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Interaction of Acyclic Tetraenes and Trienes with Transition Metals: Organoiron Compounds

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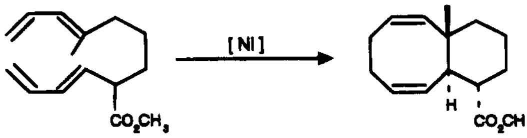
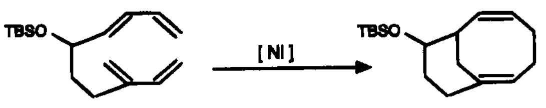
The tetraene 3,6-dimethylene-1,7-octadiene (DMOD) reacts with zerovalent [FePR$_3$] species (prepared by reduction of FeCl$_2$·*n*THF with active Mg in the presence of the donor ligand) to give $(\eta^4,\eta^4$-DMOD)FePR$_3$ compounds. The crystal structure of the PPh$_3$-stabilized derivative (space group $R\bar{3}$, $a = b = c = 20.290(9)$ Å, $\alpha = \beta = \gamma = 117.47(3)°$, $Z = 6$, $R = 0.048$, $R_w = 0.052$) confirms that the iron atom lies at the center of a square pyramid with the P atom at the apex and the two 1,3-diene fragments forming the base. That the products of the reaction of the trienes 3-methylene-1,6-heptadiene (MHD) and 3-methylene-1,7-octadiene (MOD) with zerovalent [Fe(Pr$^i_2$P(CH$_2$)$_n$PPr$^i_2$)] species ($n = 1, 2, 3$) contain a triene molecule bonded in an η^2,η^4-manner to the metal atom has been confirmed by X-ray diffraction for $(\eta^2,\eta^4$-MHD)Fe(Pr$^i_2$PC$_2$H$_4$PPr$^i_2$) (space group $P2_1/c$, $a = 11.831(1)$ Å, $b = 9.744(1)$ Å, $c = 20.917(2)$ Å, $\beta = 104.87(1)°$, $Z = 4$, R 0.042, $R_w = 0.039$). Warming a red ethereal solution of $(\eta^2,\eta^4$-MOD)Fe(Pr$^i_2$PC$_3$H$_6$PPr$^i_2$) to room temperature causes dissociation of the nonconjugated double bond of the triene to give the green, paramagnetic compound $(\eta^4$-MOD)Fe(Pr$^i_2$PC$_3$H$_6$PPr$^i_2$) which reacts with CO to give the yellow, diamagnetic compound $(\eta^4$-MOD)Fe(CO)(Pr$^i_2$PC$_3$H$_6$PPr$^i_2$).

Introduction

The transition metal catalyzed reactions of 1,3-dienes have been investigated intensively for over 30 years, and in particular those involving 1,3-butadiene form the basis of a number of industrial processes.[1] In contrast, the reactions of substrates containing two 1,3-diene fragments have received much less attention and are confined to the nickel-catalyzed [4 + 4] cycloaddition of a few 1,1′- and 1,2′-bridged species which have been studied by Wender et al.[2] Two representative reactions are shown in eqs 1 and 2 and are of particular interest in view of recent attempts to construct the taxane skeleton.



(1)



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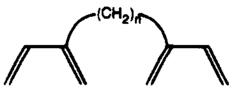
Analogous reactions involving the 2,2′-bridged species **1** have not, as far as we are aware, been reported and



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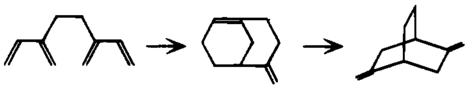
are the subject of our current research. At least on paper, the intermolecular dimerization through a double [4 + 4] cycloaddition reaction should lead to bridged 1,5-cyclooctadiene derivatives while intramolecular cycloaddition could give bicyclic products. Since it was anticipated that ring strain in the products of the reactions involving the methylene-bridged species **1** (n = 1) would hinder their formation or isolation, we initially turned our attention to the reactions of 3,6-dimethylene-1,7-octadiene (**1**, n = 2; DMOD) particularly since it has been reported that DMOD can be converted into the intramolecular Diels−Alder product **2** by a gas-phase thermolysis at 400 °C.[3] As expected, **2** rearranges to the bicyclooctane derivative **3** (eq 3).[4] It is a moot point whether the presence of transition metal species would catalyze the formation of **2** at lower temperatures or whether they would instead catalyze the further reaction.



1 (n=2) 2 3

(3)

In this and the following publication, we describe the *stoichiometric* reactions of **1** (n = 2) with zerovalent metal compounds, and the catalytic reactions and the extension to other tetraenes will be presented later. The following discussion describes the reactions of zerovalent

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[®] Abstract published in *Advance ACS Abstracts,* March 15, 1995.

(1) Parshall, G. W.; Ittel, S. D. In *Homogeneous Catalysis*; Wiley: New York, 1992.

(2) (a) Wender, P. A.; Ihle, N. C. *J. Am. Chem. Soc.* **1986**, *108*, 4678. (b) Wender, P. A.; Snapper, M. L. *Tetrahedron Lett.* **1987**, *28*, 2221. (c) Wender, P. A.; Ihle, N. C. *Tetrahedron Lett.* **1987**, *28*, 2451. (d) Wender, P. A.; Ihle, N. C.; Correia, C. R. D. *J. Am. Chem. Soc.* **1988**, *110*, 5904. (e) Wender, P. A.; Tebbe, M. J. *Synthesis* **1991**, 1089.

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(4) (a) Limberg, A. Diploma Thesis, Ruhr-Universität, Bochum, 1991. (b) Limberg, A.; Roth, W. R. Unpublished results.

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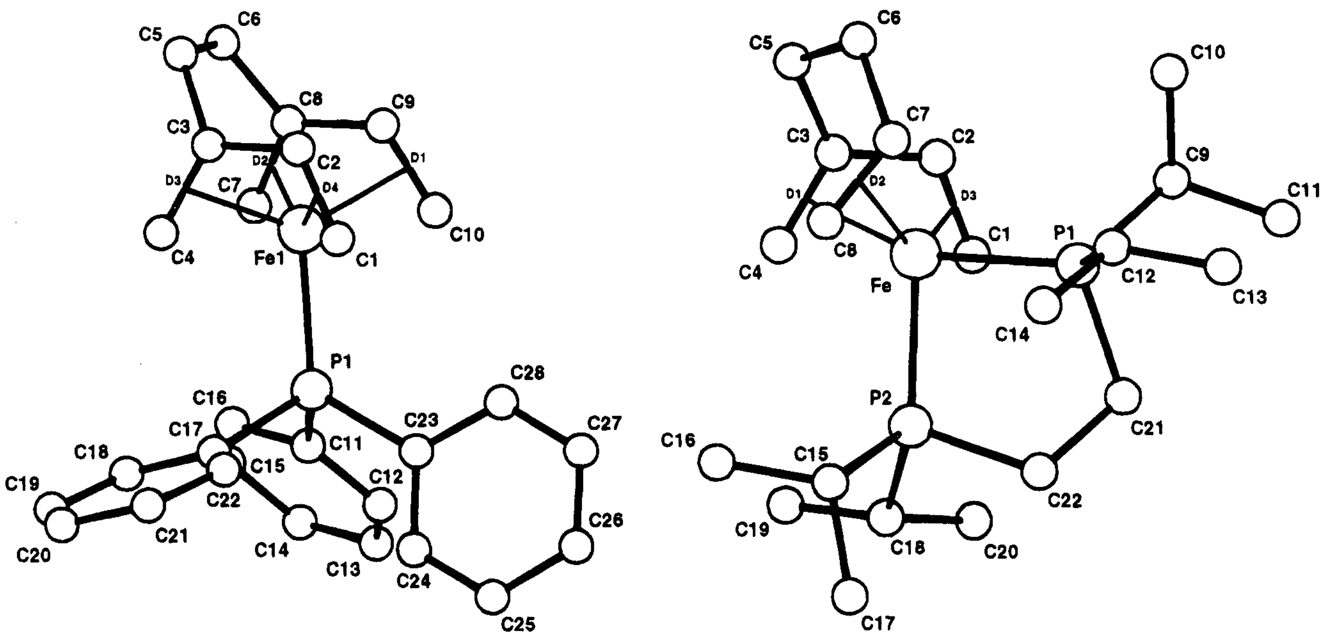
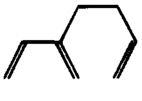


Figure 1. Molecular structure of (left) (η^4,η^4-DMOD)FePPh$_3$ (**8**) and (right) (η^2,η^4-MHD)Fe(Pr$^i{}_2$PC$_2$H$_4$PPr$^i{}_2$) (**13**).

iron species with DMOD and with the related trienes 3-methylene-1,6-heptadiene (**4**, MHD) and 3-methylene-1,7-octadiene (**5**, MOD).



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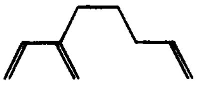

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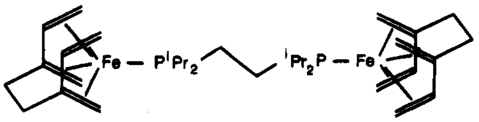
Results and Discussion

Reactions of 3,6-Dimethylene-1,7-octadiene (DMOD). Bis(1,3-butadiene)metal complexes of chromium,[5] manganese,[6] and iron[7] stabilized by monodentate P-donor ligands have been prepared by reducing the appropriate metal dichloride in the presence of the diene and ligand. These results have been extended to DMOD by using active Mg powder (prepared by thermolysis of MgH$_2$[8]) as the reducing agent. Although in the case of Cr and Mn it proved possible to isolate PMe$_3$-stabilized derivatives, the Cr compound was isolated as a green oil and could not be obtained analytically pure while the Mn compound was only formed in traces—possibly because of the low solubility of MnCl$_2$ in THF. Furthermore, both compounds were paramagnetic.

In contrast, the product of analogous reactions between iron dichloride and DMOD led to the formation in high yield of orange, stable compounds (**6**–**9**) which are moreover diamagnetic and crystalline (eq 4). Attempts to prepare a compound in which only three of the four double bonds of the tetraene are complexed to the metal atom by reacting Pr$^i{}_2$PC$_2$H$_4$PPr$^i{}_2$ were unsuccessful: a 5:1 mixture of **10** and **11** is formed indicating that the chelating property of the tetraene is stronger than that of the bidentate ligand.

$$\mathrm{FeCl_2{\cdot}nTHF + DMOD + PR_3} \xrightarrow[\mathrm{-\,MgCl_2\,/\,nTHF}]{\mathrm{Mg^*}} \quad (4)$$

$$(\eta^4,\eta^4\text{-DMOD})\mathrm{FePR_3} \quad \begin{matrix} \mathbf{6},\ \mathrm{R=Me}\ ;\ \mathbf{7},\ \mathrm{R=Et}\ ; \\ \mathbf{8},\ \mathrm{R=Ph}\ ;\ \mathbf{9},\ \mathrm{PR_3=PMe_2Ph} \end{matrix}$$



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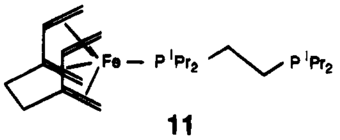

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The molecular structure has been confirmed by a crystal structure determination of the PPh$_3$-stabilized derivative **8** (Figure 1), and selected bond lengths and angles are listed in Table 1. The iron atom in **8** lies at the center of a square pyramid with the P-atom at the apex and is positioned 0.7 Å above the plane defined by the centers of the four double bonds (D1–D4). The two halves of the tetraene are bonded symmetrically to the metal atom, and within each diene fragment the bonds are identical in length. The crystal structure of (η^4-1,3-C$_4$H$_6$)$_2$FePMe$_3$ (**12**) had been determined previously,[9] and a comparison of the two structures indicates that the ethano bridge in **8** forces the terminal diene C-atoms (C1, C4, C7, C10) to occupy positions slightly farther from the metal atom than in **12** (Fe–C = 2.101(5)–2.112(7) Å for **8** and 2.080(4)–2.090(4) Å for **12**), while

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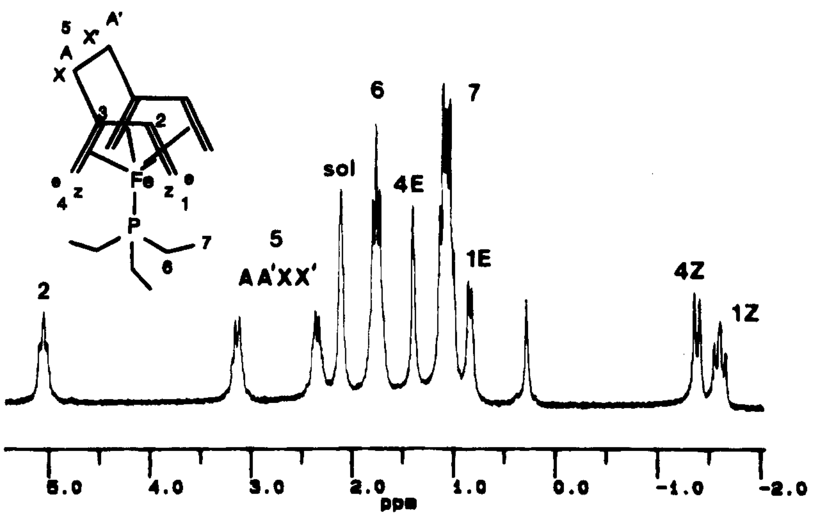


Figure 2. ^{1}H-NMR spectrum of (η^4,η^4-DMOD)FePEt$_3$ (**7**) (d_8-toluene, 300 K, 200.1 MHz).

Table 1. Selected Structural Parameters for (η^4,η^4-DMOD)FePPh$_3$ (8)

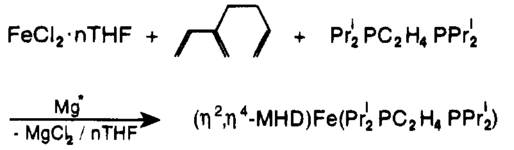
bond lengths (Å)		bond angles (deg)	
Fe−P	2.246(1)	C1−Fe−C2/C10−Fe−C9	39.8(2)/39.3(3)
Fe−C1/C10	2.101(5)/2.112(7)	C2−Fe−C3/C9−Fe−C8	40.7(2)/40.4(3)
Fe−C2/C9	2.021(5)/2.022(8)	C3−Fe−C4/C8−Fe−C7	39.8(2)/39.1(2)
Fe−C3/C8	2.021(6)/2.026(5)	C1−C2−C3/C10−C9−C8	119.7(5)/120.1(6)
Fe−C4/C7	2.104(6)/2.106(4)	C2−C3−C4/C9−C8−C7	117.8(5)/116.4(6)
C1−C2/C10−C9	1.407(7)/1.39(1)	C2−C3−C5/C9−C8−C6	118.6(6)/119.6(5)
C2−C3/C9−C8	1.407(8)/1.398(9)	C4−C3−C5/C7−C8−C6	121.8(5)/122.2(6)
C3−C4/C8−C7	1.405(9)/1.386(8)	C3−C5−C6/C8−C6−C5	113.7(7)/115.3(6)
C3−C5/C8−C6	1.517(9)/1.51(1)	P−Fe−D4/P−Fe−D1	106.6/111.3
C5−C6	1.41(1)	P−Fe−D3/P−Fe−D2	111.1/116.1
Fe−D1/D4	1.946/1.937	D4−Fe−D3/D1−Fe−D2	65.0/63.7
Fe−D2/D3	1.946/1.939	D3−Fe−D1/D4−Fe−D2	137.5/137.2

the angle formed by the two diene planes to each other increases from 10.6° in **12**[10] to 21.4° in **8**.

The NMR spectra of compounds **6−11** confirm the symmetrical arrangement of the DMOD molecule. The ^{1}H-NMR spectra are typical for (η^4-1,3-diene)iron species, and that for the PEt$_3$-stabilized compound **7** is shown in Figure 2. The proton at C-2 is relatively uninfluenced by the complexation of the tetraene to the metal atom whereas those bonded to the terminal C-atoms (C1−C4) experience the familiar high-field shift whereby those for H-1Z and H-4Z, which are directly influenced by the iron atom, are unusually large. Similar effects have been discussed previously for (η^4-1,3-butadiene)$_2$FePR$_3$ complexes.[11] The protons of the ethano bridge form an AA'XX' spin system. The ^{1}H- and the ^{13}C-NMR data are collected together in Tables 2 and 3.

Attempts to prepare complexes in which only three of the four double bonds in the DMOD molecule interact with the metal atom were unsuccessful: in the presence of Pr$^i{}_2$PC$_2$H$_4$PPr$^i{}_2$, **10** and **11** are formed (see above) while a pentane solution of **7** does not react with CO at atmospheric pressure. We were, however, able to prepare triene−iron compounds by reaction of 3-methylene-1,6-heptadiene (MHD) and 3-methylene-1,7-octadiene (MOD), and these results are discussed below.

Reactions of 3-Methylene-1,6-heptadiene (MHD) and 3-Methylene-1,7-octadiene (MOD). The product of the reaction between MHD and the zerovalent [Fe(Pr$^i{}_2$PC$_2$H$_4$PPr$^i{}_2$)] species is the expected (η^2,η^4-MHD)Fe compound **13** (eq 5) as an orange crystalline solid



(5)

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which is stable at room temperature. The NMR spectra of **13** (Tables 2 and 3) indicate that all three double bonds interact with the metal atom, and this has been confirmed by a crystal structure determination. The molecular structure is shown in Figure 1, and selected structural parameters are listed in Table 4. The arrangement of the three double bonds and the two P-atoms around the metal atom can be described either as a distorted tetragonal pyramid (with P2 at the apex; Figure 1) or alternatively as a distorted trigonal bipyramid (with P1 and the methylene group C3/C4 at the apices). The main distortions in the tetragonal pyramidal description are the displacement of the metal atom (0.7964 Å) and P1 (0.9613 Å) out of the plane formed by the center of three of the double bonds, while, in the trigonal bipyramidal description, the angle between the two apical groups (P1 and D1) is decreased from an ideal value of 180 to 154°. In the latter case, the metal atom, P2, and the centers of the two remaining double bonds (D2 and D3) lie in the same plane.

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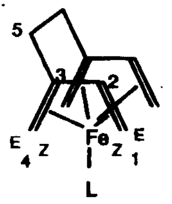
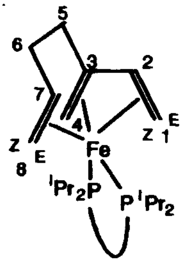
Table 2. ^{1}H-NMR Spectroscopic Data

compd,(L)	solvent (T, °C)	δ(H-*n*)						*J* (Hz)	misc
		1Z	1E	2	4Z	4E	5		
6[a] (PMe_3)	d_8-toluene (27)	−1.52 (ddd)	0.75 (ddd)	5.00 (dd)	−1.26 (d, br)	1.34 (d, br)	3.08/2.31 (m)	*J*(1Z,2) 9.2, *J*(1Z,P) 13.7, *J*(1Z,1E) 1.7, *J*(1E,2) 7.0, *J*(1E,P) 0.9, *J*(4Z,P) 11.4, *J*(4E,P) 1.2	1.43 (Me), *J*(Me,P) 7.5
7[a] (PEt_3)	d_8-toluene (−30)	−1.60 (dd)	0.85 (d)	5.06 (dd)	−1.40 (d)	1.40 (s)	3.11/2.33 (m)	*J*(1Z,2) 9.2, *J*(1Z,P), 12.4, *J*(1E,2) 6.8, *J*(4Z,P) 10.1, *J*(5,5′) 12.1/6.1, ∼−16.9/∼2.9 (AA′XX′)	1.65/1.01 (Et)
8[a] (PPh_3)	d_8-THF (27)	−1.90 (ddd)	1.08 (ddd)	4.44 (dd)	−2.18 (d)	1.44 (s)	3.23/2.23 (m)	*J*(1Z,2) 9.7, *J*(1Z,P) 13.3, *J*(1Z,1E) 1.8, *J*(1E,2), 7.2, *J*(1E,P) 0.9, *J*(2,1E) ∼8, *J*(4Z,P) 10.7, *J*(4E,P) 1.2	7.70/7.30 (Ph)
9[a] (PMe_2Ph)	d_8-toluene (27)	−1.65 (m)	0.75 (m)	5.02 (m)	−1.50 (m)	1.32 (s)	3.02/2.25 (m)	signals broad	7.43/7.10 (Ph), 1.72 (Me)
10[a,b] ($Pr^i_2PC_2H_4PPr^i_2$)	d_8-toluene (27)	−1.38 (ddd)	0.86 (d, br)	5.35 (dd)	−1.18 (d)	2.50 (s)	3.13/2.32 (m)	*J*(1Z,2) 9.6, *J*(1Z,P) 11.3, *J*(1Z,1E) 1.6, *J*(1E,2) 6.9, *J*(4Z,P) 9.6	2.58/1.42−1.16 ($Pr^i_2PC_2H_4PPr^i_2$)
11[a] ($Pr^i_2PC_2H_4PPr^i_2$)	d_8-toluene (27)	−1.35 (ddd)	0.85 (d, br)						2.55/1.42−1.22 ($Pr^i_2PC_2H_4PPr^i_2$)
13[c,d] ($Pr^i_2PC_2H_4PPr^i_2$)	d_8-toluene (27)	−1.49 (m)		5.37 (m)	−0.46(d)			*J*(4Z,P) 9.7	2.52−0.40 ($Pr^i_2PC_2H_4PPr^i_2$)
14[e,f] ($Pr^i_2PCH_2PPr^i_2$)	d_8-toluene (−30)	−0.49 (m)		5.80 (m)	−1.10 (d)	−0.70 (s)		*J*(4Z,P) 10.5	3.1−0.7 ($Pr^i_2PCH_2PPr^i_2$)
15[e,g] ($Pr^i_2PC_2H_4PPr^i_2$)	d_8-THF (−20)	−1.54 (4d)	0.63 (3d)	4.91 (t)	−1.04 (dt)	−0.76 (s)	2.21/2.04 (m)	*J*(1Z,2) 6.9, *J*(1Z,1E) 2.0, *J*(1Z,P) 14.0/6.0, *J*(1E,2) 6.1, *J*(1E,P) 8.1, *J*(4Z,E) 1.5, *J*(4Z,P) 11.0/1.5	2.91−1.51/1.7−0.6 ($Pr^i_2PC_2H_4PPr^i_2$)
16[e] ($Pr^i_2PC_3H_6PPr^i_2$)	d_8-THF (−20)	−1.16 (dt)		5.17 (t)	−1.73 (d)	−0.72 (s)		*J*(1Z,2) 7, *J*(1Z,P) 7/11, *J*(4Z,P) 10	2.74/2.57/2.4−0.8 ($Pr^i_2PC_3H_6PPr^i_2$)
17[e,h] ($Pr^i_2PC_3H_6PPr^i_2$/CO)	d_8-toluene (27)	−0.91 (m)		4.92 (m)	−0.49 (d)			*J*(4Z,P) 9.4	2.8−0.7 ($Pr^i_2PC_3H_6PPr^i_2$)

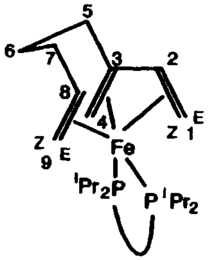
[a] Numbering scheme:



[b] Dinuclear compound. [c] Numbering scheme:



[d] δ 3.05/2.78/2.08/1.80. [e] Numbering scheme:

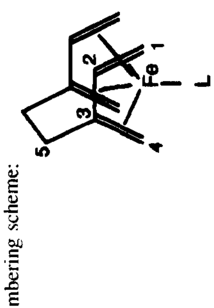


[f] δ 1.55/1.20/0.90/0.70/−0.70. [g] δ 1.64/1.25 (6), 1.92/1.39 (7), 2.39 (m, 8), 0.78 (dd 9Z), 0.98 (dd, 9E) *J*(9Z,8) 11.6, *J*(9Z,P) 1.7/1.7, *J*(9E,8) 8.9, *J*(9E,P) 14.3. [h] δ 5.90 (ddt, 8), 5.09 (br, d, 9Z), 4.99 (br, d, 9E), *J*(8,7) 6.6, *J*(8,9Z) 16.9, *J*(8,9E) 10.3.

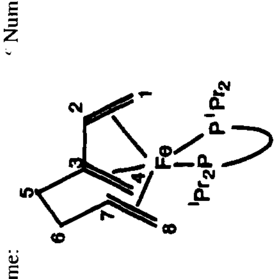
Table 3. ^{13}C-NMR Spectroscopic Data

compd (L)	solvent (T, °C)	δ(C-n) (J(C,P), Hz)									misc
		1	2	3	4	5	6	7	8	9	
7[a] (PEt_3)	d_8-toluene (−30)	34.38 (11.0)	85.47 (2.0)	101.93 (1.4)	44.84 (9.0)	37.52 (~0)					18.78/8.01 (Et)
8[a] (PPh_3)	d_8-THF (27)	36.6 (9.5)	86.3	103.4	50.5 (6.7)	36.4					139.4−126.7 (Ph)
13[b] ($Pr^i_2PC_2H_4PPr^i_2$)	d_8-toluene (27)	36.8[e] (7.9)	71.9	108.1	46.5 (9.0)	37.8[f]	32.9[f]	56.5 (7.1/2.7)	31.5[e] (9.6)		32.5−19.3 ($Pr^i_2PC_2H_4PPr^i_2$)
15[c] ($Pr^i_2PC_2H_4PPr^i_2$)	d_8-THF (−20)	30.9 (7.6/13.1)	76.2	97.1	29.7 (9.2/10.8)	33.0	25.7 (3.0)	31.2 (2.3)	43.9 (3.0/15.6)	35.2 (1.4/10.6)	31.4−19.4 ($Pr^i_2PC_2H_4PPr^i_2$)
16[c] ($Pr^i_2PC_3H_6PPr^i_2$)	d_8-THF (−20)	33.6 (7.2/12.7)	77.9	92.4	34.4 (9/11)	31.7	23.4 (~0)	29.8 (2.2)	41.2 (2.0/7.2)	36.4 (12.7)	32.3−19.3 ($Pr^i_2PC_3H_6PPr^i_2$)
17[c,d] ($Pr^i_2PC_3H_6PPr^i_2$/CO)	d_8-toluene (27)		79.1	96.9					139.5	114.4	219.5 (CO) (J(C,P) 8.0/28.0)

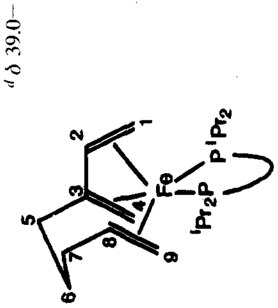
[a] Numbering scheme:



[b] Numbering scheme:



[c] Numbering scheme:

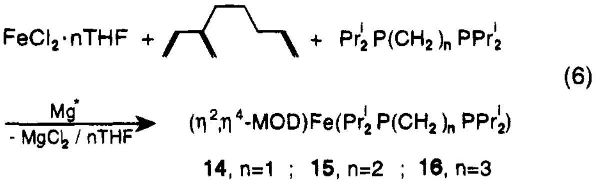


[d] δ 39.0−18.0 ($Pr^i_2PC_3H_6PPr^i_2$). [e,f] Assignment could be reversed.

Table 4. Selected Structural Parameters for (η^2,η^4-MHD)Fe($Pr^i_2PC_2H_4PPr^i_2$) (13)

bond lengths (Å)		bond angles (deg)	
Fe−P1	2.232(1)	P1−Fe−P2	86.1(1)
Fe−P2	2.237(1)	C1−Fe−C2	40.1(1)
Fe−C1	2.092(3)	C2−Fe−C3	41.0(1)
Fe−C2	2.014(3)	C3−Fe−C4	39.0(1)
Fe−C3	2.045(3)	C7−Fe−C8	38.7(1)
Fe−C4	2.142(3)	C1−C2−C3	116.3(2)
Fe−C7	2.100(3)	C2−C3−C4	115.6(2)
Fe−C8	2.086(3)	C2−C3−C5	121.6(2)
C1−C2	1.409(4)	C4−C3−C5	121.5(2)
C2−C3	1.420(3)	C3−C5−C6	109.1(2)
C3−C4	1.402(4)	C5−C6−C7	110.3(2)
C3−C5	1.504(4)	C6−C7−C8	122.9(2)
C5−C6	1.490(5)	D1−Fe−D2	90.3
C6−C7	1.524(4)	D1−Fe−D3	62.8
C7−C8	1.388(4)	D2−Fe−D3	131.1
Fe−D1	1.973	P1−Fe−D1	154.0
Fe−D2	1.974	P1−Fe−D2	97.3
Fe−D3	1.928	P1−Fe−D3	94.2

The 3-methylene-1,7-octadiene (MOD) compounds **14−16** have been prepared similarly (eq 6). These



(6)

compounds have a lower thermal stability than the MHD compound **13** and decompose above −30 °C. Isomers are possible depending upon the position adopted by the terminal alkene with respect to the 1,3-diene fragment and the conformation of the propane chain, and since we could not obtain crystals of a quality suitable for an X-ray diffraction study, the arrangement of the triene and bidentate ligand around the metal atom remains undecided. One possibility is indicated in Scheme 1. The ^{1}H-NMR spectra (Table 2) show the characteristic high field shifts for both H-1Z and H-4Z. A third signal at ca. −0.7 ppm is assigned to H-4E on the basis of extensive correlation measurements.

The reaction of the bis(diisopropylphosphino)propane-stabilized compound **16** with CO has been studied in detail (Scheme 1). Reaction in diethyl ether occurs at −30 °C to give the yellow compound **17** in which the presence of an uncomplexed double bond and a CO molecule have been confirmed spectroscopically. The same compound can be prepared by allowing a solution of **16** to warm to room temperature and then treating the resulting green solution with CO. The color change from red to green is reversible, and it is presumably the result of dissociation of the terminal alkene to give a paramagnetic (16e) species. In agreement with this interpretation, the signals in the NMR spectra of **16** at −30 °C are extremely broad while related paramagnetic compounds, e.g. (η^4-isoprene)Fe($Pr^i_2PC_3H_6PPr^i_2$), have been isolated and are also green.[12]

Experimental Section

All of the experiments described below were carried out under argon using oxygen-free dried solvents. NMR spectro-

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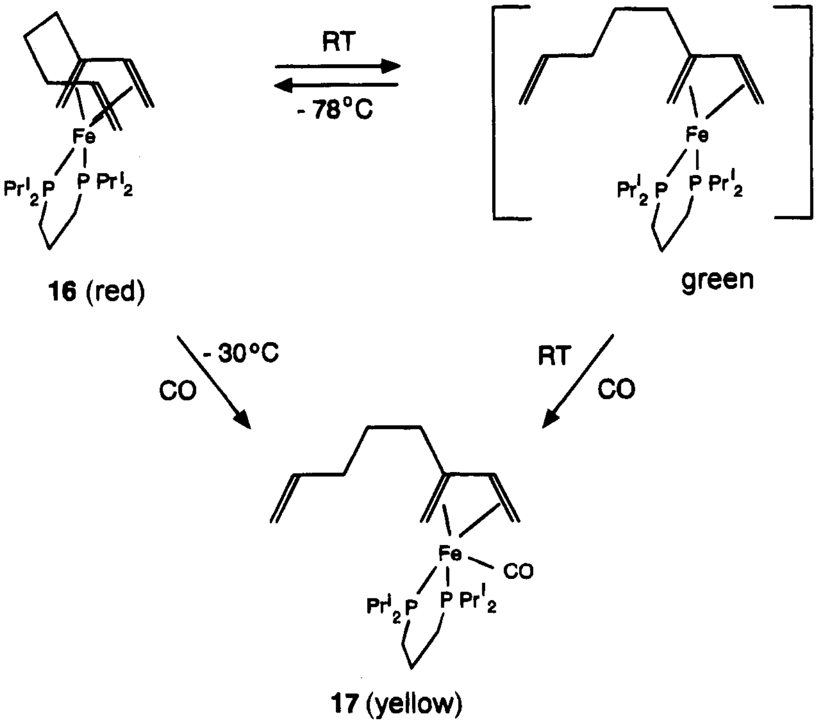
[12] Gabor, B.; Goddard, R.; Holle, S.; Jolly, P. W.; Krüger, C.; Mynott, R.; Wisniewski, W. Z. *Naturforsch.* **1995**, *50B*, 503.

Scheme 1



scopic samples were prepared under argon, and the spectra were recorded using the following Bruker instruments: WH 300, WM 300, AM 200, and AC 200. Infrared spectra were recorded as KBr disks using a Nicolet FT-7199 instrument. Mass spectra were recorded with a Finnegan MAT 311A spectrometer using 70 eV ionization energy. Elemental analyses were carried out by the microanalytical firm of Dornis and Kolbe, Mülheim an der Ruhr, Germany. The active Mg used was prepared from MgH_2.[8] $FeCl_2{\cdot}n$THF was prepared by extracting anhydrous $FeCl_2$ with THF in a Soxhlet apparatus and dried for 48 h under high vacuum: the composition was determined by elemental analysis before use.

3,6-Dimethylene-1,7-octadiene (1, *n* = 2, DMOD). The following synthesis is a modification of the published procedure.[13] A solution of 2-(bromomethyl)-1,3-butadiene (50 g, 0.34 mol)[14] in diethyl ether (400 mL) was added at room temperature over 3 h to iodine-activated Mg shavings. (4.1 g, 0.17 mol). Gentle refluxing took place, and the mixture was stirred for a further 2 h and then carefully hydrolyzed with ammonium chloride (50 g) in water (400 mL). The ether phase was separated, washed with water (3 × 150 mL), and then dried with magnesium sulfate. The compound was isolated by fractional distillation (bp 50 °C/10 mbar). Yield: 14.7 g (64.7%).

3-Methylene-1,6-heptadiene (4, MHD).[15] 2-(Bromomethyl)-1,3-butadiene (22 g, 0.15 mol)[14] in diethyl ether (200 mL) was added to (1-propen-3-yl)magnesium bromide (150 mL of a 1.0 M solution) in diethyl ether at 0 °C over 2 h. The reaction mixture was stirred for a further 2 h and the product isolated as described above (bp 52 °C/90 mbar). Yield: 10.7 g (66.7%).

3-Methylene-1,7-octadiene (5, MOD).[16] **5** was prepared as described above by reaction of (1-buten-4-yl)magnesium bromide (bp 43 °C/25 mbar). Yield: 73.3%.

(DMOD)CrPMe$_3$. $CrCl_2{\cdot}1.85$THF (1.57 g, 6.12 mmol) was suspended in THF (80 mL) and treated at −78 °C with PMe_3 (0.63 mL, 6.09 mmol), DMOD (1.00 mL, 5.88 mmol), and active Mg (0.29 g, 11.93 mmol). The reaction mixture was stirred for 24 h at −30 °C and evaported to dryness, and the resulting green residue was extracted with precooled hexane at −30 °C. The resulting extract was evaporated to give a green oil. Yield: 0.61 g (38.1%). Satisfactory analytical data could not be obtained. IR (KBr): 2970 (s), 2900 (s), 950 (s), 1100 (s), 1060 (s) cm^{-1}. MS (85 °C): *m*/*e* 262 (M^+, 34%), 186 ($M^+ - PMe_3$, 13%), 128 (M^+ − DMOD, 95%).

(DMOD)MnPMe$_3$ was prepared as described above by reaction of $MnCl_2$ at room temperature as a brown crystalline solid in 6% yield. Anal. Calcd for $C_{13}H_{23}MnP$: C, 58.9; H, 8.7; Mn, 20.7; P, 11.7. Found: C, 58.8; H, 8.8; Mn, 20.8; P, 11.6. IR (KBr): 2820 (s), 940 (s), 670 (s) cm^{-1}. MS (15 °C): *m*/*e* 265 (M^+, 47%), 189 (M^+ − PMe3, 27%), 131 (M^+ − DMOD, 31%).

(η^4,η^4-DMOD)FePMe$_3$ (6) was prepared as described below in 45.4% yield as red-orange crystals by reaction of excess PMe_3 at −30 °C. Anal. Calcd for $C_{13}H_{23}FeP$: C, 58.7; H, 8.7; Fe, 21.0; P, 11.6. Found: C, 58.6; H, 8.9; Fe, 21.1; P, 11.5. IR (KBr): 1420 (s), 1275 (s), 950 (s), 710 (s) cm^{-1}. MS (18 °C): *m*/*e* 266 (M^+, 100%), 190 ($M^+ - PMe_3$, 44%), 162 (33%), 132 (9%). ^{31}P NMR (d_8-toluene): δ 30.0. ^1H-NMR: see Table 2.

(η^4,η^4-DMOD)FePEt$_3$ (7). $FeCl_2{\cdot}n$THF (*n* = 1.32, 0.83 g, 3.73 mmol) was suspended in THF (50 mL) and treated with PEt_3 (0.55 mL, 3.73 mmol), DMOD (0.63 mL, 3.73 mmol), and active Mg (95 mg, 3.90 mmol). The reaction mixture was stirred at room temperature for 15 h and evaporated to dryness, and the residue was extracted with pentane. The orange-red pentane extract was concentrated to 20 mL and cooled to −78 °C to give the compound as red crystals which were washed with a little precooled pentane at −78 °C and dried under high vacuum. Yield: 0.60 g (52.3%). Anal. Calcd for $C_{16}H_{29}FeP$: C, 62.4; H, 9.5; Fe, 18.1; P, 10.1. Found: C, 62.3; H, 9.6; Fe 18.1; P, 10.1. IR (KBr): 2920 (s), 1035 (s), 760 (s), 710 (s) cm^{-1}. MS (60 °C): *m*/*e* 308 (M^+, 27%), 190 ($M^+ - PEt_3$, 20%), 174 (M^+ − DMOD, 14%), 118 (30%). ^{31}P NMR (d_8-toluene, −30 °C): δ 57.3. ^1H- and ^{13}C-NMR: see Figure 2 and Tables 2 and 3.

(η^4,η^4-DMOD)FePPh$_3$ (8) was prepared as described above in 4.8% yield as ruby-red crystals by reaction of PPh_3. Anal. Calcd for $C_{28}H_{29}FeP$: C, 74.4; H, 6.5; Fe, 12.4; P, 6.9. Found: C, 74.3; H, 6.6; Fe, 12.3; P, 6.6. IR (KBr): 2920 (s), 1475 (s),

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[13] Butler, G. B.; Raymond, M. A. *J. Org. Chem.* **1965**, *30*, 2410.

[14] Krug, R. C.; Yen, T. F. *J. Org. Chem.* **1956**, *21*, 1082.

[15] Kawamura, T.; Matsunaga, M.; Yonezawa, T. *J. Am. Chem. Soc.* **1978**, *100*, 92.

[16] Shea, K. J.; Kim, J.-S. *J. Am. Chem. Soc.* **1992**, *114*, 3044.

Table 5. Crystallographic Data for 8 and 13

	8	**13**
formula	$C_{28}H_{29}FeP$	$C_{22}H_{44}FeP_2$
mol wt	452.4	426.4
cryst size, mm	0.42 × 0.53 × 0.46	0.21 × 0.28 × 0.39
V, Å^3	3397.1	2330.6
D_c, g cm^{-3}	1.33	1.22
T, °C	20	20
λ(Mo), Å	0.710 69	0.710 69
Z	6	4
μ_{abs}, cm^{-1}	7.46	7.85
reflns measd	20 351 ($\pm h,\pm k,+l$)	16 637 ($\pm h,\pm k,+l$)
ind reflns	6602	8086
obsd reflns	5356	4733
no. of variables	271	358
space group (No.)	$R\bar{3}$ (148)	$P2_1/c$ (14)
a, b, c, Å	20.290(9)	11.831(1), 9.744(1), 20.917(2)
α, β, γ, deg	117.47(3)	90.0, 104.87(1), 90.0
R	0.048	0.042
R_w	0.052	0.039
res electron density, e Å^{-3}	0.45	0.30

Table 6. Final Coordinates and Equivalent Isotropic Thermal Parameters (Å^2) of the Non-Hydrogen Atoms for 8

atom	x	y	z	U_{eq}[a]
Fe1	0.9040(1)	0.6856(1)	0.6134(1)	0.033(1)
P1	1.0075(1)	0.7621(1)	0.5970(1)	0.030(2)
C1	0.7074(3)	0.4894(3)	0.3876(3)	0.056(8)
C2	0.6905(2)	0.5079(3)	0.4506(3)	0.052(8)
C3	0.7554(3)	0.6324(3)	0.5512(3)	0.05(1)
C4	0.8322(3)	0.7326(3)	0.5817(3)	0.05(1)
C5	0.7716(4)	0.6706(4)	0.6475(4)	0.08(2)
C6	0.8898(5)	0.7395(6)	0.7661(5)	0.13(2)
C7	1.0867(3)	0.8789(3)	0.8387(3)	0.057(9)
C8	0.9776(3)	0.7615(3)	0.7756(3)	0.06(1)
C9	0.9288(3)	0.6471(4)	0.6906(4)	0.07(1)
C10	0.9859(4)	0.6529(4)	0.6690(3)	0.08(1)
C11	1.2062(2)	0.9331(2)	0.7642(2)	0.032(7)
C12	1.2867(2)	0.9446(3)	0.7797(3)	0.042(8)
C13	1.4364(3)	1.0751(3)	0.9099(3)	0.05(1)
C14	1.5066(3)	1.1942(3)	1.0244(3)	0.052(8)
C15	1.4296(3)	1.1853(3)	1.0125(2)	0.049(8)
C16	1.2807(2)	1.0560(2)	0.8842(2)	0.040(7)
C17	0.9562(2)	0.7916(2)	0.5275(2)	0.033(7)
C18	1.0287(3)	0.9211(3)	0.6168(2)	0.044(8)
C19	0.9776(3)	0.9344(3)	0.5607(3)	0.05(1)
C20	0.8532(3)	0.8197(3)	0.4150(3)	0.06(1)
C21	0.7799(3)	0.6905(3)	0.3238(3)	0.050(9)
C22	0.8307(2)	0.6763(2)	0.3793(2)	0.042(8)
C23	0.9697(2)	0.6468(2)	0.4753(2)	0.039(7)
C24	1.0016(3)	0.6735(3)	0.4356(3)	0.06(1)
C25	0.9779(4)	0.5914(4)	0.3489(4)	0.07(2)
C26	0.9213(3)	0.4798(3)	0.2996(3)	0.08(1)
C27	0.8904(3)	0.4523(3)	0.3381(4)	0.07(1)
C28	0.9130(3)	0.5344(3)	0.4250(3)	0.052(9)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i{}^*a_j{}^*\bar{a}_i{\cdot}\bar{a}_j$.

1435 (s), 1085 (s), 690 (s), 530 (s) cm^{-1}. MS (130 °C): the sample decomposed. ^{31}P NMR (d_8-THF): δ 88.5. ^{1}H- and ^{13}C-NMR: see Tables 2 and 3. Crystal structure: see Figure 1 and Table 1.

(η^4,η^4-DMOD)FePMe$_2$Ph (9) was prepared as described above in 16.5% yield by reaction of PMe_2Ph. Anal. Calcd for $C_{18}H_{25}FeP$: C, 65.9; H, 7.7; Fe, 17.0; P, 9.4. Found: C, 65.8; H, 7.7; Fe, 17.1; P, 9.3. IR (KBr): 3040 (s), 3005–2800 (s), 950–870 (s), 745 (s), 700 (s), 675 (s), 575 (s), 495 (s), 480 (s) cm^{-1}. MS (70 °C): m/e 328 (M$^+$, 100%), 194 (M$^+$ − DMOD, 4.7%), 190 (M$^+$ − PMe$_2$Ph, 72.7%). ^{31}P NMR (d_8-toluene, −30 °C): δ 45.6. ^{1}H-NMR: see Table 2.

[(η^4,η^4-DMOD)Fe]$_2$($Pr^i_2PC_2H_4PPr^i_2$) (10) and (η^4,η^4-DMOD)FePPr$^i_2$C$_2$H$_4$PPr$^i_2$ (11) were prepared as a mixture (5:1 **10**:**11**) in a total yield of 40% by reaction of $Pr^i_2PC_2H_4PPr^i_2$ at −30 °C. IR (KBr): 3000–2840 (s), 1455 (s), 1435 (s), 640 (s), 620 (s) cm^{-1}. MS (**11**, 100 °C): m/e 452 (M$^+$, 42%), 318 (M$^+$ − DMOD, 13%). MS (**10**, 155 °C): m/e 642 (M$^+$, 0.5%), 508 (M$^+$ − DMOD, 29%), 452 (41%), 318 (11%). ^{31}P NMR (d_8-toluene): δ 70.6 (**10**); 68.3, 11.4, J(P,P) 23.2 Hz (**11**). ^{1}H-NMR: see Table 2.

Table 7. Final Coordinates and Equivalent Isotropic Thermal Parameters (Å^2) of the Non-Hydrogen Atoms for 13

atom	x	y	z	U_{eq}[a]
Fe	0.2635(1)	0.0758(1)	0.1470(1)	0.036(1)
P1	0.3572(1)	0.2169(1)	0.0941(1)	0.038(1)
P2	0.1435(1)	0.2523(1)	0.1487(1)	0.042(1)
C1	0.3860(2)	0.1259(3)	0.2354(1)	0.050(2)
C2	0.4020(2)	−0.0069(3)	0.2127(1)	0.049(1)
C3	0.3050(2)	−0.0974(2)	0.2033(1)	0.056(2)
C4	0.2054(3)	−0.0432(3)	0.2186(2)	0.063(2)
C5	0.3003(3)	−0.2298(3)	0.1658(2)	0.075(2)
C6	0.3201(3)	−0.2004(3)	0.0997(2)	0.072(2)
C7	0.2585(2)	−0.0679(2)	0.0716(1)	0.051(1)
C8	0.1456(2)	−0.0359(3)	0.0743(1)	0.053(2)
C9	0.5202(2)	0.2050(3)	0.1193(1)	0.050(1)
C10	0.5631(3)	0.0872(4)	0.0841(2)	0.069(2)
C11	0.5907(3)	0.3348(4)	0.1184(2)	0.075(2)
C12	0.3244(2)	0.2230(3)	0.0016(1)	0.052(2)
C13	0.3855(4)	0.3332(5)	−0.0283(2)	0.096(3)
C14	0.1951(3)	0.2269(4)	−0.0326(2)	0.074(2)
C15	−0.0100(2)	0.2449(3)	0.0964(1)	0.054(2)
C16	−0.0821(2)	0.1321(4)	0.1159(2)	0.072(2)
C17	−0.0778(3)	0.3799(4)	0.0864(2)	0.087(3)
C18	0.1224(2)	0.3318(4)	0.2264(1)	0.068(2)
C19	0.0775(3)	0.2387(5)	0.2709(2)	0.098(3)
C20	0.2310(4)	0.4080(4)	0.2656(2)	0.095(3)
C21	0.3267(2)	0.3929(2)	0.1167(2)	0.056(2)
C22	0.1969(2)	0.4040(2)	0.1120(2)	0.058(2)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i{}^*a_j{}^*\bar{a}_i{\cdot}\bar{a}_j$.

(η^2,η^4-MHD)Fe($Pr^i_2PC_2H_4PPr^i_2$) (13) was prepared as described above in 54% yield as bright red crystals by reaction of MHD and $Pr^i_2PC_2H_4PPr^i_2$ at −30 °C. Anal. Calcd for $C_{22}H_{44}FeP_2$: C, 62.0; H, 10.4; Fe, 13.1; P, 14.5. Found: C, 61.8; H, 10.4; Fe, 13.1; P, 14.7. IR (KBr): 3080 (s), 3020–2860 (s), 2820 (s), 1455 (s), 1080 (s), 885 (s), 800 (s), 690 (s) cm^{-1}. MS (110 °C): m/e 426 (M$^+$, 100%), 318 (M$^+$ − MHD, 16%), 276 (96%), 234 (88%), 192 (47%), 150 (22%). ^{31}P NMR (d_8-toluene): δ 100.7, 92.5, J(P,P) 6.8 Hz. ^{1}H- and ^{13}C-NMR: see Tables 2 and 3. Crystal structure: see Figure 1 and Table 4.

(η^2,η^4-MOD)Fe($Pr^i_2PCH_2PPr^i_2$) (14) was prepared as described above in 52% yield as a red crystalline solid by reaction of MOD and $Pr^i_2PCH_2PPr^i_2$ at −30 °C. Anal. Calcd for $C_{22}H_{44}FeP_2$: C, 62.0; H, 10.4; Fe, 13.1; P, 14.5. Found: C, 62.1; H, 10.3; Fe, 13.2; P, 14.4. IR (KBr): 3060–2800 (s), 1460 (s), 1365 (s), 1090 (s), 1055 (s), 880 (s), 745 (s), 700 (s), 595 (s) cm^{-1}. MS (110 °C): m/e 426 (M$^+$, 40%), 304 (M$^+$ − MOD, 8%), 262 (65%), 220 (63%), 205 (100%). ^{31}P NMR (d_8-toluene, −80 °C): δ 53.7, 41.5. ^{1}H-NMR: see Table 2.

(η^2,η^4-MOD)Fe($Pr^i_2PC_2H_4PPr^i_2$) (15) was prepared as described above in 86% yield as a red crystalline solid by reaction of $Pr^i_2PC_2H_4PPr^i_2$ at −30 °C. Anal. Calcd for $C_{23}H_{46}FeP_2$: C, 62.7; H, 10.5; Fe, 12.7; P, 14.1. Found: C, 62.8; H, 10.5; Fe, 12.8; P, 14.1. IR (KBr): 2960–2840 (s), 1455 (s), 1360 (s), 880 (s), 805 (s), 685 (s), 660 (s), 630 (s), 595 (s), 510 (s) cm^{-1}. MS (90 °C): m/e 440 (M$^+$, 62%), 318 (M$^+$ − MOD, 23%), 276 (88%), 234 (100%). ^{31}P NMR (d_8 -THF, −20 °C): δ 95.0, 86.8, J(P,P) 2.0 Hz. ^{1}H- and ^{13}C-NMR: see Tables 2 and 3.

(η^2,η^4-MOD)Fe($Pr^i_2PC_3H_6PPr^i_2$) (16) was prepared as described above in 66% yield by reaction of $Pr^i_2PC_3H_6PPr^i_2$ at −30 °C. Anal. Calcd for $C_{24}H_{48}FeP_2$: C, 63.4; H, 10.7; Fe, 12.3; P, 13.6. Found: C, 63.6; H, 10.8; Fe, 12.2; P, 13.5. IR (KBr): 3000–2800 (s), 1460 (s), 965 (s), 880 (s), 835 (s), 785 (s), 665 (s), 620 (s), 580 (s), 510 (s) cm^{-1}. MS (90 °C): m/e 454 (M$^+$, 2.7%), 332 (M$^+$ − MOD, 1.5%), 296 (6.7%), 248 (12%), 233 (100%). ^{31}P NMR (d_8-THF, −20 °C): δ 52.6, 44.0, J(P,P) 20.5 Hz. ^{1}H- and ^{13}C-NMR: see Tables 2 and 3.

(η^4-MOD)Fe(CO)($Pr^i_2PC_3H_6PPr^i_2$) (17). 16 (0.62 g, 1.36 mmol) was dissolved in diethyl ether (200 mL) and exposed to CO at −30 °C for 30 min. The color of the reaction mixture changed from bright red to yellow. The resulting solution was filtered through avicel and evaporated to dryness. The residue was dissolved in pentane (15 mL) and the solution filtered and cooled to −78 °C to give the compound as pale yellow needles which were washed at −78 °C with a little precooled pentane and dried under high vacuum. Yield: 0.58 g (88.2%). Anal. Calcd for $C_{25}H_{49}FeP_2O$: C, 62.1; H, 10.2; Fe, 11.6; P, 12.8. Found: C, 62.1; H, 10.0; Fe, 11.7; P, 12.8. IR (KBr): 1860 (CO), 1640 (m, C:C); 3080−2840 (s), 1460 (s), 670 (s), 625 (s), 585 (s), 560 (s). MS (110 °C): *m/e* 482 (M^+, 10%), 360 (M^+ − MOD, 58%), 332 (M^+ − MOD/CO), 290 (100%), 248 (76%), 233 (57%). ^{31}P NMR (d_8-toluene): δ 62.3, 57.4, *J*(P,P) 13.0 Hz. ^{1}H- and ^{13}C-NMR: see Tables 2 and 3.

Single-Crystal X-ray Diffraction Studies of 8 and 13. The crystal structure analyses were carried out with an Enraf-Nonius CAD-4 diffractometer. Crystallographic data and details of the refinement are listed in Table 5, and final coordinates and equivalent isotropic thermal parameters, in Tables 6 and 7. Further details are to be found in the supplementary material.

Supplementary Material Available: Detailed information on the crystal structure determinations of **8** and **13** including tables of data collection parameters, final atomic positional parameters, final thermal parameters, and interatomic distances and angles and an ORTEP diagram (17 pages). Ordering information is given on any current masthead page.

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