183. Synthesis and Structure of a New Type of Chiral Organoiron and Organoruthenium Complexes[1])

by **Christoph M. Adams, Andreas Hafner, Markus Koller, Alessandro Marcuzzi, Roland Prewo, Isabel Solana, Beverly Vincent**, and **Wolfgang von Philipsborn***

Organisch-Chemisches Institut der Universität Zürich, Winterthurerstrasse 190, CH–8057 Zürich

(28.IX.89)

The synthesis of 36 $[Fe(CO)_2L^1(\eta^4\text{-diene})]$, three $[Fe(CO)_2L^1(\eta^4\text{-enone})]$, and five $[Ru(CO)_2L^1(\eta^4\text{-diene})]$ complexes ($L^1 = Ph_3P$, Et_3P, $(EtO)_3P$, $(MeO)_3P$, $C_6H_{11}NC$) by thermal, selective CO ligand displacement in the corresponding tricarbonyl precursor complexes is described. In a second step, photochemical CO displacement by another phosphorus ligand L^2 leads to a new type of η^4-diene complexes with a centre of chirality at the metal atom (Fe, Ru). 23 Fe and three Ru complexes of this type have been prepared and characterized. In the case of complexes with unsymmetrical dienes, racemic diastereoisomers are formed which can be separated by chromatographic methods. The molecular structures of $[Fe(CO)(Ph_3P)((MeO)_3P)$(buta-1,3-diene)] (**52**), $[Fe(CO)(Ph_3P)((MeO)_3P)$(isoprene)] (**58**) and $[Fe(CO)(Et_3P)(EtO)_3P)$(hexa-2,4-dienal)] (**62a**) were determined by X-ray diffraction. All complexes were investigated by ^{13}C-, ^{31}P- and, in part, ^1H-NMR spectroscopy. At low temperatures, conformational isomers (rotamers) can be differentiated which probably arise from ψ rotation at the coordinated metal centre.

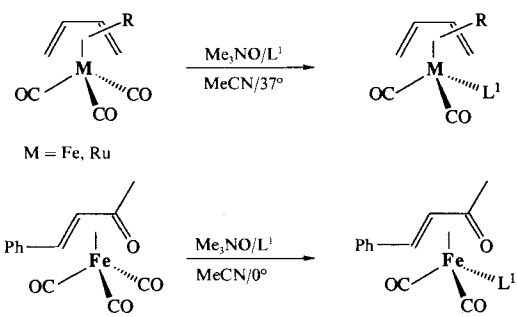
Introduction. – The $Fe(CO)_3$ moiety has been shown to act as a protecting and stabilizing group which can be used to modify the reactivity of diene systems [1]. In particular, functionalized, $[Fe(CO)_3$(butadiene)] complexes have proven to be useful synthons in the preparation of chiral molecules [2]. Modification of the tricarbonyl group by a selective replacement of one or more carbon-monoxide groups by phosphine, phosphite, or isonitrile ligands affects the electron density at the metal and thereby also influences the reactivity of the organic ligand [3]. On the other hand, an exchange of two CO groups by two different ligands L^1 and L^2 generates a chirality centre at the metal. The synthesis and resolution of chiral Fe complexes and their use in enantioselective and diastereoselective organic synthesis has become quite widespread [4]. However, chiral Fe complexes of great structural versatility have not been prepared as yet. In addition, the introduction of a chiral ligand offers a further potential for asymmetric induction, but it was shown that the stereoselectivity emanates primarily from the chirality at the Fe centre and that the phosphine chirality plays little or no role at all. This also demonstrates the potential of metal-configuration control in enantioselective catalysis [5]. *Davies* and coworkers have successfully used a chiral acetyliron complex in a variety of reactions with high stereoselectivity [6]. Alternatively, only a few $Ru(CO)_3$ complexes of 1,3-dienes have been synthesized [7], and chiral CO-displacement products are not known, to our knowledge.

[1]) Presented in part at the 'XIIIth International Conference on Organometallic Chemistry', Torino, Sept. 4–9, 1988, and at the 'Autumn Meeting of the Swiss Chemical Society', Berne, Oct. 21, 1988.

In view of these facts, we have investigated synthetic pathways for these types of complexes. We report here the synthesis of dicarbonyl- and monocarbonyl(diene)iron and corresponding Ru complexes. The structures of the novel compounds are elucidated by X-ray diffraction and multinuclear NMR studies. The details of the latter, including low-temperature conformational studies, will be reported in due course.

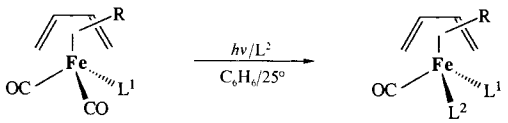
Results and Discussion. – 1. *Syntheses.* Methods for the replacement of one or more carbon-monoxide groups by phosphorus ligands have previously been reported [8], however, they suffer from disadvantages such as relatively drastic conditions, low selectivity, and low yields. This explains, why only few applications of $[Fe(CO)_2L(diene)]$ complexes in organic synthesis have been reported [3] [5a]. We envisaged a number of strategies to achieve selective and stepwise decarbonylation of the tricarbonyl(diene) metal complexes. In particular, the use of oxidizing reagents and complexing solvents was considered. It has been shown that amine oxides can promote complexation of $Fe(CO)_3$ groups to dienes [9]. Furthermore, *Kelly* and *Birch* have reported that $[Fe(CO)_3(cyclohexadiene)]$ complexes react with Me_3NO in the presence of phosphines in boiling acetone to give the corresponding dicarbonyl complexes [10]. Therefore, we used Me_3NO in combination with a ligand in various solvents of which MeCN proved most useful *(Scheme 1)*. The ratio of complex to amine oxide and to ligand is critical for the successful application of this method, and a temperature of 35–40° gave the most consistent results. The (enone)iron complexes react at room temperature, but better yields were achieved at 0°. The reactions were monitored by TLC and are complete after 3–15 h depending on the nature of the diene, ligand, and metal [11].

Scheme 1

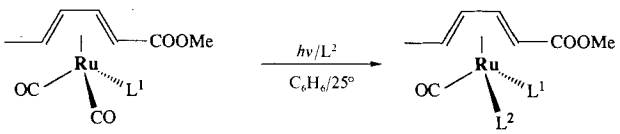


The displacement of a second CO group requires more drastic conditions. UV irradiation [12] of a benzene solution of dicarbonyl complex in the presence of an excess ($\leqslant 2$ equiv.) of ligand L^2 leads to the formation of chiral monocarbonyl complexes *(Scheme 2)*. The irradiation time depends on the diene and ligand used and varies from 1 to 18 h. The reaction can be efficiently monitored by TLC. After chromatographic purification, the products are obtained as yellow-orange oils or crystalline powders. Yields for these reactions range from 40–90% for the first step and 30–90% for the second step for Fe complexes but are lower in the case of Ru. In general, the synthesis of dicarbonylruthenium complexes presents no problems, whereas the preparation of monocarbonylruthenium complexes of functionalized 1,3-dienes *(Scheme 3)* was successful in the case of

Scheme 2

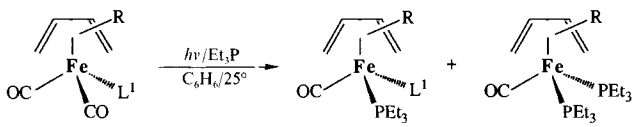


Scheme 3



R = $COOCH_3$, but failed for the corresponding aldehydes because of product instability. For optimization, the sequence of L^1 and L^2 introduction may be inverted. In some cases, when L^2 is Et_3P, a second product is obtained which arises from a different displacement reaction *(Scheme 4)*.

Scheme 4



The versatility of the CO displacement reactions is demonstrated by an application to complexes of mono- and dimethyl-substituted 1,3-dienes, functionalized 1,3-dienes, and enones effecting the introduction of phosphines, phosphites, and isonitriles. *Tables 1* and *2* contain the dienes and ligands used for the preparation of dicarbonyl and monocarbonyl complexes of Fe and Ru.

2. *Structure.* The structures of the products of the CO-displacement reactions were determined by ^{13}C-, ^{31}P-, and, in part, ^1H-NMR spectroscopy and, in three cases, by X-ray diffraction. As expected from the behaviour of the tricarbonyl precursor complexes [13] and other related dicarbonyl complexes [7b] [14], the dicarbonyl and monocarbonyl complexes in solution are also dynamic on the NMR time scale. Thus, at room temperature, the ^{13}C-NMR spectra in the fast-exchange limit allow only the observation of averaged values of chemical shifts and coupling constants. Intermediate exchange rates cause considerable line broadening and loss of spin-coupling information, especially in ^{31}P-NMR spectra. In such cases, low-temperature NMR spectra are necessary for full characterization of the complexes.

The dicarbonyl complexes are achiral for symmetric dienes and exhibit planar chirality in the case of unsymmetric dienes. At low temperature, three conformational isomers (rotamers) **I**, **II**, **III** have to be considered which are interconvertible *via* formal diene rotation (or ψ rotation at the metal centre). These rotamers are potentially distinguishable in solution by NMR spectroscopy. When the diene is symmetric, **II** and **III** form an enantiomeric pair *(Scheme 5)*.

Table 1. *Dienes and Ligands in Dicarbonyl Complexes [M(CO)$_2$L^1(diene)]* (M = Fe, unless indicated otherwise)

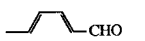
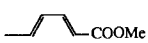
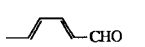
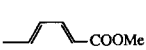
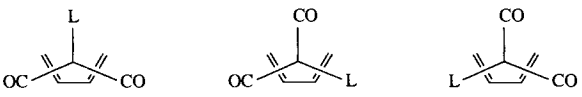
Diene	Ligand L^1 (Compound Number)
	Et_3P (**1**); $(EtO)_3P$ (**2**); $(MeO)_3P$ (**3**); Ph_3P (**4**); C_6H_{11}–NC (**5**)
	Et_3P (**6**); $(EtO)_3P$ (**7**); $(MeO)_3P$ (**8**); Ph_3P (**9**)
	$(EtO)_3P$ (**10**); $(MeO)_3P$ (**11**)
	Et_3P (**12**); $(EtO)_3P$ (**13**); $(MeO)_3P$ (**14**)
	Et_3P (**15**); $(EtO)_3P$ (**16**); $(MeO)_3P$ (**17**)
	Et_3P (**18**); $(EtO)_3P$ (**19**); $(MeO)_3P$ (**20**)
	$(EtO)_3P$ (**21**); $(MeO)_3P$ (**22**)
	Et_3P (**23**); $(EtO)_3P$ (**24**); $(MeO)_3P$ (**25**)
	$(EtO)_3P$ (**26**); $(MeO)_3P$ (**27**)
	Et_3P (**28**)
	Et_3P (**29**); $(EtO)_3P$ (**30**); $(MeO)_3P$ (**31**); Ph_3P (**32**); C_6H_{11}–NC (**33**)
	Et_3P (**34**); $(EtO)_3P$ (**35**); $(MeO)_3P$ (**36**)
	$(EtO)_3P$ (**37**); Ph_3P (**38**); C_6H_{11}–NC (**39**)
	(M = Ru): Et_3P (**40**); $(MeO)_3P$ (**41**)
	(M = Ru): Ph_3P (**42**); $(EtO)_3P$ (**43**); $(MeO)_3P$ (**44**)

Table 2. *Dienes and Ligands in Monocarbonyl Complexes [M(CO)L^{1}L^2(diene)]* (M = Fe, unless indicated otherwise)

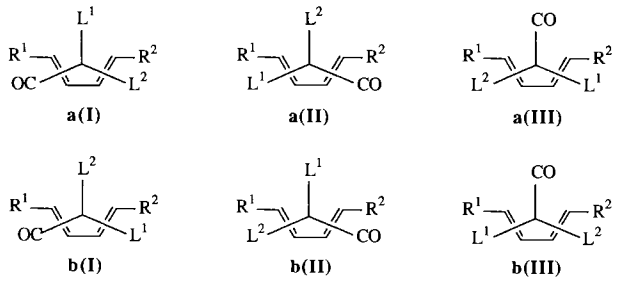
Diene	L^1, L^2 (Compound Number)
	Et_3P, Et_3P (**45**); $(EtO)_3P$, $(EtO)_3P$ (**46**); $(MeO)_3P$, $(MeO)_3P$ (**47**); Et_3P, $(EtO)_3P$ (**48**); Et_3P, $(MeO)_3P$ (**49**); $(EtO)_3P$, $(MeO)_3P$ (**50**); Ph_3P, $(EtO)_3P$ (**51**); Ph_3P, $(MeO)_3P$ (**52**)
	Et_3P, $(MeO)_3P$ (**53**)
	$(EtO)_3P$, $(EtO)_3P$ (**54**); $(MeO)_3P$, $(MeO)_3P$ (**55**); Et_3P, $(MeO)_3P$ (**56**); $(EtO)_3P$, $(MeO)_3P$ (**57**); Ph_3P, $(MeO)_3P$ (**58**)
	$(MeO)_3P$, $(MeO)_3P$ (**59**)
	$(EtO)_3P$, $(EtO)_3P$ (**60**); $(MeO)_3P$, $(MeO)_3P$ (**61**); Et_3P, $(EtO)_3P$ (**62**); $(EtO)_3P$, $(MeO)_3P$ (**63**); Ph_3P, $(MeO)_3P$ (**64**)
	Et_3P, Et_3P (**65**); Et_3P, $(EtO)_3P$ (**66**); $(EtO)_3P$, $(MeO)_3P$ (**67**) (M = Ru): Et_3P $(EtO)_3P$ (**68**); Et_3P, $(MeO)_3P$ (**69**) (M = Ru): $(EtO)_3P$, $(MeO)_3P$ (**70**)

Scheme 5



The monocarbonyl complexes have a centre of chirality at the metal atom and an additional chirality plane in the case of unsymmetric dienes. Therefore, two diastereoisomers **a** and **b** may be obtained, each of which can form three rotamers in solution *(Scheme 6)*. The diastereoisomers are separable by chromatography[2]).

Scheme 6



The chiral Fe and Ru complexes were obtained in racemic form. Attempts for resolution into the pure enantiomers are in progress [15]. ^{31}P-NMR spectra obtained at room temperature show averaged signals for the diastereoisomers **a** and **b**, but at low temperature the rotational process is frozen and sharp resonances of the different rotamers are observed *(Fig. 1)*. The relative intensities are indicative of the rotamer populations.

The CO groups of dicarbonyl compounds are diastereotopic, if the diene is unsymmetric, and two ^{13}C resonances are observed in the fast-exchange limit. Also for monocarbonyl complexes, averaged ^{13}C signals are obtained. In some cases, the diastereoisomers were separated, and the ^{13}C-NMR data of the individual isomers are reported (see *Exper. Part*). Two different ^{2}J(P, C) values are obtained from the CO resonance in both isomers at room temperature, also when the two P ligands are the same (*i.e.* bis-phosphine or bis-phosphite complexes). This reflects the influence of the coordination site on the Fe–P bond. The exchange of one CO group by a P ligand causes a significant deshielding (2–6 ppm) of the remaining CO groups. This effect is more pronounced in the monocarbonyl complexes (4–10 ppm). Moreover, the CO chemical shifts of the functional groups (CHO, COOR) are affected in the same direction, this being an indication for the modified electron-density distribution in the complexes.

Extensive variable-temperature ^{13}C-, ^{17}O-, and ^{31}P-NMR studies on the dicarbonyl and monocarbonyl complexes have been performed to determine the preferred confor-

[2]) The assignments of relative configurations of the diastereoisomers **a** and **b** in *Scheme 6*, *Fig. 1*, and in the *Exper. Part* are arbitrary, except for **58** and **62a**.

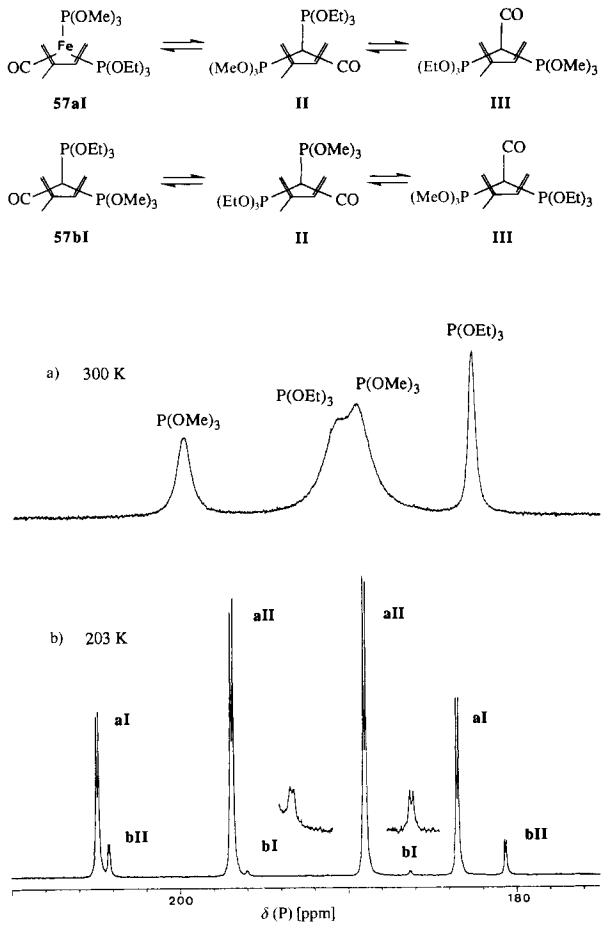


Fig. 1. *^{31}P-NMR Spectra* (162 MHz, (D_6)acetone) *of the mixture of diastereoisomers* **57a** *and* **57b** *of [Fe(CO)((EtO)$_3$P)((MeO)$_3$P)(2-methylbuta-1,3-diene)]. a)* At 300 K, *b)* at 203 K; the rotamers **57aIII** and **57bIII** are not detectable.

mations in solution in comparison with the solid-state structures. The results will be reported in a subsequent communication.

3. *X-Ray Crystallographic Studies.* The solid-state molecular structures of the chiral Fe complexes **52**, **58**, and **62** (isomer **a**) were determined by X-ray diffraction. *Tables 3* and *4* list the crystallographic data and selected bond distances and bond angles, and the molecular structures are illustrated in *Figs. 2–4*. Compounds **58** and **62a** have been separated from the respective mixtures of the diastereoisomers and crystallized from hexane/Et_2O at low temperature; **52** was crystallized from hexane.

The three complexes have a similar atomic disposition. The coordination geometry of the Fe-atom may be described as distorted square pyramid and is essentially the same as in [Fe(CO)$_3$(butadiene)] and other related complexes [16]. The base of the pyramid is

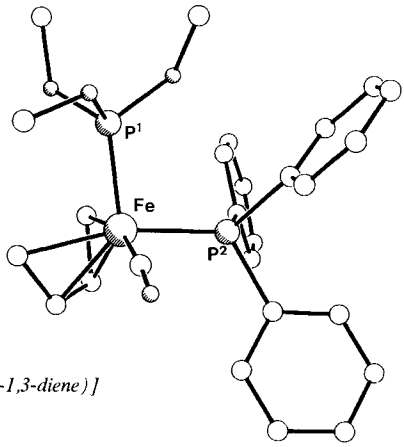


Fig. 2. *Molecular structure of* *[Fe(CO)(Ph$_3$P)((MeO)$_3$P)(buta-1,3-diene)]* (**52**): *(*R*)-isomer*

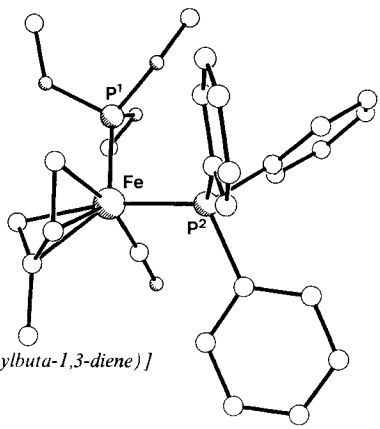


Fig. 3. *Molecular structure of* *[Fe(CO)(Ph$_3$P)((MeO)$_3$P)(2-methylbuta-1,3-diene)]* (**58**): *(*S, pS*)-isomer*

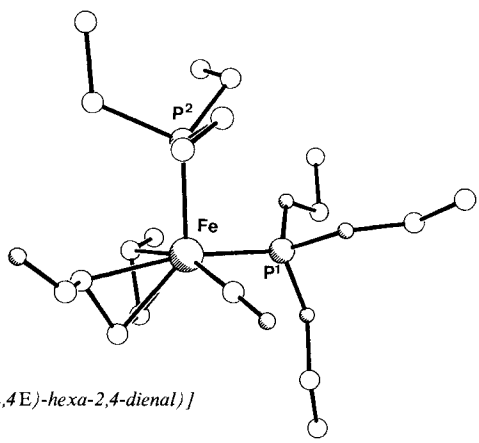


Fig. 4. *Molecular structure of* *[Fe(CO)(Et$_3$P)((EtO)$_3$P)((2*E*,4*E*)-hexa-2,4-dienal)]* (**62a**): *(*S, pS*)-isomer*

Table 3. *Experimental Details and Crystallographic Data*

	52	**58**	**62a**
Molecular Formula	$C_{26}H_{30}FeO_4P_2$	$C_{27}H_{32}FeO_4P_2$	$C_{19}H_{38}FeO_5P_2$
Formula weight	524.32	538.35	464.30
Solvent	hexane	hexane/Et_2O 1:1	hexane/Et_2O 1:1
Crystal color	yellow	yellow	brown-red
Cell Parameters			
No. of reflections refined	24	25	25
Angle range	$32 < 2\Theta < 36$	$20 < 2\Theta < 30$	$42 < 2\Theta < 46$
a [Å]	9.620 (1)	15.448 (6)	9.096 (1)
b [Å]	14.671 (2)	11.251 (3)	15.366 (1)
c [Å]	18.922 (2)	16.307 (4)	18.766 (2)
β [°]	106.34 (1)	106.38 (2)	113.35 (3)
λ [cm^{-1}]	7.37	6.97	7.79
Data Collection			
T [K]	293	293	130
$2\Theta_{max}$ [°]	64	46	64
Reflections collected	9476	5278	9080
Unique reflections	8629	4771	8357
R_{int}	0.022	0.018	0.031
Refinement			
Reflections used in refinement	6274	3463	6798
Criterion to be 'observed'	$I > 2.5\sigma(I)$	$I > 2.5\sigma(I)$	$I > 2.5\sigma(I)$
Least-squares parameters	419	373	402
Weighting scheme ($1/w$)	$\sigma^2(F) + 0.0005\,F^2$	$\sigma^2(F) + 0.0004\,F^2$	$[\sigma^2(F) + 0.0002\,F^2]/[1 - \exp(\sin\Theta/\lambda]$
R, wR	0.039, 0.041	0.039, 0.041	0.036, 0.036
Max, min residual density [e·Å^{-3}]	0.56, −0.47	0.35, −0.22	0.53, −0.44

Table 4. *Selected Bond Lengths* [Å] *and Angles* [°]

	52	**58**	**62a**		**52**	**58**	**62a**
Fe–P(1)	2.138(1)	2.127(1)	2.137(1)	P(1)–Fe–C(2)	90.4(1)	95.5(1)	95.8(1)
Fe–P(2)	2.228(1)	2.220(1)	2.228(1)	P(2)–Fe–C(2)	95.8(1)	163.0(1)	166.4(1)
Fe–C(1)	1.746(2)	1.729(3)	1.756(2)	C(1)–Fe–C(2)	165.0(2)	90.2(2)	95.8(2)
Fe–C(2)	2.104(2)	2.091(4)	2.138(2)	P(1)–Fe–C(3)	128.5(1)	133.5(1)	135.8(1)
Fe–C(3)	2.036(2)	2.063(4)	2.026(1)	P(2)–Fe–C(3)	124.0(1)	122.9(1)	126.4(1)
Fe–C(4)	2.044(2)	2.076(3)	2.059(2)	C(1)–Fe–C(3)	126.2(2)	93.8(2)	92.4(2)
Fe–C(5)	2.102(2)	2.084(4)	2.177(2)	P(1)–Fe–C(4)	131.6(1)	130.8(1)	138.1(1)
C(1)–O(1)	1.157(2)	1.155(4)	1.159(2)	P(2)–Fe–C(4)	163.9(1)	94.3(1)	96.6(1)
C(2)–C(3)	1.422(4)	1.400(5)	1.441(2)	C(1)–Fe–C(4)	94.9(2)	125.3(2)	120.6(2)
C(3)–C(4)	1.398(4)	1.415(6)	1.405(2)	P(1)–Fe–C(5)	94.1(1)	91.9(1)	100.6(1)
C(4)–C(5)	1.416(3)	1.419(6)	1.418(3)	P(2)–Fe–C(5)	89.8(1)	95.2(1)	93.5(1)
C(4)–C(6)		1.496(6)		C(1)–Fe–C(5)	92.0(2)	164.1(2)	159.5(2)
C(2)–C(6)			1.440(2)	Fe–C(1)–O(1)	175.6(2)	177.9(3)	177.0(1)
O(2)–C(6)			1.218(2)	C(2)–C(3)–C(4)	117.6(2)	117.3(4)	116.7(2)
C(5)–C(7)			1.513(3)	C(3)–C(4)–C(5)	116.2(2)	114.9(3)	119.1(1)
P(1)–Fe–P(2)	100.7(1)	101.2(1)	96.7(1)	O(2)–C(6)–C(2)			125.8(2)
P(1)–Fe–C(1)	101.0(1)	102.3(1)	99.6(1)	C(6)–C(2)–C(3)			118.9(2)
P(2)–Fe–C(1)	91.5(1)	89.8(1)	87.3(1)	C(4)–C(5)–C(7)			116.7(2)

defined by the centres of the diene double bonds, the CO ligand, and one P ligand, the second P ligand forming the apex of the pyramid. In both Ph_3P complexes (**52** and **58**), the $(MeO)_3P$ is in the apical site while the CO and Ph_3P ligands are in basal positions. In contrast, the hexadienal complex **62a** shows the basal positions occupied by CO and $(EtO)_3P$ while Et_3P is apical.

The $Fe-P(OR^1)_3$ bond distances are shorter than the corresponding $Fe-PR_3^2$ bond distances in all the three complexes. Therefore, the Fe–P bond lengths are determined by the type of P ligand and not as much by the coordination site. The introduction of a Me group at C(2) of the butadiene ligand has no significant structural consequences, since the bond angles and distances in the first coordination sphere of the Fe-atom are very closely the same in complexes **52** and **58**. The $[Fe(CO)P(OR^1)_3PR_3^2]$ moiety is flattened in **52** and **58** *vs.* the hexadienal complex **62a**, which shows smaller bond angles at the Fe-atom, probably a consequence of the presence of two terminal diene substituents. The stereochemical disposition of the P ligands reveals two diverse effects: the basal position is reserved for the ligands of higher π acidity, CO and $(RO)_3P$, except when a bulky ligand with a large cone angle is present, such as a Ph_3P [17]. Substituents on the diene system are of importance when situated at the terminal positions because of steric interaction with the apical position; for geminal dimethyl substitution, see [18].

Quantum-chemical calculations have shown that the extent of π interaction between the ligands and the metal is related to the degree of pyramidality [19]. For a square pyramid with $\theta < 100°$ (θ defines the $L_{apical}-M-L_{basal}$ bond angle), the interaction is larger in the basal site and thus stabilizes a π-acceptor ligand in this position. The situation changes in favour of the apical site for $\theta > 100°$. Complexes **52** and **58** have bond angles $\theta > 100°$ for the P and the CO ligands in contrast with **62a** showing θ values $< 100°$ *(Table 4)*. The molecular structures of **52** and **58** illustrate that the σ-donor ligand Ph_3P prefers the basal site probably for steric reasons, and because it is the weakest π acceptor. The CO ligand, a strong π acceptor, is also found in the basal position contrary to the theoretical expectation. This result probably arises because the large π-acceptor ligand $(MeO)_3P$ avoids steric congestion with the Ph_3P ligand. On the other hand, the stereochemical disposition of the ligands in the hexadienal complex **62a** is in agreement with the theoretical predictions for $\theta < 100°$, with both π-acceptor ligands in basal sites. From the structural data of the three complexes, we can conclude that the stereochemical preference of σ-donor/π-acceptor ligands is determined by electronic *and* steric factors. In addition, the effects of diene substituents have to be taken into account, as discussed above.

This work has been supported by the *Swiss National Science Fondation*, the *Ministerio de Educación y Ciencia* of Spain, and the Dr. *Helmut Legerlotz-Stiftung*. The authors acknowledge experimental contributions by *D. Rentsch* and *I. Wiedmer*.

Experimental Part

1. *General.* IR spectra were recorded on a *Perkin-Elmer 781* spectrometer. NMR spectra were recorded on *Bruker AM-400, Varian XL-200,* and *Varian XL-100* spectrometers, ^{1}H-NMR spectra in 5-mm samples tubes, ^{13}C- and ^{31}P-NMR spectra in 10-mm samples tubes; δ(H) and δ(C) are reported relative to internal TMS, δ(P) relative to 85% H_3PO_4 as an external standard. The temp. was 300 K if not indicated otherwise. $(RO)_3P$ and R_3P signals are not differentiated, but generally the first one appears at higher δ values. In ^{1}H-NMR spectra, a differentiation between J(H,H) and J(P,H) is only made where indicated. Samples were prepared under inert atmosphere in O_2-free and anh. (D_6)acetone or (D_6)benzene. Primed numbering of C-atoms refers to the Ph groups in the Ph_3P complexes. H_a and H_b denote the 'inner' and 'outer' geminal protons, resp., of the coordinated s-*cis*-buta-1,3-diene.

2. *X-Ray Crystallographic Study of* **52**, **58**, *and* **62a** (see also *Table 3*). Intensity data were collected in ω-scan mode using a *Nicolet-R3* diffractometer with an *LT-1* low-temperature attachment, with MoK_α radiation (graphite monochromator). Three standard reflections were monitored throughout each data collection; intensity variations were less than 3% in all cases. The usual corrections were applied to the data with the exception of an absorption correction. Structures were solved (heavy-atom method) and refined using the SHELXTL program system [20]. H-Atoms could be located in difference *Fourier* maps and were included in the refinement with individual isotropic temp. factors (**52** and **62a**) or using a riding model (**58**). Non-H-atoms were refined with anisotropic displacement parameters in a blocked cascade refinement on F, with approximately 100 parameters per block. The terminal C-atom of one of the Et groups of the phosphine ligand in **62a** is disordered between two positions.

3. *Syntheses.* All synthetic operations were carried out under inert atmosphere in dry, O_2-free solvents. Chromatographic separations were performed on silica gel 60 (70–230 mesh, *Merck*). [$Fe(CO)_3$(butadiene)] and [$Ru_3(CO)_{12}$] were purchased from *Strem Chemicals* and used without further purification. Starting materials were synthesized according to literature methods: [$Fe_2(CO)_9$] [21], [$Ru(CO)_3$(2,4-hexadienal)] and [$Ru(CO)_3$(methyl hexa-2,4-dienoate) [7a] [22], [$Fe(CO)_3$(diene)] [23] [24], and [$Fe(CO)_3$(heterodiene)] [18].

General Procedure for the Synthesis of [M(CO)$_2$L^1(diene)] Complexes. To a suspension of 0.45 g (4 mmol) of $Me_3NO \cdot 2\,H_2O$ in 10 ml of MeCN 5.2 mmol of phosphorus ligand and 2.5 mmol of corresponding [$M(CO)_3$(diene)] were added. The mixture was stirred at 37–40° (or 0° for heterodiene), until the starting material had disappeared (4–18 h). The mixture was extracted with hexane/Et_2O 10:1 (10 × 12 ml) and the solvent was removed under reduced pressure. The residue was chromatographed on silica gel with hexane/Et_2O as eluent and, after elimination of the solvent, the pure compounds were obtained in 40–90% yield.

General Procedure for the Synthesis of [M(CO)L^{1}L^2(diene)] Complexes. The [$M(CO)_2L^1$(diene)] (5 mmol) was dissolved in benzene, and 10 mmol of the phosphorus ligand L^2 were added. The soln. was irradiated with a high-pressure Hg lamp (*Philips HPK*, 125 W or *Hanau*, 250 W). The course of the reaction was followed by TLC, and the irradiation was continued, until no more dicarbonyl compound was detected. The soln. was filtered through *Celite* to remove any decomposed material and the solvent was removed under reduced pressure. The resulting oily residue was chromatographed on silica gel using hexane/Et_2O as eluent. Removal of the solvent yielded the pure compounds as yellow oils or crystals. In the same way, the separation of diastereoisomers was achieved.

(η^4-Buta-1,3-diene)dicarbonyl(triethylphosphine)iron (**1**). Yield: 93%. Yellow oil. ^{1}H-NMR (200.1 MHz, C_6D_6): 4.89 (*m*, H–C(2), H–C(3)); 1.36 (*m*, H_b–C(1), H_b–C(4)); 1.20 (*qd*, J = 7.5, 7.5, $P(CH_2CH_3)_3$); 0.74 (*td*, J = 7.5, 7.3, $P(CH_2CH_3)_3$); 0.36 (*m*, J(P,H) = 6, H_a–C(1), H_a–C(4)). ^{13}C-NMR (100.6 MHz, (D_6)acetone): 218.8 (*d*, J(P,C) = 14.4, CO); 83.9 (*s*, C(2), C(3)); 38.2 (*s*, C(1), C(4)); 21.2 (*d*, J(P,C) = 24, $P(CH_2CH_3)_3$); 7.9 (*s*, $P(CH_2CH_3)_3$). ^{31}P-NMR (162.0 MHz, (D_6)acetone): 55.0.

(η^4-Buta-1,3-diene)dicarbonyl(triethoxyphosphine)iron (**2**). Yield: 76%. Yellow oil. IR (film): 3055*w*, 2985*m*, 2905*m*, 1987*s*, 1925*s*, 1478*m*, 1445*m*, 1390*m*, 1030*s*. ^{1}H-NMR (200.1 MHz, C_6D_6): 5.03 (*m*, H–C(2), H–C(3)); 3.84 (*qd*, J(P,H) = J(H,H) = 7.1, $P(OCH_2CH_3)_3$); 1.68 (*m*, H_b–C(1), H_b–C(4)); 1.08 (*t*, J = 7.0, $P(OCH_2CH_3)_3$); 0.06 (*m*, H_a–C(1), H_a–C(4)). ^{13}C-NMR (50.3 MHz, (D_6)acetone): 217.2 (*d*, J(P,C) = 19.6, CO); 84.4 (*s*, C(2), C(3)); 60.9 (*d*, J(P,C) = 3.4, $P(OCH_2CH_3)_3$); 39.4 (*s*, C(1), C(4)); 16.4 (*d*, J(P,C) = 6.8, $P(OCH_2CH_3)_3$). ^{31}P-NMR (162.0 MHz, (D_6)acetone): 181.4.

(η^4-Buta-1,3-diene)dicarbonyl(trimethoxyphosphine)iron (**3**). Yield: 43%. Yellow oil. IR (film): 3050*w*, 3000*m*, 2950*m*, 2845*m*, 1987*s*, 1945*s*, 1477*m*, 1442*m*, 1030*s*. ^{1}H-NMR (400.1 MHz, C_6D_6): 4.95 (*m*, H–C(2), H–C(3)); 3.27 (*d*, J = 11.6, $P(OCH_3)_3$); 1.59 (*m*, H_b–C(1), H_b–C(4)); –0.02 (*m*, H_a–C(1), H_a–C(4)). ^{13}C-NMR (50.3 MHz, (D_6)acetone): 216.8 (*d*, J(P,C) = 19.0, CO); 84.4 (*s*, C(2), C(3)); 51.8 (*d*, J(P,C) = 3.2, $P(OCH_3)_3$); 39.2 (*s*, C(1), C(4)). ^{31}P-NMR (162.0 MHz, (D_6)acetone): 188.3.

(η^4-Buta-1,3-diene)dicarbonyl(triphenylphosphine)iron (**4**). Yield: 75%. Yellow crystals. M.p. 143–144°. ^{1}H-NMR (200.1 MHz, C_6D_6): 7.60 (*m*, H–C(2′), H–C(6′)); 7.14 (*m*, H–C(3′), H–C(5′), H–C(4′)); 4.93 (*m*, H–C(2), H–C(3)); 1.47 (*m*, H_b–C(1), H_b–C(4)); 0.0 (*m*, H_a–C(1), H_a–C(4)). ^{13}C-NMR (100.6 MHz, (D_6)acetone): 219.2

(*d*, J(P,C) = 14.1, CO); 137.4 (*d*, J(P,C) = 41, C(1')); 134.0 (*d*, J(P,C) = 8, C(2'), C(6')); 130.7 (*s*, C(4')); 129.1 (*s*, C(3'), C(5')); 85.1 (*s*, C(2), C(3)); 41.1 (*s*, C(1), C(4)). ^{31}P-NMR (162.0 MHz, (D_6)acetone): 73.3.

(η⁴-Buta-1,3-diene)dicarbonyl(cyclohexyl isocyanide)iron (**5**). Yield: 68%. Oil. IR ($CHCl_3$); 2140*s*, 1990*s*, 1930*s*. ^{1}H-NMR (400.1 MHz, C_6D_6): 5.07 (*m*, J = 7.8, 5.0, 2.5, H–C(2), H–C(3)); 2.79 (br. *m*, CH–NC); 1.54 (*m*, J = 5, 2.5, 2.1, H_b–C(1), H_b–C(4)); 1.26 (*m*, CH_2); 1.08 (*m*, 2 CH_2); 0.92 (*m*, CH_2); 0.82 (*m*, CH_2); 0.01 (*dd*, J = 7.8, 2.1, H_a–C(1), H_a–C(4)). ^{13}C-NMR (25.2 MHz, C_6D_6): 216.9 (*s*, CO); 84.6 (*s*, C(2), C(3)); 54.3 (*s*, CH–NC); 38.3 (*s*, C(1), C(4)); 32.9 (*s*, CH_2); 25.2 (*s*, CH_2); 22.9 (*s*, CH_2).

Dicarbonyl[1-4-η-((E)-penta-1,3-diene)](triethylphosphine)iron (**6**). Yield: 67%. Yellow oil. ^{13}C-NMR (100.6 MHz, (D_6)acetone): 222.3 (*s*, CO); 217.0 (*d*, J(P,C) = 21, CO); 87.3 (*s*, C(3)); 80.7 (*s*, C(2)); 51.4 (*s*, C(4)); 39.0 (*s*, C(1)); 21.1 (*d*, J(P,C) = 23, $P(CH_2CH_3)_3$); 19.5 (*s*, C(5)); 8.0 (*s*, $P(CH_2CH_3)_3$). ^{31}P-NMR (162.0 MHz, (D_6)acetone): 54.0.

Dicarbonyl[1-4-η-((E)-penta-1,3-diene)](triethoxyphosphine)iron (**7**). Yield: 56%. Yellow oil. ^{13}C-NMR (100.6 MHz, (D_6)acetone): 219.7 (*d*, J(P,C) = 11, CO); 215.3 (*d*, J(P,C) = 25, CO); 88.3 (*s*, C(3)); 80.6 (*s*, C(2)); 60.9 (*d*, J(P,C) = 3, $P(OCH_2CH_3)_3$); 54.6 (*s*, C(4)); 40.0 (*s*, C(1)); 19.2 (*s*, C(5)); 16.4 (*d*, J(P,C) = 5, $P(OCH_2CH_3)_3$). ^{31}P-NMR (162.0 MHz, (D_6)acetone): 181.7.

Dicarbonyl[1-4-η-((E)-penta-1,3-diene)](trimethoxyphosphine)iron (**8**). Yield: 87%. Yellow oil. ^{13}C-NMR (100.6 MHz, (D_6)acetone): 219.5 (*d*, J(P,C) = 10, CO); 214.9 (*d*, J(P,C) = 26, CO); 88.4 (*s*, C(3)); 80.4 (*s*, C(2)); 54.5 (*s*, C(4)); 51.8 (*s*, $P(OCH_3)_3$); 39.5 (*s*, C(1)); 19.3 (*s*, C(5)). ^{31}P-NMR (162.0 MHz, (D_6)acetone): 187.9.

Dicarbonyl[1-4-η-((E)-penta-1,3-diene)](triphenylphosphine)iron (**9**). Yield: 62%. Yellow oil. ^{13}C-NMR (100.6 MHz, (D_6)acetone): 222.5 (*s*, CO); 217.0 (*d*, J(P,C) = 23, CO); 137.1 (*d*, J(P,C) = 39, C(1')); 134.4 (*m*, C(2'), C(6')); 129.6 (*s*, C(4')); 129.1 (*m*, C(3'), C(5')); 87.5 (*s*, C(3)); 83.1 (*s*, C(2)); 53.1 (*s*, C(4)); 43.5 (*s*, C(1)); 19.4 (*s*, C(5)). ^{31}P-NMR (162.0 MHz, (D_6)acetone): 73.1.

Dicarbonyl[1-4-η-((Z)-penta-1,3-diene)](triethoxyphosphine)iron (**10**). Yield: 93%. Yellow oil. ^{1}H-NMR (400.1 MHz, C_6D_6): 5.12 (*m*, H–C(2)); 5.01 (*m*, H–C(3)); 3.82 (*dq*, J(P,H) = J(H,H) = 7.0, $P(OCH_2CH_3)_3$); 2.62 (*dqdd*, J = 8.0, 7.0, 1.5, 1.5, H–C(4)); 1.82 (*m*, H_b–C(1)); 1.44 (*ddd*, J = 9.0, 2.0, 2.0, H_a–C(1)); 1.11 (*d*, J = 7.0, CH_3); 1.08 (*t*, J = 7.0, $P(OCH_2CH_3)_3$). ^{13}C-NMR (100.6 MHz, (D_6)acetone): 218.0 (*d*, J(P,C) = 20, CO); 89.5 (*s*, C(3)); 87.2 (*s*, C(2)); 60.9 (*s*, $P(OCH_2CH_3)_3$); 50.5 (*s*, C(4)); 39.6 (*s*, C(1)); 16.5 (*s*, $P(OCH_2CH_3)_3$); 13.8 (*s*, C(5)). ^{31}P-NMR (162.0 MHz, (D_6)acetone): 178.2.

Dicarbonyl[1-4-η-((Z)-penta-1,3-diene)](trimethoxyphosphine)iron (**11**). Yield: 56%. Yellow oil. ^{13}C-NMR (100.6 MHz, (D_6)acetone): 217.5 (br., CO); 89.5 (*s*, C(3)); 87.2 (*s*, C(2)); 51.7 (*s*, $P(OCH_3)_3$); 50.6 (*s*, C(4)); 39.5 (*s*, C(1)); 13.7 (*s*, C(5)). ^{31}P-NMR (162.0 MHz, (D_6)acetone): 184.8.

Dicarbonyl[1-4-η-(2-methylbuta-1,3-diene)](triethylphosphine)iron (**12**). Yield: 34%. Yellow oil. ^{13}C-NMR (100.6 MHz, (D_6)acetone): 219.0 (*s*, CO); 216.3 (*d*, J(P,C) = 15, CO); 100.1 (*s*, C(2)); 84.0 (*s*, C(3)); 41.3 (*s*, C(1)); 37.3 (*s*, C(4)); 23.5 (*s*, CH_3–C(2)); 21.4 (*d*, J(P,C) = 24, $P(CH_2CH_3)_3$); 8.0 (*s*, $P(CH_2CH_3)_3$). ^{31}P-NMR (162.0 MHz, (D_6)acetone): 55.2.

Dicarbonyl[1-4-η-(2-methylbuta-1,3-diene)](triethoxyphosphine)iron (**13**). Yield: 56%. Yellow oil. ^{13}C-NMR (100.6 MHz, (D_6)acetone): 217.9 (*d*, J(P,C) = 11, CO); 215.3 (*d*, J(P,C) = 23, CO); 100.9 (*s*, C(2)); 84.3 (*s*, C(3)); 60.8 (*d*, J(P,C) = 3, $P(OCH_2CH_3)_3$); 42.2 (*s*, C(1)); 38.2 (*s*, C(4)); 23.1 (*s*, CH_3–C(2)); 16.4 (*d*, J(P,C) = 4, $P(OCH_2CH_3)_3$). ^{31}P-NMR (162.0 MHz, (D_6)acetone): 182.5.

Dicarbonyl[1-4-η-(2-methylbuta-1,3-diene)](trimethoxyphosphine)iron (**14**). Yield: 71%. Yellow oil. ^{13}C-NMR (100.6 MHz, (D_6)acetone): 217.5 (*d*, J(P,C) = 12, CO); 214.9 (*d*, J(P,C) = 21, CO); 101.1 (*s*, C(2)); 84.2 (*s*, C(3)); 51.7 (*s*, $P(OCH_3)_3$); 42.2 (*s*, C(1)); 37.8 (*s*, C(4)); 23.2 (*s*, CH_3–C(2)). ^{31}P-NMR (162.0 MHz, (D_6)acetone): 189.4.

Dicarbonyl[1-4-η-(2,3-dimethylbuta-1,3-diene)](triethylphosphine)iron (**15**). Yield: 37%. Yellow oil. ^{13}C-NMR (100.6 MHz, (D_6)acetone): 216.3 (*d*, J(P,C) = 7, CO); 97.6 (*s*, C(2), C(3)); 42.9 (*s*, C(1), C(4)); 21.6 (*d*, J(P,C) = 25, $P(CH_2CH_3)_3$); 21.0 (*s*, CH_3–C(2), CH_3–C(3)); 8.0 (*s*, $P(CH_2CH_3)_3$). ^{31}P-NMR (162.0 MHz, (D_6)acetone): 54.4

Dicarbonyl[1-4-η-(2,3-dimethylbuta-1,3-diene)](triethoxyphosphine)iron (**16**). Yield: 41%. Yellow oil. ^{13}C-NMR (100.6 MHz, (D_6)acetone): 215.7 (*d*, J(P,C) = 13, CO); 98.3 (*s*, C(2), C(3)); 60.7 (*s*, $P(CH_2CH_3)_3$); 43.3 (*s*, C(1), C(4)); 20.5 (*s*, CH_3–C(2), CH_3–C(3)); 16.5 (*s*, $P(OCH_2CH_3)_3$). ^{31}P-NMR (162.0 MHz, (D_6)acetone): 184.4.

Dicarbonyl[1-4-η-(2,3-dimethylbuta-1,3-diene)](trimethoxyphosphine)iron (**17**). Yield: 35%. Yellow oil. ^{13}C-NMR (100.6 MHz, (D_6)acetone): 215.3 (*d*, J(P,C) = 13, CO); 98.4 (*s*, C(2), C(3)); 51.6 (*s*, $P(OCH_3)_3$); 42.9 (*s*, C(1), C(4)); 20.5 (*s*, CH_3–C(2), CH_3–C(3)). ^{31}P-NMR (162.0 MHz, (D_6)acetone): 191.2.

Dicarbonyl[2-5-η-(2E,4E)-hexa-2,4-diene)](triethylphosphine)iron (**18**). Yield: 89%. Yellow crystals. ^{13}C-NMR (100.6 MHz, (D_6)acetone): 216.8 (*d*, J(P,C) = 6, CO); 85.0 (*s*, C(3), C(4)); 51.9 (*s*, C(2), C(5)); 21.6 (*d*, J(P,C) = 25, $P(CH_2CH_3)_3$); 19.5 (*s*, C(1), C(6)); 8.1 (*s*, $P(CH_2CH_3)_3$). ^{31}P-NMR (162.0 MHz, (D_6)acetone): 44.4.

Dicarbonyl[2–5-η-((2E,4E)-hexa-2,4-diene)](triethoxyphosphine)iron (**19**). Yield: 82%. Yellow oil. ^{13}C-NMR (100.6 MHz, (D_6)acetone): 216.0 (*d*, $J(P,C) = 9.2$, CO); 85.1 (*s*, C(3), C(4)); 60.7 (*d*, $J(P,C) = 5$, $P(OCH_2CH_3)_3$); 55.5 (*s*, C(2), C(5)); 19.1 (*s*, C(1), C(6)); 16.6 (*d*, $J(P,C) = 5$, $P(OCH_2CH_3)_3$). ^{31}P-NMR (162.0 MHz, (D_6)acetone): 182.4.

Dicarbonyl[2–5-η-((2E,4E)-hexa-2,4-diene)](trimethoxyphosphine)iron (**20**). Yield: 69%. Yellow oil. ^{13}C-NMR (100.6 MHz, (D_6)acetone): 216.0 (*d*, $J(P,C) = 9.8$, CO); 85.0 (*s*, C(3), C(4)); 55.2 (*s*, C(2), C(5)); 52.0 (*d*, $J(P,C) = 4$, $P(OCH_3)_3$); 19.2 (*s*, C(1), C(6)). ^{31}P-NMR (162.0 MHz, (D_6)acetone): 188.1.

Dicarbonyl[2–5-η-((2E,4Z)-hexa-2,4-diene)](triethoxyphosphine)iron (**21**). Yield: 54%. Yellow oil. ^{13}C-NMR (100.6 MHz, (D_6)acetone): 221.5 (*d*, $J(P,C) = 10$, CO); 214.8 (*d*, $J(P,C) = 32$, CO); 93.0 (*s*, C(4)); 83.2 (*s*, C(3)); 60.8 (*s*, $P(OCH_2CH_3)_3$); 53.1 (*d*, $J(P,C) = 9$, C(2)/C(5)); 51.7 (*d*, $J(P,C) = 11$, C(5)/C(2)); 20.4 (*s*, C(1)); 16.4 (*d*, $J(P,C) = 6$, $P(OCH_2CH_3)_3$); 14.1 (*s*, C(6)). ^{31}P-NMR (162.0 MHz, (D_6)acetone): 179.0.

Dicarbonyl[2–5-η-((2E,4Z)-hexa-2,4-diene)](trimethoxyphosphine)iron (**22**). Yield: 75%. Yellow oil. ^{13}C-NMR (100.6 MHz, (D_6)acetone): 221.2 (*d*, $J(P,C) = 10$, CO); 214.5 (*d*, $J(P,C) = 31$, CO); 93.0 (*s*, C(4)); 83.1 (*s*, C(3)); 53.5 (*d*, $J(P,C) = 9$, C(2)/C(5)); 51.7 (*d*, $J(P,C) = 3$, $P(OCH_3)_3$); 51.6 (*d*, $J(P,C) = 10$, C(5)/C(2)); 20.3 (*s*, C(1)); 14.1 (*s*, C(6)). ^{31}P-NMR (162.0 MHz, (D_6)acetone): 185.2.

Dicarbonyl[1–4-η-((E)-3-methylpenta-1,3-diene)](triethylphosphine)iron (**23**). Yield: 52%. Yellow crystals. ^{13}C-NMR (100.6 MHz, (D_6)acetone): 222.1 (*d*, $J(P,C) = 6$, CO); 216.7 (*d*, $J(P,C) = 21$, CO); 99.9 (*s*, C(3)); 81.6 (*s*, C(2)); 52.5 (*s*, C(4)); 37.7 (*s*, C(1)); 21.1 (*d*, $J(P,C) = 24$ $P(CH_2CH_3)_3$); 18.5 (*s*, CH_3); 16.2 (*s*, CH_3); 7.9 (*s*, $P(CH_2CH_3)_3$). ^{31}P-NMR (162.0 MHz, (D_6)acetone): 54.7.

Dicarbonyl[1–4-η-((E)-3-methylpenta-1,3-diene)](triethoxyphosphine)iron (**24**). Yield: 62%. Yellow crystals. ^{13}C-NMR (100.6 MHz, (D_6)acetone): 219.6 (*d*, $J(P,C) = 8.6$, CO); 215.0 (*d*, $J(P,C) = 24.8$, CO); 101.3 (*s*, C(3)); 81.6 (*s*, C(2)); 60.9 (*s*, $P(POCH_2CH_3)_3$); 55.6 (*s*, C(4)); 36.8 (*s*, C(1)); 18.4 (*s*, CH_3); 16.5 (*d*, $J(P,C) = 6$, $P(OCH_2CH_3)_3$); 16.1 (*s*, CH_3). ^{31}P-NMR (162.0 MHz, (D_6)acetone): 182.3.

Dicarbonyl[1–4-η-((E)-3-methylpenta-1,3-diene)](trimethoxyphosphine)iron (**25**). Yield: 44%. Yellow crystals. ^{13}C-NMR (100.6 MHz, (D_6)acetone): 219.6 (br., CO); 214.7 (*d*, $J(P,C) = 25$, CO); 101.4 (*s*, C(3)); 81.5 (*s*, C(2)); 55.6 (*s*, C(4)); 51.7 (*s*, $P(OCH_3)_3$); 36.4 (*s*, C(1)); 18.3 (*s*, CH_3); 16.0 (*s*, CH_3). ^{31}P-NMR (162.0 MHz, (D_6)acetone): 188.3.

Dicarbonyl[1–4-η-(4-methylpenta-1,3-diene)](triethoxyphosphine)iron (**26**). Yield: 61%. Yellow oil. ^{13}C-NMR (100.6 MHz, (D_6)acetone): 221.9 (*d*, $J(P,C) = 7$, CO); 215.2 (*d*, $J(P,C) = 34$, CO); 90.6 (*s*, C(3)); 85.4 (*s*, C(2)); 62.9 (*d*, $J(P,C) = 8$, C(4)); 60.8 (*s*, $P(OCH_2CH_3)_3$); 41.6 (*d*, $J(P,C) = 12$, C(1)); 33.4 (*s*, C(5)); 20.9 (*s*, CH_3–C(4)); 16.4 (*d*, $J(P,C) = 6$, $P(OCH_2CH_3)_3$). ^{31}P-NMR (162.0 MHz, (D_6)acetone): 178.0.

Dicarbonyl[1–4-η-(4-methylpenta-1,3-diene)](trimethoxyphosphine)iron (**27**). Yield: 65%. Yellow oil. ^{13}C-NMR (100.6 MHz, (D_6)acetone): 221.7 (*d*, $J(P,C) = 7.2$, CO); 214.8 (*d*, $J(P,C) = 34.6$, CO); 90.6 (*s*, C(3)); 85.2 (*s*, C(2)); 64.5 (*d*, $J(P,C) = 14$, C(4)); 51.7 (*d*, $J(P,C) = 4$, $P(OCH_3)_3$); 41.1 (*d*, $J(P,C) = 12$, C(1)); 33.4 (*s*, C(5)); 20.8 (*s*, CH_3–C(4)). ^{31}P-NMR (162.0 MHz, (D_6)acetone): 184.4.

Dicarbonyl[1–4-η-((E)-2-methylpenta-1,3-diene)](triethylphosphine)iron (**28**). Yield: 23%. Yellow oil. ^{1}H-NMR (400.1 MHz, (D_6)acetone): 4.81 (*d*, $J = 7.5$, H–C(3)); 2.08 (*d*, $J = 2.0$, CH_3–C(2)); 1.84 (*m*, $P(CH_2CH_3)_3$); 1.34 (*d*, $J = 1.5$, H_b–C(1)); 1.28 (*d*, $J = 6.2$, 3 H–C(5)); 1.13 (*m*, $P(CH_2CH_3)_3$); 0.0 (*m*, H_a–C(4)); –0.42 (*dd*, $J(P,H) = 11$, $J(H,H) = 1.5$, H_a–C(1)). ^{13}C-NMR (100.6 MHz, (D_6)acetone): 217.3 (*d*, $J(P,C) = 8$, CO); 215.9 (*d*, $J(P,C) = 7$, CO); 97.0 (*s*, C(2)); 88.8 (*s*, C(3)); 50.6 (*s*, C(4)); 42.3 (*s*, C(1)); 23.6 (*s*, CH_3–C(2)); 21.5 (*d*, $J(P,C) = 24$, $P(CH_2CH_3)_3$); 19.5 (*s*, C(5)); 8.0 (*s*, $P(CH_2CH_3)_3$). ^{31}P-NMR (162.0 MHz, (D_6)acetone): 49.4.

Dicarbonyl[2–5-η-((2E,4E)-hexa-2,4-dienal)](triethylphosphine)iron (**29**). Yield: 90%. Yellow crystals. ^{1}H-NMR (400.1 MHz, C_6D_6): 9.05 (*d*, $J = 7.2$, H–C(1)); 5.06 (*m*, H–C(4)); 4.47 (*dd*, $J = 6.5$, 1.5, H–C(3)); 1.47 (*m*, $P(CH_2CH_3)_3$); 1.17 (*d*, $J = 6.2$, 3 H–C(6)); 0.78 (*m*, $P(CH_2CH_3)_3$); 0.70 (*m*, H–C(5)); 0.63 (*m*, H–C(2)). ^{13}C-NMR (100.6 MHz, (D_6)acetone): 216.3 (*d*, $J(P,C) = 12$, CO); 213.1 (*d*, $J(P,C) = 5$, CO); 197.7 (br., C(1)); 89.5 (*s*, C(4)); 82.1 (*s*, C(3)); 56.5 (*s*, C(5)/C(2)); 55.0 (*s*, C(2)/C(5)); 21.0 (*d*, $J(P,C) = 26$, $P(CH_2CH_3)_3$); 19.3 (*s*, C(6)); 7.9 (*s*, $P(CH_2CH_3)_3$). ^{31}P-NMR (162.0 MHz, (D_6)acetone): 42.5.

Dicarbonyl[2–5-η-((2E,4E)-hexa-2,4-dienal)](triethoxyphosphine)iron (**30**). Yield: 90%. Yellow oil. IR (film): 2980*m*, 2905*m*, 2860*w*, 2810*w*, 2720*w*, 1995*s*, 1935*s*, 1678*s*, 1478*w*, 1440*m*, 1388*m*, 1030*s*. ^{1}H-NMR (400.1 MHz, C_6D_6): 9.22 (*d*, $J = 6.2$, H–C(1)); 5.22 (*m*, H–C(4)); 4.63 (*dd*, $J = 8.2$, 4.9, H–C(3)); 3.83 (*qd*, $J(P,H) = J(H,H) = 7.1$, $P(OCH_2CH_3)_3$); 1.32 (*d*, $J = 6.1$, 3 H–C(6)); 1.04 (*t*, $J = 7.0$, $P(OCH_2CH_3)_3$); 0.97 (*m*, H–C(5)/H–C(2)); 0.89 (*m*, H–C(2)/H–C(5)). ^{13}C-NMR (50.3 MHz, (D_6)acetone): 214.4 (*d*, $J(P,C) = 11$, CO); 213.1 (*s*, CO); 197.7 (*s*, C(1)); 89.8 (*d*, $J(P,C) = 3$, C(4)); 81.9 (*d*, $J(P,C) = 2$, C(3)); 61.7 (*d*, $J(P,C) = 5.9$, $P(OCH_2CH_3)_3$); 58.9 (*d*, $J(P,C) = 4$, C(5)/C(2)); 57.0 (*d*, $J(P,C) = 5$, C(2)/C(5)); 18.8 (*s*, C(6)); 16.5 (*d*, $J(P,C) = 6$, $P(OCH_2CH_3)_3$). ^{31}P-NMR (162.0 MHz, (D_6)acetone): 176.3. Anal. calc. for $C_{14}H_{23}FeO_6P$: C 44.94, H 6.20, P 8.28; found: C 45.16, H 6.07, P 8.15.

Dicarbonyl[2–5-η-((2E,4E)-hexa-2,4-dienal)](trimethoxyphosphine)iron (**31**). Yield: 90%. Yellow crystals. M.p. 58°. IR (film): 3005*m*, 2950*m*, 2845*w*, 2730*w*, 2000*s*, 1940*s*, 1665*s*, 1460*m*, 1025*s*. ^{1}H-NMR (400.1 MHz, C_6D_6): 9.20 (*d*, *J* = 6.2, H–C(1)); 5.16 (*m*, H–C(4)); 4.58 (*dd*, *J* = 8.6, 4.8, H–C(3)); 3.29 (*d*, *J*(P,H) = 11.4, $P(OCH_3)_3$); 1.27 (*dd*, *J* = 6.2, 1.2, 3 H–C(6)); 1.05 (*m*, H–C(5)); 0.90 (*m*, H–C(2)). ^{13}C-NMR (50.3 MHz, (D_6)acetone): 214.4 (*d*, *J*(P,C) = 16.2, CO); 212.4 (*s*, CO); 197.8 (*s*, C(1)); 89.8 (*s*, C(4)); 81.8 (*d*, *J*(P,C) = 2.7, C(3)); 58.6 (*d*, *J*(P,C) = 4.1, C(5)/C(2)); 56.4 (*d*, *J*(P,C) = 5.0, C(2)/C(5)); 52.6 (*d*, *J*(P,C) = 5.1, $P(OCH_3)_3$); 18.9 (*s*, C(6)). ^{31}P-NMR (162.0 MHz, (D_6)acetone): 182.4. Anal. calc. for $C_{11}H_{17}FeO_6P$: C 39.79, H 5.16, P 9.32; found: C 39.89, H 5.33, P 9.16.

Dicarbonyl[2–5-η-((2E,4E)-hexa-2,4-dienal)](triphenylphosphine)iron (**32**). Yield: 59%. Orange crystals. M.p. 130°. IR ($CHCl_3$): 1990*s*, 1932*m*, 1660*s*. ^{1}H-NMR (400.1 MHz, C_6D_6): 9.1 (*d*, *J* = 5.6, H–C(1)); 7.6 (*m*, H–C(2′), H–C(6′)); 7.04 (*m*, H–C(3′), H–C(5′)); 6.94 (*m*, H–C(4′)); 5.31 (*m*, H–C(4)); 4.62 (*dd*, *J* = 8.6, 3.8, H–C(3)); 1.04 (*d*, *J* = 6.2, 3 H–C(6)); 0.17 (*m*, H–C(2), H–C(5)). ^{13}C-NMR (50.4 MHz, C_6D_6): 214.9 (*d*, *J*(P,C) = 8.5, CO); 211.6 (*d*, *J*(P,C) = 4.7, CO); 196.3 (*s*, C(1)); 135.7 (*d*, *J*(P,C) = 40.2, C(1′)); 132.9–127.0 (*m*, C(2′), C(6′), C(3′), C(5′), C(4′)); 89.9 (*s*, C(4)); 82.7 (*s*, C(3)); 60.9 (*d*, *J*(P,C) = 1.7, C(5)/C(2)); 59.8 (*d*, *J*(P,C) = 4.2, C(2)/C(5)); 17.9 (*s*, C(6)). ^{31}P-NMR (162.0 MHz, (D_6)acetone): 64.5.

Dicarbonyl(cyclohexyl isocyanide)[2–5-η-((2E,4E)-hexa-2,4-dienal)]iron (**33**). Yield: 69%. Yellow oil. ^{1}H-NMR (400.1 MHz, C_6D_6): 9.28 (*d*, *J* = 4.0, H–C(1)); 5.43 (br., H–C(4)); 4.69 (*dd*, *J* = 8.6, 5, H–C(3)); 2.97 (br., CH–NC); 1.22 (*d*, *J* = 6.3, 3 H–C(6)); 1.4–1.1 (*m*, CH_2); 1.0–0.9 (*m*, CH_2, H–C(5), H–C(2)). ^{13}C-NMR (50.4 MHz, 333 K, C_6D_6): 215.4 (br. *s*, CO); 214.6 (br. *s*, CO); 195.3 (*s*, C(1)); 159.9 (br. *s*, CN); 88.9 (*s*, C(4)); 80.4 (*s*, C(3)); 55.4 (*s*, C(5)/C(2)); 54.9 (*s*, *C*H–NC); 54.6 (*s*, C(2)/C(5)); 32.9 (*s*, CH_2); 25.0 (*s*, CH_2); 23.0 (*s*, CH_2); 18.9 (*s*, C(6)).

Dicarbonyl[2–5-η-(methyl (2E,4E)-hexa-2,4-dienoate)](triethylphosphine)iron (**34**). Yield: 90%. Yellow oil. ^{13}C-NMR (100.6 MHz, (D_6)acetone): 216.6 (*d*, *J*(P,C) = 10, CO); 213.0 (*s*, CO); 174.4 (*s*, C(1)); 87.6 (*s*, C(4)); 82.5 (*s*, C(3)); 53.7 (*s*, C(5)); 50.6 (*s*, CH_3O); 44.7 (*s*, C(2)); 21.1 (*d*, *J*(P,C) = 25, $P(CH_2CH_3)_3$); 19.3 (*s*, C(6)); 7.9 (*s*, $P(CH_2CH_3)_3$). ^{31}P-NMR (162.0 MHz, (D_6)acetone): 44.1.

Dicarbonyl[2–5-η-(methyl (2E,4E)-hexa-2,4-dienoate)](triethoxyphosphine)iron (**35**). Yield: 83%. Yellow oil. ^{13}C-NMR (100.6 MHz, (D_6)acetone): 214.4 (*d*, *J*(P,C) = 17, CO); 212.4 (*s*, CO); 174.2 (*s*, C(1)); 88.3 (*s*, C(4)); 82.8 (*s*, C(3)); 61.4 (*d*, *J*(P,C) = 5, $P(OCH_2CH_3)_3$); 58.0 (*s*, C(5)); 50.9 (*s*, CH_3O); 46.1 (*s*, C(2)); 18.8 (*s*, C(6)); 16.5 (*d*, *J*(P,C) = 6, $P(OCH_2CH_3)_3$). ^{31}P-NMR (162.0 MHz, (D_6)acetone): 176.3.

Dicarbonyl[2–5-η-(methyl (2E,4E)-hexa-2,4-dienoate)](trimethoxyphosphine)iron (**36**). Yield: 72%. Yellow oil. ^{13}C-NMR (100.6 MHz, (D_6)acetone): 214.4 (*d*, *J*(P,C) = 17, CO); 212.5 (*s*, CO); 174.2 (*s*, C(1)); 88.3 (*s*, C(4)); 82.5 (*s*, C(3)); 57.6 (*s*, C(5)); 52.6 (*d*, *J*(P,C) = 5, $P(OCH_3)_3$); 50.9 (*s*, $COOCH_3$); 45.6 (*s*, C(2)); 18.9 (*s*, C(6)). ^{31}P-NMR (162.0 MHz, (D_6)acetone): 183.9.

Dicarbonyl[O–4-η-((E)-4-phenylbut-3-en-2-one)](triethoxyphosphine)iron (**37**). Yield: 80%. Dark-red oil. ^{1}H-NMR (400.1 MHz, C_6D_6): 7.33 (*m*, H–C(2′), H–C(6′)); 7.11 (*m*, H–C(3′), H–C(5′)); 6.99 (*t*, H–C(4′)); 5.49 (*dd*, *J* = 8.7, 2.4, H–C(3)); 3.89 (*m*, $P(OCH_2CH_3)_3$); 2.90 (*dd*, *J*(H,H) = 8.7, *J*(P,H) = 7.7, H–C(4)); 2.28 (*d*, *J* = 3.8, 3 H–C(1)); 1.04 (*t*, *J* = 7.0, $P(OCH_2CH_3)_3$). ^{13}C-NMR (25.2 MHz, C_6D_6): 215.3 (*d*, *J*(P,C) = 18.3, CO); 210.8 (*d*, *J*(P,C) = 9, CO); 142.1 (*s*, C(2)); 138.3 (*s*, C(1′)); 128.3 (*s*, Ph); 127.1 (*s*, Ph); 125.4 (*s*, Ph); 78.3 (*s*, C(3)); 61.0 (*d*, *J*(P,C) = 3.3, $P(OCH_2CH_3)_3$); 57.9 (*s*, C(4)); 21.2 (*s*, C(1)); 16.3 (*s*, $P(OCH_2CH_3)_3$). ^{31}P-NMR (80.9 MHz, C_6D_6): 171.2.

Dicarbonyl[O–4-η-((E)-4-phenylbut-3-en-2-one)](triphenylphosphine)iron (**38**). Yield: 68%. Orange-red crystals. M.p. 140–142°. IR (CH_2Cl_2): 2000*s*, 1935*s*, 1600*w*, 1500*w*, 1485*w*, 1435*m*. ^{1}H-NMR (200.1 MHz, C_6D_6): 7.4–7.0 (br. *m*, Ph); 6.66 (br. *m*, Ph); 5.77 (*dd*, *J* = 8.8, 1.8, H–C(3)); 2.47 (*s*, 3 H–C(1)); 1.98 (*dd*, *J*(P,H) = *J*(H,H) = 8.8, H–C(4)). ^{13}C-NMR (25.2 MHz, C_6D_6): 142.4 (*s*, C(2)); 135.5–125.4 (Ph); 79.7 (*s*, C(3)); 63.1 (*s*, C(4)); 21.5 (*s*, C(1)). Anal. calc. for $C_{30}H_{25}FeO_3P$: C 69.27, H 4.80; found: C 69.25, H 4.57.

Dicarbonyl(cyclohexyl isocyanide)[O–4-η-((E)-4-phenylbut-3-en-2-one)]iron (**39**). Yield: 68%. Orange crystals. M.p. 114°. ^{1}H-NMR (400.1 MHz, C_6D_6): 7.40 (*d*, Ph); 7.1 (*m*, Ph); 6.93 (*t*, Ph); 5.13 (*d*, *J* = 10.6, H–C(3)); 4.15 (*d*, *J* = 10.6, H–C(4)); 3.2–3.0 (br. *m*, CH–NC); 2.46 (*s*, 3 H–C(1)); 1.4–1.1 (*m*, CH_2); 1.0–0.8 (*m*, CH_2). ^{13}C-NMR (50.4 MHz, C_6D_6): 215.0 (br., CO); 200.6 (*s*, C_6H_{11}–*N*C); 147.6 (*s*, C(2)); 128.9 (*s*, C(1′)); 128.5 (*s*, Ph); 127.2 (*s*, Ph); 124.0 (*s*, Ph); 54.5 (*s*, *C*H–NC); 52.8 (*s*, C(3)/C(4)); 52.2 (*s*, C(4)/C(3)); 32.4 (*s*, CH_2); 29.3 (*s*, C(1)); 24.9 (*s*, CH_2); 22.9 (*s*, CH_2).

Dicarbonyl[2–5-η-((2E,4E)-hexa-2,4-dienal)](triethylphosphine)ruthenium (**40**). Yield: 43%. Yellow oil. IR ($CHCl_3$): 2005*s*, 1945*s*, 1650*s*. ^{1}H-NMR (200.1 MHz, C_6D_6): 9.05 (*d*, *J* = 6.9, H–C(1)); 5.25 (*m*, H–C(4)); 4.75 (*m*, H–C(3)); 1.47 (*qd*, *J*(H,H) = *J*(P,H) = 7.8, $P(CH_2CH_3)_3$); 1.28 (*dd*, *J*(H,H) = 4.7, *J*(P,H) = 1.4, 3 H–C(6)); 1.18 (*m*, H–C(5)/H–C(2)); 0.9 (*m*, H–C(2)/H–C(5)); 0.73 (*dt*, *J*(P,H) = 15.7, *J*(H,H) = 7.4, $P(CH_2CH_3)_3$). ^{13}C-NMR (50.3 MHz, C_6D_6): 195.0 (*s*, C(1)); 90.1 (*s*, C(4)/C(3)); 81.6 (*d*, *J*(P,C) = 3.9, C(3)/C(4)); 55.8 (*d*, *J*(P,C) = 2.4,

C(5)/C(2)); 47.9 (*s*, C(2)/C(5)); 20.9 (*d*, J(P,C) = 25.9, P(CH_2CH_3)$_3$); 19.5 (*s*, C(6)); 7.5 (*d*, J(P,C) = 2.8, P(CH_2CH_3)$_3$). ^{31}P-NMR (80.9 MHz, C_6D_6): 25.9.

Dicarbonyl[2–5-η-((2E,4E)-hexa-2,4-dienal)](trimethoxyphosphine)ruthenium (**41**). Yield: 59%. Yellow crystals. M.p. 51°. IR ($CHCl_3$): 2025*s*, 1965*s*, 1660*m*. ^{1}H-NMR (200.1 MHz, $CDCl_3$): 9.06 (*d*, J = 6.1, H–C(1)); 5.6 (*m*, H–C(4)); 5.2 (*m*, H–C(3)); 3.66 (*d*, J = 12.2, P(OCH_3)$_3$); 1.48 (*d*, J = 3.9, 3 H–C(6)); 1.6–1.3 (*m*, H–C(2), H–C(5)). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 196.6 (*s*, C(1)); 91.4 (*s*, C(4)/C(3)); 80.4 (*d*, J(P,C) = 5.1, C(3)/C(4)); 54.0 (*s*, C(5)/C(2)); 51.8 (*d*, J(P,C) = 2.9, P(OCH_3)$_3$); 51.0 (*s*, C(2)/C(5)); 19.2 (*s*, C(6)). ^{31}P-NMR (80.9 MHz, $CDCl_3$): 162.8.

Dicarbonyl[2–5-η-(methyl (2E,4E)-hexa-2,4-dienoate)](triphenylphosphine)ruthenium (**42**). Yield: 57%. Yellow crystals. M.p. 115°. IR ($CHCl_3$): 2010*s*, 1950*s*, 1660*s*. ^{1}H-NMR (200.1 MHz, $CDCl_3$): 8.88 (*d*, J = 5.3, H–C(1)); 7.6–7.4 (*m*, Ph); 5.76 (*m*, H–C(4)); 5.28 (*m*, H–C(3)); 1.15 (*dd*, J(H,H) = 5.9, J(P,H) = 1.5, 3 H–C(6)); 0.6 (*m*, H–C(5)/H–C(2)); 0.4 (*m*, H–C(2)/H–C(5)). ^{13}C-NMR (50.3 MHz, (D_6)acetone): 202.3 (*d*, J(P,C) = 7.5, CO); 200.1 (*d*, J(P,C) = 2.7, CO); 195.9 (*s*, C(1)); 136.4 (*d*, J(P,C) = 42.6, C(1′)); 133.5 (*d*, J(P,C) = 11.9, C(2′), C(6′)); 130.9 (*d*, J(P,C) = 1.7, C(4′)); 129.3 (*d*, J(P,C) = 10.1, C(3′), C(5′)); 92.6 (*s*, C(4)/C(3)); 82.3 (*d*, J(P,C) = 4.2, C(3)/C(4)); 59.6 (*d*, J(P,C) = 2.8, C(5)/C(2)); 56.8 (*s*, C(2)/C(5)); 18.8 (*s*, C(6)). ^{31}P-NMR (80.9 MHz, (D_6)acetone): 45.7. Anal. calc. for $C_{26}H_{23}O_3PRu$: C 60.72. H 4.47; found: C 60.99, H 4.72.

Dicarbonyl[2–5-η-(methyl (2E,4E)-hexa-2,4-dienoate)](triethoxyphosphine)ruthenium (**43**). Yield: 61%. Yellow oil. IR ($CHCl_3$): 2015*s*, 1955*s*, 1695*s*. ^{1}H-NMR (200.1 MHz, C_6D_6): 5.78 (*m*, H–C(4)); 4.93 (*m*, H–C(3)); 3.91 (*qd*, J(H,H) = J(P,H) = 7.2, P(OCH_2CH_3)$_3$); 3.45 (*s*, OCH_3); 1.41 (*dd*, J(H,H) = 5.9, J(P,H) = 3.5, 3 H–C(6)); 1.13 (*t*, J = 7.1, P(OCH_2CH_3)$_3$); 1.3–1.0 (*m*, H–C(2), H–C(5)). ^{13}C-NMR (50.4 MHz, C_6D_6): 200.7 (*d*, J(P,C) = 12.9, CO); 198.9 (*s*, CO); 173.8 (*s*, C(1)); 89.9 (*s*, C(4)/C(3)); 82.5 (*d*, J(P,C) = 5.8, C(3)/C(4)); 60.6 (*d*, J(P,C) = 3.2, P(OCH_2CH_3)$_3$); 50.4 (*s*, C(5)); 50.3 (*s*, (OCH_3)); 42.1 (*s*, C(2)); 19.3 (*s*, C(6)); 16.2 (*d*, J(P,C) = 6.6, P(OCH_2CH_3)$_3$). ^{31}P-NMR (80.9 MHz, C_6D_6): 158.7.

Dicarbonyl[2–5-η-(methyl (2E,4E)-hexa-2,4-dienoate)](trimethoxyphosphine)ruthenium (**44**). Yield: 52%. Yellow oil. IR ($CHCl_3$): 2020*s*, 1960*s*, 1695*m*. ^{1}H-NMR (200.1 MHz, C_6D_6): 5.79 (*m*, H–C(4)); 4.86 (*m*, H–C(3)); 3.43 (*s*, $COOCH_3$); 3.37 (*d*, J(P,H) = 12.2, P(OCH_3)$_3$); 1.37 (*dd*, J(H,H) = 5.9, J(P,H) = 3.5, 3 H–C(6)); 1.3–1.1 (*m*, H–C(2), H–C(5)). ^{13}C-NMR (50.3 MHz, C_6D_6): 200.3 (*d*, J(P,C) = 13.1, CO); 198.5 (br. CO); 173.7 (*s*, C(1)); 89.9 (*s*, C(4)/C(3)); 82.3 (*s*, C(3)/C(4)); 51.6 (*d*, J(P,C) = 3.1, P(OCH_3)$_3$); 50.4 (*s*, $COOCH_3$); 49.9 (*s*, C(5)); 41.5 (*s*, C(2)); 19.4 (*s*, C(6)). ^{31}P-NMR (80.9 MHz, C_6D_6): 165.3.

(η^4-Buta-1,3-diene)carbonylbis(triethylphosphine)iron (**45**). Yield: 15%. Yellow oil. ^{13}C-NMR (100.6 MHz, (D_6)acetone): 220.4 (*t*, J(P,C) = 21, CO); 216.2 (*t*, J(P,C) = 28, CO); 81.5 (br. C(2), C(3)); 35.0 (br. C(1), C(4)); 23.3 (*m*), 22.3 (*m*) (P(CH_2CH_3)$_3$); 8.4, 8.2 (*s*, P(CH_2CH_3)$_3$). ^{31}P-NMR (162.0 MHz, (D_6)acetone): 53.1 (br.), 52.6 (br.), 49.3 (br.).

(η^4-Buta-1,3-diene)carbonylbis(triethoxyphosphine)iron (**46**). Yield: 85%. Yellow oil. ^{13}C-NMR (100.6 MHz, (D_6)acetone): 217.3 (*t*, J(P,C) = 26.0, CO); 213.3 (*t*, J(P,C) = 39.6, CO); 84.4, 82.4 (*s*, C(2), C(3)); 61.0, 60.9, 59.9 (*d*, P(OCH_2CH_3)$_3$); 38.3 (*s*, C(1), C(4)); 16.6 (*m*, P(OCH_2CH_3)$_3$). ^{31}P-NMR (162.0 MHz, (D_6)acetone): 188.1 (br.); 185.1.

(η^4-Buta-1,3-diene)carbonylbis(trimethoxyphosphine)iron (**47**). Yield: 88%. Yellow oil. ^{13}C-NMR (100.6 MHz, (D_6)acetone): 216.8 (*m*, CO); 84.4, 82.3 (*s*, C(2), C(3)); 51.2 (*s*, P(OCH_3)$_3$); 37.8 (br. C(1), C(4)). ^{31}P-NMR (162.0 MHz, (D_6)acetone, 193 K): 205.4 (*d*); 188.8 (*d*); J(P,P) = 17.

(η^4-Buta-1,3-diene)carbonyl(triethoxyphosphine)(triethylphosphine)iron (**48**). Yield: 91%. Yellow oil. IR (film): 3040*w*, 2980*m*, 2935*m*, 1895*s*, 1457*m*, 1443*m*, 1386*m*, 1035*s*. ^{1}H-NMR (400.1 MHz, C_6D_6): 5.05 (*m*, H–C(2)/H–C(3)); 4.91 (*m*, H–C(3)/H–C(2)); 3.92–3.78 (*m*, P(OCH_2CH_3)$_3$); 1.70–0.89 (*m*, H_b–C(1), H_b–C(4), P(CH_2CH_3)$_3$, P(OCH_2CH_3)$_3$, –0.69 (*m*, H_a–C(1)/H_a–C(4)); –0.61 (*m*, H_a–C(4)/H_a–C(1)). ^{13}C-NMR (100.6 MHz, (D_6)acetone): 218.5 (*dd*, J(P,C) = 32.4, 16.4, CO); 81.3 (*s*, C(2), C(3)); 60.5 (*d*, J(P,C) = 5.6, P(OCH_2CH_3)$_3$); 37.1 (br. *s*, C(1)/C(4)); 36.1 (br. *s*, C(4)/C(1)); 21.6 (*d*, J(P,C) = 22.6, P(CH_2CH_3)$_3$); 16.7 (*d*, J(P,C) = 4.8, P(OCH_2CH_3)$_3$); 8.1 (*s*, P(CH_2CH_3)$_3$). ^{31}P-NMR (162.0 MHz, (D_6)acetone): 182.2 (br.); 54.3 (*d*); J(P,P) = 21.0.

(η^4-Buta-1,3-diene)carbonyl(triethylphosphine)(trimethoxyphosphine)iron (**49**). Yield: 72%. Yellow oil. IR (film): 3040*w*, 2960*m*, 2940*m*, 2910*m*, 2880*m*, 2840*m*, 1895*s*, 1458*m*, 1425*w*, 1378*w*, 1030*s*. ^{1}H-NMR (200.1 MHz, C_6D_6): 5.04 (*m*, H–C(2)/H–C(3)); 4.88 (*m*, H–C(3)/H–C(2)); 3.37 (*d*, J = 10.6, P(OCH_3)$_3$); 1.59 (*qd*, J(H,H) = J(P,H) = 7.5, P(CH_2CH_3)$_3$); 1.50–1.20 (*m*, H_b–C(1), H_b–C(4)); 1.00 (*dt*, J(P,H) = 14, J(H,H) = 7.5, P(CH_2CH_3)$_3$); –0.57–(–)0.72 (*m*, H_a–C(1), H_a–C(4)). ^{13}C-NMR (100.6 MHz, (D_6)acetone): 218.5 (*dd*, J(P,C) = 28.8, 18.1, CO); 81.5 (*s*, C(2)/C(3)); 81.1 (*s*, C(3), C(2)); 51.7 (*d*, J(P,C) = 5.3, P(OCH_3)$_3$); 36.3 (br., C(1), C(4)); 21.5 (*d*, J(P,C) = 22.6, P(CH_2CH_3)$_3$); 8.0 (*s*, P(CH_2CH_3)$_3$). ^{31}P-NMR (162.0 MHz, (D_6)acetone): 188.2 (br.); 53.9 (*d*); J(P,P) = 18.1.

(η^4-Buta-1,3-diene)carbonyl(triethoxyphosphine)(trimethoxyphosphine)iron (**50**). Yield: 44%. Yellow oil. ^{13}C-NMR (100.6 MHz, (D_6)acetone): 217.1 (*dd*, J(P,C) = 30, 23, CO); 82.6 (*s*, C(2)/C(3)); 82.1 (*s*, C(3)/C(2)); 60.1 (*d*, J(P,C) = 3, P(O*C*H$_2$CH$_3$)$_3$); 51.1 (*s*, P(OCH$_3$)$_3$); 38.5 (*s*, C(1)/C(4)); 37.4 (*s*, C(4)/C(1)); 16.5 (*d*, J(P,C) = 6, P(OCH$_2$*C*H$_3$)$_3$). ^{31}P-NMR (162.0 MHz, (D_6)acetone): 196.1 (br.); 186.0 (br.).

(η^4-Buta-1,3-diene)carbonyl(triethoxyphosphine)(triphenylphosphine)iron (**51**). Yield: 15%. Yellow crystals. IR ($CHCl_3$): 3060*w*, 2985*m*, 2930*w*, 2900*w*, 1895*s*, 1481*w*, 1436*m*, 1388*w*, 1030*s*. ^{1}H-NMR (200.1 MHz, (D_6)acetone): 7.5 (*m*, H–C(2′)/H–C(6′)); 7.4 (*m*, H–C(3′), H–C(4′), H–C(5′)); 5.07 (*m*, H–C(2)/H–C(3)); 4.56 (*m*, H–C(3)/H–C(2)); 3.93 (*qd*, J = 7.1, 1.0, P(OC*H*$_2$CH$_3$)$_3$); 1.40 (*m*, H$_b$–C(1)/H$_b$–C(4)); 1.12 (*t*, J = 7.1, P(OCH$_2$C*H*$_3$)$_3$); 0.60 (*m*, H$_b$–C(4), H$_b$–C(1)); –0.69 (*m*, H$_a$–C(1)/H$_a$–C(4)); –0.90 (*m*, H$_a$–C(4)/H$_a$–C(1)). ^{13}C-NMR (100.6 MHz, (D_6)acetone): 219.5 (*dd*, J(P,C) = 25.8, 16.8, CO); 139.1 (*d*, J(P,C) = 35.2, C(1′)); 134.4 (*s*, C(2′), C(6′)); 129.7 (*s*, C(4′)); 128.3 (*s*, C(3′), C(5′)); 84.2 (*s*, C(2)/C(3)); 81.4 (*d*, C(3)/C(2)); 60.7 (*d*, J(P,C) = 6.2, P(O*C*H$_2$CH$_3$)$_3$); 43.6 (*s*, C(1)/C(4)); 36.2 (*s*, C(4)/C(1)); 16.5 (*d*, J(P,C) = 4.6, P(OCH$_2$*C*H$_3$)$_3$). ^{31}P-NMR (162.0 MHz, (D_6)acetone): 185.8 (br.); 77.1.

(η^4-Buta-1,3-diene)carbonyl(trimethoxyphosphine)(triphenylphosphine)iron (**52**). Yield: 31%. Yellow crystals. M.p. 105°. IR ($CHCl_3$): 3060*w*, 3010*m*, 2950*m*, 2845*w*, 1898*s*, 1480*m*, 1446*m*, 1028*s*. ^{1}H-NMR (400.1 MHz, C_6D_6): 7.75–7.65 (*m*, H–C(2′), H–C(6′)); 7.15–7.0 (*m*, H–C(3′), H–C(4′), H–C(5′)); 5.35 (*m*, H–C(2)/H–C(3)); 4.88 (*m*, H–C(3)/H–C(2)); 3.37 (*d*, J = 11.0, P(OCH$_3$)$_3$); 1.85 (*d*, J = 6.7, H$_b$–C(1)/H$_b$–C(4)); 1.08 (*m*, H$_b$–C(4)/H$_b$–C(1)); –0.07 (*m*, H$_a$–C(1)/H$_a$–C(4)); –0.26 (*m*, H$_a$–C(4)/H$_a$–C(1)). ^{13}C-NMR (100.6 MHz, (D_6)acetone): 219.4 (*dd*, J(P,C) = 26.6, 15.6, CO); 138.9 (*d*, J(P,C) = 35.5, C(1′)); 134.3 (*d*, J(P,C) = 4.3, C(2′), C(6′)); 129.8 (*s*, C(4′)); 127.9 (*s*, C(3′), C(5′)); 84.2 (*s*, C(2)/C(3)); 81.0 (*s*, C(3)/C(2)); 51.9 (*d*, J(P,C) = 6, P(OCH$_3$)$_3$); 43.0 (*s*, C(1)/C(4)); 35.5 (*s*, C(4), C(1)). ^{31}P-NMR (162.0 MHz, (D_6)acetone): 191.5; 76.7. Anal. calc. for $C_{26}H_{30}FeO_4P_2$: C 59.56, H 5.77; found: C 59.80, H 6.00.

Carbonyl[1–4-η-((E)-penta-1,3-diene)](triethylphosphine)(trimethoxyphosphine)iron (**53**). Yield: 78%. Yellow crystals. ^{13}C-NMR (100.6 MHz, (D_6)acetone; 2 diastereoisomers): 219.8 (*dd*, J(P,C) = 30.4, 11.2, CO); 218.4 (*dd*, J(P,C) = 41.0, 10.4, CO); 85.3 (*s*, C(3)); 79.3 (*s*, C(2)); 77.7 (*s*, C(3)); 51.7 (*m*, P(OCH$_3$)$_3$); 48.3 (*s*); 46.7 (*s*) (C(4)); 37.5 (*s*), 37.1 (*s*) (C(1)); 21.7 (*d*, J(P,C) = 22), 21.1 (*d*, J(P,C) = 21) (P(*C*H$_2$CH$_3$)$_3$); 19.8 (*s*, C(5)); 8.2 (*d*), 8.0 (*d*) (P(CH$_2$*C*H$_3$)$_3$). ^{31}P-NMR (162.0 MHz, (D_6)acetone): *isomer a:* 195.7; 52.6; *isomer b:* 183.0 (*d*); 50.6 (*d*); J(P,P) = 16.

Carbonyl[1–4-η-(2-methylbuta-1,3-diene)]bis(triethoxyphosphine)iron (**54**). Yield: 50%. Yellow oil. ^{13}C-NMR (100.6 MHz, (D_6)acetone): 217.0 (*dd*, J(P,C) = 36, 14, CO); 97.1 (*s*, C(2)); 82.9 (*s*, C(3)); 60.0 (*d*, J(P,C) = 3.5, P(O*C*H$_2$CH$_3$)$_3$); 59.7 (*d*, J(P,C) = 2.9, P(O*C*H$_2$CH$_3$)$_3$); 40.3 (*s*, C(1)); 37.3 (*s*, C(4)); 23.1 (*s*, CH$_3$–C(2)); 16.6 (*d*, J(P,C) = 6, P(OCH$_2$*C*H$_3$)$_3$). ^{31}P-NMR (162.0 MHz, (D_6)acetone): 192.0 (br.); 183.3 (br.).

Carbonyl[1–4-η-(2-methylbuta-1,3-diene)]bis(trimethoxyphosphine)iron (**55**). Yield: 55%. Yellow oil. ^{13}C-NMR (100.6 MHz, (D_6)acetone): 216.7 (*dd*, J(P,C) = 36, 14, CO); 97.3 (*s*, C(2)); 82.7 (*s*, C(3)); 51.3 (*d*, J(P,C) = 4.3); 51.1 (*s*) (P(O*C*H$_3$)$_3$); 40.0 (*s*, C(1)); 36.4 (*s*, C(4)); 23.1 (*s*, CH$_3$–C(2)). ^{31}P-NMR (162.0 MHz, (D_6)acetone): 198.1 (br.); 188.1 (br.).

Carbonyl[1–4-η-(2-methylbuta-1,3-diene)](triethylphosphine)(trimethoxyphosphine)iron (**56**). Yield: 25%. Yellow oil. ^{13}C-NMR (100.6 MHz, (D_6)acetone; 2 diastereoisomers): 218.8 (*t*, J(P,C) = 14); 217.9 (*dd*, J(P,C) = 38, 8.5) (CO); 95.5 (*s*, C(2)); 81.4 (*s*), 84.0 (*s*), 82.6 (*s*) (C(3)); 51.8 (*m*, P(O*C*H$_3$)$_3$); 39.2 (br., C(1)); 35.8 (*s*, C(4)); 23.5 (*s*, CH$_3$–C(2)); 21.8 (*d*, J(P,C) = 23); 21.1 (*d*, J(P,C) = 22) (P(*C*H$_2$CH$_3$)$_3$); 8.0 (br. *s*, P(CH$_2$*C*H$_3$)$_3$). ^{31}P-NMR (162.0 MHz, (D_6)acetone): *isomer a:* 196.7 (br.); 54.6 (*d*, J(P,P) = 17.5); *isomer b:* 182.7 (*d*); 53.9 (*d*); J(P,P) = 26.

Carbonyl[1–4-η-(2-methylbuta-1,3-diene)](triethoxyphosphine)(trimethoxyphosphine)iron (**57**). Yield: 34%. Yellow oil. ^{13}C-NMR (100.6 MHz, (D_6)acetone; 2 diastereoisomers): 216.8 (*dd*, J(P,C) = 34.7, 15.5, CO); 97.4 (*s*), 97.1 (*s*) (C(2)); 82.8 (*s*), 82.7 (*s*), (C(3)); 60.1 (*s*), 59.9 (*s*) (P(O*C*H$_2$CH$_3$)$_3$); 51.3 (*s*), 51.1 (*s*) (P(O*C*H$_3$)$_3$); 40.3 (br.), 36.9 (br.) (C(1)/C(4)); 23.1 (*s*, CH$_3$–C(2)); 16.6 (*s*), 16.5 (*s*) (P(OCH$_2$*C*H$_3$)$_3$). ^{31}P-NMR (162.0 MHz, (D_6)acetone): 199.8 (br.); 191.0 (br.); 189.5 (br.); 182.6 (br.).

Carbonyl[1–4-η-(2-methylbuta-1,3-diene)](trimethoxyphosphine)(triphenylphosphine)iron (**58**). Yield: 70%. Yellow crystals. ^{13}C-NMR (100.6 MHz, (D_6)acetone; main isomer): 219.0 (*dd*, J(P,C) = 27.6, 10.4, CO); 139.0 (*d*, J(P,C) = 35, C(1′)); 134.3 (*s*, C(2′), C(6′)); 129.7 (*s* (C(4′)); 128.3 (*s*, C(3′), C(5′)); 95.6 (*s*, C(2)); 84.2 (*s*, C(3)); 52.0 (*d*, J(P,C) = 5, P(OCH$_3$)$_3$); 40.7 (*s*, C(1)); 36.6 (*s*, C(4)); 22.3 (*s*, CH$_3$–C(2)). ^{31}P-NMR (162.0 MHz, (D_6)acetone): 191.4 (br.); 78.4 (*d*, J(P,P) = 8).

Carbonyl[2–5-η-((2E,4E)-hexa-2,4-diene)]bis(trimethoxyphosphine)iron (**59**). Yield: 42%. Orange oil. ^{13}C-NMR (100.6 MHz, (D_6)acetone, 203 K): 218.2 (*dd*, J(P,C) = 41, 10, CO); 86.2 (*s*), 83.2 (*s*) (C(3)/C(4)); 55.7 (*s*, C(2)/C(5)); 51.4 (*s*), 51.0 (*s*) (P(OCH$_3$)$_3$); 50.1 (*s*, C(5)/C(2)); 19.9 (*s*), 19.4 (*s*) (C(1)/C(6)). ^{31}P-NMR (162.0 MHz, (D_6)acetone, 213 K): 194.9 (*d*); 187.2 (*d*); J(P,P) = 6.4.

Carbonyl[2–5-η-((2E,4E)-hexa-2,4-dienal)]bis(triethoxyphosphine)iron (**60**). Yield: 45%. Yellow oil. ^{13}C-NMR (100.6 MHz, (D_6)acetone, 203 K): 217.6 (*dd*, J(P,C) = 45.1, 17.5, CO); 202.6 (*s*, C(1)); 86.1 (*s*, C(4)/C(3)); 84.8 (*s*, C(3)/C(4)); 60.6 (*d*, J(P,C) = 3, P(OCH_2CH$_3$)$_3$); 56.8 (*s*, C(5)/C(2)); 53.9 (*s*, C(2)/C(5)); 19.3 (*s*, C(6)); 16.8 (*d*, J(P,C) = 5, P(OCH$_2$$CH_3$)$_3$). ^{31}P-NMR (162.0 MHz, (D_6)acetone): 183.6 (br.); 182.4 (br.); 177.1 (br.); 174.4 (br.).

Carbonyl[2–5-η-((2E,4E)-hexa-2,4-dienal)]bis(trimethoxyphosphine)iron (**61**). Yield: 48%. Yellow oil. ^{13}C-NMR (100.6 MHz, (D_6)acetone, 203 K): 217.3 (*dd*, J(P,C) = 45.0, 17.5, CO); 203.4 (*s*, C(1)); 86.3 (*d*, C(4)/C(3)); 84.9 (*d*, C(3)/C(4)); 56.5 (*d*, C(5)/C(2)); 53.8 (*d*, C(2)/C(5)); 52.1 (*s*, P(OCH_3)$_3$); 19.4 (*s*, C(6)). ^{31}P-NMR (162.0 MHz, (D_6)acetone): 187.8 (br.); 180.3 (br.).

Carbonyl[2–5-η-((2E,4E)-hexa-2,4-dienal)](triethoxyphosphine)(triethylphosphine)iron (**62**). Yield: 28%. *Isomer a:* 11%, yellow crystals; *isomer b:* 17%, yellow oil. IR ($CHCl_3$): *isomer a:* 2980*s*, 2940*m*, 2905*m*, 2820*w*, 2735*w*, 1908*s*, 1680*m*, 1642*s*, 1460*m*, 1388*m*, 1035*s*; *isomer b:* 2980*s*, 2940*m*, 2905*m*, 2810*w*, 2735*w*, 1905*s*, 1643*s*, 1458*m*, 1442*m*, 1390*m*, 1035*s*. ^{1}H-NMR (400.1 MHz, C_6D_6): *isomer b:* 9.30 (*d*, J = 7.2, H–C(1)); 5.29 (*m*, H–C(4)); 4.56 (*dd*, J = 7.8, 4.7, H–C(3)); 3.77–3.64 (*m*, P(OCH_2CH$_3$)$_3$); 1.85 (*m*, P(CH_2CH$_3$)$_3$); 1.45 (*t*, J = 5.5, 3 H–C(6)); 1.06 (*m*, P(OCH$_2$CH_3)$_3$, P(CH$_2$CH_3)$_3$); 0.67 (*m*, H–C(5)/H–C(2)); 0.39 (*m*, H–C(2)/H–C(5)). ^{13}C-NMR (100.6 MHz, (D_6)acetone): *isomer a:* 216.5 (*dd*, J(P,C) = 47.8, 7.9, CO); 198.7 (*s*, C(1)); 89.7 (*s*, C(4)); 75.6 (*s*, C(3)); 61.6 (*d*, J(P,C) = 8, P(OCH_2CH$_3$)$_3$); 55.3 (*s*, C(5)/C(2)); 52.6 (*s*, C(2)/C(5)); 19.7 (*d*, J(P,C) = 20.7, P(CH_2CH$_3$)$_3$); 19.2 (*s*, C(6)); 16.5 (*s*, P(OCH$_2$$CH_3$)$_3$); 8.0 (*s*, P(CH$_2$$CH_3$)$_3$); *isomer b:* 219.1 (*dd*, J(P,C) = 43.5, 13.4, CO); 200.8 (*s*, C(1)); 85.3 (*s*, C(4)/C(3)); 82.3 (*s*, C(3)/C(4)); 61.5 (*d*, J(P,C) = 7.2, P(OCH_2CH$_3$)$_3$); 56.2 (*s*, C(5)/C(2)); 48.8 (*s*, C(2)/C(5)); 21.2 (*d*, J(P,C) = 23.0, P(CH_2CH$_3$)$_3$); 19.3 (*s*, C(6)); 16.5 (*s*, P(OCH$_2$$CH_3$)$_3$); 8.0 (*s*, P(CH$_2$$CH_3$)$_3$). ^{31}P-NMR (162.0 MHz, (D_6)acetone): *isomer a:* 173.2 (*d*); 42.0 (*d*), J(P,P) = 40.4; *isomer b:* 169.5; 42.9. Anal. calc. for $C_{19}H_{38}FeO_5P_2$: C 49.15, H 8.25; found (*isomer b*): C 49.00, H 8.33.

Carbonyl[2–5-η-((2E,4E)-hexa-2,4-dienal)](triethoxyphosphine)(trimethoxyphosphine)iron (**63**). Yield: 38%. Yellow oil. ^{13}C-NMR (100.6 MHz, (D_6)acetone, 203 K, 2 main isomers): 217.5 (*dd*, J(P,C) = 44.5, 17.0, CO); 217.4 (*dd*, J(P,C) = 44.5, 18.5, CO); 202.8 (*s*), 202.3 (*s*) (C(1)); 86.3 (*s*), 86.2 (*s*) (C(4)/C(3)); 85.0 (*s*), 84.8 (*s*) (C(3)/C(4)); 60.7 (*d*, J(P,C) = 2), 60.5 (*d*, J(P,C) = 2) (P(OCH_2CH$_3$)$_3$); 57.0 (*s*), 56.2 (*s*) (C(5)/C(2)); 54.0 (*s*), 53.7 (*s*) (C(2)/C(5)); 52.0 (*s*), 51.6 (*s*) (P(OCH_3)$_3$); 19.5 (*s*), 19.2 (*s*) (C(6)); 16.8 (*s*), 16.6 (*s*) (P(OCH$_2$$CH_3$)$_3$). ^{31}P-NMR (162.0 MHz, (D_6)acetone, 203 K): *isomer a:* 183.5 (*s*); 181.8 (*s*); *isomer b:* 189.7 (*d*); 176.5 (*d*); J(P,P) = 9.

Carbonyl[2–5-η-((2E,4E)-hexa-2,4-dienal)](trimethoxyphosphine)(triphenylphosphine)iron (**64**). Yield: 18%. *Isomer a:* 12%, yellow crystals, m.p. 128°; *isomer b:* 6%, yellow oil. IR ($CHCl_3$): *isomer a:* 3060*w*, 3005*m*, 2950*m*, 2840*w*, 2730*w*, 1915*s*, 1648*s*, 1482*w*, 1435*m*, 1030*s*; *isomer b:* 3060*w*, 3005*m*, 2950*m*, 2840*w*, 2740*w*, 1910*s*, 1710*m*, 1650*s*, 1482*w*, 1435*m*, 1030*w*. ^{1}H-NMR (400.1 MHz, C_6D_6): *isomer b:* 9.51 (*d*, J = 6.9, H–C(1)); 7.81 (*m*, H–C(2′)/H–C(6′)); 7.15–7.00 (*m*, H–C(3′)/H–C(4′)/H–C(5′)); 5.44 (*m*, H–C(4)); 4.67 (*dd*, J = 8.3, 4.6, H–C(3)); 3.09 (*d*, J(P,H) = 9.8, P(OCH_3)$_3$); 1.31 (*m*, 3 H–C(6)); 0.89 (*m*, H–C(5)/H–C(2)); 0.29 (*m*, H–C(2)/H–C(5)). ^{13}C-NMR[3]) (100.6 MHz, (D_6)acetone): *isomer a:* 216.4 (*m*, CO); 198.7 (br., C(1)); 138.9 (*d*, J(P,C) = 36.4 C(1′)); 134.4 (*s*, C(2′), C(6′)); 129.9 (*s*, C(4′)); 128.5 (*s*, C(3′), C(5′)); 91.2 (*s*, C(4)); 75.8 (*s*, C(3)); 64.5 (*s*, C(5)); 57.0 (*s*, C(2)); 52.4 (*s*, P(OCH_3)$_3$); 17.7 (*s*, C(6)); *isomer b:* 218.7 (*dd*, J(P,C) = 44.4, 12.5, CO); 201.2 (*s*, C(1)); 138.4 (*d*, J(P,C) = 36.9, C(1′)); 134.6 (*s*, C(2′), C(6′)); 129.9 (*s*, C(4′)); 128.5 (*s*, C(3′), C(5′)); 87.1 (*s*, C(4)); 84.7 (*s*, C(3)); 60.9 (*s*, C(5)); 57.4 (*s*, C(2)); 52.2 (*s*, P(OCH_3)$_3$); 18.5 (*s*, C(6)). ^{31}P-NMR (162.0 MHz, (D_6)acetone): *isomer a:* 178.0 (*d*); 69.5 (*d*); J(P,P) = 19.7; *isomer b:* 174.6 (*s*); 69.5 (*s*). Anal. calc. for $C_{28}H_{32}FeO_5P_2$: C 59.38, H 5.70; found (*isomer a*): C 59.34, H 5.45; found (*isomer b*): C 59.17, H 5.47.

Carbonyl[2–5-η-(methyl (2E,4E)-hexa-2,4-dienoate)]bis(triethylphosphine)iron (**65**). Yield: 16%. Orange oil. ^{13}C-NMR (100.6 MHz, (D_6)acetone): 221.7 (*dd*, J(P,C) = 32.9, 13.2, CO); 177.4 (*s*, C(1)); 85.2 (*s*, C(4)/C(3)); 83.8 (*s*, C(3)/C(4)); 50.3 (*s*, OCH$_3$); 44.8 (*s*, C(5)/C(2)); 42.4 (*s*, C(2)/C(5)); 22.7 (*d*, J(P,C) = 21, P(CH_2CH$_3$)$_3$); 20.6 (*d*, J(P,C) = 18, P(CH_2CH$_3$)$_3$); 19.1 (*s*, C(6)); 8.8 (*s*, P(CH$_2$$CH_3$)$_3$); 8.3 (*s*, P(CH$_2$$CH_3$)$_3$). ^{31}P-NMR (162.0 MHz, (D_6)acetone): 43.1 (*d*); 40.3 (*d*); J(P,P) = 2.

Carbonyl[2–5-η-(methyl (2E,4E)-hexa-2,4-dienoate)](triethoxyphosphine)(triethylphosphine)iron (**66**). Yield: 58%. Yellow oil. ^{13}C-NMR (100.6 MHz, (D_6)acetone; 2 diastereoisomers): 218.9 (*dd*, J(P,C) = 40.4, 15.4, CO); 216.0 (*dd*, J(P,C) = 46.9, 8.5, CO); 175.5 (*s*, C(1)); 87.6 (*s*), 83.9 (*d*), 81.0 (*s*) (C(4)/C(3)); 61.3 (*m*, P(OCH_2CH$_3$)$_3$); 50.1 (*d*, OCH$_3$); 50.0–40.0 (C(2)/C(5)); 21.2 (*d*, J(P,C) = 22, P(CH_2CH$_3$)$_3$); 19.2 (*s*, C(6)); 16.5 (*s*), 16.4 (*s*) (P(OCH$_2$$CH_3$)$_3$); 8.0 (*s*, P(CH$_2$$CH_3$)$_3$). ^{31}P-NMR (162.0 MHz, (D_6)acetone): *isomer a:* 182.7 (*d*); 46.0 (*d*); J(P,P) = 8.0; *isomer b:* 174.3 (*d*); 44.0 (*d*); J(P,P) = 36.4.

---

[3]) Both diastereoisomers **64a** and **64b** show the presence of rotational isomers in the ^{1}H-, ^{13}C-, and ^{31}P-NMR spectra at r.t. The signals reported refer to the main isomers.

Carbonyl[2–5-η-(methyl (2E,4E)-hexa-2,4-dienoate)](triethoxyphosphine)(trimethoxyphosphine)iron (**67**). Yield: 54% (*isomer a:* 25%, *isomer b:* 29%). Yellow oils. ^{13}C-NMR (100.6 MHz, (D_6)acetone, 203 K): *isomer a:* 214.9 (*dd*, J(P,C) = 47.1, 8.8, CO); 175.9 (*s*, C(1)); 89.4 (*s*, C(4)); 77.8 (*s*, C(3)); 60.4 (*s*, $P(OCH_2CH_3)_3$); 51.5 (*s*, $P(OCH_3)_3$); 51.1 (*s*, $COOCH_3$); 45.0 (*s*, C(5)); 41.3 (*s*, C(2)); 19.5 (*s*, C(6)); 16.7 (*s*, $P(OCH_2CH_3)_3$); *isomer b:* 217.5 (*dd*, J(P,C) = 45.7, 15.2 CO); 175.7 (*s*, C(1)); 84.4 (*s*, C(4)/C(3)); 82.6 (*s*, C(3)/C(4)); 60.3 (*s*, $P(OCH_2CH_3)_3$); 51.5 (*s*, $P(OCH_3)_3$; 51.0 (*s*, $COOCH_3$); 44.6 (*s*, C(5)); 41.3 (*s*, C(2)); 19.2 (*s*, C(6)); 16.9 (*s*, $P(OCH_2CH_3)_3$). ^{31}P-NMR (162.0 MHz, (D_6)acetone): *isomer a:* 184.7 (br.); 184.3 (br.); *isomer b:* 189.5 (br.); 173.5 (br.).

Carbonyl[2–5-η-(methyl (2E,4E)-hexa-2,4-dienoate)](triethoxyphosphine)(triethylphosphine)ruthenium (**68**). Yield: 11%. Yellow oil. IR ($CHCl_3$): 1930*s*, 1730*w*, 1680*m*. ^{1}H-NMR (200.1 MHz, C_6D_6): 5.9 (*m*, H–C(4)); 4.9 (*m*, H–C(3)); 3.71 (*m*, $P(OCH_2CH_3)_3$); 3.64 (*s*, OCH_3); 2.1–0.6 (*m*, $P(CH_2CH_3)_3$, H–C(2), H–C(5), 3 H–C(6), $P(CH_2CH_3)_3$, $P(OCH_2CH_3)_3$). ^{13}C-NMR (50.3 MHz, C_6D_6): *isomer a*[4]): 174.7 (br., C(1)); 89.3 (*s*, C(4)/C(3)); 76.1 (*t*, J(P,C) = 3.4, C(3)/C(4)); 60.4 (*d*, J(P,C) = 5.8, $P(OCH_2CH_3)_3$); 49.9 (*s*, OCH_3); 48.0–39.6 (*m*, C(2), C(5)); 21.5 (*d*, J(P,C) = 24.8, $P(CH_2CH_3)_3$); 19.1 (*d*, J(P,C) = 3, C(6)); 16.2 (*d*, J(P,C) = 6.3, $P(OCH_2CH_3)_3$); 7.6 (*d*, J(P,C) = 1.7, $P(CH_2CH_3)_3$). ^{31}P-NMR (80.9 MHz, C_6D_6): *isomer a:* 153.5 (*d*); 27.1 (*d*); J(P,P) = 29.5; *isomer b:* 164.7 (*d*); 26.5 (*d*); J(P,P) = 11.0.

Carbonyl[2–5-η-(methyl (2E,4E)-hexa-2,4-dienoate)](triethylphosphine)(trimethoxyphosphine)ruthenium (**69**). Yield: 10%. Yellow oil[5]). IR ($CHCl_3$): 1920*s*, 1690*m*. ^{1}H-NMR (200.1 MHz, C_6D_6): 5.9 (*m*, H–C(4)); 4.9 (*m*, H–C(3)); 3.49 (*s*, $COOCH_3$); 3.43 (*d*, J(P,H) = 11.4, $P(OCH_3)_3$); 1.87 (*m*, $P(CH_2CH_3)_3$); 1.41 (*d*, J(H,H) = 6.6, 3 H–C(6)); 1.05 (*dt*, J(P,H) = 15.0, J(H,H) = 7.5, $P(CH_2CH_3)_3$); 1.2–0.8 (*m*, H–C(5)/H–C(2)); 0.65 (*m*, H–C(2)/H–C(5)). ^{13}C-NMR (50.3 MHz, C_6D_6): 174.9 (*d*, J(P,C) = 3.4, C(1)); 84.8 (*d*, J(P,C) = 3.2, C(4)/C(3)); 81.6 (*d*, J(P,C) = 3.2, C(3)/C(4)); 52.1 (*d*, J(P,C) = 4.9, $P(OCH_3)_3$); 49.8 (*s*, $COOCH_3$); 45.6, 44.6, 41.2 (C(2), C(5)); 21.6 (*dd*, J(P,C) = 23.9, 2.3, $P(CH_2CH_3)_3$); 19.9 (*d*, J(P,C) = 3.4, C(6)); 7.6 (*qd*, J(P,C) = 2.4, $P(CH_2CH_3)_3$). ^{31}P-NMR (80.9 MHz, C_6D_6): 154.5 (*d*); 26.2 (*d*); J(P,P) = 28.5.

Carbonyl[2–5-η-(methyl (2E,4E)-hexa-2,4-dienoate)](triethoxyphosphine)(trimethoxyphosphine)ruthenium (**70**). Yield: 12.5% (*isomer a:* 7.1%, yellow oil; *isomer b:* 5.4%, yellow oil). ^{1}H-NMR (400.1 MHz, CD_2Cl_2): *isomer a* (247 K, main rotamer): 5.41 (*m*, H–C(4)); 4.81 (*m*, H–C(3)); 3.88 (*m*, $P(OCH_2CH_3)_3$); 3.48 (*s*, OCH_3); 3.44 (*d*, J(P,H) = 12, $P(OCH_3)_3$); 1.31 (*dd*, J(H,H) = 6.1, J(P,H) = 3.3, 3 H–C(6)); 1.23 (*t*, J(H,H) = 7.0, $P(OCH_2CH_3)_3$); 0.75 (*m*, H–C(5)/H–C(2)); 0.58 (*m*, H–C(2)/H–C(5)); *isomer b* (259 K, main rotamer): 5.42 (*m*, H–C(4)); 4.84 (*m*, H–C(3)); 3.78 (*m*, $P(OCH_2CH_3)_3$); 3.54 (*d*, J(P,H) = 12.1, $P(OCH_3)_3$); 3.45 (*s*, $COOCH_3$); 1.37 (*dd*, J(H,H) = 5.9, J(P,H) = 3.2, 3 H–C(6)); 1.18 (*t*, J(H,H) = 7.0, $P(OCH_2CH_3)_3$); 0.78 (*m*, H–C(5)/H–C(2)); 0.55 (*m*, H–C(2)/H–C(5)). ^{13}C-NMR (100.6 MHz, CD_2Cl_2): *isomer a* (228 K, main rotamer): 202.2 (*s*, CO); 175.7 (*s*, C(1)); 90.5 (*s*, C(4)/C(3)); 75.9 (*s*, C(3)/C(4)); 59.4 (*s*, $P(OCH_2CH_3)_3$); 51.1 (*s*, $P(OCH_3)_3$); 51.0–38.0 (C(2), C(5), $COOCH_3$); 18.2 (*s*, C(6)); 16.1 (*d*, J(P,C) = 7.2, $P(OCH_2CH_3)_3$); *isomer b* (213 K, main rotamer): 202.1 (*s*, CO); 174.6 (*s*, C(1)); 91.4 (*s*, C(4)/C(3)); 76.1 (*s*, C(3)/C(4)); 60.0 (*s*, $P(OCH_2CH_3)_3$); 50.9 (*m*, $P(OCH_3)_3$, $COOCH_3$); 39.4 (*d*, C(2), C(5)); 18.7 (*s*, C(6)); 16.2 (*d*, J(P,C) = 6.8, $P(OCH_2CH_3)_3$). ^{31}P-NMR (80.9 MHz, C_6D_6): *isomer a:* 171.3 (br.); 153.3 (br.); 166.0 (*d*); 162.7 (*d*); J(P,P) = 40.0; *isomer b:* 173.4 (*d*); 156.8 (*d*), J(P,P) = 38.7; 163.6 (br.), 158.9 (br.).

REFERENCES

[1] E.J. Corey, G. Moinet, *J. Am. Chem. Soc.* **1973,** *95,* 7185; G. Evans, B.F.G. Johnson, J. Lewis, *J. Organomet. Chem.* **1975,** *102,* 507; D.H.R. Barton, A.A.L. Gunatilaka, T. Nakanishi, H. Patin, D.D. Widdowson, B.R. Worth, *J. Chem. Soc., Perkin Trans. 1* **1976,** 821; G.D. Annis, E.M. Hebblethwaite, S.V. Ley, *J. Chem. Soc., Chem. Commun.* **1980,** 297; D. Farcasiu, G. Marino, *J. Organomet. Chem.* **1983,** *253,* 243.

[2] J. Morey, D. Grée, P. Mosset, L. Toupet, G. Grée, *Tetrahedron Lett.* **1987,** *28,* 2959; M. Franck-Neumann, M. Sedrati, M. Mokhi, *Angew. Chem.* **1986,** *98,* 1138; A. Hafner, H. Bieri, R. Prewo, W. von Philipsborn, A. Salzer, *ibid.* **1983,** *95,* 736; A. Hafner, W. von Philipsborn, A. Salzer, *ibid.* **1985,** *97,* 136.

[3] A.J. Birch, W.D. Raverty, S.-Y. Hsu, A.J. Pearson, *J. Organomet. Chem.* **1984,** *260,* C59; L.A.P. Kane-Maguire, *J. Chem. Soc.* **1971,** 1602.

[4] H. Brunner, *Adv. Organomet. Chem.* **1980,** *18,* 151; M. Brookhart, J.R. Tucker, G.R. Husk, *J. Am. Chem. Soc.* **1983,** *105,* 258.

---

[4]) Main diastereoisomer; small signals of second isomer (*b*) not listed.

[5]) According to TLC and NMR spectra, only one diastereoisomer was formed.

[5] a) J. A. S. Howell, M. J. Thomas, *J. Chem. Soc., Dalton Trans.* **1983,** 1401; b) M. Brookhart, D. Timmers, J. R. Tucker, G. D. Williams, G. R. Husk, H. Brunner, B. Hammer, *J. Am. Chem. Soc.* **1983,** *105,* 6721.

[6] N. Aktogu, H. Felkin, S. G. Davies, *J. Chem. Soc., Chem. Commun.* **1982,** 1303; S. G. Davies, I. M. Dordor-Hedgecok, P. Warner, R. H. Jones, K. Prout, *J. Organomet. Chem.* **1985,** *285,* 213; G. J. Baird, S. G. Davies, *ibid.* **1983,** *248,* C1.

[7] a) S. Ruh, W. von Philipsborn, *J. Organomet. Chem.* **1977,** *127,* C59; S. Zobl-Ruh, W. von Philipsborn, *Helv. Chim. Acta* **1981,** *64,* 2378; b) T. H. Whitesides, R. A. Budnik, *Inorg. Chem.* **1975,** *14,* 664.

[8] L. Gmelin, 'Handbook of Inorganic Chemistry', 'Organoiron Compounds', 8th edn., Part B6, Springer Verlag, Berlin, Heidelberg, New York 1981, p. 25ff, and ref. cit. therein.

[9] Y. Shvo, E. Hazum, *J. Chem. Soc., Chem. Commun.* **1975,** 829; F. Birenczwaig, H. Shamai, Y. Shvo, *Tetrahedron Lett.* **1979,** 2947.

[10] L. F. Kelly, A. J. Birch, *J. Organomet. Chem.* **1985,** *286,* C5.

[11] C. M. Adams, Ph. D. Thesis, University of Zürich, 1987.

[12] E. Koerner v. Gustorf, Z. Pfajfer, F. W. Grewels, *Z. Naturforsch.* **1971,** *266,* 66; O. Jaenicke, R. C. Kerber, P. Kirsch, E. A. Koerner v. Gustorf, R. Rumin, *J. Organomet. Chem.* **1980,** *187,* 361, and ref. cit. therein; G. L. Geoffroy, M. S. Wrighton, 'Organometallic Photochemistry', Academic Press, New York, 1979, Chapt. 2.

[13] L. Kruzynski, J. Takats, *J. Am. Chem. Soc.* **1974,** *96,* 932; L. Kruzynski, J. Takats, *Inorg. Chem.* **1976,** *15,* 3140.

[14] M. A. Busch, R. J. Clark, *Inorg. Chem.* **1975,** *14,* 226; C. B. Ungermann, K. G. Caulton, *J. Organomet. Chem.* **1975,** *94,* C9; J. A. S. Howell, D. T. Dixon, J. C. Kola, *ibid.* **1984,** *266,* 69; J. A. S. Howell, G. Walton, *J. Chem. Soc., Chem. Commun.* **1986,** 622.

[15] M. Koller, Diploma Thesis, University of Zürich, 1988.

[16] O. S. Mills, G. Robinson, *Acta Crystallogr.* **1963,** *16,* 758; A. J. Pearson, P. R. Raithby, *J. Chem. Soc., Dalton Trans.* **1981,** 884; F. H. Herbstein, M. G. Reisner, *Acta Crystallogr., Sect. B* **1977,** *33,* 3304.

[17] Ch. A. Tolman, *Chem. Rev.* **1977,** *77,* 313.

[18] C. M. Adams, G. Cerioni, A. Hafner, H. Kalchhauser, W. von Philipsborn, R. Prewo, A. Schwenk, *Helv. Chim. Acta* **1988,** *71,* 1116.

[19] A. R. Rossi, R. Hoffmann, *Inorg. Chem.* **1975,** *14,* 365; M. Elian, R. Hoffmann, *ibid.* **1975,** *14,* 1058.

[20] G. M. Sheldrick, SHELXTL, An Integrated System for Solving, Refining, and Displaying Crystal Structures from Diffraction Data, Version 5.1, 1985.

[21] W. P. Fehlhammer, W. A. Herrmann, K. Oefele, in 'Handbuch der Präparativen Anorganischen Chemie', 3. Aufl., Ed. G. Brauer, Ferdinand Enke Verlag, Stuttgart, 1981, Bd. 3, S. 1827.

[22] A. Marcuzzi, Diploma Thesis, University of Zürich, 1988.

[23] G. F. Emerson, J. E. Mahler, R. Kochhar, R. Pettit, *J. Org. Chem.* **1964,** *29,* 3620; R. K. Kochhar, R. Pettit, *J. Organomet. Chem.* **1966,** *6,* 272; R. B. King, T. A. Manuel, F. G. A. Stone, *J. Inorg. Nucl. Chem.* **1961,** *16,* 233; H. W. Whitlock, C. Reich, W. D. Woessner, *J. Am. Chem. Soc.* **1971,** *93,* 2483.

[24] Ref. [8] p. 163ff and ref. cit. therein.