The Reaction of Dienes with [Fe(Pr'2P(CH2)nPPr'2)] Species


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

Dedicated to Prof. Dr. h. c. mult Günther Wilke on the occasion of his 70th birthday

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The structure of the compounds formed upon reacting Fe(Pr'2P(CH2)nPPr'2)Cl2 (n = 1−3) and active-Mg with acyclic and cyclic 1,3-, 1,4- and 1,5-dienes depends upon the nature of the diene and upon the length of the methylene-chain bridging the two P-atoms of the bidentate ligand. For example, isoprene reacts to give either (η2-isoprene)FePPPr'2C2H4PPr'2 or (η2-isoprene)Fe(Pr'2PC3H6PPr'2) while the products of the reaction with 1,5-hexadiene are (η2-1-methylpentadienyl)Fe(Pr'2PC3H6PPr'2)H or (η2,η2-1,5-hexadienyl)Fe(Pr'2PC3H6PPr'2).

The crystal structures of the last two compounds have been established by X-ray diffraction. The penultimate species catalyses the linear dimerization of 1,5-hexadiene.

Introduction

The reactions between dienes and zerovalent-iron species have been studied for almost seventy years. Most interest has centered on the behaviour of 1,3-dienes and on carbonyl-stabilized compounds [1] and much less attention has been given to derivatives involving either non-conjugated dienes or P-donor ligands. Our interest in this topic stems from the observation that (η2-C4H6)FeL3 species react with 1,3-dienes with reductive coupling of the allyl groups followed by diene exchange (e.g. eq. (1)), whereby the nature of the final product of the reaction depends upon the type of the donor ligand bonded to the metal atom [2].

\[ \text{(η2-C4H6)Fe(PMe3)}_2 + 2 \text{PMe3} \rightarrow \text{FePMel}_3 \]

We have now extended these studies to the reaction between zerovalent Fe(Pr'2P(CH2)nPPr'2) species (generated in situ by reacting the corresponding dichloride with active-Mg [3]) and acyclic and cyclic 1,3-, 1,4- and 1,5-dienes.

Before presenting our results, it is useful to classify the known carbonyl-free diene-iron compounds. Most common are compounds of the type (η2-1,3-diene)FeL3 [1]; considerably less common are the (η2-1,3-diene)2FeL species, while only one example of an (η2-1,3-diene)FeL2 compound has been reported. Compounds containing acyclic, non-conjugated dienes apparently have not been prepared previously.

The (η2-1,3-diene)FeL3 compounds have been prepared by several methods including the reduction of an iron(II)-salt in the presence of the diene and a ligand [2, 4−6], the reaction of vapoured iron with the diene and ligand [7], the reaction of (η2-1,3-C4H6)Fe(PR'3)2 [4] or (η2-C4H6)Fe(PMe3)2 [8] with further diene, the reaction of (η2-C4H6)FeL2 with the diene [2] or the reductive coupling of the organic groups in (pentadienyl)2FePPPr' species [9]. The only example of an (η2-1,3-diene)FeL2 species, (η2,2,3-dimethyl-1,3-butadienyl)Fe(Pr'2PC3H6PPr'2), has been reported in a doctoral thesis as the product of the reaction between the diene and a related (η2-CH2=CH2)2Fe species [10].

Results and Discussion

Reactions of 1,3-dienes

The products of the reaction of excess 1,3-butadiene with the intermediate zerovalent [Fe(Pr'2P(CH2)nPPr'2)]-species (n = 1−3; Pr'2PC3H6PPr'2 = dippm, Pr'2PC3H4PPr'2 = dippe, Pr'2PC3H6PPr'2 = dipp) are ligand dependent. Whereas the compounds containing dipp and dipp react to give (η2,1,3-C4H6)2Fe-compounds (1), that containing dippe leads to the formation...
of the \((\eta^5\text{-1-ethylcyclohexadienyl})\)iron-hydride (2) (Scheme 1).

\[
\text{Fe(Pr'2P(CH2)nPPr'2)Cl}_2 + 2 \xrightarrow{\text{2,3}} \text{Mg}^+ \quad \text{MgCl}_2
\]

\[n=2\]

\[n=1,3\]

\[\text{Scheme 1}\]

2 has been prepared previously by reacting \((\text{CH}_2;\text{CH}_2)_2\text{Fe(Pr'2PC}_2\text{H}_4\text{PPr'2})\) with 1,3-cyclohexadiene [10] or by reacting \((\eta^3\text{-C}_3\text{H}_5)_2\text{Fe(Pr'2PC}_2\text{H}_4\text{PPr'2})\) with either 1,3-butadiene or 4-vinyl-1-cyclohexene [2]. If the reaction involving the dippe-stabilized intermediate is carried out in the presence of an equimolar amount of butadiene ([Fe]:[1,3-butadiene] = 1:1), then a mixture of 2 and 1 \((n=2)\) is obtained \((2:1 = 4:3)\). With \(n=2\), 1 reacts further at room temperature to give 2 whereas with \(n=1\) or 3, 1 is stable at this temperature.

In contrast to the reactions with 1,3-butadiene, the dippe-stabilized compound reacts with excess isoprene to give the \((\eta^4\text{-1,3-diene})\)Fe-species 3 in high yield whereas the only product which could be isolated from the reaction with the dippp-stabilized system is the green, paramagnetic compound 4 (Scheme 2).

\[
\text{FePr'2P(CH3)2PPr'2)Cl}_2 + 2 \xrightarrow{\text{2,3}} \text{Mg}^+ \quad \text{MgCl}_2
\]

\[n=2\]

\[n=3\]

\[\text{Scheme 2}\]

Compound 3 has been prepared previously by reacting \((\eta^3\text{-C}_3\text{H}_5)_2\text{Fe(Pr'2PC}_2\text{H}_4\text{PPr'2})\) with isoprene [2], and although isomers are possible, depending upon the mutual arrangement of the two diene molecules, the NMR-spectroscopic data indicate that only one is formed; this is assumed to have the structure shown in Scheme 2 in analogy to related phosphite-stabilized complexes [7]. The two isomers of piperylene behave differently (Scheme 3). cis-Piperylene reacts with both the dippe- and dippp-stabilized species to the \((\eta^5\text{-pentadienyl})\)iron-hydride (5) whereas no reaction is observed in the presence of dippm. trans-Piperylene, in contrast, reacts with the dippe-stabilized species to give the \((\eta^4\text{-1,3-diene})\)_2Fe-compound 6.

\[
\text{FePr'2P(CH3)2PPr'2)Cl}_2 + \text{Mg}^+ \quad \text{MgCl}_2
\]

\[\text{Scheme 3}\]

This difference in behaviour is attributed to the position adopted by the methyl group with respect to the metal atom in the intermediate \((\eta^5\text{-1,3-diene})\)Fe-species and is reminiscent of the agostic interaction between Me-group and iron atom which has been studied by NMR spectroscopy for \([(\eta^3\text{-1-anti-MeC}_3\text{H}_4)\text{Fe(P(OR)3)}_3]^+\) [11]. The NMR spectra of 5 are temperature dependent. At \(-80^\circ\text{C}\) two phosphorus signals are observed \((126.3\text{ and }109.9\text{ ppm})\), while the \(^{13}\text{C}\) and \(^{1}\text{H}\) NMR spectra of the \(\eta^5\text{-pentadienyl}\) group consists of the expected five and seven signals, respectively. At \(0^\circ\text{C}\) a rapid pairwise exchange occurs and the spectra simplify to one phosphorus signal \((118.5\text{ ppm})\), three carbon signals and four proton signals. This could be the result of either rotation or li-
bration of the FeL₂H-fragment (eq. (2)) or of the rearrangement of the \( \eta^5 \)-pentadienyl group through the intermediacy of \( \eta^3 \)- and \( \eta^1 \)-bonded species in a manner similar to that discussed previously for the \( (\eta^7 \)-pentadienyl)\( (\eta^5 \)-pentadienyl)-FePR₃ system [9].

![Diagram](image)

A compound related to 5, viz. \((\eta^5 \)-1-methylpentadienyl)\( \text{Fe}(\text{Pr}'₂\text{PC₃H₆PPr}'₂)\)H (7), is the product of an analogous reaction involving 2,4-hexadiene (as a mixture of three isomers). 7 is, however, more conveniently prepared from 1,5-hexadiene as discussed further below.

The product of the reaction of 2,3-dimethylbutadiene with both the dippe- and dippp-stabilized systems is the green, paramagnetic species \((\eta^4 \)-2,3-dimethylbutadiene)\( \text{Fe}(\text{Pr}'₂\text{P}((\text{CH}_2)_n\text{PPr}'₂)(n = 2, 3). \) The latter has been reported previously to be the product of the reaction between \( (\text{CH}_2 : \text{CH}_2) \cdot \text{Fe}(\text{Pr}'₂\text{PC}_3\text{H}_6\text{PPr}'₂) \) and the diene [10]. Both compounds are formed in good yield and have been identified by their elemental analysis and mass spectra.

**Reactions of 1,4-dienes**

The reactions of the \( \text{Fe}(\text{Pr}'₂\text{P}((\text{CH}_2)_n\text{PPr}'₂)\)-species \((n = 1 - 3) \) with 1,4-dienes did not lead to the isolation of identifiable products. 1,4-Pentadiene reacts with the dippe-stabilized species to give a mixture of at least four compounds \((^{31}\text{P NMR})\), while a reaction mixture containing dippp did not react below 0°C, and above this thermal decomposition occurred. Similar behaviour was observed in all three cases for reactions involving 1,4-hexadiene.

**Reactions of 1,5-dienes**

In contrast to 1,4-dienes, reactions with 1,5-hexadiene occurred smoothly and led to the formation of a single organoiron compound in high yield. Here again, the structure of the product is dependent upon the bidentate ligand: the product of the reaction involving dippe is the \((\eta^5 \)-1-methyl-pentadienyl)iron-hydride (7), while in the presence of dippp the paramagnetic \((\eta^2 \eta^2 \)-1,5-hexadiene)iron-species (8) is formed (Scheme 4).

![Scheme 4](image)

8 is also formed in the reaction of \((\eta^5 \)-pentadienyl)\( \text{Fe}(\text{Pr}'₂\text{PC}_3\text{H}_6\text{PPr}'₂)\)H (5, \( n = 3 \) ) with 1,5-hexadiene as the product of the reductive coupling of the pentadienyl group and hydride atom followed by diene exchange.

The crystal structures of both 7 and 8 have been established by X-ray diffraction. The molecular structure of 7 is shown in Fig. 1 with selected bond distances and angles. The molecule can be thought of as an octahedral \( d^6 \) iron complex with the pentadienyl ligand occupying three coordination sites. The open face of the pentadienyl ligand is arranged above P₂, but this does not appear to have an electronic cause since the pentadienyl ligands in both \((\eta^5 \)-1-ethyl-cyclohexadienyl)\( \text{Fe}(\text{Pr}'₂\text{PC}_3\text{H}_6\text{PPr}'₂)\)H and \((\eta^5 \)-cyclohexadienyl)\( \text{Fe}(\text{Pr}'₂\text{PC}_3\text{H}_6\text{PPr}'₂)\)H also have different orientations in the solid state [10]. The Fe–H distance of 1.43(2) Å is shorter than that found in neutron diffraction studies, e.g. 1.609(2) Å for the polyhydrido complex \( \text{FeH}_6\text{Mg}_4\text{X}_4(\text{THF})_8 \) [12], so its position must be treated with caution. The H atom is situated, however, approximately \( \text{trans} \) to C1 \( \text{[H–Fe–C1} 170.3(9)° \). The molecular structure of 8 is shown in Fig. 2. Disorder prevents a detailed discussion of the structure but the analysis reveals that the Fe atom is tetrahedrally co-ordinated and that the hexadiene ligand can adopt both cisoid and transoid conformations on the metal. In both cases the double bonds line up approximately parallel to one Fe–P direction when viewed towards the Fe atom, as is observed for the bis(ethylene) complexes \((\eta^5 \text{C}_2\text{H}_4)_2\text{Fe}(\text{Pr}'₂\text{PC}_3\text{H}_6\text{PPr}'₂)\) [10] and \((\eta^2-
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Fig. 1. Molecular structure of (rj5-syn, Me-pentadienyl) Fe(Pr2PC2H4PPr2)H (7) with selected bond distances (Å) and angles (°): Fe–P1 2.171(1), Fe–P2 2.187(1), Fe–H 1.43(2), Fe–C1 2.177(1), Fe–C2 2.078(1), Fe–C3 2.085(1), Fe–C4 2.069(1), Fe–C5 2.183(1), C1–C2 1.406(2), C2–C3 1.424(2), C3–C4 1.413(2), C4–C5 1.409(2), P1–C7 1.855(1), P2–C8 1.857(1), C7–C8 1.526(2), P1–Fe–P2 88.2(1), P1–Fe–H 75.9(9), P2–Fe–H 86.3(9), C1–Fe–C5 82.4(1), C1–Fe–H 170.3(9).

Fig. 2. Molecular structure of [(rj2,2–l,5-hexadiene)–Fe(PrSPC3H6PPr2)] (8). The hexadiene molecule is disordered (C18a–C21a:C18b–C21b 70:30). Selected bond distances (Å) and angles (°) (Cm,n is the midpoint between the atoms Cm and Cn): Fe–P1 2.280(1), Fe–P2 2.291(1), Fe–C16 2.088(3), Fe–C17 2.089(3), Fe–C20a 2.081(4), Fe–C21a 2.118(4), C16–C17 1.388(4), C17–C18a 1.628(6), C18a–C19a 1.469(7), C19a–C20a 1.505(6), C20a–C21a 1.413(6), P1–Fe–P2 95.0(1), P1–Fe–C16 118.2(2), P1–Fe–C20a,21a 111.5(2), P2–Fe–C16,17 115.1(2), P2–Fe–C20a,21a 112.2(2), C16,17–Fe–C20a, 21a 105.2(4).

C2H42Fe(PEt3)2 [13]. The difference in the formal oxidation states of the Fe atom in 7(II) and 8(0) is reflected in different Fe–P distances in the two compounds [average, 7:2.179(1) vs. 8:2.286(1) Å].

Gas chromatographic analysis of the solution after isolation of 7 indicated that the excess 1,5-hexadiene had dimerized during the reaction, and further investigation showed that 7 catalyses the dimerization of the diene at room temperature. The reaction is slow and only 18 cycles at room temperature were observed after 24 h. The product mixture was separated by preparative GC and shown by NMR spectroscopy to consist of the four isomers 9 (15%), 10 (55%), 11 (22%) and 12 (8%) (see experimental section).

The presence of dippe is necessary to generate an active catalyst as shown by the fact that (η5-pentadienyl)Fe(Pr2PC2H4PPr2)H (5) and (η5-C3H5)2Fe(Pr2PC2H4PPr2) are equally effective (or ineffective!) as 7 while systems containing dippp, e.g. (η5-pentadienyl)Fe(Pr2PC2H4PPr2)H or strongly bonded organic ligands, e.g. (η5-C3H5)2FePPr2C3H5PPr2 or (η5-cyclohexadienyl)-Fe(Pr2PC2H4PPr2)H, are inactive as is (η5-C3H5)2Fe(PMe3)2. Interestingly, the combination Fe(Pr2PC2H4PPr2)Cl2/active-Mg has only slight activity suggesting that side products or the MgCl2 formed suppress the reaction. Further work will be necessary before a plausible mechanism can be formulated.

Reactions of cyclic dienes

Our investigations with cyclic dienes have been limited to examples involving 4-vinyl-1-cyclohexene and cyclohexadiene.
The dippe- and dippp-stabilized species react with vinylcyclohexene at $-40^\circ$C to give the $(\eta^2,\eta^3$-1-vinyl-3,4,5-cyclohexenyl)iron-hydride complexes 13 (eq. (3)).

13 rearranges at $-30^\circ$C, presumably by a conventional hydride-addition/elimination process, to give 2. The dippp-stabilized derivative 13 behaves differently and (although the dippp-analogue to 2 is a known compound whose crystal structure has been established by X-ray diffraction [10]) decomposition to paramagnetic material is observed. In contrast, the dippm-stabilized species reacts with vinylcyclohexene to give $(\eta^5$-1-ethylcyclohexadienyl)Fe(Pr$_2$P(CH$_2$)$_2$PPr$_2$)$_2$H directly.

Analogous reactions with 1,4-cyclohexadiene led to the formation of $(\eta^5$-cyclohexadienyl)Fe(Pr$_2$P(CH$_2$)$_2$PPr$_2$)$_2$H ($n = 2,3$) even at $-78^\circ$C. These species have been reported previously as the products of the reaction involving 1,3-cyclohexadiene, and the structure of the dippp-stabilized compound has been confirmed by an X-ray diffraction study [10].

**Discussion**

The investigations described above (Schemes 2–4 and eq. (3)) indicate that small changes in the bidentate P-donor ligand can have a dramatic effect upon the course of reaction. The structure of the final product is apparently the result of the subtle interplay of a number of effects which include differences in the geometry of the Fe(Pr$_2$P(CH$_2$)$_2$PPr$_2$)-fragment, the strength of the metal-diene interaction, and the proximity of H-atoms on the organic ligand to the metal. The H-transfer from diene to metal is of considerable significance and, since some of the compounds are obvious candidates for molecular modelling, we are at present pursuing this approach and anticipate that it will provide us with a deeper mechanistic insight.

**3. Experimental Section**

The general experimental conditions and instrumentation have been described in an earlier publication [2]. The IR spectra of the compounds described below have been measured as KBr-discs and many show a medium absorption at 2030 cm$^{-1}$ which is not present if the measurements are carried out at low temperature. Since this absorption is observed irrespective of whether dippe or dippp is bonded to the iron atom, we suspect that it is associated with a rearrangement product involving the transfer of an H-atom from a P-bonded isopropyl group to the metal atom.

3.1 Reactions with 1,3-butadiene

FeCl$_2$.nTHF ($n = 1.43$, 0.40 g, 1.74 mmol) was dissolved in THF (40 ml) and treated with dippp (0.56 ml, 1.74 mmol) at room temperature. The solution was cooled to $-78^\circ$C and treated with excess 1,3-butadiene (ca. 1 ml) and active-Mg (44 mg, 1.8 mmol). The reaction mixture was stirred at $-30^\circ$C for 16 h and the resulting brown-green suspension evaporated to dryness in vacuo at $-30^\circ$C and the residue extracted with pentane (3×30 ml) at $-30^\circ$C. The compound is also the product of the reaction involving 1,3-cyclohexadiene, and the structure of the dippp-stabilized compound has been confirmed by an X-ray diffraction study [10].

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the NMR-spectroscopic data with those of an authentic sample prepared either by reacting (CH$_2$:CH$_2$)$_2$Fe(Pr'$_2$PC$_2$H$_4$PPPr'$_2$) with 1,3-cyclohexadiene [10] or by reacting ($\eta^4$-C$_4$H$_4$)$_2$Fe(Pr'$_2$PC$_2$H$_4$PPPr'$_2$) with butadiene or 4-vinyl-1-cyclohexene [2]. $^{31}$P NMR (d$_8$-toluene, $-30 \, ^\circ\mathrm{C}$): $\delta$ 116.7. $^1$H NMR (d$_8$-toluene): $\delta$ 5.87 (t, 1H), 4.24 (d, 2H), 2.45 (1H), 2.45/1.15 (Et)-1-ethylcyclohexadienyl group; $-4.04$ (FeH).

If the reaction is carried out by reacting an equimolar amount of butadiene, instead of excess, at 0 $^\circ\mathrm{C}$, then a 4:3 mixture (total yield 40%) of the above compound 2 and ($\eta^4$-I,3-butenadiene)$_2$FePPPr'$_2$C$_2$H$_4$PPPPr'$_2$ (1, n = 2) is formed. 1 (n = 2) has been characterized by comparison of the spectroscopic data ($^{31}$P NMR (d$_8$-toluene, $-30 \, ^\circ\mathrm{C}$): $\delta$ 64.5, 9.3, J(PP) 22.0 Hz; $^1$H NMR (d$_8$-toluene, $-30 \, ^\circ\mathrm{C}$): $\delta$ 4.3 (H-2), ca. 0.8–1.0 (H-1E), $-1.1$ (H-1Z) with those for the related compounds containing Pr'$_2$PC$_2$H$_4$PPPPr'$_2$ (1, n = 3, see above) and Pr'$_2$PCH$_2$PPPPr'$_2$ (1, n = 1, see below). Furthermore, NMR-spectroscopic evidence indicates that 1 (n = 2) rearranges to 2 at room temperature.

($\eta^4$-I,3-C$_4$H$_6$)$_2$FePPPr'$_2$C$_2$H$_4$PPPPr'$_2$ (1, n = 1)

Prepared in an analogous manner to that described above as a yellow compound in 60% yield by reacting Fe(Pr'$_2$PCH$_3$PPPPr'$_2$)$_2$Cl$_2$, active-Mg and excess butadiene at $-40 \, ^\circ\mathrm{C}$.

C$_{2}$$_{2}$H$_{12}$FeP$_{2}$

Calcd C 61.2 H 10.2 Fe 13.6 P 15.1%

Found C 60.1 H 10.4 Fe 14.1 P 15.5%

MS (100 $^\circ$C): m/e 412 (M$^+$), 358 (M$^+$$-$$C$_4$H$_8$), 304 (M$^+$$-$$2$C$_4$H$_8$). $^{31}$P NMR (d$_8$-toluene, $-80 \, ^\circ\mathrm{C}$): $\delta$ 70.0, $-6.2$, J(PP) 4.6 Hz. $^1$H NMR (d$_8$-toluene, $-80 \, ^\circ\mathrm{C}$): $\delta$ 4.39 (br, H-2), 0.92 (H-1E), $-1.02$ (H-1Z).

The compound apparently contains ($\eta^4$-1,3-C$_4$H$_6$)$_2$Fe(Pr'$_2$PCH$_3$PPPPr'$_2$) as an impurity [MS (90 $^\circ$C): m/e 358 (M$^+$), 304 (M$^+$$-$$C$_4$H$_8$)] which would account for the broadness of the absorptions in the $^1$H NMR spectrum.

3.2 Reactions with isoprene
($\eta^4$-isoprene)$_2$FePPPr'$_2$C$_2$H$_4$PPPPr'$_2$ (3)

This compound has been prepared as a yellow solid in 88% yield by reacting Fe(Pr'$_2$PCH$_3$PPPPr'$_2$)$_2$Cl$_2$, active-Mg and excess isoprene in THF at $-30 \, ^\circ\mathrm{C}$. Details of the characterization have been reported in [2]. $^1$H NMR (d$_8$-toluene, $-30 \, ^\circ\mathrm{C}$): $\delta$ 3.92 (H-3), 1.93 (2-Me), 0.87 (H-1E), $-1.21$ (H-4Z), $-1.36$ (H-1Z).

($\eta^4$-Isoprene)Fe(Pr'$_2$PC$_3$H$_6$PPPPr'$_2$) (4)

Prepared as described above as a green solid in 17% yield by reacting Fe(Pr'$_2$PC$_3$H$_6$PPPPr'$_2$)$_2$Cl$_2$, active-Mg and excess isoprene in THF at $-30 \, ^\circ\mathrm{C}$. MS (90 $^\circ$C): m/e 400 (M$^+$), 332 (M$^+$$-$$C$_5$H$_8$). IR (KBr): $\nu$ 3010, 1180.

3.3. Reactions with piperylene
($\eta^5$-pentadienyl)Fe(Pr'$_2$PC$_2$H$_4$PPPPr'$_2$)H (5, n = 2)

Prepared as described above in 42% yield as a yellow solid by reacting Fe(Pr'$_2$PC$_2$H$_4$PPPPr'$_2$)$_2$Cl$_2$, active-Mg and cis-piperylene in THF at $-30 \, ^\circ\mathrm{C}$.

C$_{19}$H$_{48}$FeP$_{2}$

Calcd C 59.1 H 10.4 Fe 14.5 P 16.1%

Found C 58.7 H 10.9 Fe 14.3 P 16.0%

IR (KBr): $\nu$ 3080, 3060, (FeH) 1900, 1500. – MS (77 $^\circ$C): m/e 386 (M$^+$), 318 (M$^+$$-$$C$_5$H$_8$), $^{31}$P NMR (d$_8$-toluene, $-80 \, ^\circ\mathrm{C}$): $\delta$ 126.3, 109.9, J(PP) 65 Hz; (0 $^\circ$C) 118.5. $^1$H NMR (d$_8$-toluene, 0 $^\circ$C): $\delta$ 5.41 (H-3), 4.77 (H-2/4), $-0.30$ (H-1a/5a), $-18.1$ (t, FeH, J(PP) 71 Hz); (J(PP) 54.2/4.31 (H-2/4), 2.58 (H-5s), 2.33 (H-1s), 0.29 (H-1a), $-0.48$ (H-5a), $-18.61$ (dd, FeH, J(PP) 72 Hz). $^{13}$C NMR (d$_8$-toluene, 0 $^\circ$C): $\delta$ 89.7 (C-2/4), 84.4 (C-3), 46.7 (C-1/5); 28.6 (PCH$_2$), 21.9 (PCH$_3$), 18.9/18.8/18.4 (Me); (J(PP) 80 $^\circ$C): $\delta$ 91.1/88.0 (C-2/4), 84.4 (C-3), 48.6/44.8 (C-1/5), 29.3/25.9 (PCH$_2$), 19.8–17.7 (Me).

($\eta^5$-Pentadienyl)Fe(Pr'$_2$PC$_3$H$_6$PPPPr'$_2$)H (5, n = 3)

Prepared in an analogous manner to the compound described above from cis-piperylene at $-30 \, ^\circ\mathrm{C}$ as a yellow solid in 63% yield.

C$_{2}$$_{2}$H$_{14}$FeP$_{2}$

Calcd C 60.0 H 10.5 Fe 14.0 P 15.5%

Found C 59.9 H 10.4 Fe 14.0 P 15.7%

IR (KBr): $\nu$ 3040, (FeH) 1920, 1500. – MS (70 $^\circ$C): m/e 400 (M$^+$). $^{31}$P NMR (d$_8$-toluene, $-80 \, ^\circ\mathrm{C}$): $\delta$ 74.7, 62.3, J(PP) 26.7 Hz. $^1$H NMR (d$_8$-toluene, $-30 \, ^\circ\mathrm{C}$): $\delta$ 5.29 (br, H-3), 4.36 (br, H-2/4), $-1.07$ (br, H-1a/5a), $-17.36$ (t, FeH, J(PP) 76.3 Hz).

($\eta^4$-trans-Piperylene)$_2$FePPPr'$_2$C$_2$H$_4$PPPPr'$_2$ (6)

Prepared as a yellow-brown oily solid in 27% yield as described above by reacting Fe(Pr'$_2$PC$_2$H$_4$PPPPr'$_2$)$_2$Cl$_2$, active-Mg and excess piperylene (trans:cis = 2:1) in THF at $-30 \, ^\circ\mathrm{C}$.
Satisfactory analytical data could not be obtained and the compound was identified by comparison of the spectroscopic data with those for (η²-trans-piperylene)Fe(PMe₂)₃ [4]. ³¹P NMR (d₆-toluene, -30 °C): δ 55.7, 10.0. ¹H NMR (d₅-toluene, -30 °C): δ 4.34 (H-2), 4.14 (H-3), -0.61 (H-1Z), -0.90 (H-4Z).

### 3.4 Reactions with 2,4-hexadiene

(η²-1-syn,Me-pentadienyl)Fe(PrSPC₃H₆PPr₂)H (7)

Prepared in 40% yield by reacting Fe(Pr₂PC₃H₆PPr₂)Cl₂ with active-Mg and 2,4-hexadiene (as a 16.5:68.4:14.7 mixture of the trans, trans, cis and cis, cis-isomers) at -30 °C. The compound is more conveniently prepared by reacting 1,5-hexadiene and details of its characterization are given below.

### 3.5 Reactions with 2,3-dimethylbutadiene

(η²-2,3-dimethylbutadiene)Fe(Pr₂PC₃H₆PPr₂) (8)

Prepared as described above as a green solid in 44% yield by reacting 2,3-dimethylbuta-1,3-diene at -78 °C.

C₂₇H₄₄FeP₂

| C₆0.9 H 10.4 Fe 13.5 P 15.0% | Found C 60.4 H 11.3 Fe 13.3 P 14.9% |

IR (KBr): ν 3010, 1315. - MS (80 °C): m/e 414 (M⁺), 332 (M⁺ - C₆H₁₀). Crystal structure determination: see Fig. 2.

This compound has been isolated previously from the reaction between Fe(Pr₂PC₃H₆PPr₂)Cl₂ and allylmagnesium chloride (1:2) in THF (yield 45%) as well as of the reaction between (η²-pentadienyl)-Fe(Pr₂PC₃H₆PPr₂)H (5, n = 3) and 1,5-hexadiene (yield 60%).

(η²-1-Methylpentadienyl)Fe(Pr₂PC₃H₆PPr₂)H (7)

Prepared as described above by reacting Fe(Pr₂PC₃H₆PPr₂)Cl₂ with 1,5-hexadiene and active-Mg in THF at -30 °C. The compound is isolated as a yellow solid in 68% yield.

C₂₂H₄₂FeP₂

| C₆0.0 H 10.5 Fe 14.0 P 15.5% | Found C 58.1 H 10.6 Fe 14.0 P 15.6% |

IR (KBr): ν (FeH) 1900, (C=C) 1515. - MS (60 °C): m/e 400 (M⁺), 318 (M⁺ - C₆H₁₀). ³¹P NMR (d₆-toluene, -80 °C): δ 119.2, 113.8. J(P,P) 55 Hz. ¹H NMR (d₅-toluene, -80 °C): δ 5.39 (H-5), 3.10 (t, H-4, 7 Hz), 8.80 (m, H-1, 1.7 Hz), 2.31 (H-6), 1.56 (Me-1s), -0.07 (H-5a), -18.17 (dd, FeH, J(PH) 66 Hz). ¹³C NMR (d₅-toluene, -80 °C): δ 91.29 (C-3), 88.71/78.06 (C-2/4), 46.13 (C-5), 53.87 (C-1) 21.29 (Me); 27.10/25.16/23.25/21.3 (PCH), 19.3-15.7 (dippe). The compound is also formed as the product of an analogous reaction with 2,4-hexadiene (see above). Crystal structure determination: see Fig. 1.

### Catalytic dimerization of 1,5-hexadiene

In a typical reaction (η²-1-syn,Me-pentadienyl)-Fe(Pr₂PC₃H₆PPr₂)H (7) and 1,5-hexadiene ([Fe]: diene = 1:100) were reacted in n-heptane at room temperature. Complete conversion corresponding to 18 catalytic cycles was reached after 24 h. The product mixture was shown by GC/MS [MS after hydrogenation: m/e 170 (M⁺)] to consist of four isomeric dimers in the ratio 15:55:22:8. The dimers were separated by preparative GC (53 m Deoxil 410) and characterized by NMR spectroscopy, (η²-Pentadienyl)Fe(Pr₂PC₃H₆PPr₂)H (5, n = 2) and (η²-C₆H₁₀)₂Fe(Pr₂PC₃H₆PPr₂) were equally effective catalysts whereas Fe(Pr₂PC₃H₆PPr₂)Cl₂/active-Mg was only slightly active. The following compounds, among others, were inactive: (η²-pentadienyl)Fe(Pr₂PC₃H₆PPr₂)H (5, n = 3), (η²-2-MeC₃H₆)₂Fe(Pr₂PC₂H₆PPr₂).
(η^3-C₅H₅)₂Fe(PMe₃)₂, (η^5-C₅H₇)₂FePPPr₂C₂H₄PPPr₂
(1, n = 2), (η^5-cyclohexadienyl)-
Fe(Pr²P₃H₄PPPr₂)H.

9. ^1H NMR (CDCl₃): δ 5.71 (H-2), 5.62 (H-8), 5.18 (H-4), 4.95 (H-1), 4.86 (H-9), 2.69 (H-3), 2.40 (H-6), 2.02 (H-7), 1.49 (H-10), 1.22 (H-11), 0.73 (H-12). ^13C NMR (CDCl₃): δ 137.8 (C-2, J(C,H)
153 Hz), 137.7 (C-8, J(C,H) 152 Hz), 137.4 (C-5),
124.3 (C-4, J(C,H) 152 Hz), 114.9 (C-9, J(C,H)
155 Hz), 114.2 (C-1, J(C,H) 155 Hz), 41.5 (C-6, J(C,H)
126 Hz), 38.0 (C-7, J(C,H) 125 Hz), 31.9 (C-3,
J(C,H) 126 Hz), 25.6 (C-11, J(C,H) 125 Hz), 18.0
(C-10, J(C,H) 126 Hz), 12.1 (C-12, J(C,H)
126 Hz) - numbering scheme shown below.

NMR spectroscopic assignment: the ^1H-(400 MHz) and ^13C-(100.6 MHz) assignments are un-
ambiguous and were made with the aid of COSY
and C,H-shift correlated 2D spectra (J(C,H)) and
DEPT spectra. In addition, in the case of 12, in-
verse 'TOCSY, C,H-correlated spectra (long range
C,H coupling constants) and 2D-INADEQUATE
[14] spectra were used.

3.7 Reactions of 4-vinyl-1-cyclohexene
(η^3-η^5-1-vinyl-3,4,5-cyclohexadienyl)-
Fe(Pr²P₃C₂H₄PPPr₂)H (13, n = 2)

FeCl₂·nTHF (n = 1.375, 0.56 g, 2.478 mmol) and
dippe (0.77 ml, 2.478 mmol) in THF (40 ml) were
stirred at room temperature, cooled to −78 °C and
treated with 4-vinyl-1-cyclohexene (0.31 ml, 2.478
mmol) and active-Mg (60 mg, 2.5 mmol). The mix-
ture was stirred at −40 °C for 16 h to give a brown
solution which was evaporated to dryness at
−78 °C. The residue was extracted with pentane
(3×30 ml) at −78 °C and the resulting yellow solu-
tion was evaporated to give the compound as a
yellow solid. Yield 0.50 g (47%).

C₂₂H₄₄FeP₂
Calcd C 62.0 H 10.3 Fe 13.2 P 14.6%
Found C 61.4 H 10.6 Fe 13.3 P 14.6%

IR (KBr, −100 °C): ν 3000, 1880 (FeH), 1510
(C:C) − MS (80 °C): m/e 426 (M⁺), 318, 276, 234;
identical with (η^5-1-ethylcyclopentadienyl)Fe(Pr²P₃-
PC₂H₄PPPr₂)H [10], see above. ^31P NMR (d₆-tolu-
en, −60 °C): δ 102.0, 95.1, J(P,P) 15.3 Hz. ^1H
NMR (d₆-toluene, −60 °C): δ 4.72 (t, H-6, J(5,6)
6 Hz, J(7,6) 6 Hz), 4.08 (q, H-2, J(1E, 2) 8.0 Hz
J(1Z, 2) 11.4 Hz), 3.83 (q, H-5, J(4b,5), 4.2 Hz,
J(6,5) 6 Hz), 2.82 (td, H-1E, J(2E, 1E) 8.0 Hz), 2.75
(q, H-7), 2.67 (dd, H-1Z, J(2Z, 1Z) 11.4 Hz), 2.59
(d, H-4a, J(4a, 4b) 11.9 Hz), 2.50 (s, H-3), 2.32 (dt,
H-4b, J(4b,5), 4.2 Hz, J(4b,4a) 11.9 Hz), 1.87 (d, H-8a, J(8a,8b) 13.6 Hz), 0.90 (d,
H-8b), −14.70 (t, FeH, J(H,P₃) 80.6 Hz, J(H,P₃)
80.6 Hz) 2.22−0.36 (dippe) − numbering scheme
shown below. ^13C NMR (d₆-toluene, −60 °C): δ
76.7 (C-2, J(P,C) 2.2/3.9 Hz, J(C,H) 152 Hz), 75.2
(C-6, J(C,H) 162 Hz), 54.3 (C-5, J(P,C) 2.1/7.5 Hz,
J(C,H) 153 Hz), 48.8 (C-7, J(P,C) 6.4/10.7 Hz.
The Reaction of Dienes with [Fe(Pr₄P(CH₂)₅PPr₄)] Species

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J(C,H) 155 Hz), 48.6 (C-1, 7(P,C) 1 Hz, 7(C,H) 128 Hz), 23.5 (C-8, J(CH) 128 Hz); 31.6-17.9 (dippp) – numbering scheme shown below.

The structure and signal assignments are unambiguous and are based upon COSY, C,H-shift correlated 2D NMR spectra, DEPT(13)C and ¹H NMR spectra with selective decoupling of ³¹P.

At -30 °C the NMR-spectroscopic samples rearranged completely to (η3-1-ethylcyclohexadienyl)Fe(Pr₄PC₃H₆PPr₂)H (2) [10]. ³¹P NMR (d₈-toluene): δ 117.7. ¹H NMR (d₈-toluene): δ 5.88 (br, H-1), 4.29 (br, H-2), 2.35 (br, H-4/5), 1.94 (d, H-3), 1.08 (H-6), -4.79 (t, FeH), J(PH) 57.3 Hz) – numbering scheme shown below.

(η3-1-Vinyl-3,4,5-cyclohexenyl)-Fe(Pr₄PC₃H₆PPr₂)H (13, n = 3)

Prepared as described above by reacting FeCl₂·nTHF, dippp, 4-vinyl-1-cyclohexene and active-Mg in THF at -30 °C. Isolated as a yellow crystalline solid in 62% yield.

C₂₃H₄₀FeP₂
Calcd C 62.7 H 10.5 Fe 12.7 P 14.1%
Found C 62.8 H 10.4 Fe 12.6 P 14.1%

IR (KBr): ν 3020, 1940 (FeH). 13P NMR (d₈-toluene, -30 °C): δ 50.4; a singlet is observed between -80 °C and +60 °C. ¹H NMR (d₈-toluene, -30 °C): δ 6.58 (H-1), 4.42 (H-2), 2.60 (H-5), 2.26 (H-4), 1.80 (H-3), 1.6-0.6 (dippp) – numbering scheme shown above for 2; no Fe–H ligand could be observed between -80 °C and +60 °C. ¹C NMR (d₈-toluene, -30 °C): δ 84.77 (C-2), 78.32 (C-1), 38.83 (C-4), 37.20 (C-3), 32.11 (C-5), 12.63 (C-6), 28.6/28.2 (dippp) – numbering scheme shown above for 2.

3.8 Reactions of cyclohexadiene
(η3-cyclohexadienyl)Fe(Pr₄PC₃H₆PPr₂)H [10]

Prepared as described above by reacting FeCl₂·nTHF (n = 1.375, 0.52 g, 2.30 mmol), dippp (0.72 ml, 2.30 mmol), 1,4-cyclohexadiene (0.22 ml, 2.30 mmol) and active-Mg (55 mg, 2.30 mmol) were suspended in THF (40 ml) at -78 °C. An immediate reaction occurred to give a yellow suspension. The reaction mixture was evaporated to dryness at -78 °C and the residue extracted with pentane (150 ml) at -78 °C. The pentane solution was concentrated to 5 ml, cooled to -78 °C and the resulting yellow solid dried under high vacuum. Yield 0.32 g (35% theory). The compound was identified by comparison of the spectroscopic data with those for an authentic sample prepared as above from 1,3-cyclohexadiene at 0 °C or -78 °C (yield ca. 80%) [10]. ³¹P NMR (d₈-toluene, -30 °C): 119.0. ¹H NMR (d₈-toluene, -30 °C): δ 5.92 (H-1), 4.56 (H-2), 2.58/2.24/1.86 (H-3/4/CH), 1.0-0.8 (dippp), -19.63 (t, FeH, J(PH) 69.3 Hz) – numbering scheme shown below.

(η3-Cyclohexadienyl)Fe(Pr₄PC₃H₆PPr₂)H [10]

Prepared as described above by reacting FeCl₂·nTHF, dippp, 1,4-cyclohexadiene and active-Mg in THF at -40 °C. Yellow crystals (yield 38%). The compound was identified by comparison of the spectroscopic data with those for an authentic sample prepared at 0 °C [10]. ³¹P NMR (d₈-toluene, -30 °C): δ 71.3; (-80 °C) 75.3, 66.5. ¹H NMR (d₈-toluene, -30 °C): δ 5.73 (H-1), 4.67 (H-2), 2.46 (H-4), 1.91 (H-5), 2.24-0.8 (dippp), -19.01 (t, FeH, J(PH) 72.9 Hz) – numbering scheme shown above.
Table I. Atomic coordinates and equivalent isotropic thermal parameters (Å²) of 7 with standard deviations in parentheses.

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<th>z</th>
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$^a$ $U_{eq} = 1/3 \sum_{ij} U_{ij} a_i^* a_j^*$ $a_i a_j$

Crystal structure analysis of (η²-1-syn,Me-pentadienyl)Fe(PrP_3C_2H_4PPr_3)H (7)

Molecular formula C_{20}H_{24}FeP_2, molecular weight 400.4 g mol^{-1}, crystal color yellow-brown, crystal size 0.25 x 0.35 x 0.60 mm, a = 8.251(1), b = 11.248(1), c = 23.071(1) Å, V = 2141.2 Å³, T = 100 K. d_{calc} = 1.24 g cm^{-3}, μ = 8.50 cm^{-1}, Z = 4, orthorhombic, space group P2_1_2_1_2_1. Enraf-Nonius CAD4 diffractometer, λ = 0.71069 Å, scan mode o-wθ, 7086 measured reflections (±h, ±k, ±l), [(sinθ)/λ]_{max} 0.70 Å^{-1}, 622 independent reflections, 5991 observed reflections (I>2σ(I)) for 377 refined parameters, structure solved by heavy atom method, H atom positions and isotropic thermal parameters refined, R = 0.022, R_w = 0.028 [w = 1/σ²(F_{o})], residual electron density 0.62 e Å^{-3} [15,16]. Atomic positional parameters, including the hydride H atom, and equivalent isotropic thermal parameters are given in Table I.

Crystal structure analysis of [(η²,η⁷-1,5-hexadiene)Fe(PrP_3C_2H_4PPr_3)] (8)

Molecular formula C_{21}H_{24}FeP_2, molecular weight 414.4 g mol^{-1}, crystal color black, crystal size 0.46 x 0.49 x 0.49 mm, a = 9.663(2), b = 17.026(3), c = 14.344(3) Å, β = 105.41(1)°, V = 2275.2 Å³, T = 100 K, d_{calc} = 1.21 g cm^{-3}, μ = 8.02 cm^{-1}, Z = 4, monoclinic, space group P2_1/m. Enraf-Nonius CAD4 diffractometer, λ = 0.71069 Å, scan mode o-2θ, 5596 measured reflections (±h, ±k, ±l), [(sinθ)/λ]_{max} 0.65 Å^{-1}, 5204 independent reflections, 4709 observed reflections (I>2σ(I)) for 231 refined parameters, structure solved by heavy atom method, C18-C21 ordered and refined isotropically, H atom positions calculated and fixed (U_{H} = 0.03 Å²) in the final refinement stages, R = 0.042, R_w = 0.056 [w = 1/σ²(F_{o})], residual electron density 0.79 e Å^{-3} [15,16]. Atomic positional parameters and equivalent isotropic thermal parameters are given in Table II.
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[16] Further details of the crystal structure investigation 
(listings of hydrogen atom positional parameters, 
anisotropic thermal parameters, distances and 
angles) may be obtained from the Fachinfor-
mationzentrum Karlsruhe, Gesellschaft für wissen-
schaftlich-technische Information mbH, D-76344 
Eggenstein-Leopoldshafen, Germany, on quoting 
the depository number CSD 58744, the names of the 
authors and the journal citation.