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Bidentate ferrocenylphosphines and their palladium(II)dichloride complexes — X-ray structural and NMR spectroscopic investigations and first results of their characteristics in the Pd-catalysed cooligomerisation of 1,3-butadiene with CO_2

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Dedicated to Professor Stanisław Pasynkiewicz on the occasion of his 70th birthday.

Abstract

The chiral 1,1′-bis(di(+)-menthylphosphino)ferrocene (dmenpf, **1b**) and achiral 1,1′-bis(diisopropylphosphino)ferrocene (disoppf, **1a**) were prepared from the corresponding tertiary chlorophosphines **2b** and **2a** and the dilithiated ferrocene–TMEDA complex as analytically pure crystals. The synclinic eclipsed conformation of the Cp rings and the Cp(1)–Fe–Cp(1)′ angle in **1b** was determined to be 175.0(2)° by X-ray structure analysis. With $H_2[PdCl_4]$ **1a** forms the bimetallic complex (disoppf)$PdCl_2$ (**3a**). In contrast to the structure of the free ligand disoppf (**1a**), the X-ray structure of **3a** and the NMR spectra in solution as well as in the solid state show that the P atoms are chemically and magnetically equivalent. The conformation of the Cp rings converts from an eclipsed to a staggered conformation. The ferrocene-based ligands show significant activity in the Pd-catalysed cooligomerisation of 1,3-butadiene with CO_2 © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Phosphines; Chiral ligands; Ferrocenes; X-ray structure; NMR; CPMAS; Catalysis; CO_2; Lactone

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1. Introduction

Ferrocenylphosphines **1** (R = alkyl or aryl) are well known bidentate ligands in coordination chemistry and catalysis [1,2]. In comparison with bis(phosphine)ligands of the type $R_2P(CH_2)_nPR_2$ with a flexible alkyl backbone, ferrocenylbiphosphines show different steric and electronic properties due to their rigid backbone.

Additionally, the formation of bimetallic complexes by coordination of the phosphine moiety and studies concerning their structural and electronic properties have been the subject of several reports [3]. Another point of interest is the influence on the selectivity and the speed of reactions using these complexes in homogeneous catalysis.

Here we report on the synthesis and structural characterisation of some bidentate ferrocenylphosphines (Fig. 1) and their palladium(II)dichloride complexes. First results of the Pd-catalysed δ-lactone synthesis will be presented (see Fig. 6).

2. Results and discussion

For the preparation of symmetrically substituted 1,1′-ferrocenylbiphosphines (**1**) the 1,1′-dilithiated ferrocene–TMEDA complex [4] is an excellent starting material [5,6]. It is treated with two equivalents of $ClP(^iPr)_2$ (**2a**) or (+)-$ClP(men)_2$ (**2b**), respectively at

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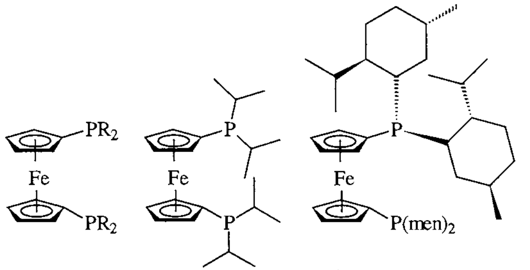

1 **1a** **1b**

Fig. 1. Symmetrically substituted ferrocenylbiphospines: 1,1′-bis(diisopropylphosphino)ferrocene (disoppf, **1a**) and 1,1′-bis(di(+)menthylphosphino)ferrocene (dmenpf, **1b**).

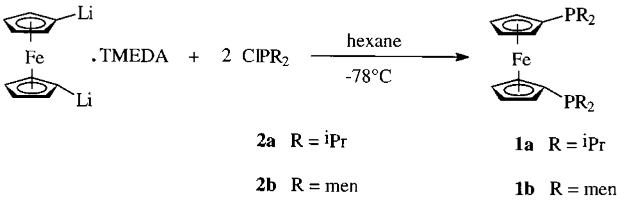

Fig. 2. Reaction scheme for the synthesis of symmetrically substituted 1,1′-ferrocenyldiphosphines (**1**).

− 78°C to yield analytically pure oils of achiral disoppf (**1a**) and chiral and optically pure (+)-dmenpf (**1b**) (Fig. 2).

*2.1. 1,1′-Bis-(diidopropylphosphino)ferrocene (**1a**)*

1,1′-Bis(diisopropylphosphino)ferrocene (**1a**) is well-known in the literature since 1985 [7]; the crystal structure was determined recently [8]. In accordance with its solid-state structure, the ^{31}P-CPMAS NMR spectrum (Fig. 3(a)) shows two singlets due to the two different types of phosphorus atoms in the molecule.

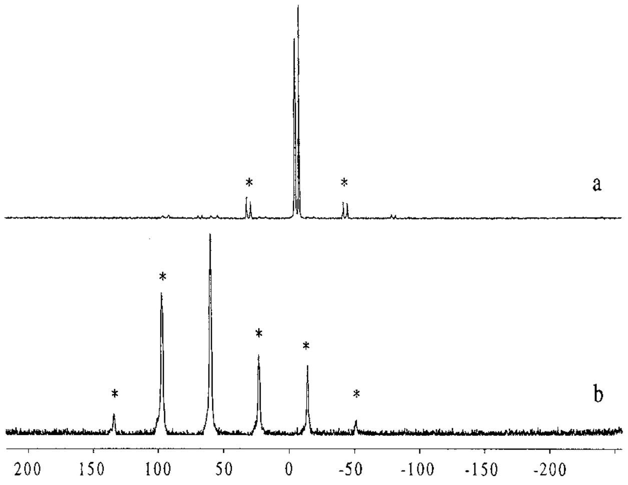

Fig. 3. Solid-state ^{31}P-CPMAS NMR spectra of (a) disoppf (**1a**) at 25°C and $\nu_R = 6$ kHz and (b) (disoppf)PdCl$_2$ (**3a**) at 25°C and $\nu_R = 6$ kHz; x-axis, ppm; (*) spinning side bands.

Table 1
Selected bond lengths (Å) and angles (°) for (disoppf)PdCl$_2$ (**3a**)

Bond lengths			
Fe–Cp(1) [a]	1.633(3)	P(1)–C(1)	1.809(3)
Fe–P(1)	3.424(3)	P(1)–C(7)	1.860(3)
Pd–Cl(1)	2.3526(9)	P(1)–C(10)	1.860(3)
Pd–P(1)	2.2941(9)	d_P [b]	0.0119(3)
Bond angles			
Cp(1)–Fe–Cp(1)′	179.9(3)	C(1)–Cp(1)–Cp(1)′–C(1)′	32.5(3)
P(1)–Fe–P(1)′	89.4(3)	tilt-angle α	3.7(3)
Cl(1)–Pd–Cl(1)′	87.53(5)	Cl(1)′–Pd–P(1)′	84.57(3)
P(1)′–Pd–P(1)	103.59(4)	P(1)–Pd–Cl(1)	84.57(3)
Pd–P–C(7)	114.9(2)	C(7)–P–C(10)	105.0(2)
C(10)–P–C(1)	101.0(2)	C(1)–P–Pd	119.82(10)

[a] Cp(1) and Cp(1)′ are the centroids of the C(1)–C(5) and C(1)′–C(5)′ rings.

[b] Deviation d_p of the P atoms from the mean Cp plane.

*2.2. Dichloro-1,1′-bis(diisopropylphosphino)-ferrocene–palladium(II) (disoppf)PdCl$_2$ (**3a**) [9]*

Dichloro-1,1′-bis(diisopropylphosphino)ferrocene–palladium(II) (disoppf)PdCl$_2$ (**3a**) was prepared from H$_2$[PdCl$_4$] with one equivalent of disoppf (**1a**) in ethanol at room temperature and was isolated as red crystals from the crude reaction mixture. It crystallises in the orthorhombic space group *Pnna*. The elementary cell contains four molecular units. The Pd atom has approximately a square-planar coordination sphere. The angle P–Pd–P′ (103.59(4)°; see Table 1, Fig. 4) is significantly wider than in the complex (dppf)PdCl$_2$·CH$_2$Cl$_2$ (**4**) (97.98(4)°) [6]. The P–Cl and Pd–P distances in **3a** are in the same order of magnitude as in **4**. The conformation of the Cp rings in **3a** is staggered due to the coordination of the P atoms to the Pd centre. The torsion angle C(1)–Cp(1)–Cp(1)′–C(1)′ is 32.5(3)°. In contrast to the solid-state structure of the free ligand

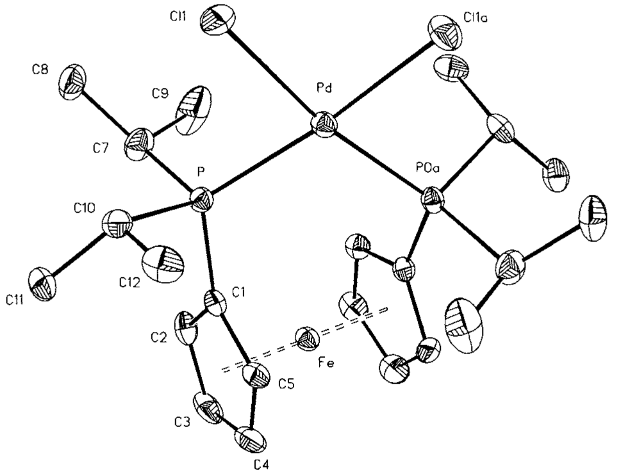

Fig. 4. ORTEP plot of (disoppf)PdCl$_2$ (**3a**) with non-H atoms as 30% thermal vibration ellipsoids.

disoppf (**1a**) [8], the P atoms in **3a** are equivalent. This is in accordance with the ^{31}P-NMR spectrum of **3a** in solution as well as in the solid state. The ^{31}P resonance of the complex **3a** in solution is shifted downfield with $\Delta\delta = 66.0$ ppm relative to **1a**.

Corresponding downfield shifts are also found in the ^{1}H spectrum for all resonances and in the ^{13}C spectrum for the carbon atoms of the Cp system. The solid-state ^{31}P-NMR spectrum of the bimetallic complex shows just one resonance at $\delta = 65.8$ ppm (Fig. 3(b)). In agreement with its X-ray crystal structure, the phosphorus atoms are chemically and magnetically equivalent.

The bond lengths Fe–P (3.424(9) Å) are slightly shorter than in disoppf (**1a**) (Fe–P 3.5161(1) Å and Fe–P′ 3.555(1) Å). The tetrahedral angles C–P–C around the P atoms are broadened out. All other distances and angles correspond to the values found for the ligand disoppf (**1a**) [8].

2.3. 1,1′-Bis(di-(+)-menthylphosphino)ferrocene (dmenpf) (1b)

The synthesis of **1b** was recently described by Brunner and Janura [10]. (+)-Menthylchloride was prepared by reaction of (+)-menthol with the Lukas reagent ($ZnCl_2$–HCl) following a modification of the published procedure [11]. The corresponding Grignard derivative was reacted with PCl_3 to yield (+)-chlorodimenthylphosphine. Further reaction with 1,1′-dilithioferrocene–TMEDA complex results in formation of **1b**.

Surprisingly, the treatment of (+)-dmenpf (**1b**) with $H_2[PdCl_4]$, following thus the same procedures for disoppf (**1a**), did not result any bimetallic palladium–dichloride complex. The low reactivity of **1b** may be explained by its specific structural properties, the limited rotation around the Cp–Fe–Cp axis caused by the bulky menthyl substituents. Therefore a physical closeness between the phosphorus atoms and the palladium centre is not possible.

2.4. X-ray crystal structure analysis

1,1′-Bis(di-(+)-menthylphosphino)ferrocene (**1b**) crystallises from hexane in the orthorhombic chiral space group $P2_12_12$ with two molecules per elementary cell. For more detailed information see Ref. [12]. The molecule has a twofold axis on the Fe-atom, the conformation of the Cp-rings is synclinic eclipsed with a torsion angle C(1)–Cp(1)–C(1)′–Cp(1)′ of 64.6(6)° (see Table 2, Fig. 5). The P atoms are just slightly displaced from the planes of the Cp rings. The Cp rings are not exactly coplanar, the tilt angle is 6.0(2)° and the angle Cp(1)–Fe–Cp(1)′ is 175.0(2)°. These values are significantly smaller than in disoppf (**1a**) (Cp(1)–Fe–Cp(1)′ = 179.3(1)°) [8]. This is probably caused by the steric influence of the bulky menthyl substituents. Consequently the C–P–C angles are enlarged. The distance between the Fe atom and the centre Cp(1) of the Cp ring (1.656(2) Å) is in the same order of magnitude as in **1a** (1.651(2) Å). The P–C bond lengths are within the range found for comparable compounds [13]. However, the distance between P and C(1) with (1.819(3) Å) is smaller than to the carbon atoms C(6) and C(16).

Table 2
Selected bond lengths (Å) and angles (°) for (+)-dmenpf (**1a**)

Bond lengths			
Fe–Cp(1)	1.656(3)	P–C(1)	1.819(3)
Fe–P	3.509(3)	P–C(6)	1.875(3)
d_P [a]	−0.0137(3)	P–C(16)	1.890(3)
Bond angles			
Cp(1)–Fe–Cp(1)′	175.0(2)	C(1)–Cp(1)–Cp(1)′–C(1)′	64.6(2)
C(1)–P–C(6)	104.4(2)	C(2)–C(1)–P	119.1(3)
C(1)–P–C(16)	104.21(13)	C(5)–C(1)–P	135.4(3)
C(6)–P–C(16)	103.13(14)	P(1)–Fe–P′	89.4(2)
Tilt angle α	6.0(2)		

[a] Deviation d_P of the P atoms from the mean Cp plane.

2.5. Pd-catalysed cooligomerisation of CO_2 with 1,3-butadiene

The Pd(0)-catalysed cooligomerisation of CO_2 and 1,3-butadiene to 2-ethyliden-6-hepten-5-olid (δ-lactone) is a promising way to use CO_2 as a C_1-building block in organic chemistry [14] (Fig. 6). Here we report on

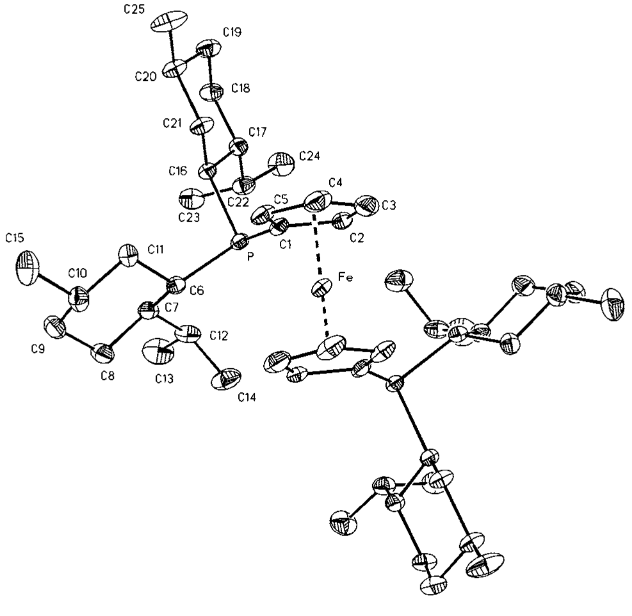

Fig. 5. ORTEP plot of 1,1′-bis(di-(+)-menthylphosphino)ferrocene (**1b**) with non-H atoms as 30% thermal vibration ellipsoids.

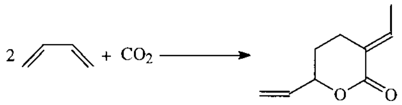

Fig. 6. Pd-catalysed telomerisation of 1,3-butadiene with CO_2.

the first results of the activity of the ferrocene-based ligands in this reaction. A detailed study dealing with this topic will be published separately (Table 3).

The values for selectivity and turnover number (TON) differ drastically from phosphine to phosphine and from Pd compound to Pd compound. As the main difference especially between **1a** and **1b** is the bulkiness of the alkyl groups attached to the phosphorus atoms, steric reasons in this special case may apply.

The elucidation of further reasons is the object of current work, especially in situ NMR and in situ IR studies.

3. Conclusions

Symmetrically substituted ferrocenylphosphines can be prepared easily from tertiary chlorophosphines in a one-step synthesis. The symmetry of the structure can be completely different in the free phosphine and the corresponding metal complex. We showed that they are promising components to form homogeneous as well as heterogeneous catalysts with several transition metals.

We already realised the successful use of ferrocenylphosphines and their palladium complexes in transition-metal-catalysed C,C-bond formation reactions with CO_2 as C_1-building block [15].

Table 3
Results of the Pd-catalysed cooligomerisation of CO_2 with butadiene

Pd compound	Phosphane	Selectivity to δ-lactone (%)	TON [a]
$Pd(OAc)_2$	**1a**	63	80
$Pd(OAc)_2$	**1b**	71	78
$Pd(OAc)_2$	dppf [b]	20	13
$Pd(acac)_2$	**1a**	70	73
$Pd(acac)_2$	**1b**	0	0
$Pd(acac)_2$	dppf	3	2
(Cp)Pd(allyl)	**1a**	7	2
(Cp)Pd(allyl)	**1b**	65	81
(Cp)Pd(allyl)	dppf	9	3
$Pd_2(dba)_3$ [c]	**1a**	0	0
$Pd_2(dba)_3$	**1b**	60	60
$Pd_2(dba)_3$	dppf	0	0

[a] TON, turnover number (mole product per mole Pd).
[b] dppf, 1,1′-bis(diphenylphosphino)ferrocene.
[c] dba, dibenzylidenacetone.

4. Experimental

4.1. General

Commercially available reagents were used without further purification. All reactions were carried out using standard Schlenk techniques. Solvents were dried by standard methods and freshly distilled prior use.

4.2. Crystallographic data collection and processing

For all structures data were collected on an Enraf–Nonius DAD4 diffractometer in the $\omega/2\theta$ scan mode using graphite monochromated Mo–K_α radiation. The intensities were corrected for Lorentz and polarisation effects. A correction for absorption was done for (disoppf)$PdCl_2$ (**3a**). The reduction of data was done with the program MOLEN [16], the structures were solved with SHELXS-86 [17] and the structure refinement was obtained with SHELXL-93 [18].

4.3. Solution NMR spectroscopy

NMR spectra were recorded on a Bruker AC 200 (operating at 200.13 Hz for ^1H, 50.29 MHz for ^{13}C or 81.00 MHz for ^{31}P) or a Varian Unity Inova 400 (operating at 399.98 Hz for ^1H, 100.59 Hz for ^{13}C or 161.92 MHz for ^{31}P) spectrometer. ^1H and ^{13}C shifts are given in ppm downfield from internal TMS. ^{31}P chemical shifts are given in ppm downfield from external 85% H_3PO_4.

4.4. Solid-state NMR spectroscopy

$^{31}P\{^1H\}$-CPMAS spectra were obtained at 161.92 MHz using the standard xpolar1 pulse sequence supplied with the VNMR software from VARIAN. ^{31}P chemical shifts are given in ppm downfield from external 85% H_3PO_4. Rotating frequencies ν_R are specified at the particular spectra.

4.5. Gas chromatography

For the quantitative determination of the δ-lactone a 25 m CP-Sil 5 (100% dimethylsiloxane) column was used in a Chrompack CP 9000 GC. (Separation conditions: 180°C isotherm, 35 kPa, injector: 250°C, detector (FID): 280°C, carrier gas: nitrogen, internal standard: pentadecane.)

4.6. Further analytical methods

IR spectroscopic data were recorded on a Perkin–Elmer FT-IR 16-PC spectrometer. EI mass spectra were measured on a Finnigan MAT SS-Q 710 (70 eV) spectrometer. Elemental analyses were performed using a

LECO CHNS 932 analyser at the Laboratory of Organic Chemistry of the Friedrich-Schiller University (Jena, Germany).

4.7. Syntheses

4.7.1. Preparation of chlorodi-(+)-menthylphosphine (2b)

Chlorodi-(+)-menthylphosphine (**2b**) was synthesised according to the literature procedures starting from (+)-menthol [11].

4.7.2. Preparation of 1,1′-dilithioferrocene–TMEDA complex

1,1′-Dilithioferrocene–TMEDA complex was synthesised according to the literature procedure [4] and isolated by filtration as an orange pyrophoric powder.

4.7.3. Preparation of 1,1′-bis(diisopropylphosphino)-ferrocene (disoppf) (1a) [7,8]

To a vigorously stirred suspension of 12.8 g (70.8 mmol) 1,1′-dilithioferrocene–TMEDA complex [4] in 100 ml hexane 14.3 g (93.7 mmol) chlorodiisopropylphosphine (**2a**) was added dropwise at −78°C. The reaction mixture was stirred for further 30 min and then warmed up slowly to 20°C. After hydrolysis with 15 ml water, the organic layer was separated, dried with Na_2SO_4 and the solvent was removed in vacuo. The obtained orange oil was analytically pure. Within a few hours at 5°C orange crystals of disoppf (**1a**) were formed (11.4 g, 27.2 mmol, 58%) m.p. 48–51°C.

IR (KBr pellet, cm^{-1}): 2968, 2947, 2925, 2895, 2861, 1463, 1379, 1360, 1156, 1029, 806, 503, 488.

MS *m/z* 418 (26%) [M^+], 376 (25%), 375 (100%) [M^+–C_3H_7], 333 (12%), 299 (3%), 289 (12%), 257 (10%), 246 (25%), 217 (15%), 186 (13%), 152 (14%), 121 (21%), 97 (4%), 56 (9%), 43 (19%).

^{1}H-NMR [C_6D_6]: $\delta = 1.09$ (dd, 12H, (C-7)H_3 (C-10)H_3, $^3J_{HH} = 7.0$ Hz; $^3J_{PH} = 3.2$ Hz); 1.16 (d, 12H, (C-8)H_3, (C-11)H_3, $^3J_{HH} = 7.0$ Hz); 1.90 (dsept, 4H, (C-6)H, (C-9)H, $^3J_{HH} = 7.0$ Hz, $^2J_{PH} = 1.6$ Hz); 4.18 (m, 4H, (C-2)H, (C-5)H); 4.27 (m, 4H, (C-3)H, (C-4)H).

$^{13}C\{^1H\}$-NMR [C_6D_6]: $\delta = 20.1$ (d, 4C, CH_3, C-7, C-10, $^2J_{CP} = 11$ Hz); 20.6 (s, 4C, CH_3, C-8, C-11); 23.7 (d, 4C, CH, C-6, C-9, $^1J_{CP} = 14$ Hz); 71.8 (s, 4C, CH, C-3, C-4), 72.4 (d, 4C, CH, C-2, C-5, $^2J_{CP} = 11$ Hz); 77.4 (d, 2C, C_q, C-1, $^1J_{CP} = 21$ Hz).

$^{31}P\{^1H\}$-NMR [C_6D_6]: $\delta = -0.2$ (s). Anal. Calc. (%): C, 63.2; H, 8.9; Found: C, 62.6; H, 8.3.

4.7.4. Preparation of dichloro-1,1′-bis(diisopropylphosphino)ferrocene–palladium(II) (3a)

$PdCl_2$ (17.9 mg, 0.101 mmol) was suspended in 2 ml of ethanol and treated with 2 ml of concentrated hydrochloric acid. The obtained solution was stirred at 50°C for 30 min and filtered over 5 cm of kieselgur. At 20°C, 26.2 mg (0.064 mmol) 1,1′-bis(diisopropylphosphino)ferrocene (disoppf, **1a**), dissolved in 2 ml of diethylether, were added and the mixture was stirred for a further 10 min. At −35°C orange–red crystals were formed, filtered and washed five times with a total amount of 100 ml of water and then dried in vacuo. Yield: 22.4 mg (0.038 mmol, 38%); m.p. 296°C (decomposition).

IR (KBr pellet, cm^{-1}): 3905, 3082, 2963, 2926, 2968, 1459, 1166, 1039, 822, 653, 499.

MS *m/z* 596 (13%) [M^+], 468 (10%), 418 (2%), 375 (39%), 333 (3%), 302 (13%), 259 (8%), 246 (17%), 217 (38%), 182 (19%), 139 (53%), 121 (17%), 97 (42%), 66 (25%), 41 (100%) [C_3H_5].

^{1}H-NMR [$CDCl_3$]: $\delta = 1.19$ (dd, 12H, (C-7)H_3, (C-10)H_3, $^3J_{HH} = 6.9$ Hz, $^3J_{PH} = 15.8$ Hz); 1.60 (dd, 12H, (C-8)H_3, (C-11)H_3; $^3J_{HH} = 7.2$ Hz; $^3J_{PH} = 17.7$ Hz); 3.00 (dsept, 4H, (C-6)H, (C-9)H, $^3J_{HH} = 7.1$ Hz, $^2J_{PH} = 2.4$ Hz); 4.48 (s, 4H, Cp system); 4.58 (s, 4H, Cp system).

$^{13}C\{^1H\}$-NMR [C_6D_6]: $\delta = 19.2$ (s, 4C, CH_3, C-7, C-10); 20.2 (d, 4C, CH_3, C-8, C-11, $^3J_{CP} = 2$ Hz); 28.5 (m, 4C, CH, C-6, C-9); 72.5 (s, 4C, Cp system); 74,2 (s, 6C, Cp system).

$^{31}P\{^1H\}$-NMR [C_6D_6]: $\delta = 65.8$ (s). Anal. Calc. (%): C, 44.4; H, 6.1; Cl, 11.9; Found: C, 44.1; H, 5.8; Cl, 11.7.

Crystal data for **3a**: $C_{22}H_{36}Cl_2FeP_2Pd$, $M_r = 595.60$ g mol^{-1}, brown prism, size $0.35 \times 0.32 \times 0.28$ mm^3, orthorhombic, space group P_{nna}, $a = 16.058(1)$, $b = 19.985(1)$, $c = 8.883(1)$ Å, $V = 2422.8(3)$ Å^3, $T = -90$°C, $Z = 4$, $\rho_{calc.} = 1.633$ g cm^{-3}, $\mu(Mo–K_\alpha) = 17.01$ cm^{-1}, psi-scan, $trans_{min}$: 0.228, $trans_{max}$: 0.273, $F(000) = 1216$, 4247 reflections in $h(0/20)$, $k(-16/21)$, $l(-11/8)$, measured in the range $2.54 \le \Theta \le 26.31$°, 2466 independent reflections, 1801 reflections with $F_o > 4\sigma(F_o)$, 200 parameters, 0 restraints, $R_{1obs} = 0.030$, $wR^2_{obs} = 0.067$, $R_{1all} = 0.058$, $wR^2_{all} = 0.079$, Goodness-of-fit = 1.071, largest difference peak and hole: 0.504/ −0.395 e Å^{-3}.

4.7.5. Preparation of 1,1′-bis(di-(+)-menthylphosphino)ferrocene (1b)

1,1′-Dilithioferrocene–TMEDA complex (3.2 g, 10.2 mmol) [4] was suspended in 50 ml hexane and stirred vigorously. A solution of 7.0 g (20.3 mmol) chlorodi-(+)-menthylphosphine (**2b**) in 50 ml hexane was added dropwise at −78°C. The reaction mixture was stirred for 1 h and then allowed to reach 20°C. The orange-coloured reaction mixture was quenched with 20 ml of water. The aqueous layer was separated and washed twice with 20 ml of hexane. The combined organic layers were dried with Na_2SO_4, filtered and the solvent was removed in vacuo. The obtained orange oil was dissolved in 10 ml hexane. Within a few days orange crystals of **1b** were formed at 25°C (6.4 g, 78%); m.p. 221–223°C; $[\alpha]_D^{20} = +199.3$ (c = 2, CHCl$_3$).

IR (KBr pellet, cm^{-1}): 1638, 1384, 1366, 1191, 1181, 1155, 1032, 819.

MS m/z 804 (6%) $[M^+ + 1]$, 802 (29%) $[M^+ - 1]$, 663 (9%), 525 (18%), 493 (37%), 401 (10%), 353 (8%), 249 (65%), 217 (39%), 186 (64%), 137 (8%), 95 (25%), 83 (100%) [M$^+$–CH$_2$, –C$_3$H$_7$, –CpPMen$_2$, –CpPMen, –Fe], 55 (56%), 43 (26%).

^{1}H-NMR [C$_6$D$_6$]: $\delta = 0.85$ (dd, 12H, (C-13)H$_3$, (C-23)H$_3$, $^3J_{HH} = 6.4$ Hz, $^3J_{HH} = 7.0$ Hz, $^5J_{PH} = 16.2$ Hz); 1.07 (dd, 12H, (C-14)H$_3$, (C-24)H$_3$, $^3J_{HH} = 6.2$ Hz, $^3J_{HH} = 6.8$ Hz, $^5J_{PH} = 16.0$ Hz); 1.13 (d, 12H, (C-15)H$_3$, (C-25)H$_3$, $^3J_{HH} = 7.0$ Hz); 1.29–1.86 (m, 24H); 2.15 (m, 3H, CH); 2.41 (d, 3H, CH$_2$, $J_{PH} = 12.7$ Hz); 3.13–3.23 (m, 6H, CH); 4.32–4.39 (m, 8H, Cp system).

^{13}C{^{1}H}-NMR [C$_6$D$_6$]: $\delta = 15.9$ (s, 2C, CH$_3$, C-13); 16.3 (d, 2C, C-23); 21.9 (d, 2C, C-14); 22.3 (d, 2C, C-24); 23.0 (s, 4C, CH$_3$, C-15, C-25); 26.2 (m, 4C, CH$_2$, $J_{CP} = 9$ Hz); 27.2 (dd, 4C, CH, $J_{CP} = 26$ Hz); 34.1 (s, 2C, CH); 35.5 (s, 4C, CH$_2$); 38.5 (d, 4C, CH, $J_{CP} = 65$ Hz); 39.8 (s, 2C, CH$_2$); 41.1 (s, 2C, CH$_2$); 45.3 (d, 2C, CH, $J_{CP} = 15$ Hz); 47.5 (d, 2C, CH, $J_{CP} = 22$ Hz); 70.0 (s, 2C, CH, C-3, C-3′); 71.2 (s, 2C, CH, C-4, C-4′); 72.2 (m, 2C, CH, C-2′, C-5); 77.1 (d, 2C, CH, C-2, C-5′, $^2J_{CP} = 29$ Hz), 78.4 (d, 2C, C$_q$, C-1, C-1′, $^1J_{Cp} = 20$ Hz).

^{31}P{^{1}H}-NMR [C$_6$D$_6$]: $\delta = -25.2$ (s). Anal. Calc.(%): C, 74.8; H, 10.5; P, 7.7; Found: C, 74.7; H, 9.8; P, 7.3.

Crystal data for **1b**: $C_{50}H_{84}FeP_2$, $M_r = 802.96$ g mol^{-1}, orange prism, size $0.40 \times 0.40 \times 0.36$ mm^3, orthorhombic, space group $P2_12_12$, $a = 9.671(2)$, $b = 26.913(5)$, $c = 9.075(2)$ Å, $V = 2362.0(8)$ Å^3, $T = -90$°C, $Z = 2$, $\rho_{calc.} = 1.129$ g cm^{-3}, $\mu(\text{Mo–K}_\alpha) = 4.18$ cm^{-1}, $F(000) = 880$, 3052 reflections in $h(-12/0)$, $k(-34/0)$, $l(0/11)$, measured in the range $2.37 \le \Theta \le 27.42°$, 3052 independent reflections, 2592 reflections with $F_o > 4\sigma(F_o)$, 240 parameters, 0 restraints, $R_{1obs} = 0.033$, $wR^2_{obs} = 0.086$, $R_{1all} = 0.053$, $wR^2_{all} = 0.143$, Goodness-of-fit = 1.190, Flack-parameter 0.00(3), largest difference peak and hole: 0.374/−0.195 e Å^{-3}.

4.8. Standard procedure for catalytic runs

Under an atmosphere of argon a 160 ml stainless steel autoclave was charged with the phosphine (0.048 mmol) and the Pd compound (0.048 mmol). A total of 30 ml acetonitrile was added, the reactor was closed and cooled down to −30°C. 1,3-butadiene (70.3 mmol, 3.8 g) was transferred into the autoclave from a lecture bottle with a Teflon tube (for a short period of time Teflon is resistant to butadiene). After warming up to 25°C the autoclave was pressurised with 8 atm of CO$_2$ (100 mmol). The reaction was started by heating the mixture to 70°C for 15 h. After cooling down the reactor to 25°C the reaction mixture was filtered over 5 cm of alumina to remove the catalyst and analysed by GC.

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