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The preparation of bis(η^3-allyl)iron(II) complexes and their reactions with 1,3-dienes

B. Gabor, S. Holle, P.W. Jolly and R. Mynott

Max-Planck-Institut für Kohlenforschung, D-45466 Mülheim an der Ruhr (Germany)

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Abstract

The title compounds were prepared by treating $\mathrm{Fe(PR_3)_2Cl_2}$ or $\mathrm{Fe(R_2P(CH_2)_nPR_2)Cl_2}$ with allylmagnesium chloride. Some of them were also made by reaction of $\mathrm{Fe(PR_3)_2Cl_2}$ with isopropylmagnesium chloride, or with active-magnesium and allyl chloride, or by reaction between tris(η^3-allyl)iron and bis(dimethylphosphino)ethane. The new compounds were characterized by NMR spectroscopy and shown to be formed as a mixture of two isomers that differ in the mutual arrangement of the two allyl groups. The reactions of the bis(allyl)iron compounds with 1,3-dienes were studied: complexes containing η^4-1,3-$\mathrm{C_4H_6}$, η^4-1-$\mathrm{C_3H_5C_4H_5}$ or η^5-1-ethylcyclohexadienyl groups were isolated from the reaction with 1,3-butadiene. The reaction between (η^3-$\mathrm{C_3H_5)_2Fe(^iPr_2PC_2H_4P^iPr_2)}$ and 1,3-cyclohexadiene gave (η^5-cyclohexadienyl)$\mathrm{Fe(^iPr_2PC_2H_4P^iPr_2)H}$.

Key words: Iron; Allyl; Diene; Cyclohexadienyl

1. Introduction

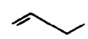
In continuation of our investigations of the chemistry of the donor-ligand stabilized bis(η^3-allyl)metal complexes of the transition metals [1-3], we have turned our attention to species containing iron. Although (η^3-$\mathrm{C_3H_5)_2Fe(CO)_2}$ was first reported almost 25 years ago [4], the only other bis(η^3-allyl)iron compounds described since contain either the 2-methylallyl group, *e.g.* (η^3-2-$\mathrm{MeC_3H_4)_2Fe(PMe_3)_2}$ [5], or the η^3-pentadienyl group, *e.g.* (η^3-1-$\mathrm{CH_2:CHC_3H_4)_2Fe(PMe_3)_2}$ and (η^3-1-$\mathrm{CH_2:CHC_3H_4)_2Fe(Et_2PC_2H_4PEt_2)}$ [6]. Crystal structure determinations of the last two compounds indicate that they have a C_2-symmetry, with the metal atom lying at the centre of a pseudo-octahedron. The allyl groups adopt a *cis*-arrangement with the two *meso*-C-atoms pointing away from the $\mathrm{FeP_2}$ fragment.

We report here the preparation of examples containing the η^3-$\mathrm{C_3H_5}$ group and describe their reactions with 1,3-dienes.

2. Results and discussion

2.1. Preparation

The (η^3-$\mathrm{C_3H_5)_2Fe(PR_3)_2}$ and (η^3-$\mathrm{C_3H_5)_2Fe(R_2P(CH_2)_nPR_2)}$ compounds (**1**-**7**, **9**-**11**; see Table 1) and (η^3-2-$\mathrm{MeC_3H_4)_2Fe(^iPr_2PCH_2P^iPr_2)}$ (**12**) have been prepared by the conventional reaction between allylmagnesium chloride and either a preformed $\mathrm{Fe(PR_3)_2Cl_2}$ or $\mathrm{Fe(R_2P(CH_2)_nPR_2)Cl_2}$ compound or $\mathrm{Fe(THF)_nCl_2}$ in the presence of a monodentate or bidentate phosphine (*e.g.* eqn. (1)).

$\mathrm{Fe(PMe_3)_2Cl_2} + 2$  MgCl $\longrightarrow$

$$(\eta^3\text{-}\mathrm{C_3H_5)_2Fe(PMe_3)_2} + 2\mathrm{MgCl_2} \qquad (1)$$

1

Some of them were also prepared by treating the dichloride with allyl lithium (**1**, **10**) or with active-Mg (prepared by thermolysis of $\mathrm{MgH_2}$ [7]) and allyl bromide (**10**, **12**). The complex (η^3-$\mathrm{C_3H_5)_2Fe(Me_2PC_2H_4PMe_2)}$ (**8**) could only be obtained by the reaction of (η^3-$\mathrm{C_3H_5)_3Fe}$ with the bidentate ligand. (η^3-$\mathrm{C_3H_5)_2Fe(^iPr_2PC_2H_4P^iPr_2)}$ (**10**) was also obtained,

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Correspondence to: Professor P.W. Jolly.

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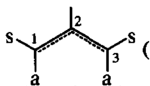
TABLE 1. Selected ^{1}H NMR spectroscopic data for the $(\eta^3\text{-}C_3H_5)_2Fe(PR_3)_2$ and $(\eta^3\text{-}C_3H_5)_2Fe(R_2P(CH_2)_nPR_2)$ compounds **1–12** measured in d_8-toluene

		$\delta ^1$H [a]					
$PR_3/R_2P(CH_2)_nPR_2$ (*n*)	*T* (°C)	1s	3s	1a	3a	2	Ligand
PMe_3 (**1**; isomer-I)	−80	1.87	1.76	0.47	−0.52	4.05	0.84br
(**1**; isomer-II)		1.97	1.97	1.67	−0.23	3.83	0.84br
		1.87 [e]	0.76	1.47	0.82	5.46	0.84br
PEt_3 (**2**; isomer-I)	−80	2.38	1.54	–	−0.17	4.29	1.4–0.8
PMe_2Ph (**3**; isomer-I)	−30	2.35q	1.70d	0.52dd	−0.34dd	4.09m	6.8–7.0(Ph), 1.20/1.01(Me)
PPh_2Me (**4**; isomer-I) [b]	−30	2.88	1.92	0.97	0.07	4.70	2.00/1.04(Me),
		3.08 [e]	1.99	0.11	0.52	4.56	6.6–7.7(Ph)
$P(OMe)_3$ (**5**; isomer-I)	−30		2.45/1.63/0.44 (1:2:1)			4.18	3.40t
$^iPr_2PCH_2P^iPr_2$ (**6**; isomer-I)	−30	2.85	1.42d	0.85	0.42dd	3.51m	2.90(t, CH_2), 2.14/1.62(CH), 1.27/1.09/0.81/0.69(Me)
$Ph_2PCH_2PPh_2$ (**7**; isomer-I)	−30	3.05	1.91	–	−0.17	3.79	4.79(CH_2)
$Me_2PC_2H_4PMe_2$ (**8**; isomer-I) [d]	−30	1.49	1.35d	−0.29dd	−0.69dd	3.40m	2.33/1.88(C_2H_4), 1.47/0.71(d, Me)
$Et_2PC_2H_4PEt_2$ (**9**; isomer-I)	−30	–	–	−0.14m	−0.25m	3.94	1.8–0.8
$^iPr_2PC_2H_4P^iPr_2$ (**10**; isomer-I) [d]	−30	1.80	1.39d	0.10	−0.20	3.25	2.40(C_2H_4), 2.37/1.61(CH), 1.2–0.8(Me)
$Ph_2PC_3H_6PPh_2$ (**11**; isomer-II)	−80	3.42	2.64	2.53d	0.12	3.82	7.0 (br, Ph)
		2.79d [e]	0.30	1.18	0.77t	5.80	
$^iPr_2PCH_2P^iPr_2$ (**12**; isomer-I) [c]	−30	2.68	–	0.42d	–	2.24(Me)	2.81(CH_2), 1.61(CH), 1.3–0.6(Me)

[a] 

(H-1 *trans* to P): the assignments are based on C,H- and COSY-90-correlated spectra.

[b] **4** is assigned a *cis*-structure even though the allyl groups are inequivalent; see text.

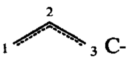
[c] $(\eta^3\text{-}2\text{-}MeC_3H_4)_2Fe(R_2PCH_2PR_2)$ compound.

[d] Solvent; d_8-THF.

[e] 11s, 13s, 11a, 13a, 12; see structural diagram II for numbering scheme.

TABLE 2. ^{13}C NMR spectroscopic data for the $(\eta^3\text{-}C_3H_5)_2Fe(PR_3)_2$ and $(\eta^3\text{-}C_3H_5)_2Fe(R_2P(CH_2)_nPR_2)$ compounds measured in d_8-toluene

		$\delta ^{13}$C [a]			
$PR_3/R_2P(CH_2)_nPR_2$ (*n*)	*T* (°C)	1	3	2	Ligand
PMe_3 (**1**; isomer-I, 43%)	−80	37.9{18.9}	39.7	81.7	19.2br [e]
(**1**; isomer-II, 57%)		34.5	49.0	85.5	19.5(20)/18.6(18)
		41.1 [d]	41.6	86.3	
PMe_2Ph (**3**; isomer-I, 90%)	−30	39.6{18.2}	40.5{7.4}	83.2{4.8}	143.6–127.5(Ph), 20.5{30}/16.1{21.3}(Me)
PPh_2Me (**4**; isomer-I) [b]	−30	41.0(13.5)	39.9	81.0	21.7(25.7)/14.7(12)(Me)
		44.6(13) [d]	40.3	81.9	146–127(Ph)
$^iPr_2PCH_2P^iPr_2$ (**6**; isomer-I)	−30	31.0{12.8}	34.4{6.8}	86.4{4.0}	33.5(12.5)(CH_2), 30.7{15.7}/27.9{6.2}(CH), 20.2/20.1/19.7/19.3(Me)
$Ph_2PC_3H_6PPh_2$ (**11**; isomer-II)	−80	44.7(9)	43.3	86.6	143–125.2(Ph),
		42.0 [d]	56.2	87.1	31.2(26)/26.3(20)/21.4(CH_2)
$^iPr_2PCH_2P^iPr_2$ (**12**; isomer-I) [c]	−30	31.9/31.7(1/3), 90.3(2), 25.4(2-Me)			28.4(CH_2), 23.3(CH), 19.7/19.3/17.8/17.6(Me)

[a] 

C-1 *trans* to P; *J*(PC) in parentheses; *J*(PC) + *J*(P′C) curly brackets.

[b] see text.

[c] $(\eta^3\text{-}2\text{-}MeC_3H_4)_2Fe(R_2PCH_2PR_2)$ compound.

[d] 11, 13, 12; see structural diagram II for numbering scheme.

[e] 21.7/14.3(2:1) −110°C/d_8-THF.

albeit in low yield, from the following reaction with i-propylmagnesium chloride (eqn. (2)).

$$\mathrm{Fe(^iPr_2PC_2H_4P^iPr_2)Cl_2 + 2Me_2CHMgCl} \xrightarrow{-2\mathrm{MgCl_2}}$$

$$\mathrm{[(Me_2CH)_2Fe(^iPr_2PC_2H_4P^iPr_2)]} \xrightarrow{-4[\mathrm{H}]}$$

$$(\eta^3\text{-}\mathrm{C_3H_5})_2\mathrm{Fe(^iPr_2PC_2H_4P^iPr_2)} \quad (2)$$

10

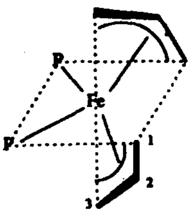
This presumably involves the initial generation of an $(\text{i-}C_3H_7)_2Fe$ species, which reacts further by a double β-H transfer process in which the fate of the four H atoms is unknown.

Compounds 1–12 were isolated as yellow to orange solids which decompose above *ca.* 0°C. Many are sufficiently volatile to allow mass spectra to be recorded: fragmentation proceeds by the consecutive elimination of the allyl groups and of the donor ligand molecules.

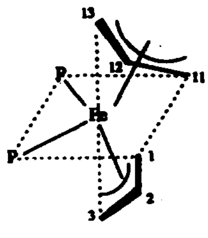
2.2. NMR and structural characterization

The compounds are diamagnetic (18e systems) and ^{1}H- and ^{13}C-NMR spectroscopic data are listed in Tables 1 and 2. The ^{31}P-NMR spectral data are given in the Experimental section.

The spectra of the compounds are consistent with a pseudo-octahedral structure in which each η^3-allyl group formally occupies two coordination positions around the central metal atom. In contrast to the previously known examples containing substituted allyl groups [5,6], the compounds are formed as a mixture of two isomers (I, II) that differ in the relative arrangement of the two iron-bonded allyl groups. In I, the two *meso*-C atoms point away from the FeP_2 fragment and the molecule has a twofold axis (C_2), whereas in II the two *meso*-C atoms point in different directions and the molecule has no symmetry (C_1).



I (C_2)



II (C_1)

Formally, the two forms can be interconverted by rotation of one of the allyl groups by 180°C about the metal–allyl axis. A third possible isomer, in which both *meso*-C atoms point towards the FeP_2 fragment, is not observed, and is presumably destabilized by steric interference between the *meso*-H atoms and the donor ligands. Structure I is that revealed previously by X-ray crystallography for $(\eta^3\text{-1-CH}_2:\text{CHC}_3\text{H}_4)_2\text{Fe(PMe}_3)_2$ and $(\eta^3\text{-1-CH}_2:\text{CHC}_3\text{H}_4)_2\text{Fe(Et}_2\text{PC}_2\text{H}_4\text{PEt}_2)$ [6], whereas II was previously unknown.

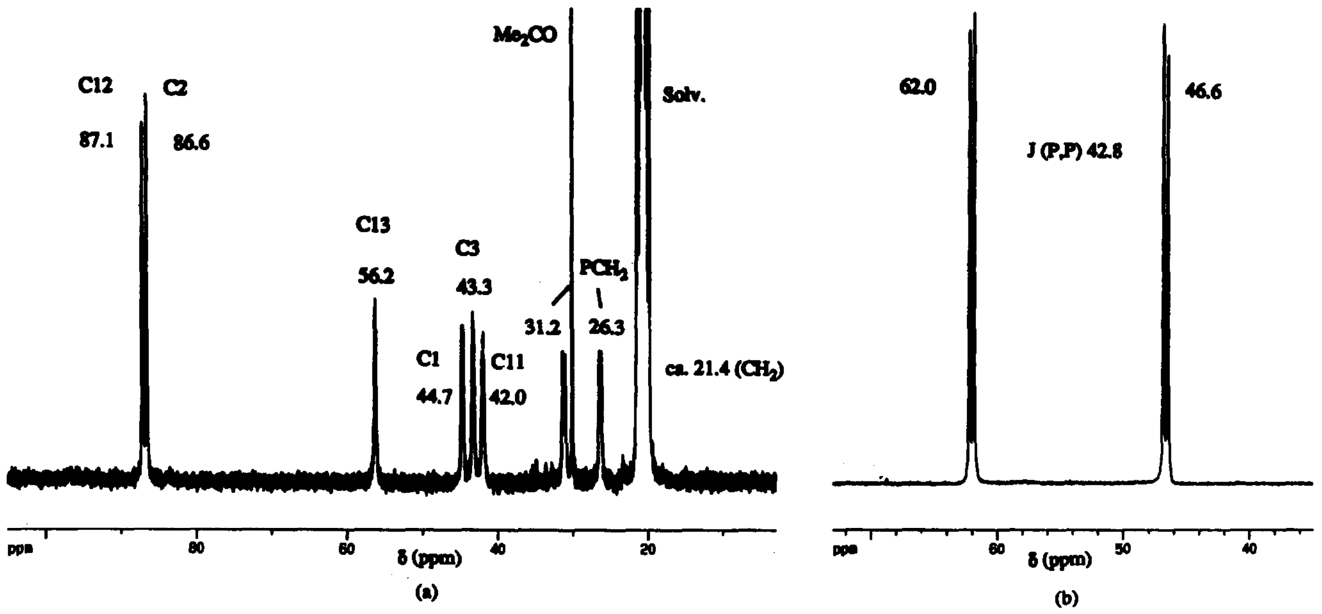


Fig. 1. The NMR spectra of $(\eta^3\text{-C}_3\text{H}_5)_2\text{Fe(Ph}_2\text{PC}_3\text{H}_6\text{PPh}_2)$ (11): (a) ^{13}C{^{1}H}-NMR spectrum and (b) ^{31}P{^{1}H}-NMR spectrum; −80°C in d_8-toluene. The assignments, in particular those for C-1 and C-3 (see Table 2), have been confirmed by ^{13}C, ^{1}H chemical shift correlated and COSY 2D-NMR spectra.

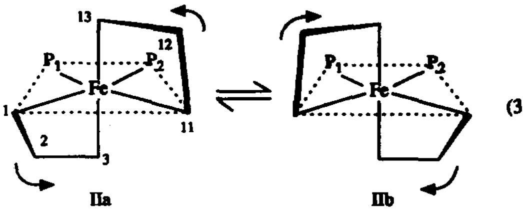
The η^3-allyl groups in isomer-I are equivalent and the NMR spectrum contains 5 signals for the H atoms and 3 for the C atoms, whereas in isomer-II the η^3-allyl groups are different and 10 signals are observed for the H atoms and 6 for the C atoms. The ^{13}C-NMR signals of the terminal allyl carbon atoms of I are apparent triplets (X part of AA'X spin system; A,A' $= {}^{31}$P, X $= {}^{13}$C) due to coupling with phosphorus. In agreement with the suggested octahedral geometry, the splitting ($1/2[J_{PC}+J_{P'C}]$) for one carbon atom (C-1) is significantly larger than that for the other, consistent with the presence of a larger *quasi-trans* coupling in this case but only *quasi-cis* coupling for C-3. Even at low temperature the signals for II are frequently too broad to allow observation of the phosphorus–carbon couplings as a result of exchange (see below).

The available data (further reaction or partial decomposition to give paramagnetic material prevented us from obtaining satisfactory spectra in a number of cases) are not sufficient for conclusive generalizations concerning the relationship between the two isomers. It appears, however, that their relative stabilities are highly dependent upon the particular phosphorus ligands present. Nevertheless, if the preparation and isolation is carried out at −30°C, isomer-I is formed exclusively in all cases except that involving $Ph_2PC_3H_6PPh_2$, for which only isomer-II is detected (Fig. 1). Samples enriched in isomer-II were obtained by carrying out the reaction and product isolation at −80°C for systems involving PMe_3 (**1**), PEt_3 (**2**), PMe_2Ph (**3**), and $^iPr_2PC_2H_4P^iPr_2$ (**10**). In the case of the reaction involving PMe_3, the use of allyllithium (instead of allylmagnesium chloride) at −80°C gave a sample containing mainly II.

The relationship between the two isomers has been investigated in greatest detail for the PMe_3-stabilized compound **1** and is discussed below. A sample prepared at −80°C (see above) has been shown by ^{31}P- and ^{13}C-NMR spectroscopy to consist of *ca.* 43% of isomer-I and *ca.* 57% of isomer-II.

The NMR spectra of I in solution remain practically unaltered between −110°C and 0°C. Isomer-II, in contrast, shows dynamic behaviour above *ca.* −80°C. Three processes can be distinguished, and these are considered separately below.

1) At −80°C, the terminal C-atoms within each allyl group exchange without the allyl groups themselves undergoing site exchange; *i.e* at this temperature II is not stereochemically rigid but undergoes equilibration with its mirror image (eqn. (3)); the arrows show the direction of movement of the allyl groups in the isomerization process).



(3)

IIa IIb

The ^{31}P 2D-EXSY spectrum shows cross peaks between the signals of the two phosphorus atoms and at the same time a ^{13}C 2D-EXSY spectrum reveals cross peaks between the signals from C-1 and C-3 and between C-11 and C-13 but not between the carbon atoms in different allyl groups. The 2D exchange spectra also show that this exchange process does not involve I as an intermediate, since no cross peaks are observed between the signal from this isomer and the phosphorus ligands in II (Fig. 2). Analysis of the ^{31}P and ^{13}C 2D-EXSY spectra at −80°C gives an exchange rate for this process of 15 s^{-1}, from which the free energy of activation ($\Delta G^{\ddagger}$) can be calculated as 42 kJ mol^{-1}. The 2D exchange spectra were recorded at low temperature to obtain information about the exchange process because there was a serious overlap of signals at intermediate temperatures and the sample rearranged at higher temperatures.

2) At −30°C (AMX-300) the two allyl groups exchange with each other, and as a result the signals

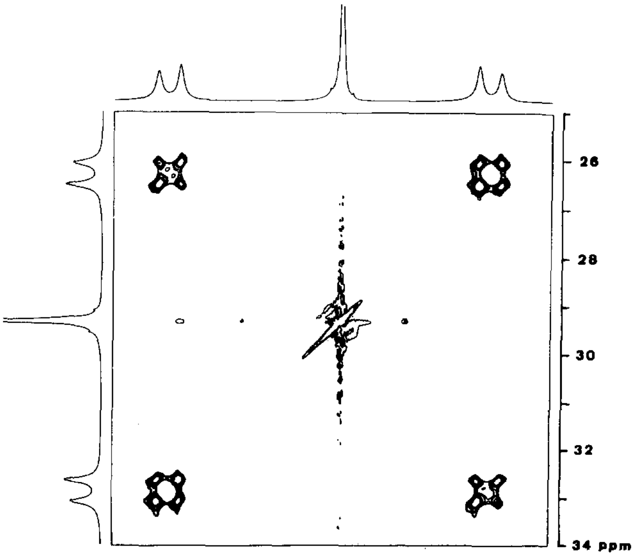


Fig. 2. 121.4 MHz ^{31}P 2D-EXSY spectrum of $(\eta^3\text{-}C_3H_5)_2Fe(PMe_3)_2$ (**1**) at −80°C. Whereas the phosphorus signals for the isomer-II at 26.2 and 32.8 ppm have strong cross peaks due to exchange, none are observed between these resonances and the singlet from isomer-I at 29.3 ppm.

from the two phosphorus atoms, the six carbon atoms, and the ten hydrogen atoms coalesce to give respectively one signal, two broad signals (δ_C (*terminal*) 41.5 ppm, δ_C(*meso*) 86.3 ppm) and three broad signals (δ(*meso*-H) *ca.* 4.5 ppm, δ(*syn*/*anti*-H) 1.6 ppm and 0.8 ppm) respectively. The 1D ^{1}H- and ^{13}C-NMR spectra at −30°C show that the signals of the isomer-I remain sharp during this process, clearly indicating that it is not involved as an intermediate.

3) Above 0°C, an irreversible conversion of II into I occurs.

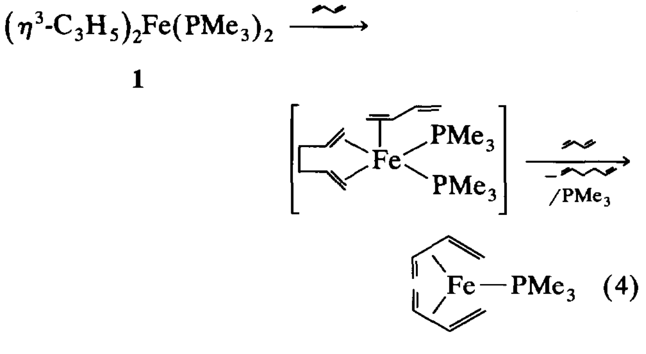
Process 2 and 3 presumably proceed by the familiar mechanism involving the intermediate rearrangement of an η^3-allyl group into the η^1-allyl form but we were unable to confirm this unambiguously from the ^{1}H-NMR spectra. The difference in stability between the two isomers (II is kinetically stable even though I is the more thermodynamically stable) probably results from steric interactions between the allyl groups and the P-donor ligands. An additional indication that these molecules are indeed sterically strained comes from the ^{13}C-NMR spectrum of isomer-I at −110°C: two signals are observed in the ratio 2:1 for the P-bonded methyl groups, indicating that at this temperature rotation about the Fe–P bond is restricted.

The results discussed above for $(\eta^3\text{-}C_3H_5)_2Fe(PMe_3)_2$ (**1**) are not general for all of the compounds shown in Table 1. For example, isomer-II of $(\eta^3\text{-}C_3H_5)_2Fe(Ph_2PC_3H_6PPh_2)$ (**11**, Fig. 1) shows no tendency to isomerize below the decomposition point.

The spectroscopic results for $(\eta^3\text{-}C_3H_5)_2Fe(PPh_2Me)_2$ (**4**) are anomalous: although 10 signals are observed for the H-atoms and 6 signals for the C-atoms and the ^{31}P-NMR spectrum is that for an AB-spin system, the NMR parameters are otherwise more consistent with those for I. For example, the chemical shifts for the two *meso*-H atoms are almost identical (4.70 and 4.56 ppm) and J(P, P) is small (8.0 Hz). These values contrast with those for $(\eta^3\text{-}C_3H_5)_2(PMe_3)_2$ (δ_H(*meso*) 3.83 and 5.36, J(P, P) 55.4 Hz) and suggest that **4** has structure I in which the symmetry has been lowered. That this is the result of differences in the coordination geometry of the PPh_2Me ligands is supported by the unexpectedly large difference between the chemical shifts of the P-methyl C atoms (δ_C 21.7/14.7).

2.3. Reactions

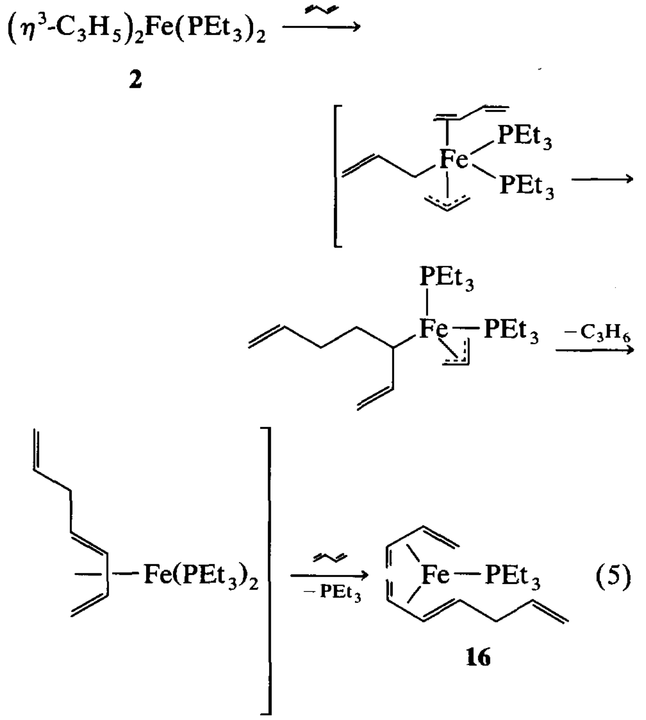
We investigated the reactions of selected $(\eta^3\text{-}C_3H_5)_2Fe$ species with 1,3-dienes. $(\eta^3\text{-}C_3H_5)_2Fe(PMe_3)_2$ (**1**) reacts with 1,3-butadiene to give the $(\eta^4\text{-}1,3\text{-}C_4H_6)_2Fe$ compound **13**, presumably as the product of a butadiene-induced reductive coupling of the allyl groups followed by diene exchange (eqn. (4)).



(4)

13

The PEt_3 analogue **14** is one of the products of the reaction between $(\eta^3\text{-}C_3H_5)_2Fe(PEt_3)_2$ (**2**) and 1,3-butadiene. However, the main products of this reaction are $(\eta^4\text{-}1\text{-}C_3H_5C_4H_5)_2FePEt_3$ (**15**) and $(\eta^4\text{-}C_4H_6)(\eta^4\text{-}1\text{-}C_3H_5C_4H_5)FePEt_3$ (**16**) and these can be understood as the products of the 1,2-insertion of butadiene molecules into the Fe–allyl bond followed by β-H transfer (*e.g.* eqn. (5)).



(5)

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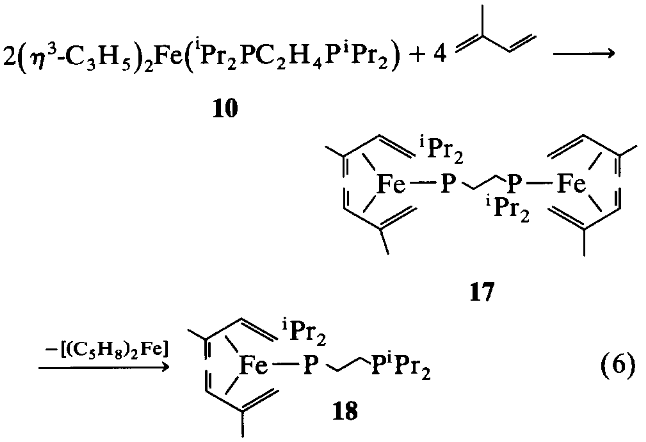
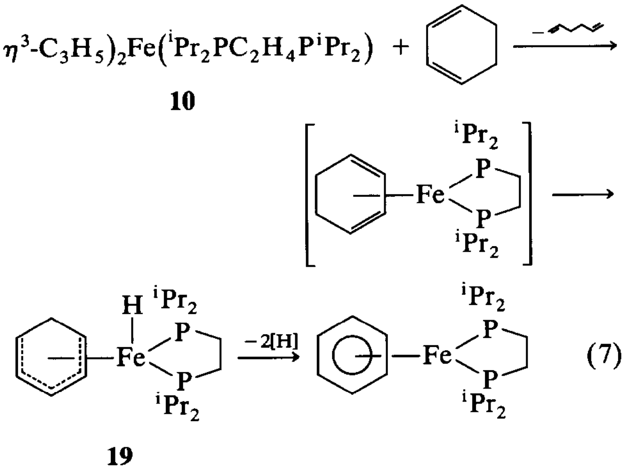
The compounds $(\eta^4\text{-}C_4H_6)_2FePR_3$ were prepared either by reaction of $(\eta^4\text{-}C_4H_6)Fe(PR_3)_3$ with butadiene [9], reduction of iron salts in the presence of a donor ligand and butadiene [9–11], by cocondensation of the ligands with vaporized iron [12–15], or by ligand exchange [16,17].

$(\eta^4\text{-}1,3\text{-}diene)_2Fe$ species have also been isolated from the reaction of $(\eta^3\text{-}C_3H_5)_2Fe(^iPr_2PC_2H_4P^iPr_2)$ (**10**) with isoprene. The ^{31}P-NMR spectra indicate that initially a dinuclear species with a bridging bidentate ligand (**17**) is formed, and that this reacts further at 30°C in solution to give the mononuclear compound **18** (eqn. (6)).



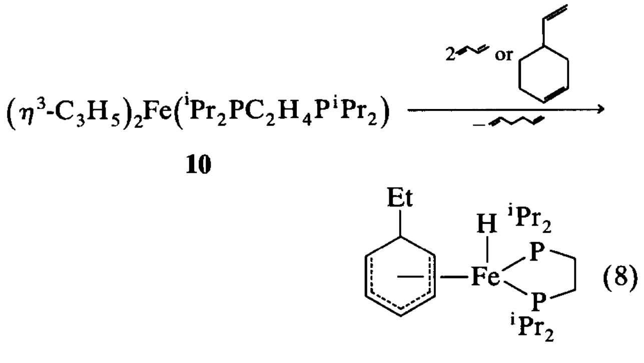
A third compound, (η^4-isoprene)Fe($^iPr_2PC_2H_4P^iPr_2$), was detected in a mass spectrometer when **17** was heated to 97°C [*m/e* 386 (M^+), 318 ($M^+ - C_5H_8$)] but was not isolated. Although isomers are possible for **17** and **18**, depending upon the relative arrangement of the pairs of isoprene molecules [12], the data suggest that only one is formed. Compound **18** can also be prepared in high yield by reducing Fe($^iPr_2PC_2H_4P^iPr_2$)Cl_2 with activated-Mg in the presence of isoprene.

Completely different behaviour is observed upon reaction of **10** with 1,3-cyclohexadiene or 1,3-butadiene, (η^5-cyclohexadienyl)iron-hydride species being formed. The product of the reaction with 1,3-cyclohexadiene is **19**, and this could be converted into the corresponding (η^6-benzene)Fe species by refluxing in toluene, the fate of the dihydrogen being unknown (eqn. (7)).



19

The reaction of **10** with 1,3-butadiene gives the η^5-1-ethylcyclohexadienyl species **20**. The same compound is also the product of the reaction between **10** and 4-vinyl-1-cyclohexene, suggesting that the butadiene is initially dimerized and then reacts further (eqn. (8)).



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Both **19** and **20** are already known: **19** is the product of the reaction between Fe($^iPr_2PC_2H_4P^iPr_2$)Cl_2, active-Mg and 1,3-cyclohexadiene [18], while a related compound has been identified in the product mixture formed in the reaction of 1,3-cyclohexadiene and $P(OMe)_3$ with vaporized-Fe [12] and **20** has been prepared by reacting $(CH_2{:}CH_2)_2Fe(^iPr_2PC_2H_4P^iPr_2)$ with 1,3-cyclohexadiene, and the structure of the related $^iPr_2PC_3H_6P^iPr_2$-stabilized compound has been determined by X-ray diffraction [18].

3. Experimental section

Most of the compounds described below are thermally labile and air sensitive and all experiments were carried out at low temperatures under argon using oxygen-free solvents. $Fe(PMe_3)_2Cl_2$ [19,20], $Fe(PEt_3)_2Cl_2$ [18], $Fe(P(OMe)_3)_2Cl_2$ [19], $Fe(^iPr_2PCH_2{}^iPr_2)Cl_2$ [18], $Fe(^iPr_2PC_2H_4P^iPr_2)_2Cl_2$ [18,21] and $Fe(Ph_2PC_2H_4PPh_2)Cl_2$ [22] were prepared by published procedures. $Fe(PPh_2Me)_2Cl_2$, $Fe(PMe_2Ph)_2Cl_2$, $Fe(Ph_2PCH_2PPh_2)Cl_2$ and $Fe(Et_2PC_2H_4PEt_2)Cl_2$ (as a mixture with $Fe(Et_2PC_2H_4PEt_2)_2Cl_2$ [23]) were prepared similarly by treating $Fe(THF)_nCl_2$ ($n = ca.$ 1.5; prepared by extracting $FeCl_2$ with THF in a Soxhlet apparatus) with the donor ligand in THF at room temperature. Infrared spectra were recorded as KBr disks with a Nicolet 7199 FT spectrometer. Mass spectra were recorded with a Varian CH-5 spectrometer. NMR spectra were recorded with the following Bruker FT instruments: AMX 400 (^1H), AMX 300 (^1H, ^{13}C, ^{31}P), AM 200 (^1H, ^{31}P), AC 200 (^1H, ^{31}P). Microanalyses were carried out by Dornis and Kolbe, Microanalytical Laboratory, Mülheim an der Ruhr.

3.1. $(\eta^3\text{-}C_3H_5)_2Fe(PMe_3)_2$ (1)

A suspension of $Fe(PMe_3)_2Cl_2$ (0.99 g, 3.6 mmol) in diethyl ether was cooled to −30°C and ethereal allylmagnesium chloride (16.4 ml of a 0.43 M solution, 7.10

mmol) was added slowly. The mixture was stirred overnight at −30°C, the solvent was then removed under high vacuum at −30°C, and the dark residue extracted with cold pentane. The extract was filtered, concentrated, and cooled to −78°C to give the compound as orange crystals, which were dried *in vacuo* at −30°C (they decompose above *ca.* 0°C). Yield 0.60 g (58%). Found: C, 49.5; H, 9.7; Fe, 19.4; P, 21.3%. $C_{12}H_{28}FeP_2$ calc.: C, 49.7; H, 9.7; Fe, 19.3; P, 21.4%. IR(KBr): ν 1480, 1225, 1185, 1005. MS (30°C): *m/e* 290 (M^+), 249 ($M^+-C_3H_5$), 214 (M^+-PMe_3), 173 ($M^+-C_3H_5/PMe_3$). ^{31}P-NMR (d_8-THF, −30°C): δ 28.3: isomer-I. The product of an analogous reaction involving allyllithium at −78°C is a mixture of I and II: ^{31}P-NMR (d_8-toluene, −80°C): δ 29.3: isomer-I (43%); 32.8/26.2, *J*(P, P) 54.4: isomer-II (57%). ^{1}H- and ^{13}C-NMR spectroscopic data: see Tables 1 and 2. The following compounds were prepared similarly.

3.1.1. $(\eta^3\text{-}C_3H_5)_2Fe(PEt_3)_2$ (2)

Orange (dec. > 0°C). Yield 60%. Found: C, 56.7; H, 10.7; Fe, 15.4; P, 17.1. $C_{18}H_{40}FeP_2$ calc.: C, 57.8; H, 10.7; Fe, 15.0; P, 16.6%. IR (KBr): ν 3030m, 1485sh, 1225w, 1190w, 875m. MS (25°C): *m/e* 374 (M^+), 333 ($M^+-C_3H_5$), 292 ($M^+-2C_3H_5$), 256 (M^+-PEt_3), 215 ($M^+-C_3H_5/PEt_3$). ^{31}P-NMR (d_8-toluene, −80°C): δ 42.1: isomer-I (80%); 47.1/40.5, *J*(P, P) 39: isomer-II (17%). ^{1}H-NMR spectroscopic data; see Table 1.

3.1.2. $(\eta^3\text{-}C_3H_5)_2Fe(PMe_2Ph)_2$ (3)

Orange (dec. > 0°C). Yield 65%. Decomposition prevented analysis. MS (75°C): *m/e* 414 (M^+), 373 ($M^+-C_3H_5$), 332 ($M^+-2C_3H_5$), 276 (M^+-PMe_2Ph), 235 ($M^+-C_3H_5/PMe_2Ph$), 193, 138. ^{31}P-NMR (d_8-toluene, −100°C): δ 31.0: isomer-I (*ca.* 20%); 36.5: isomer-II (*ca.* 80%): (−30°C) 35.8. ^{1}H- and ^{13}C-NMR spectroscopic data: see Tables 1 and 2.

3.1.3. $(\eta^3\text{-}C_3H_5)_2Fe(P(OMe)_3)_2$ (5)

Yellow (dec. > 0°C). Yield 20%. Decomposition prevented analysis. IR (KBr): ν 3050, 1490, 1285. MS (36°C): *m/e* 386 (M^+), 345 ($M^+-C_3H_5$), 262 ($M^+-P(OMe)_3$), 221 ($M^+-C_3H_5/P(OMe)_3$). ^{31}P-NMR (d_8-toluene, −30°C): δ 191.9. ^{1}H-NMR spectroscopic data; see Table 1.

3.1.4. $(\eta^3\text{-}C_3H_5)_2Fe({}^iPr_2PCH_2P^iPr_2)$ (6)

Orange (dec. > 0°C). Yield 78%. Found: C, 59.8; H, 10.6; Fe, 13.9; P, 15.6. $C_{19}H_{40}FeP_2$ calc.: C, 59.1; H, 10.4; Fe, 14.5; P, 16.1%. IR (KBr): ν *ca.* 3050, 1495sh, 1220, 1195, 1000. MS (50°C): *m/e* 386 (M^+), 345 ($M^+-C_3H_5$), 206, 205. ^{31}P-NMR (d_8-toluene, −80°C): δ 39.8. ^{1}H- and ^{13}C-NMR spectroscopic data: see Tables 1 and 2.

3.1.5. $(\eta^3\text{-}C_3H_5)_2Fe(Et_2PC_2H_4PEt_2)$ (9)

Orange (dec. > 0°C). Yield 24%. Decomposition prevented analysis. MS (65°C): *m/e* 344 (M^+), 303 ($M^+-C_3H_5$), 233, 231. ^{31}P-NMR (d_8-toluene, −30°C): δ 85.2. ^{1}H-NMR spectroscopic data: see Table 1.

3.1.6. $(\eta^3\text{-}C_3H_5)_2Fe({}^iPr_2PC_2H_4P^iPr_2)$ (10)

Orange (dec. > 0°C). Yield 94%. Found: C, 57.7; H, 10.4; Fe, 14.1; P, 15.5. $C_{20}H_{42}FeP_2$ calc.: C, 60.0; H, 10.5; Fe, 14.0; P, 15.5%. IR (KBr): ν *ca.* 3060, 1220, 1200. MS (60°C): *m/e* 400 (M^+), 359 ($M^+-C_3H_5$), 318 ($M^+-2C_3H_5$), 276. ^{31}P-NMR (d_8-toluene, −80°C): δ 101.7: isomer-I (94%); 96.8/92.3, *J*(P, P) 29.6: isomer-II (6%): (−30°C) 98.6. ^{1}H-NMR spectroscopic data: see Table 1.

The compound was also prepared by reacting $Fe({}^iPr_2PC_2H_4P^iPr_2)Cl_2$ with allyllithium (yield 85%) or with active-Mg [7] and allyl bromide (yield 15%) or with i-C_3H_7MgCl (yield 12%).

3.1.7. $(\eta^3\text{-}C_3H_5)_2Fe(Ph_2PC_3H_6PPh_2)$ (11)

Orange (dec. > 0°C). Yield 28%. Found: C, 70.0; H, 7.1; Fe, 10.8; P, 12.0. $C_{33}H_{36}FeP_2$ calc.: C, 72.0; H, 6.6; Fe, 10.2; P, 11.3%. ^{31}P-NMR (d_8-toluene, −100°C): δ 62.1/46.7, *J*(P, P) 42.7: isomer-II. ^{1}H- and ^{13}C-spectroscopic data: see Tables 1 and 2 and Fig. 1.

3.1.8. $(\eta^3\text{-}C_3H_5)_2Fe(PPh_2Me)_2$ (4) and $(\eta^3\text{-}C_3H_5)_2Fe(Ph_2PCH_2PPh_2)$ (7)

These were prepared similarly for spectroscopic purposes but were not purified. ^{31}P-NMR (d_8-toluene, −30°C): δ 59.4/54.7, *J*(P, P) 8.0: isomer-I, **4**. ^{31}P-NMR (d_8-toluene, −30°C): δ 39.4: **7**. ^{1}H- and ^{13}C-NMR spectroscopic data: see Tables 1 and 2.

3.1.9. $(\eta^3\text{-}C_3H_5)_2Fe(Me_2PC_2H_4PMe_2)$ (8)

$(\eta^3\text{-}C_3H_5)_3Fe$ (1.17 g, 6.5 mmol) was dissolved in diethyl ether (60 ml) at −78°C and treated with excess $Me_2PC_2H_4PMe_2$ (2 ml, 11.8 mmol). The mixture was stirred at −30°C for 3 days and the resulting yellow precipitate isolated and dried at −78°C *in vacuo*. Yield 0.9 g (48% theory). Samples invariably contained traces of $(\eta^3\text{-}C_3H_5)_3Fe$, and attempted analysis resulted in an explosion. MS (30°C): *m/e* 288 (M^+), 247 ($M^+-C_3H_5$), 203. ^{31}P-NMR (d_8-THF, −30°C): δ 75.3. ^{1}H-NMR spectroscopic data: see Table 1. See also reference [24*].

3.1.10. $(\eta^3\text{-}2\text{-}MeC_3H_4)_2Fe({}^iPr_2PCH_2P^iPr_2)$ (12)

Prepared as an orange solid (dec. > 0°C) by treating $Fe({}^iPr_2PCH_2P^iPr_2)Cl_2$ (0.41 g, 1.1 mmol) with acti-

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* Reference number with asterisk indicates a note in the list of references.

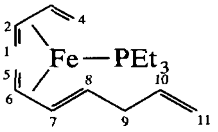
vated-Mg [7] (*ca.* 60 mg) and 2-methylallyl chloride (0.2 ml, 2.18 mmol) in THF (40 ml) at -30°C. Yield 27%. Found: C, 60.9; H, 10.6; Fe, 13.4; P, 15.0. $C_{21}H_{44}FeP_2$ calc.: C, 60.9; H, 10.6; Fe, 13.5; P; 15.0%. IR (KBr); ν 3040, 1230, 1155. ^{31}P-NMR (d_8-toluene, -30°C): δ 39.71. ^{1}H- and ^{13}C-NMR spectroscopic data: see Tables 1 and 2. The compound was also prepared (yield 21%) by reaction of $Fe(THF)Cl_2$, $^iPr_2PCH_2P^iPr_2$ with 2-methylallylmagnesium chloride in ether.

3.1.11. Reaction of (η^3-C_3H_5)$_2$Fe(PMe$_3$)$_2$ (1) with 1,3-butadiene

A solution of **1** (0.22 g, 0.76 mmol) in toluene (20 ml) was treated with an excess of butadiene (5 ml) at -30°C. The mixture was kept at 60°C for 24 h to give (η^4-1,3-C_4H_6)$_2$FePMe$_3$ (**13**), obtained as orange-yellow crystals from pentane. The product was identified by comparison of its NMR spectroscopic data with those of an authentic sample [9,10]. Yield 0.1 g (55% theory).

3.1.12. Reaction of (η^3-C_3H_5)$_2$Fe(PEt$_3$)$_2$ (2) with 1,3-butadiene

(a) Compound **2** (0.54 g, 1.44 mmol) and an excess of butadiene (5 ml) were dissolved in diethyl ether (40 ml) and the mixture was stirred at room temperature for 24 h. Orange crystals (0.2 g) were obtained from pentane and shown by NMR spectroscopy to be a mixture of (η^4-1,3-C_4H_6)$_2$FePEt$_3$ (**14**) and (η^4-1,3-C_4H_6)(η^4-1-$C_3H_5C_4H_5$)FePEt$_3$ (**16**) (**14**:**16** = 37:61). **14** was identified by comparison of the NMR spectroscopic data with those of an authentic sample [9] while the data for **16** are listed below. MS (20°C): *m/e* 322 (M^+), 268 ($M^+ - C_4H_6$), 174 ($M^+ - C_4H_6/C_7H_{10}$), 146. ^{31}P-NMR (d_8-THF, -30°C): δ 50.6. ^{1}H-NMR (d_8-THF, -30°C): δ 5.67 (m, H-10), 4.8 (d, H-11Z), 4.71 (d, H-11E), 4.50 (m, H-2), 4.5 (t, H-3/6), 4.22 (m, H-7), 2.2/1.32 (H-9), 2.12/2.09/1.23 (Et), 0.85/0.78 (H-5E/4E), 0.71 (d, H-1E), -0.92 (m, H-8), -1.40/-1.46/-1.50 (m, H-5Z/H-4Z/H-1Z), *J*(1E,2), 6.9, *J*(1Z,2) 8.9, *J*(2,3) 4.9, *J*(3,4E) 7.1, *J*(5Z,6) 9.1, *J*(6,7) 5.0, *J*(7,8Z) 8.4, *J*(8,9) 3.4/10.7, *J*(9,10) 7.1/5.7, *J*(9.9′) -14.8, *J*(1Z,P) 13.1, *J*(8Z,P) 11.8, *J*(9,P) 0—numbering scheme shown below.



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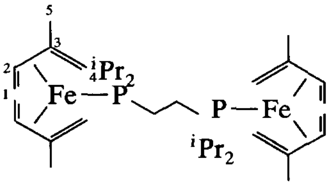
(b) Compound **2** (0.40 g, 1.07 mmol) was treated with two equivalents of butadiene (0.2 ml, 2.0 mmol) in diethyl ether (60 ml) at -30°C and the mixture allowed to warm to room temperature. Orange crystals were isolated from pentane and shown by NMR spectroscopy to consist of a mixture of (η^4-1,3-C_4H_6)$_2$FePEt$_3$ (**14**), (η^4-1,3-C_4H_6)(η^4-1-$C_3H_5C_4H_5$)FePEt$_3$ (**16**) and (η^4-1-$C_3H_5C_4H_5$)$_2$FePEt$_3$ (**15**) (49:27:24; ^{31}P-NMR). MS (60°C): *m/e* 362 (M^+), 350, 306, 208 $M^+ - C_7H_{10}$), 178. ^{31}P-NMR (d_8-THF, -30°C): δ 48.0.

3.1.13. Reaction of (η^3-C_3H_5)$_2$Fe($^iPr_2PC_2H_4P^iPr_2$) (10) with isoprene

Compound **10** (0.68 g, 1.70 mmol) was stirred with excess of isoprene (5 ml) in diethyl ether (60 ml) at room temperature for 16 h. The product, [(isoprene)$_2$-Fe]$_2$($^iPr_2PC_2H_4P^iPr_2$) (**17**) was obtained as yellow crystals from pentane. Yield 0.45 g (82% theory). It was characterized by the NMR spectroscopic data shown below; satisfactory analytical data could not be obtained because the sample decomposed above 0°C. ^{31}P-NMR (d_8-toluene, -30°C): δ 65.4, ^{1}H-NMR (d_8-toluene, -30°C): δ 3.95 (t, H-2), 2.49 (C_2H_4), 2.47/1.23/1.19 (i-C_3H_7), 1.94 (s, H-5), 1.06 (m, H-1E), 0.89 (s, H-4E), -1.19 (t, H-1Z), -1.33 (d, H-4Z), *J*(1E,2) 7.2, *J*(1Z,2) 9.0, *J*(1Z,P) 16.2, *J*(4Z,P) 14.2—numbering scheme shown below.



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The ^{31}P-NMR spectrum of a solution of **17** in d_8-toluene suggests that at 30°C the compound reacts further to give (η^4-isoprene)$_2$Fe($P^iPr_2C_2H_4P^iPr_2$) (**18**) (δ ^{31}P 64.7, 11.6, *J*(P,P) 21.8), while the mass spectrum of **17** at 97°C shows peaks (*m/e* 386, 318, 276, 234, 219, 192, 124) attributable to (η^4-isoprene)Fe-($^iPr_2PC_2H_4P^iPr_2$).

An authentic sample of (η^4-isoprene)$_2$Fe($^iPr_2P$-$C_2H_4P^iPr_2$) (**18**) was prepared by treating Fe($^iPr_2P$-$C_2H_4P^iPr_2$)Cl$_2$ (0.40 g, 1.03 mmol) with activated-Mg (*ca.* 25 mg) and isoprene (0.5 ml, 4.90 mmol) in THF (40 ml) at -30°C for 2 h. It was isolated as a yellow powder from pentane. Yield 0.41 g (88% theory). Found: C, 63.09; H, 10.95; Fe, 12.35; P, 13.58. $C_{24}H_{48}FeP_2$ calc.: C, 63.44; H, 10.57; Fe, 12.33; P, 13.66%. ^{31}P-NMR (d_8-toluene, -30°C): δ 63.3, 9.4, *J*(P,P) 21. ^{1}H-NMR (d_8-toluene, -30°C): δ 3.92 (H-2), 2.45/2.25/1.74/1.56 ($^iPr_2PC_2H_4P^iPr_2$), 1.93 (H-5), 0.87(H-4E), -1.21(H-1Z), -1.36(H-4Z)—numbering scheme shown above for **17**.

3.1.14. Reaction of $(\eta^3\text{-}C_3H_5)_2Fe(^iPr_2PC_2H_4P^iPr_2)$ (10) with 1,3-cyclohexadiene

Compound **10** (0.2 g, 0.5 mmol) was treated with 1,3-cyclohexadiene (50 μl, 0.5 mmol) in diethyl ether (50 ml) at -30°C and the mixture allowed to warm to room temperature. The product, (η^5-cyclo-hexadienyl) $Fe(^iPr_2PC_2H_4P^iPr_2)H$ (**19**), was isolated as yellow crystals. Yield 0.16 g (80% theory). It was identified by comparison of its NMR spectroscopic data with those of an authentic sample [18] prepared by reaction of $Fe(^iPr_2PC_2H_4P^iPr_2)Cl_2$ with active-Mg, and 1,3-cyclohexadiene. ^{31}P-NMR (d_8-toluene, -30°C): δ 118.96. MS (80°C): m/e 398 (M^+).

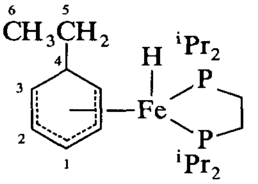
Compound **19** reacts further during 6 h in refluxing toluene to give $(\eta^6\text{-}C_6H_6)Fe(^iPr_2PC_2H_4P^iPr_2)$ as a red crystalline compound: ^{31}P-NMR (d_8-toluene): δ 110.5. ^{1}H-NMR (d_8-toluene): δ 4.76 (t, C_6H_6, J(P,H) 2.1); 1.69 m, 1.04 (m, J(P,H) 13.3), 0.97 (m, J(P,H) 11.4)—$^iPr_2PCH_2$. MS: m/e 396 (M^+), 318 ($M^+ - C_6H_6$).

3.1.15. Reaction of $(\eta^3\text{-}C_3H_5)_2Fe(^iPr_2PC_2H_4P^iPr_2)$ (10) with 1,3-butadiene

Compound **10** (0.86 g, 2.15 mmol) was treated with an excess of butadiene (15 ml) in diethyl ether (80 ml) at -30°C and the mixture was then kept to room temperature for 4 days. The product, (η^5-1-ethyl-cyclohexadienyl)$Fe(^iPr_2PC_2H_4P^iPr_2)H$ (**20**), was isolated yellow crystals. Yield 0.5 g (55% theory). Found: C, 61.14; H, 10.50; Fe, 12.32; P, 13.78. $C_{22}H_{44}FeP_2$ calc.: C, 61.97; H, 10.33; Fe, 13.14; P, 14.55%.

The compound was also the product (yield *ca.* 90%) of the reaction between **10** and 4-vinyl-1-cyclohexene in diethyl ether at room temperature, and was identified by comparison of its spectroscopic data with those of a sample prepared by reaction of $(CH_2:CH)_2$-$Fe(^iPr_2PC_2H_4P^iPr_2)$ with 1,3-cyclohexadiene [18].

IR (KBr): ν (FeH) 1900, 1850. ^{31}P-NMR (d_8-THF, -30°C): δ 116.1. ^{1}H-NMR (d_8-toluene, -20°C): δ 5.88 (t, H-1), 4.25 (d, H-2), 2.52 (t, H-4), 2.43/1.14 (Et), 2.01 (d, H-3), -2.75 (FeH, -80°C); 1.61/1.36/0.87/0.85/0.76 ($^iPr_2PCH_2$)—numbering scheme shown below.



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