1,1′-Bis(methylphenylphosphanyl)ferrocene: Synthesis and Complexes with the Tetracarbonylchromium Fragment

Gerhard E. Herberich* and Stefan Moss

Institut für Anorganische Chemie, Technische Hochschule Aachen,
D-52056 Aachen, Germany

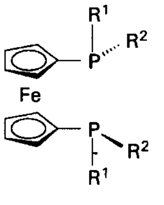
Received February 27, 1995

Key Words: Ferrocene, 1,1′-bis(methylphenylphosphanyl)- / Chromium, carbonyl-, phosphane derivatives

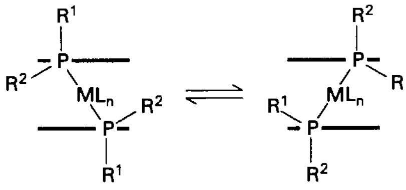
1,1′-Bis(methylphenylphosphanyl)ferrocene (mppf) (**2**) was synthesized from dilithioferrocene and PMePh(OC_6H_4-4-Me). The diastereomers *rac*-**2** and *meso*-**2** were separated by fractional crystallization from ethanol. The tetracarbonylchromium complexes (*rac*-**2**)Cr(CO)$_4$ (*rac*-**5**) and (*meso*-**2**)Cr(CO)$_4$ (*meso*-**5**) were obtained photochemically from hexacarbonylchromium and mppf in near quantitative yield. The structures of *rac*-**2**, *rac*-**5**, and *meso*-**5** were determined by X-ray crystallographic analysis.

Ferrocenylphosphanes, both chiral and achiral, play an important role as ligands in many areas of chemistry, especially in coordination chemistry, enantioselective organic synthesis, and homogeneous catalysis[1]. 1,1′-Bis(diphenylphosphanyl)ferrocene (dppf) is probably the most widely used ferrocenediylbisphosphane ligand, and its coordination chemistry has been studied in great detail[2].

In this paper we consider ligands of type **1**. When the two substituents R^1 and R^2 are equal as in dppf the ligand displays effective C_{2v} symmetry. Most commonly, dppf is coordinated to a single metal centre as a chelating ligand. In this situation it possesses a synclinal sandwich conformation. For instance, (dppf)Mo(CO)$_4$ exists as two enantiomers **A** and **B** ($R^1 = R^2 =$ Ph) which, according to NMR-spectroscopic observation, rapidly interconvert[3]. This internal motion is governed by a symmetrical double-minimum potential.



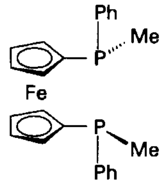
1



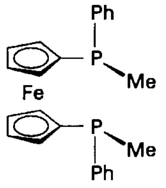
ML_n = Mo(CO)$_4$

For different substituents R^1 and R^2 stereoisomerism comes into play. The ligands **1** then exist in two chiral forms with effective C_2 symmetry and as *meso* form which possesses effective C_s symmetry in its synperiplanar conformation. In racemic complexes as e.g. *rac*-**1** · Mo(CO)$_4$ the two conformations **A** and **B** are no longer equal in energy and one will be preferred to the other. The case of the *meso* form is entirely analogous. It is obvious from this discussion that ligands **1** with different substituents at the phosphorus atom offer better stereocontrol when used as auxiliaries in catalysis.

Previous work on 1,1′-bis(phosphanyl)ferrocene ligands Fe($C_5H_4PR^1R^2$)$_2$ with two different substituents at the phosphorus atom comprises a preliminary communication on *tert*-butylphenyl derivatives (R^1 = *t*Bu, R^2 = Ph)[4] and a report on isopropylphenyl derivatives (R^1 = *i*Pr, R^2 = Ph)[5]. We decided to study the as yet unknown Fe(C_5H_4PMePh)$_2$ (mppf) (**2**) and give here a first account of the ensuing chemistry.



rac-**2**



meso-**2**

Results

Synthesis of mppf and Separation of the Diastereoisomers

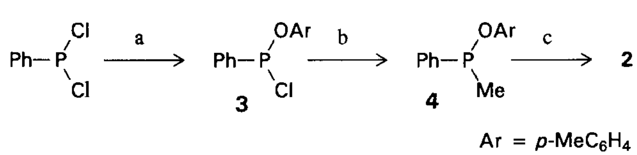
The synthesis of **2** is summarized in Scheme 1[6]. Dichlorophenylphosphane was treated with 4-methylphenol (1:1) in the presence of pyridine to give chloro(4-methylphenoxy)phenylphosphane (**3**). Treatment of **3** with methyllithium at low temperature afforded methyl(4-methylphenoxy)phenylphosphane (**4**) with good chemoselectivity. Finally, dilithioferrocene Fe[C_5H_4Li(tmeda)]$_2$[7] was treated with **4** to give the two diastereomers *rac*- and *meso*-**2** in a 3:1 ratio.

The two diastereomers can be separated by crystallization from ethanol. The racemic isomer *rac*-**2** readily forms clusters of orange needles. The composition of the mother liquor is typically *rac*:*meso* = 1:4. After concentration of the solution *meso*-**2** crystallizes slowly as thin orange plate-

Chem. Ber. **1995**, *128*, 689–693 © VCH Verlagsgesellschaft mbH, D-69451 Weinheim, 1995 0009–2940/95/0707–0689 $ 10.00+.25/0

lets. We note that equilibration at temperatures above 140 °C (e.g. in the melt at 200 °C for 15 min) produces mixtures with *rac*:*meso* = 45:55 and subsequent crystallization from ethanol gives a further crop of *rac*-**2**. In principle, all material can thus be transformed into the more valuable isomer.

Scheme 1

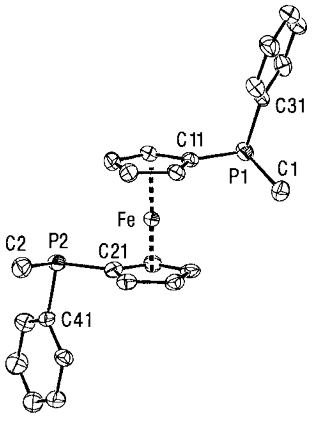


a: ArOH, py / hexane, 0 °C
b: MeLi / Et$_2$O, -78 °C
c: Fe{C$_5$H$_4$Li(tmeda)}$_2$ / hexane, r. t., inverse addition

Structure of *rac*-mppf

The structure of *rac*-**2** was determined by X-ray diffraction analysis (Figure 1). The ferrocene skeleton shows very small to insignificant deviations from idealized geometry (Table 1). The cyclopentadienyl rings are planar and coplanar; their rotational position corresponds to an anticlinally staggered conformation with a torsion angle (C11−X1−X2−C21, where X1 and X2 are the Cp ring centroids) of 139.7°. The phenyl groups are arranged perpendicularly to the *exo* faces of the ferrocene skeleton with dihedral angles of 71.1(2) (for the Ph group C31···C36) and 88.8(2)° (for the Ph group C41···C46). This orientation of the PMePh substituents seems to be energetically most favorable.

Figure 1. Molecular structure of *rac*-**2**; selected bond lengths [pm]: Fe−C(Cp)$_{av}$ 204.8 [203.2(4)−206.3(5)], C−C(Cp)$_{av}$ 141.0 [137.4(7)−145.2(7)], P1−C1 181.5(6), P1−C11 180.9(5), P1−C31 184.3(4), P2−C2 184.2(5), P2−C21 182.9(5), P2−C41 184.0(4)



Synthesis of (mppf)Cr(CO)$_4$ Complexes

The tetracarbonylchromium complexes (*rac*-**2**)Cr(CO)$_4$ (*rac*-**5**) and (*meso*-**2**)Cr(CO)$_4$ (*meso*-**5**) can readily be obtained from hexacarbonylchromium and mppf. Under photochemical conditions in toluene both mppf isomers afford the corresponding diastereomers *rac*- and *meso*-**5** as stable yellow crystals in near quantitative yield. The corresponding thermal synthesis[8] (140 °C, in xylene, 3 h, 63% yield) is complicated by partial epimerization and hence is of no further interest.

Table 1. Structural parameters of the ferrocene skeleton

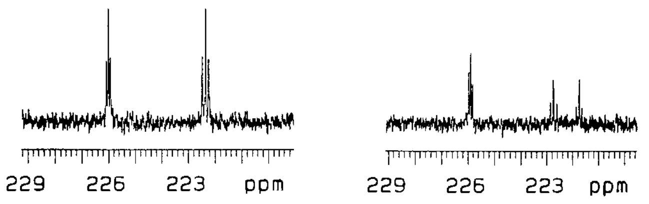
	rac-**2**	*rac*-**5**	*meso*-**5**
conformation	anticlinal eclipsed	synclinal staggered	synperiplanar eclipsed
τ [°] [a]	139.7	42.2	11.1
θ [°] [b]	1(4)	4(2)	2(2)
X$_A$FeX$_B$ [°]	178.6	179.2	177.6
PFeP [°]	140.5	59.4	65.0
P···P [pm]	648.4(3)	361.4(1)	340.9(1)
d_P [pm] [c]	-4.8(2), -1.9(2)	8.3(1), -8.8(1)	9.5(1), 7.6(1)
d_C [pm] [d]	0.56, 0.29	0.50, 0.45	0.23, 0.14

[a] Torsion angle $\tau = C_A{-}X_A{-}X_B{-}C_B$, where C_A is C-1 in Cp ring A (likewise for C_B); X_A, X_B are the centroids of the two Cp rings. − [b] Dihedral angle θ between the two Cp rings. The values show no significant deviation from zero. − [c] Deviation d_P of the linked P atom from the Cp least-squares plane. A positive sign means that the P atom is on the same side of the Cp ring as the Fe atom. − [d] Mean deviation d_C of the C atoms in a Cp ring from their least-squares plane.

(*rac*-**2**)Cr(CO)$_4$ (*meso*-**2**)Cr(CO)$_4$
rac-**5** *meso*-**5**

The purity of the new compounds can best be monitored by ^{31}P{^{1}H}-NMR spectroscopy, while the ^{13}C{^{1}H}-NMR spectra allow unambiguous identification of the diastereomers (Figure 2). *rac*-**5** displays effective C_2 symmetry in solution with two pairs of chemically equivalent CO groups. In contradistinction to this situation, *meso*-**5** shows effective mirror symmetry. While its equatorial CO groups (those *trans* to one of the two phosphorus atoms) are symmetry-related, the two axial CO groups (*cis* to both phosphorus atoms) are chemically inequivalent. Hence, three CO signals are observed in this case with an approximate 2:1:1 intensity ratio. It also follows that the CO groups *trans* to a phosphorus atom resonate at lower field.

Figure 2. ^{13}C{^{1}H}-NMR spectra of carbonyl region for *rac*-**5** (left) and *meso*-**5** (right)



Structures of (*rac*-mppf)Cr(CO)$_4$ and (*meso*-mppf)Cr(CO)$_4$

The molecular structure of (*rac*-**1**)Cr(CO)$_4$ (Figure 3 for *rac*-**5**) is of approximate C_2 symmetry with very small distortions of the ferrocene skeleton (Table 1). The sandwich conformation is synclinally staggered with a torsion angle of 42.2°. The conformation of the PMePh substituents places the phenyl groups in a roughly perpendicular orientation relative to the *exo* face of the cyclopentadienyl rings [with dihedral angles C11-5/C31-6 76.1(1)° and C21-5/C41-6 73.6(1)°].

In the case of (*meso*-**1**)Cr(CO)$_4$ (Figure 4 for *meso*-**5**, Table 1) the sandwich conformation is nearly synperiplanar with a torsion angle of 11.1°. This forces the Cr(CO)$_4$ fragment to bend sideways and to twist somewhat to avoid close non-bonding intramolecular contacts. The phenyl groups are again in a perpendicular orientation relative to the *exo* face of the cyclopentadienyl rings [with dihedral angles C11-5/C31-6 85.7(2)° and C21-5/C41-6 87.6(2)°].

Figure 3. Molecular structure of *rac*-**5**; selected bond lengths [pm]: Cr–P1 237.14(8), Cr–P2 238.38(9), Cr–C3 184.9(4), Cr–C4 184.7(3), Cr–C5 185.8(4), Cr–C6 187.4(3), C3–O3 114.4(6), C4–O4 114.3(4), C5–O5 114.9(6), C6–O6 114.8(5), Fe–C(Cp)$_{av}$ 203.7 [201.4(3)–206.2(4)], C–C(Cp)$_{av}$ 141.9 [139.3(5)–144.0(4)]

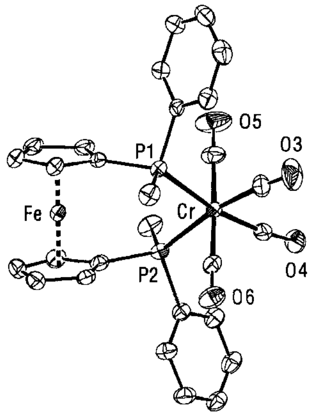
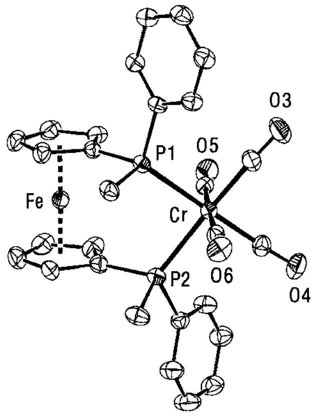


Figure 4. Molecular structure of *meso*-**5**; selected bond lengths [pm]: Cr–P1 240.44(9), Cr–P2 238.34(9), Cr–C3 184.7(4), Cr–C4 183.9(3), Cr–C5 185.5(4), Cr–C6 187.8(4), C3–O3 115.9(4), C4–O4 116.4(4), C5–O5 116.7(4), C6–O6 115.4(4), Fe–C(Cp)$_{av}$ 204.1 [202.9(3)–205.9(3)], C–C(Cp)$_{av}$ 142.6 [140.3(6)–144.7(5)]



Conclusion

Our synthesis of the diastereomeric mppf ligands **2** first modified PhPCl$_2$. The use of 4-methylphenoxy derivatives ensured sufficient chemoselectivity in the methylation step; monitoring of the preparations by means of NMR spectroscopy was greatly facilitated by the *para*-methyl substituents. We also note that our preparation of the mppf isomers can easily be upscaled and is not fully optimized.

The structural results suggest that the use of different substituents at the phosphorus atom does indeed induce a strong preference for one of the two alternative dispositions of the substituents R^1 and R^2. The smaller one of the two substituents (Me) extends into the equatorial region. In the related work on *rac*- and *meso*-Fe(C$_5$H$_4$PPh*i*Pr)$_2$ the phenyl groups are smaller than the isopropyl substituents and are roughly placed into the equatorial plane[5], in nice agreement with our interpretation. This effect should be of considerable interest for the design of chiral auxiliary ligands on the basis of *rac*-**2**.

We thank Dr. *U. Englert* for advice with the structural work and *T. Gossen* for the NMR measurements. This work was generously supported by *VEBA OEL AG* and the *Fonds der Chemischen Industrie.*

Experimental

Reactions were carried out under nitrogen by means of conventional Schlenk techniques. Pentane and hexane were distilled from Na/K alloy and THF from sodium benzophenone ketyl. Sand and alumina were heated in a high vacuum at 300 °C prior to use; alumina was deactivated (7% H$_2$O, deoxygenated) after cooling. – Melting points: sealed capillaries, uncorrected. – NMR: WP-80 PFT (^{1}H, 80.1 MHz), Bruker; WH-270 PFT (^{31}P, 109.3 MHz), Bruker; Varian Unity 500 (^{1}H, 500 MHz; ^{13}C, 125.7 MHz; ^{31}P, 202.3 MHz); Varian VXR 300 (^{1}H, 300 MHz; ^{13}C, 75.4 MHz); vt = virtual triplet; ^{1}H and ^{13}C spectra are referenced to internal TMS, ^{31}P spectra to external H$_3$PO$_4$ (85%). – MS: Varian MAT CH-5-DF. – IR: Perkin-Elmer 1720 X FTIR.

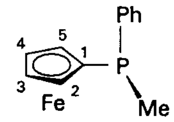
1. *Chloro(4-methylphenoxy)phenylphosphane* (**3**): A solution of *p*-cresol (20.4 g, 188 mmol) and pyridine (15.2 ml) in hexane (125 ml) was added dropwise (within 2 h) with stirring to dichlorophenylphosphane (25.5 ml, 188 mmol) in hexane (125 ml) at 0 °C. Stirring was continued at 0 °C for 2 h. After warming of the mixture to ambient temp., the pyridinium chloride formed was removed by filtration. Distillative workup gave three fractions: 5.2 g of PhPCl$_2$ (b.p. 32–40 °C/5 · 10^{-6} bar), 30.6 g of **3** (b.p. 108–129 °C/5 · 10^{-6} bar), and 7.8 g of PhP(OC$_6$H$_4$Me-*p*)$_2$ (b.p. 170–190 °C/5 · 10^{-6} bar); yield of spectroscopically (NMR) pure **3** 77% (based on PhPCl$_2$ consumed), colorless liquid. – ^{1}H NMR (80 MHz, C$_6$D$_6$): δ = 2.01 (s, Me), 6.77–7.89 (m, 9H, aromatic H). – ^{13}C{^{1}H} NMR[9] (75 MHz, C$_6$D$_6$): δ = 20.55 (s, Me); Ph: 128.65 (d, $^3J_{PC}$ = 9.2 Hz, C$_m$), 130.16 (d, $^2J_{PC}$ = 28.2 Hz, C$_o$), 130.49 (s, C$_p$), 141.0 (d, $^1J_{PC}$ = 30 Hz, C$_i$); *p*-C$_6$H$_4$: 119.75 (d, $^3J_{PC}$ = 8.5 Hz, C$_o$), 131.89 (s, C$_m$), 134.04 (s, C$_p$), 152.89 (d, $^2J_{PC}$ = 6.1 Hz, C$_i$). – ^{31}P{^{1}H} NMR (109 MHz, C$_6$D$_6$): δ = 175.2.

2. *Methyl(4-methylphenoxy)phenylphosphane* (**4**): A solution of methyllithium in Et$_2$O (0.5 M, 407 ml, 203 mmol) was added dropwise with stirring (within 4 h) at –78 °C to **3** (51.0 g, 203 mmol) in Et$_2$O (200 ml). Stirring was continued for 12 h. After warming up to ambient temp., the solvent was partially (400 ml) distilled off, and pentane (400 ml) was added to the residue. The precipitate of LiCl was filtered off through a 3-cm layer of sand. Distillative workup (20-cm Vigreux column, 105–6 °C/2 · 10^{-6} bar) gave 38.0 g of spectroscopically (NMR) pure **4** (81%); colourless liquid. – ^{1}H NMR (80 MHz, C$_6$D$_6$): δ = 1.45 (d, $^2J_{CH}$ = 7.3 Hz, PMe), 2.03 (s, *p*-Me), 6.77–7.89 (m, 9H, aromatic H). – ^{13}C{^{1}H} NMR[9] (126 MHz, C$_6$D$_6$): δ = 20.82 (d, $^1J_{PC}$ = 18.6 Hz, PMe); Ph: 128.72 (d, $^3J_{PC}$ = 7.3 Hz, 2 C$_m$), 129.41 (d, $^2J_{PC}$ = 21.9 Hz, 2 C$_o$), 129.67 (s, C$_p$), 143.92 (d, $^1J_{PC}$ = 23.6 Hz, C$_i$); *p*-Tolyl: 20.51 (s, *p*-Me), 118.88 (d, $^3J_{PC}$ = 11.1 Hz, C$_o$), 130.23 (s, C$_m$), 131.57 (s, C$_p$), 155.74 (d, $^2J_{PC}$ = 8.3 Hz, C$_i$). – ^{31}P{^{1}H} NMR (202 MHz, C$_6$D$_6$): δ = 114.8.

3. *1,1'-Bis(methylphenylphosphanyl)ferrocene* (mppf) (**2**): Butyllithium in hexane (2.5 M, 66 ml, 166 mmol) was added to ferrocene (15.1 g, 81 mmol) in hexane (400 ml). *N,N,N',N'*-Tetramethylethylenediamine (tmeda) (25.4 ml, 168 mmol) was then added dropwise. After stirring at ambient temp. for 6 h, a solution of **4** (38.0 g, 165 mmol) in hexane (50 ml) was added with stirring within 30 min, and stirring was continued for 24 h. The reaction mixture was then hydrolyzed by addition of water (30 ml). The resulting yellow solid was collected by filtration and suspended in sodium hydroxide solution (1 M, 150 ml). The raw product was extracted with toluene/ether (1:1) and chromatographed on a short column of alumina. Ferrocene and CpFe(C_5H_4PMePh) were eluted with hexane as separate orange bands, and mppf was eluted with toluene/hexane (1:1). Removal of the eluents left 19.6 g (56%) of mppf as orange powder with *rac*-**2**:*meso*-**2** = 75:25 ($^{31}P\{^1H\}$ NMR).

a) *rac*-**2**: Two crystallizations from ethanol gave 8.6 g (25%) of *rac*-**2** as orange needles, *de* = 98% ($^{31}P\{^1H\}$ NMR); m.p. 120.5–121.5°C. – ^1H NMR (500 MHz, C_6D_6): δ = 1.47 (d, J = 3.7 Hz, 2 PMe); Cp: 4.12 (dtd, J = 2.4, 1.2, 1.2 Hz[14], 2 2-H), 4.14 (tdd, J = 2.4, 1.2, 0.8 Hz[14], 2 4-H), 4.17 (td, J = 2.4, 1.2 Hz, 2 3-H), 4.23 (dtd, J = 2.4, 1.2, 1.2 Hz[14], 2 5-H); 7.03 (2 H_p), 7.09 (4 H_m), 7.43 (4 H_o). – $^{13}C\{^1H\}$ NMR[9,15] (126 MHz, C_6D_6): δ = 12.81 ("d", N = 11.5 Hz, PMe); Cp: 69.80 (vt, N = 2.2 Hz, C-2), 71.55 (vt, N = 2.5 Hz, C-3), 72.21 (vt, N = 7.4 Hz, C-4), 75.25 (m, N = 28.5 Hz, C-5), 79.34 (m, N = 10.8 Hz, C-1); Ph: 128.18 (s, C_p), 128.42 (vt, N = 6.3 Hz, C_m), 131.66 (m, N = 18.9 Hz, C_o), 142.93 (m, N = 15.3 Hz, C_i). – $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6): δ = –39.71. – $C_{24}H_{24}FeP_2$ (430.3): calcd. C 67.00, H 5.62; found C 66.96, H 5.64; mol. mass 430 (MS).

b) *NMR Assignments for rac*-**2**: The $^1H\{^{31}P\}$-NMR spectrum for the Cp ring is of type ABCD. The protons α to the phosphorus atom appear as dt signals while those in the β-position appear as td signals, both with ^3J = 2.4 and ^4J = 1.2 Hz as expected for ferrocenes[17]. NOE spectra furnished the required additional information. Irradiation into the PMe signal effected a strong intensity enhancement for one (at δ = 4.12) of the two H_α signals. Using the numbering scheme defined in Formula C, we assigned the signal at δ = 4.12 to 2-H. Irradition into the second H_α signal (at δ = 4.23) produced an intensity enhancement for one (at 4.17, but not at 4.14) of the two H_β signals. This completes the assignment of all Cp ring protons and an H,C-COSY spectrum allowed us to assign all Cp ring C atoms.

C 

c) *meso*-**2**: The first crystallization of *rac*-**2** left a mother liquor with *rac*:*meso* = 1:4. Slow crystallization of 0.73 g of this material from ethanol (60 ml) afforded 0.39 g of *meso*-**2** as orange platelets, *de* = 96% ($^{31}P\{^1H\}$ NMR), m.p. 103–4°C. – ^1H NMR (500 MHz, C_6D_6): δ = 1.48 (d, J = 4.0 Hz, 2 PMe); Cp: 4.10 (m, 2H), 4.16 (m, 4H), 4.26 (m, 2H); Ph: 7.02 (2 H_p), 7.07 (4 H_m), 7.42 (4 H_o). – $^{13}C\{^1H\}$ NMR[9,15] (126 MHz, C_6D_6): δ = 12.72 (m, N = 10.4 Hz, PMe); Cp: 69.73 ("d", N = 1.1 Hz, C-2), 71.45 (vt, N = 2.0 Hz, C-3), 72.23 (m, N = 7.7 Hz, C-4), 75.68 (m, N = 27.4 Hz, C-5), 79.07 ("d", N = 18.9 Hz, C-1); Ph: 128.16 (s, C_p), 128.44 ("d", N = 6.3 Hz, C_m), 131.60 ("d", N = 18.5 Hz, C_o), 143.19 ("d", N = 15.1 Hz, C_i). – $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6): δ = –39.59. – $C_{24}H_{24}FeP_2$ (430.3): calcd. C 67.00, H 5.62; found C 67.27, H 5.87; mol. mass 430 (MS).

4. *[(rac-1,1'-Bis(methylphenylphospanyl)ferrocene]tetracarbonylchromium* (*rac*-**5**): A solution of $Cr(CO)_6$ (443.5 mg, 2.02 mmol) and *rac*-**2** (880.5 mg, 2.05 mmol) in toluene (180 ml) was irradiated (medium-pressure mercury lamp) until the ν(CO) band of $Cr(CO)_6$ (1982 cm^{-1}) could no longer be detected. After filtration the solvent was removed to give 1.09 g (91%) of *rac*-**5** as yellow crystals, m.p. 227–9°C. – ^1H NMR (500 MHz, C_6D_6): δ = 1.80 (vt, N = 6.1 Hz, 2 PMe); Cp: 3.79 (m, 2H), 3.87 (s br, 2H), 4.07 (s br, 2H), 4.54 (m, 2H); Ph: 6.97 (2H), 7.09 (4H), 7.58 (4H). – $^{13}C\{^1H\}$ NMR[9,15] (126 MHz, $CDCl_3$): δ = 17.50 (m, N = 25.5 Hz, PMe); Cp: 70.56 (s), 70.68 (s), 73.85 (vt, N = 7.1 Hz), 75.70 (vt, N = 18.9 Hz), 80.45 (m, N = 7.1 Hz, C-1); Ph: 128.03 (vt, N = 8.3 Hz, C_m), 128.68 (s, C_p), 129.51 (vt, N = 9.3 Hz, C_o), 140.75 (m, N = 37.6 Hz, C_i); 222.38 (vt, N = 31.3 Hz, CO_{ax}), 226.03 (vt, N = 18.6 Hz, CO_{eq}). – $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$): δ = 27.37. – MS (70 eV), *m/z* (%): 594 (23) [M^+], 482 (100) [M^+ – 4 CO]. – IR (toluene): ν(CO) = 2005 s, 1912 s, 1890 cm^{-1} vs. – $C_{28}H_{24}CrFeO_4P_2$ (594.3): calcd. C 56.59, H 4.07; found C 56.28, H 4.19.

5. *[(meso-1,1'-Bis(methylphenylphosphanyl)ferrocene]tetracarbonylchromium* (*meso*-**5**): In the same manner $Cr(CO)_6$ (101 mg, 0.46 mmol) and *meso*-**2** (197 mg, 0.46 mmol) in toluene (80 ml) gave 250 mg (92%) of *meso*-**5** as yellow crystals, m.p. 218–20°C. – ^1H NMR (500 MHz, C_6D_6): δ = 1.77 (vt, N = 5.8 Hz, PMe); Cp: 3.84 (m, 2H), 3.90 (s br, 2H), 3.97 (s br, 2H), 4.52 (s br, 2H); Ph: 7.00 (2H), 7.10 (4H), 7.66 (4H). – $^{13}C\{^1H\}$ NMR[9] (126 MHz, $CDCl_3$): δ = 19.10 (m, N = 25.5 Hz, PMe); Cp: 70.58 (vt, N = 4.3 Hz), 71.22 (vt, N = 5.5 Hz), 72.05 (vt, N = 5.8 Hz), 74.36 (vt, N = 11.4 Hz), 83.92 (m, N = 36.7 Hz, C-1): Ph: 128.23 (vt, N = 8.7 Hz, C_m), 129.07 (s, C_p), 130.04 (vt, N = 10.4 Hz, C_o), 139.37 (m, N = 37.1 Hz, C_i); 221.78 (t, J = 14.9 Hz, CO_{ax}), 222.77 (t, J = 15.2 Hz, CO_{ax}), 225.92 (t, J = 18.1 Hz, CO_{eq}). – $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$): δ = 28.28. – MS (70 eV), *m/z* (%): 594 (10) [M^+], 482 (100) [M^+ – 4 CO]. – IR (toluene): ν(CO) = 2004 s, 1914 s, 1886 cm^{-1} vs. – $C_{28}H_{24}CrFeO_4P_2$ (594.3): calcd. C 56.59, H 4.07; found C 56.62, H 4.32.

6. *Structure Determination of rac*-**2**, *rac*-**5**, *and meso*-**5**: Suitable crystals of *rac*-**2** were obtained from a warm ethanol solution while *rac*- and *meso*-**5** were crystallized from hexane/CH_2Cl (8:1). The crystal data and refinement parameters are listed in Table 2. Ge-

Table 2. Crystal data and structure refinement parameters

compound	*rac*-**2**	*rac*-**5**	*meso*-**5**
formula	$C_{24}H_{24}FeP_2$	$C_{28}H_{24}CrFeO_4P_2$	$C_{28}H_{24}CrFeO_4P_2$
formula weight	430.25	594.29	594.29
crystal system	orthorhombic	monoclinic	triclinic
space group	*Pnn*2 (No. 34)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
a [pm]	2921.6(3)	855.3(2)	1240.3(9)
b [pm]	1212.1(2)	1806.5(3)	1304(2)
c [pm]	583.9(1)	1774.6(2)	846(1)
α [°]	90	90	107.7(2)
β [°]	90	103.7(1)	98.8(2)
γ [°]	90	90	84.6(1)
V [nm^3]	2.068(1)	2.664(3)	1.286(6)
d_{calcd} [g cm^{-3}]	1.38	1.48	1.53
Z	4	4	2
F(000)	896	1216	608
μ [cm^{-1}]	73.93	10.92	95.63
radiation, λ [pm]	Cu-K_α (154.06)	Mo-K_α (71.07)	Cu-K_α (154.06)
scanmode	ω	ω-2θ	ω-2θ
scanrange [°]	$5 < \theta < 70$	$0 < \theta < 30$	$5 < \theta < 62$
total no. of data	3148	8454	4194
unique observed data	2377, $I > 3\sigma(I)$	3899, $I > 2\sigma(I)$	3301, $I > 2\sigma(I)$
no. of variables	244	325	326
absorption correction	emp, psi-scans	emp, psi-scans	emp, DIFABS [18]
min, max transmission	0.5943, 0.9941	0.8394, 0.9950	
sec extinction coefficient	$2.23 \cdot 10^{-7}$	not refined	$1.67 \cdot 10^{-6}$
residuals R	0.055	0.039	0.047
R_w [$w^{-1} = \sigma^2(F_O)$]	0.064	0.044	0.057
GOF	3.031	1.406	1.893
max res density [10^{-6} e pm^{-3}]	0.9	0.5	0.29

ometry and intensity data were collected on Enraf-Nonius CAD4 diffractometers equipped with graphite monochromators. The structures were solved by Patterson and difference Fourier methods[19]. In the final full-matrix refinement, non-hydrogen atoms were refined with anisotropic thermal parameters, and hydrogen atoms were included as riding in standard positions (C–H = 0.98 Å). A statistical weighting scheme $w^{-1} = \sigma^2(F_o)$ was used for all reflections[20]. The polarity of the *c* axis in our crystal of *rac*-**2** could be determined: inversion results in $R = 0.113$, $R_w = 0.143$.

---

[1] A. Togni, T. Hayashi (Eds.), *Ferrocenes*, VCH Verlagsgesellschaft, Weinheim, **1995**.

[2] K.-S. Gan, T. S. A. Hor, *1,1′-Bis(diphenylphosphino)ferrocene – Coordination Chemistry, Organic Syntheses, and Catalysis* in ref.[1].

[3] I. R. Butler, W. R. Cullen, T.-J. Kim, S. J. Rettig, J. Trotter, *Organometallics* **1985**, *4*, 972–980.

[4] I. R. Butler, W. R. Cullen, T.-J. Kim, F. W. B. Einstein, T. Jones, *J. Chem. Soc., Chem. Commun.* **1984**, 719–721; W. R. Cullen, T.-J. Kim, *Organometallics* **1985**, *4*, 346–351.

[5] L.-K. Liu, J.-C. Chen, *Bull. Inst. Chem. Acad. Sinica* **1991**, *38*, 43–53.

[6] For a different synthetic methodology see the preparation of $CpFe(C_5H_4PMePh)$: V. S. Tolkunova, A. S. Peregudov, Yu. Yu. Gorelikova, A. I. Krylova, E. N. Tsvetkov, V. D. Vil'chevskaya, D. N. Kravtsov, *Metalloorg. Khim.* **1991**, *4*, 446–452; *Organomet. Chem. USSR* **1991**, *4*, 216–219; V. S. Tolkunova, E. N. Tsvetkov, A. S. Peregudov, A. I. Krylova, Yu. Yu. Gorelikova, V. D. Vil'chevskaya, D. N. Kravtsov, *Metalloorg. Khim.* **1989**, *2*, 661–667 [*Chem. Abstr.* **1990**, *112*, 158519s].

[7] M. D. Rausch, G. A. Moser, C. F. Meade, *J. Organomet. Chem.* **1973**, *51*, 1–11; J. J. Bishop, A. Davison, M. L. Katcher, D. W. Lichtenberg, R. E. Merrill, J. C. Smart, *ibid.* **1971**, *27*, 241–249; M. D. Rausch, D. C. Ciappenelli, *ibid.* **1967**, *10*, 127–136; cf. also: I. R. Butler, W. R. Cullen, J. Ni, S. J. Rettig, *Organometallics* **1985**, *4*, 2196–2201.

[8] Cf. the synthesis of $(dppf)Cr(CO)_4$: A. W. Rudie, D. W. Lichtenberg, M. L. Katcher, A. Davison, *Inorg. Chem.* **1978**, *17*, 2859–2863.

[9] Assignments of Ph carbon atoms are based on analogy (cf. PPh_3[10], *p*-cresol[11], $P(OPh)_3$[12]), APT (attached proton test, for C_i)[13], relative integrated intensities (C_o, C_m vs. C_p), and on J_{PC} values (C_o vs. C_m).

[10] T. Bundgaard, H. J. Jakobsen, *Acta Chem. Scand.* **1972**, *26*, 2548–2549.

[11] P. C. Lauterbur, *J. Am. Chem. Soc.* **1961**, *83*, 1846–1852; E. Breitmeier, W. Voelter, *^{13}C NMR Spectroscopy*, Verlag Chemie, Weinheim, **1974**.

[12] H.-O. Kalinowski, S. Berger, S. Braun, *^{13}C-NMR-Spektroskopie*, Georg Thieme-Verlag, Stuttgart, **1984**.

[13] H. Günther, *NMR-Spektroskopie*, 3rd ed., Georg Thieme-Verlag, Stuttgart, **1992**.

[14] Coupling constants are noted in the order $^3J_{HH}$, $^4J_{HH}$, $^nJ_{PH}$ with $n = 3, 4$.

[15] The ^{13}C signals are the X part of an ABX-type spectrum (very close to an AA′X spectrum)[16]. The individual pattern varies from a virtual triplet "vt" over a multiplet "m" to a socalled "filled-in" doublet "d" depending on the values of the different coupling constants J_{AX}, J_{BX}, and J_{AB}. The pseudo-coupling constant $N = |J_{AX} + J_{BX}|$ which denotes the distance between the two prominent outer lines of the multiplet is given.

[16] P. S. Pregosin, R. W. Kunz, *^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes* in *NMR, Basic Principles and Progress* (Eds.: P. Diehl, E. Fluck, R. Kosfeld), vol. 16, Springer-Verlag, Berlin, **1979**.

[17] R. W. Crecely, K. M. Crecely, J. H. Goldstein, *Inorg. Chem.* **1969**, *8*, 252–254.

[18] N. Walker, D. Stuart, *Acta Crystallogr., Sect. A*, **1983**, *39*, 158–166.

[19] B. A. Frenz, *The Enraf-Nonius CAD4-SDP – a Real-Time System for Concurrent X-Ray Data Collection and Crystal Structure Determination* in *Computing in Crystallography* (Eds.: H. Schenk, R. Olthof-Hazekamp, H. von Koningsveld, G. C. Bassi), Delft University Press, Delft, **1978**; *SDP-PLUS*, Version 1.1, (**1984**) and *VAXSDP*, Version 2.2 (**1985**).

[20] Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-401568 (*rac*-**2**), -401567 (*rac*-**5**), -401566 (*meso*-**5**), the names of the authors, and the journal citation.

[95028]