)bis(triethylphosphane)iron (17b)**. At room temperature 1 mmol of **15a,b** was dissolved in THF and hexane, respectively, and 2 mmol of DBU was added. The reaction mixture was flushed with CO, and the progress of the reaction to **17a,b** was monitored by IR.

**17a**: very slow reaction, which could not be taken to completeness; preferred formation of **18**. Yield: ca. 10% of **17a** after 5 d. IR:  $\nu$  (cm<sup>-1</sup>) = 1970 (m, CO), 1900 (st, CO).

**17b**: evolution of the  $\nu$ (CO) bands, see Figure 1. IR:  $\nu$  (cm<sup>-1</sup>) = 1973 (m, CO), 1904 (st, CO).

**NMR Tube Experiment for the DBU Assisted Preparation of Dicarbonyl[ $\eta^2$ -(trimethylsilyl)ethenone-C,O]-bis(triethylphosphane)iron (17c)**. A 24.0 mg (3.99 × 10<sup>-3</sup> mmol) amount of the acyl compound **16c** was dissolved in 0.60 mL of C<sub>6</sub>D<sub>6</sub>, transferred into a NMR tube placed in a Schlenk tube, and cooled to 0 °C. A 9.0 mg (5.77 × 10<sup>-3</sup> mmol) amount DBU in 0.20 mL of C<sub>6</sub>D<sub>6</sub> was carefully added and frozen. The flask was evacuated and filled with CO. In the sealed NMR tube the reaction mixture was then allowed to warm to room

Table 6

reacn time (min)	16c <sup>a</sup>	17c <sup>a</sup>	18 <sup>a</sup>
5	76	14	10
20	74	9	17
50	61	21	18
105	50	13	37
195	31	20	49
300	9	4	87
420	7	3	90

<sup>a</sup> Relative concentrations in % from <sup>31</sup>P NMR data.

temperature. The reaction was monitored by <sup>31</sup>P NMR and <sup>1</sup>H NMR spectroscopy (see Table 6).

**Preparation of Dicarbonyl[ $\eta^2$ -(trimethylsilyl)ethenone-C,O]bis(triethylphosphane)iron (17c) from 1a,b and HC-(SiMe<sub>3</sub>)=C=O**. A 480 mg (0.79 mmol) amount of Fe(CO)<sub>2</sub>(PET<sub>3</sub>)<sub>2</sub>I<sub>2</sub> was reduced in ether as described above and reacted with 180 mg (1.25 mmol) of (trimethylsilyl)ketene. The solvent was removed in vacuo at 0 °C to yield 347 mg (95%) of **17c**. Anal. Calcd for C<sub>19</sub>H<sub>40</sub>FeO<sub>3</sub>P<sub>2</sub>Si: C, 49.32; H, 8.72; Fe, 12.08. Found: C, 49.16; H, 8.91; Fe, 12.02. IR (ether):  $\nu$  (cm<sup>-1</sup>) = 1973, 1905 (s, CO), 1608 (m, C<sub>2</sub>O). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 0.14 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>), 0.93 (dt, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, <sup>3</sup>J<sub>PH</sub> = 15.1 Hz, 18H, P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>), 1.35–1.62 (m, 12H, P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>), 3.89 (t, <sup>4</sup>J<sub>PH</sub> = 2.3 Hz, 1H, C=CHCSiMe<sub>3</sub>). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 1.1 (s, Si(CH<sub>3</sub>)<sub>3</sub>), 7.9 (s, P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>), 17.2 (pseudo-t, J<sub>virt</sub> = 12 Hz, P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>), 64.6 (s, C=CHCSiMe<sub>3</sub>), 182.4 (t, <sup>2</sup>J<sub>PC</sub> = 15 Hz,  $\eta^2$ -C,O), 213.5 (t, <sup>2</sup>J<sub>PC</sub> = 20 Hz, CO), 220.1 (t, <sup>2</sup>J<sub>PC</sub> = 30 Hz, CO). <sup>31</sup>P NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 54.3. MS (EI, 70 eV):  $m/z$  (%) = 462 (<1) [M<sup>+</sup>], 348 [M<sup>+</sup> - ketene], 320 [Fe(PET<sub>3</sub>)<sub>2</sub>CO]<sup>+</sup>, 292 (100) [Fe(PET<sub>3</sub>)<sub>2</sub>]<sup>+</sup>, 264, 146, 118 [PET<sub>3</sub>]<sup>+</sup>, 90.

**Spectroscopic Pursuit of the Reaction of 17c with Fe-(CO)<sub>2</sub>(PET<sub>3</sub>)<sub>2</sub>I<sub>2</sub>**. To a solution of 22.1 mg (4.78 × 10<sup>-3</sup> mmol) of **17c** in 5 mL of diethyl ether was added a solution of 60.3 mg (10.0 × 10<sup>-3</sup> mmol) of Fe(CO)<sub>2</sub>(PET<sub>3</sub>)<sub>2</sub>I<sub>2</sub>. The reaction was monitored by <sup>31</sup>P NMR and IR spectroscopy. After approximately 1 h complete conversion to Fe(CO)<sub>3</sub>(PET<sub>3</sub>)<sub>2</sub> and free (trimethylsilyl)ketene was observed. A brown, oily, and spectroscopically inactive residue remained. In a control experiment the decay of pure **17c** was pursued under the same conditions. After 2 h slow formation of the free ketene, Fe-(CO)<sub>3</sub>(PET<sub>3</sub>)<sub>2</sub>, and Fe(CO)<sub>2</sub>(PET<sub>3</sub>)<sub>3</sub> (10% each) together with Fe-(CO)<sub>2</sub>(PET<sub>3</sub>)<sub>2</sub>(HC(SiMe<sub>3</sub>)=C=O) (80%) was noticed.

**Reaction of 17c with CO**. 120 mg (0.26 mmol) amount of the ketene complex **17c** was dissolved in 20 mL of hexane and stirred in a Schlenk tube under 1 bar of CO. After 2 h the formation of Fe(CO)<sub>3</sub>(PET<sub>3</sub>)<sub>2</sub> was complete. All volatile components were distilled off and monitored by GC. (Trimethylsilyl)ketene was identified by comparison with the authentic material. The residue was identified spectroscopically as **18**. IR (hexane): HC(SiMe<sub>3</sub>)=C=O,  $\nu$  (cm<sup>-1</sup>) = 2118 (m,  $\nu$ (CCO)); **18**, 1876 (s,  $\nu$ (CO)). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): **18**,  $\delta$  = 1.06 (m, 18H, P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>), 1.57 (m, 12H, P(CH<sub>2</sub>CH<sub>3</sub>)). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 8.0 (s, P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>), 28.9 (pt, <sup>3</sup>J<sub>PC</sub> = 15 Hz, P(CH<sub>2</sub>-CH<sub>3</sub>)<sub>3</sub>), 215.8 (t, <sup>2</sup>J<sub>PC</sub> = 29 Hz, CO). <sup>31</sup>P NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 70.2.

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**Supporting Information Available**: Tables of crystal data and structure refinement parameters, atomic coordinates, bond lengths, bond angles, anisotropic displacement parameters, and hydrogen coordinates of **7a**, **8a<sup>z</sup>**, **9b**, and **14a** (23 pages). Ordering information is given on any current masthead page.

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