The Reaction of Dienes with [Fe(Pr₂₂P(CH₂)₆PPr₂)] Species

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

Dedicated to Prof. Dr. 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(Pr₂₂P(CH₂)₆PPr₂)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 (η⁴-isoprene)FePPPr₂C₂H₄PPr₂ or (η⁴-isoprene)Fe(Pr₂PC₃H₆PPr₂) while the products of the reaction with 1,5-hexadiene are (η⁴-1-methylpentadienyl)Fe(Pr₂PC₃H₆PPr₂)H or (η⁴,η⁵-1,5-hexadiene)Fe(Pr₂PC₃H₆PPr₂). 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 (η⁴-C₃H₅)₂Fe<PMe₃)₂ — —

The (η⁴-C₃H₅)₂Fe<PMe₃)₂ 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].

(η⁴-C₃H₅)₂Fe<PMe₃)₂ + 2PMe₃ — — → Fe<PMe₃)(η⁴-C₃H₅)

We have now extended these studies to the reaction between zerovalent Fe(Pr₂₂P(CH₂)₆PPr₂)-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 (η⁴-1,3-diene)FeL₃ [1]; considerably less common are the (η⁴-1,3-diene)₂FeL species, while only one example of an (η⁴-1,3-diene)FeL₂ compound has been reported. Compounds containing acyclic, non-conjugated dienes apparently have not been prepared previously.

The (η⁴-1,3-diene)FeL₂ 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 vapourized iron with the diene and ligand [7], the reaction of (η⁴-1,3-C₃H₆)Fe(Pr₂P) [4] or (η⁴-C₃H₆)Fe(PMe₃) [8] with further diene, the reaction of (η⁴-C₃H₅)₂FeL₂ with the diene [2] or the reductive coupling of the organic groups in (pentadienyl)₂FePR₃ species [9]. The only example of an (η⁴-1,3-diene)FeL₂ species, (η⁴-2,3-dimethyl-1,3-butadiene)Fe(Pr₂PC₃H₆PPr₂), has been reported in a doctoral thesis as the product of the reaction between the diene and a related (η⁴-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(Pr₂₂P(CH₂)₆PPr₂)]-species (n = 1–3; Pr₂PC₃H₆PPr₂ = dipm, Pr₂PC₃H₆PPr₂ = dippe, Pr₂PC₃H₆PPr₂ = dippp) are ligand dependent. Whereas the compounds containing dipm and dippp react to give (η⁴-1,3-C₄H₆)₂Fe-compounds (1), that containing dippe leads to the formation

* Reprint requests to Prof. Dr. P. W. Jolly.

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of the \((\eta^5\text{-1-ethylcyclohexadienyl})\text{iron-hydride}\) (2) (Scheme 1).

Scheme 1

\[
\text{Fe(Pr}'_2\text{P(CH}_2\text{)}_2\text{PPr}'_2\text{Cl}_2 + 2 \rightarrow \text{Mg}^+ \quad \text{Fe(Pr}'_2\text{P(CH}_2\text{)}_2\text{PPr}'_2\text{Cl})}
\]

\(n=2\)
\(n=1,3\)

\(2\) has been prepared previously by reacting \((\text{CH}_2\text{; CH}_2\text{)}_2\text{Fe(Pr}'_2\text{P(C}_2\text{H}_4\text{)PPr}'_2\text{)}\) with 1,3-cyclohexadiene [10] or by reacting \((\eta^3\text{-C}_3\text{H}_5\text{)}_2\text{Fe(Pr}'_2\text{P(C}_2\text{H}_4\text{)PPr}'_2\text{)}\) 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 \([\text{Fe}]:[1,3\text{-butadiene}] = 1:1\), 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 \((\eta^4\text{-1,3-diene})\text{Fe-species} 3\) 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).

Scheme 2

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

\(n=3\)
\(n=2\)

Compound 3 has been prepared previously by reacting \((\eta^3\text{-C}_3\text{H}_5\text{)}_2\text{Fe(Pr}'_2\text{P(C}_2\text{H}_4\text{)PPr}'_2\text{)}\) 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 \((\eta^5\text{-pentadienyl})\text{iron-hydride} 5\) whereas no reaction is observed in the presence of dippm. trans-Piperylene, in contrast, reacts with the dippe-stabilized species to give the \((\eta^4\text{-1,3-diene})\text{Fe-compound} 6\).

Scheme 3

\[
\text{FePr}'_2\text{P(CH}_2\text{)}_2\text{PPr}'_2\text{Cl} + \text{Mg}^+
\]

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})\text{Fe-species} and is reminiscent of the agostic interaction between Me-group and iron atom which has been studied by NMR spectroscopy for \([\eta^5\text{-1-anti-MeC}_3\text{H}_4\text{Fe(PO}_3\text{)}_3]^+\) [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 η⁵-pentadienyl group through the intermediacy of η³- and η¹-bonded species in a manner similar to that discussed previously for the (η⁵-pentadienyl)(η⁵-pentadienyl)-FePR₃ system [9].

A compound related to 5, viz. (η⁵-1-methylpentadienyl)Fe(Pr₂PC₃H₆PPr₂)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 (η⁴-2,3-dimethylbutadiene)Fe(Pr₄P(CH₂)₆PPr₂) (n = 2,3). The latter has been reported previously to be the product of the reaction between (CH₂:CH₂)₂Fe(Pr₄PCH₂CH₂CH₂CH₂CH₂PPr₂) 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 Fe(Pr₄P(CH₂)₆PPr₂)-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 (³¹P 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 (η⁵-1-methylpentadienyl)iron-hydride (7), while in the presence of dippp the paramagnetic (η⁵,η²-1,5-hexadiene)iron-species (8) is formed (Scheme 4).

8 is also formed in the reaction of (η⁵-pentadienyl)Fe(Pr₄PCH₂CH₂CH₂CH₂CH₂PPr₂)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 d⁶ 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 (η⁵-1-ethylcyclohexadienyl)Fe(Pr₄PCH₂CH₂CH₂CH₂CH₂PPr₂)H and (η⁵-cyclohexadienyl)Fe(Pr₄PCH₂CH₂CH₂CH₂CH₂PPr₂)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 FeHₓMgₓX₄(THF)₈ [12], so its position must be treated with caution. The H atom is situated, however, approximately trans to C1 [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 (η⁵-C₆H₆)₂Fe(Pr₄PCH₂CH₂CH₂CH₂PPr₂) [10] and (η²-
Fig. 1. Molecular structure of \( \eta^5-1\text{-syn, Me-pentadienyl}) \text{Fe(Pr}^2\text{PC}_2\text{H}_4\text{PPr}^2\text{)}\)H \(\text{(7)}\) 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 \( \left(\eta^2,\eta^2-1,5\text{-hexadiene}\right)\text{Fe(Pr}^2\text{PC}_3\text{H}_6\text{PPr}^2\text{)}\) (8). The hexadiene molecule is disordered \(\text{(C18a–C21a:C18b–C21b 70:30)}\). 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–P3 2.291(1), Fe–C16 2.088(3), Fe–C17 2.089(3), Fe–C20a 2.081(4), Fe–C20b 2.081(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–C16 95.0(1), P1–Fe–C20a 111.5(2), P2–Fe–C16 115.1(2), P2–Fe–C20a 112.2(2), C16–C17–Fe–C20a 105.2(4).

C$_2$H$_4$$_2$Fe(PEt$_3$)$_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 \( \eta^5\text{-pentadienyl})\text{Fe(Pr}^2\text{PC}_3\text{H}_4\text{PPr}^2\text{)}\)H \(\text{(5)}\) and \( \eta^5\text{-C}_3\text{H}_5\text{Fe(Pr}^2\text{PC}_2\text{H}_4\text{PPr}^2\text{)}\) \(\text{(6)}\) are equally effective (or ineffective!) as 7 while systems containing dippp, e.g. \( \eta^5\text{-pentadienyl})\text{Fe(Pr}^2\text{PC}_3\text{H}_4\text{PPr}^2\text{)}\)H or strongly bonded organic ligands, e.g. \( \eta^4\text{-C}_3\text{H}_5\text{FePPPr}_2\text{C}_2\text{H}_4\text{PPr}^2\text{)}\) or \( \eta^5\text{-cyclohexadienyl})\text{Fe(Pr}^2\text{PC}_3\text{H}_4\text{PPr}^2\text{)}\)H, are inactive as is \( \eta^5\text{-C}_3\text{H}_5\text{Fe(PMe}_3\text{)}\) \(\text{(6)}\). Interestingly, the combination Fe(Pr$^2$PC$_2$H$_4$PPr$_2$)$_2$Cl$_2$/active-Mg has only slight activity suggesting that side products or the MgCl$_2$ 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 \((\eta^2,\eta^3-1\text{-vinyl-3,4,5-cyclohexenyl})\)iron-hydride complexes \(13\) (eq. (3)).

\[ \text{Fe(Pr}_2\text{P(CH}_2\text{)}_3\text{PPr}_2)_2\text{Cl}_2 + \text{Mg}^+ \rightarrow \text{Fe(Pr}_2\text{P(CH}_2\text{)}_3\text{PPr}_2)_2\text{H} \]  

\(13\) \((n = 2)\) rearranges at \(-30^\circ C\), presumably by a conventional hydride-addition/elimination process, to give \(2\). The dippp-stabilized derivative \((13, n = 3)\) 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 \((\eta^7-1\text{-ethylcyclohexadienyl})\)Fe(Pr\(_2\)PCH\(_2\)PPr\(_2\))H directly.

Analogous reactions with 1,4-cyclohexadiene led to the formation of \((\eta^5\text{-cyclohexadienyl})\)Fe(Pr\(_2\)P(CH\(_2\))\(_3\)PPr\(_2\))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\(_2\))\(_3\)PPr\(_2\))-fragment, the strength of the metal-diene interaction, and the proximity of H-atoms on the organic ligand to the metal atom. 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

\((\eta^4,1,3\text{-Butadiene})_2\text{FePPr}_2\text{C}_3\text{H}_6\text{PPr}_2\) \((1, n = 3)\)

FeCl\(_2\) in THF \((n = 1.43, 0.40\text{ g}, 1.74\text{ mmol})\) was dissolved in THF \((40\text{ ml})\) and treated with dippp \((0.56\text{ ml}, 1.74\text{ mmol})\) at room temperature. The solution was cooled to \(-78^\circ C\) and treated with excess 1,3-butadiene \((ca. 1\text{ ml})\) and active-Mg \((44\text{ mg}, 1.8\text{ mmol})\). 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 \((3 \times 30\text{ ml})\) at \(-30^\circ C\). The pentane extract was concentrated to 15 ml and cooled to \(-78^\circ C\) to give the compound as a yellow solid. Yield 0.53 g (69%).

\[ C_{23}H_{46}\text{FeP}_2 \]

Calcd C 62.7 H 10.5 Fe 12.7 P 14.1%  
Found C 62.0 H 10.6 Fe 13.0 P 14.4%

IR (KBr): \(v 3020\).  
MS (110 \(^\circ\)C): \(m/e 440 (M^+)\), \(386 (M^+-C_4H_6)\), \(332 (M^+-2C_4H_6)\).  
\(^{31}\)P NMR (d\(_8\)-toluene, \(-30^\circ C\)): \(\delta 60.8, -0.2\).  
\(^{1}H\) NMR (d\(_8\)-toluene, \(-30^\circ C\)): \(\delta 4.36 (dd, H-2, J(IE, 2) 6.6\text{ Hz}, J(IZ, 2) 8.4\text{ Hz})\), \(0.90 (H-1E)\), \(-1.15 (dd, H-1E, J(IZ, P) 11.4\text{ Hz})\).

The compound is also the product of the reaction between \((\eta^7,\eta^3-1,5\text{-hexadiene})\)Fe(Pr\(_2\)PC\(_3\)H\(_4\)PPr\(_2\)) and butadiene in diethyl ether at room temperature.

\((\eta^5\text{-Ethylcyclohexadienyl})\)Fe(Pr\(_2\)PC\(_3\)H\(_4\)PPr\(_2\))H \((2)\)

Prepared as described above as a yellow solid by reacting Fe(Pr\(_2\)PC\(_3\)H\(_4\)PPr\(_2\))Cl\(_2\) with active-Mg and excess butadiene in THF at room temperature (yield 45%) and identified by comparison of...
the NMR-spectroscopic data with those of an authentic sample prepared either by reacting (CH₃:C₂H₂)₃Fe(Pr₄PC₆H₄PPr₂) with 1,3-cyclohexadiene [10] or by reacting (η⁵-C₃H₅)₃Fe(Pr₄PC₂H₄PPr₂) with butadiene or 4-vinyl-1-cyclohexene [2]. ³¹P NMR (d₈-toluene, –30 °C): δ 116.7. ¹H NMR (d₈-toluene): δ 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 °C, then a 4:3 mixture (total yield 40%) of the above compound 2 and (η⁴-I,3-butadiene)₂FePPr₂C₂H₄PPr₂ (I, n = 2) is formed. I (n = 2) has been characterized by comparison of the spectroscopic data (³¹P NMR (d₈-toluene, –30 °C): δ 64.5, 9.3, J(PP) 22.0 Hz; ¹H NMR (d₈-toluene, –30 °C): δ 3.43 (H-2), ca. 0.8–1.0 (H-1 E), –1.1 (H-1 Z) with those for the related compounds containing Pr₄PC₂H₄PPr₂ (I, n = 3, see above) and Pr₄PCH₂PPr₂ (I, n = 1, see below). Furthermore, NMR-spectroscopic evidence indicates that I (n = 2) rearranges to 2 at room temperature.

(η⁴-I,3-C₃H₅)₂FePPr₂C₂H₄PPr₂ (I, n = 1)

Prepared in an analogous manner to that described above as a yellow compound in 60% yield by reacting Fe(Pr₄PC₂H₄PPr₂)Cl₂, active-Mg and excess butadiene at –40 °C.

C₃H₁₂FeP₂
Calcd C 61.0 H 10.2 Fe 13.6 P 15.1%
Found C 60.1 H 10.4 Fe 14.1 P 15.5%

MS (100 °C): m/e 412 (M⁺), 358 (M⁺–C₆H₆), 304 (M⁺–2C₆H₆); ³¹P NMR (d₈-toluene, –80 °C): δ 128.8, 130.9, J(PP) 265 Hz; ¹H NMR (d₈-toluene, –80 °C): δ 4.39 (br, H-2), 0.92 (H-1 E), –1.02 (H-1 Z).

The compound apparently contains (η⁴-I,3-C₃H₅)₃Fe(Pr₄PCH₂PPr₂) as an impurity [MS (90 °C): m/e 358 (M⁺), 304 (M⁺–C₆H₆)] which would account for the broadness of the absorptions in the ¹H NMR spectrum.

3.2 Reactions with isoprene
(η⁴-isoprene)₂FePPr₂C₂H₄PPr₂ (3)

This compound has been prepared as a yellow solid in 88% yield by reacting Fe(Pr₄PC₂H₄PPr₂)Cl₂, active-Mg and excess isoprene in THF at –30 °C. Details of the characterization have been reported in [2]. ¹H NMR (d₈-toluene, –30 °C): δ 3.92 (H-3), 1.93 (2-Me), 0.87 (H-1 E), –1.21 (H-4 Z), –1.36 (H-1 Z).

(η⁴-Isoprene)₃Fe(Pr₄PC₂C₆H₄PPr₂) (4)

Prepared as described above as a green solid in 17% yield by reacting Fe(Pr₄PC₂C₆H₄PPr₂)Cl₂, active-Mg and excess isoprene in THF at –30 °C. MS (90 °C): m/e 400 (M⁺), 332 (M⁺–C₆H₆). IR (KBr): ν 3010, 1180.

3.3. Reactions with piperylene
(η⁴-pentadienyl)Fe(Pr₄PC₂C₆H₄PPr₂)H (5, n = 2)

Prepared as described above in 42% yield as a yellow solid by reacting Fe(Pr₄PC₂C₆H₄PPr₂)Cl₂ active-Mg and cis-piperylene in THF at –30 °C.

C₃H₁₀FeP₂
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): ν 3080, 3060, (FeH) 1900, 1500. – MS (77 °C): m/e 386 (M⁺), 318 (M⁺–C₆H₆), ³¹P NMR (d₈-toluene, –80 °C): δ 126.3, 109.9, J(PP) 65 Hz; ¹H NMR (d₈-toluene, 0 °C): 118.5. ¹H NMR (d₈-toluene, 0 °C): δ 5.41 (H-3), 4.77 (H-2/4), –0.30 (H-1 a/5 a), –18.1 (t, FeH, J(PP) 71 Hz); (–80 °C): δ 5.49 (H-3), 5.42/4.31 (H-2/4), 2.58 (H-5 s), 2.33 (H-1 s), 0.29 (H-1 a), –0.48 (H-5 a), –18.61 (dd, FeH, J(PP) 72 Hz). ¹³C NMR (d₈-toluene, 0 °C): δ 89.7 (C-2/4), 84.4 (C-3), 46.7 (C-1/5), 28.6 (PCH), 21.9 (PCH₂), 18.9/18.8/18.4 (Me); (–80 °C): δ 91.1/88.0 (C-2/4), 84.4 (C-3), 48.6/44.8 (C-1/5), 29.3/25.9 (PCH), ~28.0 (PCH₂), 19.8–17.7 (Me).

(η⁵-Pentadienyl)Fe(Pr₄PC₂C₆H₄PPr₂)H (5, n = 3)

Prepared in an analogous manner to the compound described above from cis-piperylene at –30 °C as a yellow solid in 63% yield.

C₃H₁₀FeP₂
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): ν 3040, (FeH) 1920, 1500. – MS (70 °C): m/e 400 (M⁺). ³¹P NMR (d₈-toluene, –80 °C): δ 74.7, 62.3, J(PP) 26.7 Hz. ¹H NMR (d₈-toluene, –30 °C): δ 5.29 (br, H-3), 4.36 (br, H-2/4), –1.07 (br, H-1 a/5 a), –17.36 (t, FeH, J(PP) 76.3 Hz).

(η⁴-trans-Piperylene)₂FePPr₂C₂H₄PPr₂ (6)

Prepared as a yellow-brown oily solid in 27% yield as described above by reacting Fe(Pr₄PC₂C₆H₄PPr₂)Cl₂ with active-Mg and excess piperylene (trans:cis = 2:1) in THF at –30 °C.
Satisfactory analytical data could not be obtained and the compound was identified by comparison of the spectroscopic data with those for \((\eta^2\text{-isoprene})_2\text{FePPr}_2\text{C}_3\text{H}_5\text{PPr}_2\) and \((\eta^1\text{-trans-piperylene})\text{Fe}(\text{PMc})_3\) [4]. \(^{31}\)P NMR (d₅-toluene, \(-30^\circ\text{C}\)): δ 55.7, 10.0, J(PP) 21 Hz. \(^1\)H NMR (d₅-toluene, \(-30^\circ\text{C}\)): δ 4.34 (H-2), 4.14 (H-3), –0.61 (H-1Z), –0.90 (H-4Z).

### 3.4 Reactions with 2,4-hexadiene

\((\eta^5\text{-1-syn,Me-pentadienyl})\text{Fe}(\text{Pr'2PCH}_2\text{PPr'2})\text{H} (\text{7})\)

Prepared in 40% yield by reacting \(\text{Fe(Pr'2PC}_2\text{H}_4\text{PPr'2)}\text{Cl}_2\) with active-Mg and 2,4-hexadiene (as a 16.5:68.4:14.7 mixture of the \((\text{trans,trans,trans,cis}\) and \((\text{cis,cis, cis})\)-isomers) at \(-30^\circ\text{C}\). 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

\((\eta^5\text{-2,3-dimethylbutadiene})\text{Fe}(\text{Pr'2PC}_2\text{H}_4\text{PPr'2})\) (7)

Prepared as described above as a green solid in 44% yield by reacting 2,3-dimethylbuta-1,3-diene at \(-78^\circ\text{C}\).

\(\text{C}_{20}\text{H}_{42}\text{FeP}_2\)

Calcd C 60.9 H 10.5 Fe 14.0 P 15.5%, Found C 59.9 H 10.6 Fe 13.9 P 15.4%.

IR (KBr): ν 3020. – MS (100 °C): m/e 414 (M⁺), 332 (M⁺–C₆H₁₀). Crystal structure determination: see Fig. 2.

The same compound is the product of the reaction between \(\text{Fe(Pr'2PC}_2\text{H}_4\text{PPr'2})\text{Cl}_2\) and allylmagnesium chloride (1:2) in THF (yield 45%) as well as of the reaction between \((\eta^5\text{-pentadienyl})\text{Fe(Pr'2PC}_2\text{H}_4\text{PPr'2})\text{H} (\text{5}, n = 3)\) and 1,5-hexadiene (yield 60%).

\((\eta^5\text{-1-Methylpentadienyl})\text{Fe}(\text{Pr'2PC}_2\text{H}_4\text{PPr'2})\text{H} (\text{7})\)

Prepared as described above by reacting \(\text{Fe(Pr'2PC}_2\text{H}_4\text{PPr'2})\text{Cl}_2\) with 1,5-hexadiene and active-Mg in THF at \(-30^\circ\text{C}\). The compound is isolated as a yellow solid in 68% yield.

### 3.6 Reactions with 1,5-hexadiene

\((\eta^2\text{-1,5-hexadiene})\text{Fe}(\text{Pr'2PC}_2\text{H}_6\text{PPr'2})\) (8)

Prepared as described above by reacting \(\text{Fe(Pr'2PC}_2\text{H}_6\text{PPr'2})\text{Cl}_2\) with 1,5-hexadiene and active-Mg in THF at \(-50^\circ\text{C}\). The compound is isolated as a dark green solid in 90% yield.

\(\text{C}_{22}\text{H}_{44}\text{FeP}_2\)

Calcd C 60.9 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.

In a typical reaction \((\eta^2\text{-1-syn,Me-pentadienyl})\text{-Fe(Pr'2PC}_2\text{H}_6\text{PPr'2})\text{H} (\text{7})\) 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 De- xil 410) and characterized by NMR spectroscopy. \((\eta^5\text{-Pentadienyl})\text{Fe(Pr'2PC}_2\text{H}_6\text{PPr'2})\text{H} (\text{5}, n = 2)\) and \((\eta^5\text{-C}_3\text{H}_5)\text{Fe(Pr'2PC}_2\text{H}_6\text{PPr'2})\) were equally effective catalysts whereas \(\text{Fe(Pr'2PC}_2\text{H}_6\text{PPr'2})\text{Cl}_2\) active-Mg was only slightly active. The following compounds, among others, were inactive: \((\eta^5\text{-pentadienyl})\text{Fe(Pr'2PC}_2\text{H}_6\text{PPr'2})\text{H} (\text{5}, n = 3)\), \((\eta^2\text{-MeC}_3\text{H}_5)_2\text{Fe(Pr'2PCH}_2\text{H}_2\text{PPr'2})\).
(η3-C3H3)2Fe(PMe3)2, (η4-C6H6)2FePPr2C2H4PPr2 (1, n = 2), (η5-cyclohexadienyl)-
Fe(Pr'2PC2H4PPr2)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(CH)), 153 Hz), 137.7 (C-8, J(CH) 152 Hz), 137.4 (C-5), 124.3 (C-4, J(CH) 152 Hz), 114.9 (C-9, J(CH) 155 Hz), 114.2 (C-1, J(CH) 155 Hz), 41.5 (C-6, J(CH) 126 Hz), 38.0 (C-7, J(CH) 125 Hz), 31.9 (C-3, J(CH) 126 Hz), 25.6 (C-11, J(CH) 125 Hz), 18.0 (C-10, J(CH) 126 Hz), 12.1 (C-12, J(CH) 126 Hz) – numbering scheme shown below.

10. 1H NMR (CDCl3): δ 5.74 (H-2), 5.63 (H-8), 5.1 (H-4), 4.95 (H-1), 4.87 (H-9), 2.69 (H-3), 2.02 (H-7), 1.86 (H-6), 1.41 (H-10), 1.28 (H-11), 0.72 (H-12). 13C NMR (CDCl3): δ 137.8 (C-8, J(CH) 151 Hz), 137.7 (C-5), 137.4 (C-2, J(CH) 153 Hz), 122.9 (C-4, J(CH) 153 Hz), 114.8 (C-9, J(CH) 155 Hz), 114.0 (C-1, J(CH) 155 Hz), 50.7 (C-6, J(CH) 126 Hz), 38.1 (C-7, J(CH) 127 Hz), 32.0 (C-3, J(CH) 126 Hz), 25.6 (C-11, J(CH) 126 Hz), 12.0 (C-12, J(CH) 126 Hz) – numbering scheme shown below.

11. 1H NMR (CDCl3): δ 5.84 (H-8), 5.73 (H-2), 5.05/4.96 (H-9), 5.00/4.94 (H-1), 4.81/4.76 (H-10), 2.20 (H-7), 2.14 (H-3), 2.01 (H-6), 1.99 (H-4), 1.45/1.37 (H-11), 0.82 (H-12). 13C NMR (CDCl3): δ 150.8 (C-5), 138.7 (C-8, J(CH), 152 Hz), 137.5 (C-2, J(CH) 152 Hz), 115.2 (C-1, J(CH) 155 Hz), 114.4 (C-9, J(CH) 155 Hz), 109.4 (C-10, J(CH) 154 Hz), 48.0 (C-4, J(CH) 127 Hz), 38.3 (C-3, J(CH) 127 Hz), 32.7 (C-6, J(CH) 125 Hz), 31.9 (C-7, J(CH) 127 Hz), 25.9 (C-11, J(CH) 125 Hz), 11.7 (C-12, J(CH) 125 Hz) – numbering scheme shown below.

12. 1H NMR (CDCl3): δ 5.76 (H-8), 5.43 (H-2), 5.41 (H-3), 4.95/4.88 (H-9), 4.73/4.68 (H-10), 2.81 (H-4), 2.13 (H-7), 2.02 (H-6), 1.56 (H-1), 1.49/1.29 (H-11), 0.78 (H-12). 13C NMR (CDCl3): δ 151.8 (C-5), 138.7 (C-8, J(CH) 152 Hz), 133.9 (C-3, J(CH) 153 Hz) 124.1 (C-2, J(CH) 153 Hz), 114.4 (C-9, J(CH) 155 Hz), 108.3 (C-10, J(CH) 155 Hz), 45.1 (C-4, J(CH) 128 Hz), 33.8 (C-6, J(CH) 126 Hz), 32.2 (C-7, J(CH) 128 Hz), 26.8 (C-11, J(CH) 127 Hz), 13.1 (C-1, J(CH) 126 Hz), 11.9 (C-12, J(CH) 126 Hz) – numbering scheme shown below.

NMR spectroscopic assignment: the 1H-(400 MHz) and 13C-(100.6 MHz) assignments are unambiguous and were made with the aid of COSY and C,H-shift correlated 2D spectra (1J(CH)) and DEPT spectra. In addition, in the case of 12, inverse TOCSY, C,H-correlated spectra (long range C,H-correlation) were used.

3.7 Reactions of 4-vinyl-1-cyclohexene
(η5-C6H6-1-vinyl-3,4,5-cyclohexenyl)-
Fe(Pr'2PC2H4PPr2)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 mixture was stirred at −40 °C for 16 h to give a brown solution which was evaporated to dryness at 0.1 mmHg. The residue was extracted with pentane (3×30 ml) at −78 °C and the resulting yellow solution 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 (η5-1-ethylcyclopentadienyl)Fe(Pr'2PC2H4PPr2)H [10], see above. 31P NMR (d6-toluene, −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(1E, 2) 8.0 Hz, 2.75 (q, H-7), 2.67 (dd, H-1Z, J(1Z,2) 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), 1.37 (d, H-8a, J(8a, 8b) 13.6 Hz), 0.90 (d, H-8b), −14.70 (t, FeH, J(H,P1) 80.6 Hz, J(H,P2) 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(CH) 152 Hz), 75.2 (C-6, J(CH) 162 Hz), 54.3 (C-5, J(P,C) 2.1/7.5 Hz, J(CH) 153 Hz), 48.8 (C-7, J(P,C) 6.4/10.7 Hz).
The structure and signal assignments are unambiguous and are based upon COSY, C,H-shift correlated 2D NMR spectra, DEPT (13C) and 1H NMR spectra with selective decoupling of 31P.

At -30 °C the NMR-spectroscopic samples rearranged completely to

\[ \eta^2-1\text{-ethylenecyclohexadienyl}Fe(P(\text{Pri}_2\text{P}(\text{C}_2\text{H}_4\text{PPri}_2))\text{H} \] (2) [10]. 31P NMR (d8-toluene): \( \delta 117.7 \). 1H NMR (d8-toluene): \( \delta 5.88 \) (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.

\[ \eta^2-\text{1-Vinyl-3,4,5-cyclohexenyl}-Fe(P(\text{Pri}_2\text{P}(\text{C}_2\text{H}_4\text{PPri}_2))\text{H} \] (13, \( n = 3 \))

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

\[ C_{22}H_{46}FeP_2 \]

Caled C 62.7 H 10.5 Fe 12.7 P 14.1%.

\[ \text{Found C 62.8 H 10.4 Fe 12.6 P 14.1%} \]

IR (KBr): \( \nu 3020, 1940 \text{ (FeH)}, 1505 \text{ (C:C)} \). - MS (70 °C): m/e 412 (M+), 304 (M+ -CH3). 31P NMR (d8-toluene, -30 °C): \( \delta 50.4 \); a singlet is observed between -80 °C and +60 °C. 1H NMR (d8-toluene, -30 °C): \( \delta 6.58 \) (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. 13C NMR (d8-toluene, -30 °C): \( \delta 84.77 \) (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

\[ \eta^2-\text{Cyclohexadienyl}Fe(P(\text{Pri}_2\text{P}(\text{C}_2\text{H}_4\text{PPri}_2))\text{H} \] [10]

FeCl2·nTHF (n = 1.375, 0.52 g, 2.30 mmol), dippm (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): \( \delta 5.92 \) (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.

\[ \eta^2-\text{Cyclohexadienyl}Fe(P(\text{Pri}_2\text{P}(\text{C}_2\text{H}_4\text{PPri}_2))\text{H} \] [10]

Prepared as described above by reacting FeCl2·nTHF, dippm, 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): \( \delta 71.3 \); (-80 °C) 75.3, 66.5. 1H NMR (d8-toluene, -30 °C): \( \delta 5.73 \) (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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α Ueq = 1/3 Σ Σ Ui j a i α j a j.

Crystal structure analysis of
(η²-1-syn,Me-pentadienyl)Fe(Pr s PC3H5PPr s)H (7)

Molecular formula C20H24FeP2, molecular weight 400.4 gmol⁻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, dcal = 1.24 g cm⁻³, µ = 8.50 cm⁻¹, Z = 4, orthorhombic, space group P2₁2₁2₁ [No. 19]. Enraf-Nonius CAD4 diffractometer, λ = 0.71069 Å, scan mode ω-2θ, 7086 measured reflections (±h, ±k, ±l), [(sinθ)/λ]max = 0.70 Α⁻¹, 6226 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, Rw = 0.028 [w = 1/σ²(Fo)], 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,η²-1,5-hexadiene)Fe(Pr s PC3H5PPr s)] (8)

Molecular formula C21H44FeP2, molecular weight 414.4 gmol⁻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, dcal = 1.21 g cm⁻³, µ = 8.02 cm⁻¹, Z = 4, monoclinic, space group P2₁/m [No. 14]. Enraf-Nonius CAD4 diffractometer, λ = 0.71069 Å, scan mode ω-2θ, 5596 measured reflections (±h, ±k, ±l), [(sinθ)/λ]max = 0.65 Α⁻¹, 5204 independent reflections, 4709 observed reflections [I>2σ(I)] for 213 refined parameters, structure solved by heavy atom method, C18-C21 ordered and refined isotropically, H atom positions calculated and fixed (UH = 0.03 Å²) in the final refinement stages, R = 0.042, Rw = 0.056 [w = 1/σ²(Fo)], 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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Further details of the crystal structure investigation (listings of hydrogen atom positional parameters, anisotropic thermal parameters, distances and angles) may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number CSD 58744, the names of the authors and the journal citation.