STEREOSELECTIVE METHYLATION OF 1-(DIPHENYLPHOSPHANYL)-2-[(METHOXYCARBONYL)METHYL]FERROCENE. THE CRYSTAL STRUCTURES OF THE METHYLATED ESTER AND ITS PALLADIUM(II) COMPLEX WITH AN AUXILIARY 2-[(DIMETHYLAMINO)METHYL]PHENYL LIGAND.

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Received March 20, 2007
Accepted July 2, 2007

Dedicated to Professor Štefan Toma on the occasion of his 70th birthday.

Treatment of racemic 1-(diphenylphosphanyl)-2-[(methoxycarbonyl)methyl]ferrocene successively with $NaN(SiMe_3)_2$ and methyl iodide affords the C-alkylated product, 1-(diphenylphosphanyl)-2-[1-(methoxycarbonyl)ethyl]ferrocene (**6**), as a mixture of diastereoisomers in ca. 10:1 ratio, from which the major ($S,R_p/R,S_p$)-diastereoisomer is easily isolated by crystallisation. ($S,R_p/R,S_p$)-**6** reacts with $[Pd(L^{NC})(MeCN)_2]ClO_4$ (L^{NC} = 2-[(dimethylamino-κ*N*)-methyl]phenyl-κC^1) to give the cationic bis-chelate complex ($S,R_p/R,S_p$)-$[Pd(L^{NC})$(**6**-κ$^2O,P$)]-ClO_4 (**9**). The structures of ($S,R_p/R,S_p$)-**6** and **9** have been determined by single-crystal X-ray diffraction. Hydrolysis of ester **6** to the corresponding carboxylic acid proved to be difficult, being complicated by racemisation at the chiral carbon atom and oxidation of the phosphanyl group.

Keywords: Ferrocenes; Phosphanes; Esters; Alkylation; Chiral ligands; Palladium; Crystal structure determination.

Chiral ferrocene donors derived from C-chiral [1-(dimethylamino)ethyl]-ferrocene (Ugi's amine) have found widespread use as catalyst components to various transition metal-mediated organic reactions. Compounds of type **I** (Chart 1; R is usually the methyl group and X, Y and Z are various donor moieties) typically result from diastereoselective metallation/functionalisation reactions and subsequent modifications of the introduced substitutents[1]. Obviously, this synthetic approach relies on the availability of the starting chiral compounds as well as on the compatibility of the introduced groups and their transformations. Whereas the former aspect does not impose any

Collect. Czech. Chem. Commun. 2007, Vol. 72, No. 8, pp. 985–995

doi:10.1135/cccc20070985

practical limitations, the latter reduces the scope of the accessible derivatives, particularly in the case of ferrocenylphosphanes modified with phosphane-incompatible (typically polar) donor groups. Hence, the development of alternative preparative methods is desirable to circumvent the mentioned synthetic restrictions.

It has been reported that ferrocenylmethyl derivatives $FcCH_2G$ (Fc = ferrocenyl) bearing electron-withdrawing groups G can be selectively deprotonated and alkylated at the methylene group[2]. In a search for synthetic methods leading to new ferrocene phosphanylcarboxylic acids[3] related to acid **1** [4] (see Chart 1), we have recently made use of this approach in the synthesis of nitrile **5** from *rac*-[2-(diphenylphosphanyl)ferrocenyl]acetonitrile (**2**)[4a], showing that the alkylation reaction proceeds in diastereoselective manner to produce preferably the (S,R_p/R,S_p) diastereoisomer[5]. In order to extend the scope of this reaction, we decided to study deprotonation/alkylation of the related ester **3** [4a]. Herein we report on diastereoselective methylation of **3** to give ester **6** and attempts at hydrolysis of the latter compound. We also present the synthesis and structural characterisation of a palladium(II) complex involving ester **6** as an O,P-chelating donor.

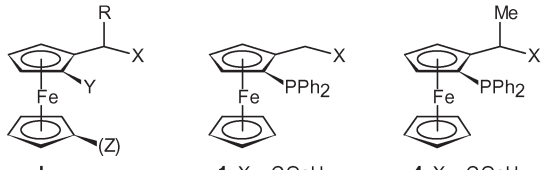
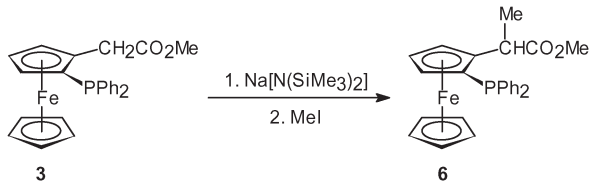


CHART 1

RESULTS AND DISCUSSION

The synthesis of ester **6** is outlined in Scheme 1. The compound was prepared by selective deprotonation of racemic ester **3** with $NaN(SiMe_3)_2$ (in THF at –78 °C) followed by quenching of the formed anion with methyl iodide. Subsequent purification by column chromatography afforded pure alkylated ester **6** as an orange, air-stable solid in 65% yield. NMR analysis revealed that the compound results as a mixture of two diastereoisomers in the ratio ca. 10:1. The isomers could not be separated chromatographically. However, simple recrystallisation from hot heptane gave the pure major diasteroisomer, which was assigned (S,R_p/R,S_p) configuration on the basis of structure determination (see below). Apparently, the nucleophile attacks

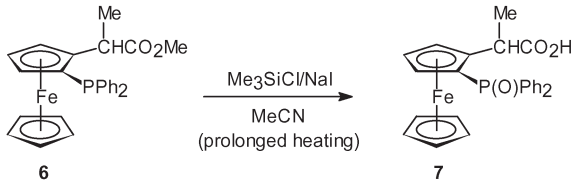
the intermediate anion preferably from the less sterically encumbered side, more distant from the bulky phosphanyl substitutent. Similar preference has been observed in the alkylation of **2**[5].



3 **6**

SCHEME 1

Ester **6** can be regarded as a precursor to hitherto unknown acid **4**, which is an isomer of 2-[1-(diphenylphosphanyl)ethyl]ferrocenecarboxylic acid[6]. Indeed, simple treatment of **6** with potassium hydroxide in a methanol–THF–water mixture gave acid **4**, but as a mixture of all possible stereoisomers (i.e., (S,R_p/R,S_p) and (R,R_p/S,S_p) pairs in a near-to-statistical ratio 5:4) due to concomitant racemisation at the tertiary carbon atom. In search for a milder method that would not cause the racemisation, K_2CO_3[7] and KO(*t*-Bu)[8] have been used without success. Finally, a procedure utilising a Me_3SiCl–NaI mixture in refluxing acetonitrile[9] afforded diastereomerically pure product, though in the form of phosphane oxide **7** (Scheme 2), presumably because of extended reaction times (2 days at reflux).

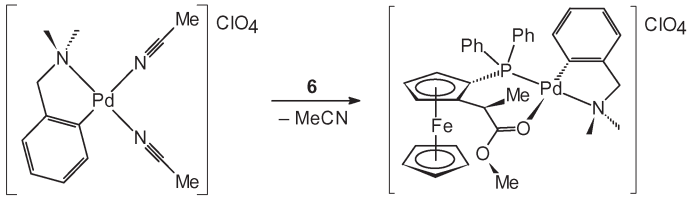


6 **7**

SCHEME 2

The coordination ability of **6** was examined in the reaction with bis(acetonitrile){2-[(dimethylamino-κ*N*)methyl]phenyl-κ*C*[1]}palladium(II) perchlorate (**8**). The replacement of acetonitrile ligands in **8** with ester **6** proceeded smoothly to afford cationic O,P-chelate complex **9** (Scheme 3). Spectral data of **9** are in accordance with the suggested structure, clearly indicating the coordination of both phosphane and the ester carbonyl groups. The phosphorus resonance in ^{31}P NMR spectrum appears markedly shifted to lower fields (Δ_P = 55.2; $\Delta_P = \delta_P(\mathbf{9}) - \delta_P(\mathbf{6})$) which is in accordance with coordination through the phosphorus atom. On the other hand, the slight low-field shift of the C=O signal in ^{13}C NMR spectra (Δ_C = 5.9) as

well as the shift of the $\nu_{C=O}$ band in the IR spectra to lower energies ($\Delta\nu$ = –71 cm^{-1}) imply coordination via the ester moiety. The presence of the perchlorate counter-ion is manifested by strong IR bands at 1089 (ν_3) and 623 (ν_4) cm^{-1}.



8 **9**

SCHEME 3

*Crystal Structures of (S,R_p/R,S_p)-**6** and **9***

The major diastereoisomer of **6** crystallises with the symmetry of the centrosymmetric space group *C*2/*c*. Views of the molecular structure are shown in Fig. 1 together with selected geometric data. The geometric parameters are rather unexceptional; however, the structure clearly corroborates the anticipated stereochemical preference of the alkylation reaction. The methyl substituent in **6** is located above the ferrocene moiety while the methoxycarbonyl group is directed to the opposite side and, simultaneously, bent away from the ferrocene unit (see the alternative view in Fig. 1). The dihedral angle subtended by the Cp(1) and carboxyl {C(13)O(1)O(2)} planes is 57.3(4)° (see Fig. 1 for the definition of the ring planes). The ferrocene cyclopentadienyl rings are tilted at an angle of 2.7(2)° and, as indicated by the torsion angle C(11)–C(1)–C(2)–P of 7.9(5)°, void of any significant torsion.

The structure of the cation of complex **9** is shown in Fig. 2 and the selected geometric parameters are listed in Table I. The observed bond lengths and angles do not differ much from those in a complex featuring the non-alkylated ester **3**, [Pd(L^{NC})(**3**-κ^2*O*,*P*)][4a]. Particularly, the ligand bite angle P–Pd–O(1) (98.03(7)°) is similar to that in the reference compound (97.78(3)°).

Palladium and its four ligating atoms in **9** are coplanar within 0.025 Å but the coordination sphere shows noticeable angular deformation. The the P–Pd–O(1) and P–Pd–C(27) angles are opened due to, respectively, the steric demands of the chelating ester and interactions between the palladium-bonded benzene ring and the bulky diphenylphosphanyl group. This opening is fully compensated by the closure of the remaining interligand angles

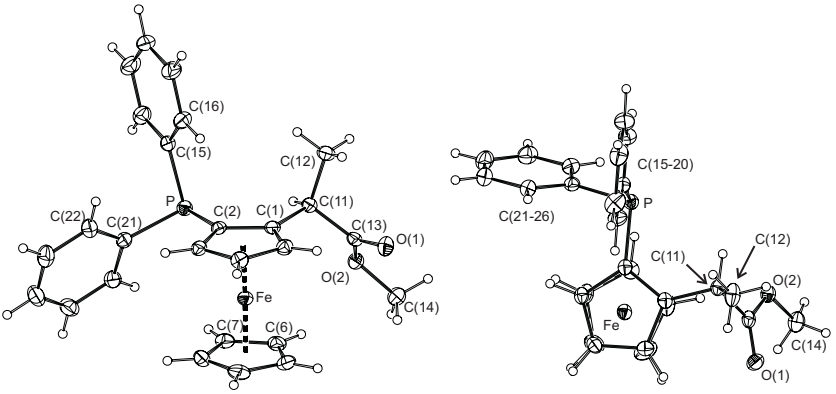


FIG. 1

Two alternative PLATON plots of the major diastereoisomer of **6**; the molecule of the (S,R_p) isomer from the (S,R_p)/(R,S_p) pair present in the centrosymmetric unit cell is shown. Displacement ellipsoids enclose the 30% probability level. Selected distances (in Å) and angles (in °): Fe–Cg(1) 1.640(2), Fe–Cg(2) 1.658(2), C(1)–C(11) 1.511(5), C(11)–C(12) 1.540(5), C(11)–C(13) 1.513(5), C(13)–O(1) 1.206(4), C(13)–O(2) 1.343(4), O(2)–C(14) 1.454(4), P–C(2) 1.819(3), P–C(15) 1.840(3), P–C(21) 1.841(4); ∠Cp(1),Cp(2) 2.7(2), C(1)–C(11)–C(12) 109.2(3), C(1)–C(11)–C(13) 110.0(3), O(1)–C(13)–O(2) 123.4(3), C(13)–O(2)–C(14) 115.4(3), C(2)–P–C(15) 101.4(2), C(2)–P–C(21) 101.7(2), C(15)–P–C(21) 101.2(2). Definitions: Cp(1) and Cp(2) are the cyclopentadienyl rings C(1–5) and C(6–10), respectively. Cg(1) and Cg(2) denote their centroids

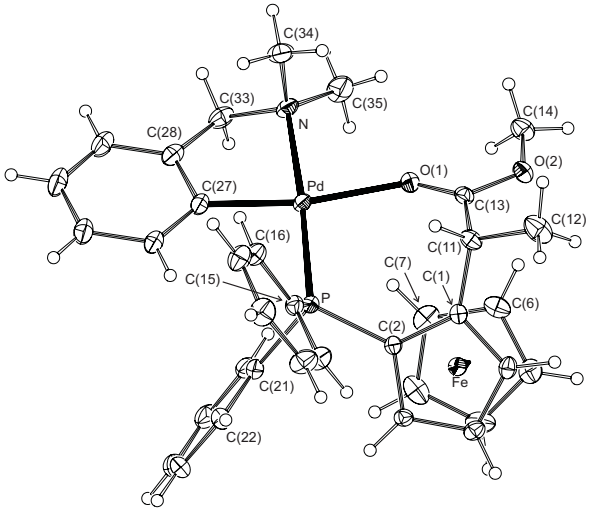


FIG. 2

PLATON plot of the cation in the structure of complex **9**. Displacement ellipsoids are shown with 30% probability

P(1)–Pd–N and N–Pd–C(27) which, in turn, is aided by the spatial constraints within the *ortho*-palladated ring. The coordination plane {PdPO(1)-NC(27)} is tilted with respect to the ferrocene unit, leaning towards the ester moiety. The dihedral angle of the coordination and Cp(1) planes is 35.5(4)° while the carboxyl and coordination planes are mutually rotated at an angle of 26.9(4)°. The *ortho*-metallated aryl benzene deviates from the coordination plane by 14.9(2)°.

On going from free **6** to its O,P-coordinated form, there is clearly detectable a lengthening of the C=O bond (ca. 0.02 Å) and a slightly more pronounced shortening of the C–O (0.03 Å) bond. Somewhat unexpectedly,

TABLE I
Selected interatomic distances (in Å) and angles (in °) for the cation in complex **9**[a]

Distances		Angles	
Pd–P	2.2503(9)	P–Pd–O(1)	98.03(7)
Pd–O(1)	2.161(3)	P–Pd–C(27)	93.5(1)
Pd–N	2.151(3)	N–Pd–O(1)	85.6(1)
Pd–C(27)	2.004(3)	N–Pd–C(27)	82.8(1)
Fe–Cg(1)	1.647(2)	∠Cp(1),Cp(2)	3.6(2)
Fe–Cg(2)	1.660(2)		
C(1)–C(11)	1.513(5)	C(1)–C(11)–C(12)	112.6(3)
C(11)–C(12)	1.503(5)	C(1)–C(11)–C(13)	110.2(3)
C(11)–C(13)	1.514(5)	O(1)–C(13)–O(2)	122.3(3)
C(13)–O(1)	1.229(4)	Pd–O(1)–C(13)	139.2(2)
C(13)–O(2)	1.312(4)	C(13)–O(2)–C(14)	117.9(3)
O(2)–C(14)	1.453(5)	C(2)–P–C(15)	101.0(2)
P–C(2)	1.809(3)	C(2)–P–C(21)	102.1(1)
P–C(15)	1.833(4)	C(15)–P–C(21)	106.6(2)
P–C(21)	1.826(4)	Pd–P–C[b]	112.7(1)–116.8(1)
N–C(33)	1.488(5)	C(33)–N–C(34)	110.3(3)
N–C(34)	1.487(5)	C(33)–N–C(35)	109.1(3)
N–C(35)	1.466(5)	C(34)–N–C(35)	109.4(3)
C(28)–C(33)	1.488(5)	C(26)–N(33)–N	109.4(3)

[a] Definitions: Cp(1) and Cp(2) are the cyclopentadienyl rings C(1–5) and C(6–10), respectively. Cg(1) and Cg(2) denote their centroids. [b] The range of Pd–P–C(2,15,21) angles.

the C(11)–C(12) in **9** is by almost 0.04 Å shorter than in the non-coordinated ester. Also detectable are some minor changes in the conformation of the pendant ester. As manifested by the C(2)–C(1)–C(11)–C(13) torsion angles 139.3(2) and 76.0(4)° for **6** and **9**, respectively, the ester side arm in **9** is rotated along the C(1)–C(11) bond more below the Cp(1) plane. This corresponds with a less acute dihedral angle of the carboxyl and Cp(1) planes (compare 60.5(4)° for **9** with 57.3(4)° for **6**). By contrast, the conformation at the C(11)–C(13) bond remains nearly the same (compare C(1)–C(11)–C(13)–O(1) 70.0(4)° for **6** and 71.4(4)° for **9**).

CONCLUSIONS

1-(Diphenylphosphanyl)-2-[(methoxycarbonyl)methyl]ferrocene can be deprotonated and methylated at the activated methylene group to give ester **6**. The reaction proceeds in a stereoselective fashion, the stereochemical preference reflecting the steric influence of the bulky ferrocene and phosphane moieties. As exemplified by the synthesis and structure determination of **9**, ester **6** readily forms O,P-chelate complexes when combined with a suitable metal complex precursor.

EXPERIMENTAL

General

Syntheses were performed under argon atmosphere and with exclusion of the direct daylight. THF was freshly distilled from potassium/benzophenone ketyl, dichloromethane was dried over anhydrous potassium carbonate and then distilled from calcium hydride. Acetonitrile was distilled from P_2O_5 and stored over activated 4 Å molecular sieves. Other solvents utilised for chromatography and crystallisations were used as received from commercial sources (Merck, Lach-Ner). THF solution of $NaN(SiMe_3)_2$ was purchased from Aldrich. Compounds **3** [4a] and **8** [10] were prepared following the literature procedures.

Melting points were determined on a Kofler apparatus and are uncorrected. NMR spectra were measured on a Varian Unity Inova 400 spectrometer (^1H, 399.95; ^{13}C, 100.58; ^{31}P, 161.90 MHz) at 298 K. Chemical shifts (δ, ppm) are given relative to internal tetramethylsilane (^1H and ^{13}C) or external 85% aqueous H_3PO_4 (^{31}P); coupling constants (*J*) are given in Hz. IR spectra (ν, cm^{-1}) were recorded on an FTIR Nicolet Magna 760 instrument in the range of 400–4000 cm^{-1}. Mass spectra were obtained on a ZAB-SEQ VG Analytical spectrometer.

1-(Diphenylphosphanyl)-2-[1-(methoxycarbonyl)ethyl]ferrocene (**6**)

A solution of $NaN(SiMe_3)_2$ (0.38 ml of 1 M in THF, 0.38 mmol) was added dropwise to a stirred solution of *rac*-**3** (111 mg, 0.25 mmol) in THF (10 ml) at –78 °C, whereupon the colour of the reaction mixture turned from orange to red. The mixture was stirred at –78 °C for

15 min and allowed to warm to room temperature while stirring for another 30 min. Then, it was cooled again to –78 °C and treated with methyl iodide (178 mg, 1.90 mmol; the colour changed back to amber). After the addition, the cooling bath was removed and stirring continued at room temperature for 1 h. Saturated aqueous NaCl solution and diethyl ether (10 ml each) were added. The organic phase was separated, dried over anhydrous $MgSO_4$ and evaporated under vacuum. The rusty orange residue was purified by column chromatography on silica gel, eluting with diethyl ether. Evaporation of the solvent afforded ester **6** as a yellow oil, which solidified upon standing at 4 °C. Yield 74 mg (65%). A small amount of the product was further crystallised from hot heptane. M.p. 111 °C (heptane). ^{1}H NMR ($CDCl_3$): major isomer 1.01 (d, $^3J_{HH}$ = 7.2, 3 H, CHC**H**$_3$); 3.80 (s, 3 H, CO_2CH_3); 3.81 (m, 1 H, C_5H_3); 3.87 (dq, $^3J_{HH}$ = 7.3, $^4J_{PH}$ = 4.2, 1 H, C**H**CH_3); 3.97 (s, 5 H, C_5H_5); 4.30 (apparent t, J = 2.5, 1 H, C_5H_3); 4.65 (m, 1 H, C_5H_3); 7.10–7.58 (m, 10 H, PPh_2). ^{13}C{^{1}H} NMR ($CDCl_3$): 21.83 (CH**C**H_3); 38.70 (d, $^3J_{PC}$ = 12, **C**HCH_3); 51.37 (CO_2**C**H_3); 69.54 (d, J_{PC} = 2.5, C_5H_3 **C**H); 69.59 (C_5H_3 **C**H); 69.60 (C_5H_5); 70.81 (d, J_{PC} = 4, C_5H_3 **C**H); 74.89 (d, $^1J_{PC}$ = 7, C_5H_3 **C**-P); 92.79 (d, $^2J_{PC}$ = 26, C_5H_3 **C**-CH); 128.03 (d, $^3J_{PC}$ = 2, PPh_2 **C**H$_m$); 128.04 (PPh_2 **C**H$_p$); 128.11 (d, $^3J_{PC}$ = 2, PPh_2 **C**H$_m$); 129.08 (PPh_2 **C**H$_p$); 132.61 (d, $^2J_{PC}$ = 19, PPh_2 **C**H$_o$); 134.95 (d, $^2J_{PC}$ = 21, PPh_2 **C**H$_o$); 137.24, 139.82 (2 × d, $^1J_{PC}$ = 9, PPh_2 **C**$_{ipso}$); 175.01 (**C**O_2CH_3). ^{31}P{^{1}H} NMR ($CDCl_3$): –24.4 (s, major isomer); –23.1 (s, minor isomer). IR (Nujol): 1729 s, 1433 s, 1350 m, 1322 m, 1308 w, 1253 m, 1238 m, 1195 s, 1170 s, 1159 s, 1089 m, 1003 m, 952 w, 819 s, 791 w, 741 vs, 700 vs, 502 s. MS (EI+), *m/z* (%): 456 (100, $M^{\bullet+}$), 425 (5, $[M – MeO]^+$), 413 (52), 347 (9), 331 (8), 271 (10), 212 (33), 183 (13, $[PPh_2 – 2\ H]^+$), 121 (12, $[C_5H_5Fe]^+$). HR MS (EI+): calculated for $C_{26}H_{25}{}^{56}FeO_2P$ 456.0942, found 456.0933.

2-[2-(Diphenylphosphanyl)ferrocenyl]propanoic Acid (**4**)

Degassed 3 M aqueous solution of KOH (2 ml, 6 mmol) was added to a solution of ester **6** (35 mg, 0.08 mmol) in methanol and THF (2 ml each) and the resulting clear mixture was heated at reflux for 24 h. After cooling to room temperature, the solution was concentrated under reduced pressure and the residue acidified with 3 M HCl (5 ml). The aqueous phase was extracted twice with dichloromethane, the combined extracts were washed with water and saturated aqueous NaCl solution, dried over anhydrous $MgSO_4$, and evaporated. The crude product was purified by chromatography on silica gel (elution with dichloromethane–methanol, 10:1) to give racemic **4** as an orange solid after evaporation. Yield 25 mg (74%).

Diastereoisomer A: ^{1}H NMR ($CDCl_3$): 1.04 (d, $^3J_{HH}$ = 7.1, 3 H, CHC**H**$_3$); 3.82 (m, 1 H, C_5H_3); 3.85 (dq, $^3J_{HH}$ = 7.1, $^4J_{PH}$ = 4.3, 1 H, C**H**CH_3); 3.98 (s, 5 H, C_5H_5); 4.30 (apparent t, J = 2.5, 1 H, C_5H_3); 4.64 (m, 1 H, C_5H_3); 7.10–7.60 (m, 10 H, PPh_2). ^{31}P{^{1}H} NMR ($CDCl_3$): –24.5 (s).

Diastereoisomer B: ^{1}H NMR ($CDCl_3$): 1.67 (d, $^3J_{HH}$ = 7.2, 3 H, CHC**H**$_3$); 3.88 (m, 1 H, C_5H_3); 3.90 (dq, $^3J_{HH}$ = 7.3, $^4J_{PH}$ = 3.2, 1 H, C**H**CH_3); 4.01 (s, 5 H, C_5H_5); 4.35 (apparent t, J = 2.5, 1 H, C_5H_3); 4.49 (m, 1 H, C_5H_3); 7.10–7.60 (m, 10 H, PPh_2). ^{31}P{^{1}H} NMR ($CDCl_3$): –23.8 (s). MS (EI+, direct inlet), *m/z* (%): 442 (67, $M^{\bullet+}$), 398 (100, $[M – CO_2]^+$), 321 (12), 293 (9), 213 (41), 183 (25), 121 (25).

(*S*,*R*$_p$/*R*,*S*$_p$)-2-[2-(Diphenylphosphoryl)ferrocenyl]propanoic Acid (**7**)

Chlorotrimethylsilane (0.08 ml, 0.6 mmol) was added to a stirred solution of ester **6** (68 mg, 0.15 mmol) and sodium iodide (90 mg, 0.6 mmol) in acetonitrile (20 ml). The mixture was heated at reflux for 48 h. After cooling to room temperature, water (10 ml) was added to

quench the reaction. The organic phase was separated and water phase was extracted with dichloromethane. The combined organic layers were washed with water and saturated aqueous NaCl solution, dried over anhydrous $MgSO_4$, and evaporated. Subsequent chromatography (silica gel, dichloromethane/methanol, 10:1) and evaporation of the solvent afforded **7** as a light orange solid. Yield 36 mg (54%). ^{1}H NMR ($CDCl_3$): 1.29 (d, $^3J_{HH}$ = 7.0, 3 H, CHC**H**$_3$); 3.54 (q, $^3J_{HH}$ = 7.1, 1 H, C**H**CH$_3$); 3.91 (m, 1 H, C_5H_3); 4.14 (s, 5 H, C_5H_5); 4.46 (m, 1 H, C_5H_3); 4.68 (m, 1 H, C_5H_3); 7.40–7.82 (m, 10 H, PPh_2); 13.71 (br s, 1 H, COOH). ^{31}P{^{1}H} NMR ($CDCl_3$): 37.1 (s).

[SP-4-3]-{2-[(Dimethylamino-κ*N*)methyl]phenyl-κC^1}{1-(diphenylphosphanyl-κ*P*)-2-[1-(methoxycarbonyl-κO^1)ethyl]ferrocene}palladium(II) Perchlorate (**9**)

Ester **6** (11.4 mg, 0.025 mmol) and bis(acetonitrile){2-[(dimethylamino-κ*N*)methyl]phenyl-κC^1}-palladium(II) perchlorate (**8**; 10.6 mg, 0.025 mmol) were dissolved in dichloromethane (3 ml). The solution was stirred at room temperature in the dark for 1 h, then filtered through a PTFE syringe filter (pore size 45 μm), and the product crystallised by diffusion of diethyl ether to afford **9** as an orange crystalline solid. Yield 15 mg (75%). ^{1}H NMR ($CDCl_3$): 1.21 (d, $^3J_{HH}$ = 7.1, 3 H, CHC**H**$_3$); 2.94 (d, $^4J_{PH}$ = 2.1, 3 H, NCH$_3$); 3.06 (q, $^3J_{HH}$ = 7.1, 1 H, C**H**CH$_3$); 3.10 (d, $^4J_{PH}$ = 3.4, 3 H, NCH$_3$); 3.49 (m, 1 H, C_5H_3); 3.79 (dd, $^2J_{HH}$ = 13.9, $^4J_{PH}$ = 3.7, 1 H, C**H**$_2$NCH$_3$); 4.16 (s, 3 H, COOCH$_3$); 4.25 (s, 5 H, C_5H_5); 4.37 (apparent t, *J* = 2.5, 1 H, C_5H_3); 4.57 (m, 1 H, C_5H_3); 4.61 (d, $^2J_{HH}$ = 13.8, 1 H, C**H**$_2$NCH$_3$); 6.26–6.38 (m, 2 H, C_6H_4); 6.82–7.00 (m, 2 H, C_6H_4); 7.34–7.88 (m, 10 H, PPh_2). ^{13}C{^{1}H} NMR ($CDCl_3$): 15.09 (CH**C**H$_3$); 37.62 (**C**HCH$_3$); 49.67 (d, $^4J_{PC}$ = 3, NCH$_3$); 50.83 (d, $^3J_{PC}$ = 2.5, NCH$_3$); 55.25 (CO_2**C**H$_3$); 69.11 (d, J_{PC} = 6, C_5H_3 **C**H); 70.71 (C_5H_5); 71.37 (d, J_{PC} = 2, C_5H_3 **C**H); 72.73 (d, J_{PC} = 7, C_5H_3 **C**H); 73.08 (d, $^1J_{PC}$ = 4, C_5H_3 **C**-P); 89.18 (d, $^2J_{PC}$ = 15, C_5H_3 **C**-CH); 123.40, 125.22 (2 × C_6H_4 **C**H); 125.83 (d, J_{PC} = 6, C_6H_4 **C**H); 128.37, (d, J_{PC} = 12, PPh_2 **C**H); 129.45 (d, J_{PC} = 11, PPh_2 **C**H); 131.29, 132.55 (2 × PPh_2 **C**H$_p$); 133.64 (d, J_{PC} = 12, PPh_2 **C**H); 136.05 (d, J_{PC} = 15, PPh_2 **C**H); 138.41 (d, J_{PC} = 13, C_6H_4 **C**H); 141.11 (d, J_{PC} = 4, C_6H_4 **C**$_{ipso}$); 147.61 (d, J_{PC} = 3, C_6H_4 **C**$_{ipso}$); 180.87 (**C**O$_2$CH$_3$); signals due to PPh_2 **C**$_{ipso}$ were not found. ^{31}P{^{1}H} NMR ($CDCl_3$): 30.8 (s). IR (Nujol): 1658 s, 1583 w, 1324 m, 1168 w, 1089 composite vs, 1053 sh, 1023 m, 997 m, 841 m, 815 w, 752 m, 743 s, 697 m, 623 m, 503 m. For $C_{35}H_{37}ClFeNO_6PPd$ (796.3) calculated: 52.79% C, 4.68% H, 1.76% N; found: 52.46% C, 4.57% H, 1.71% N.

X-ray Crystallography

Crystals suitable for X-ray diffraction analysis were grown by recrystallisation from hot heptane (**6**: orange block, 0.10 × 0.15 × 0.20 mm^3) and by diffusion of diethyl ether into a dichloromethane solution (**9**; orange bar, 0.10 × 0.10 × 0.50 mm^3). Full-set diffraction data (±*h*±*k*±*l*) were collected on a Nonius Kappa CCD diffractometer equipped with an Oxford Cryostream cooler (Oxford Instruments) using graphite-monochromatised MoKα radiation (λ = 0.71073 Å). The data for **9** were corrected for absorption by a Gaussian method based on the indexed crystal shape as incorporated in the diffractometer software[11]. The relevant crystallographic data are given in Table II.

The structures were solved by direct methods (SIR97 [12]) and refined by full-matrix least-squares procedure on F^2 (SHELXL97 [13]). The perchlorate counter ion is disordered and was modelled as if contributed from two moieties mutually rotated along the O(3)–Cl bond. The two orientations were refined with isotropic displacement parameters constrained in the re-

TABLE II
Crystallographic data, data collection and structure refinement parameters for **6** and **9**

Parameter	**6**	**9**
Formula	$C_{26}H_{25}FeO_2P$	$C_{35}H_{37}ClFeNO_6PPd$
M	456.28	796.33
T, K	150(2)	150(2)
Crystal system	monoclinic	triclinic
Space group	*C*2/*c* (No. 15)	*P*-1 (No. 2)
a, Å	12.4734(4)	9.7769(2)
b, Å	11.4241(4)	11.8703(4)
c, Å	31.078(1)	16.5640(6)
α, °		70.183(2)
β, °	90.220(2)	76.180(2)
γ, °		80.923(2)
V, Å^3	4428.5(3)	1749.92(9)
Z	8	2
D, g ml^{-1}	1.369	1.511
μ(MoKα), mm^{-1}	0.773	1.095
T[a]	[e]	0.708–0.921
Diffractions total	19165	28128
Unique/observed[b] diffractions	3980/2954	7988/6702
R_{int}[c], %	5.2	5.21
No. of parameters	273	414
R observed diffractions, %[d]	4.67	4.25
R, *wR* all data, %[d]	7.87, 10.5	5.40, 11.4
Δρ, e Å^{-3}	0.45, –0.38	1.36, –0.96[f]

[a] The range of transmission coefficients. [b] Diffractions with $I_o > 2\sigma(I_o)$. [c] $R_{int} = \Sigma|F_o^2 - F_o^2(\text{mean})|/\Sigma F_o^2$, where $F_o^2(\text{mean})$ is the average intensity for symmetry-equivalent diffractions. [d] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma w(F_o^2)^2]^{1/2}$. [e] Not corrected. [f] Residual electron density in the space accommodating the disordered perchlorate anion.

spective atom pairs (i.e., U_{iso}(O*n*A) = U_{iso}(O*n*B), where *n* = 4–6) and converged to 37:63 (A:B) occupancies. All other non-hydrogen atoms were refined with anisotropic displacement parameters while the hydrogen atoms were included in the calculated positions and refined as riding atoms with U_{iso}(H) set to 1.5U_{eq} (methyl) or 1.2U_{eq} (all other) of their bonded atoms. Geometric calculations were performed with a recent version of the PLATON program[14]. The calculated values are given in one decimal with respect to their estimated standard deviations.

CCDC 640903 (**6**) and 640904 (9) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

This work was financially supported by the Grant Agency of the Charles University (grant No. 318/2005/B-CH/PrF) and represents a part of the long-term research projects supported by the Ministry of Education, Youth and Sports of the Czech Republic (projects Nos MSM0021620857 and LC06070).

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