SYNTHESIS AND STRUCTURES OF (η^3-METHALLYL)PALLADIUM(II) COMPLEXES WITH PHOSPHANYLFERROCENECARBOXYLIC LIGANDS

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Dedicated to Professor Jaroslav Podlaha on the occasion of his 70th birthday.

Di-μ-chlorobis{(η^3-methallyl)palladium(II)} (**1**) reacts with two equivalents of 1′-(diphenylphosphanyl)ferrocene-1-carboxylic acid (Hdpf) and *rac*-[2-(diphenylphosphanyl)ferrocen-1-yl]acetic acid (*rac*-Hpfa) to give complexes with P-monodentate phosphanylcarboxylic ligands: [PdCl(η^3-CH$_2$C(Me)CH$_2$)(L-κP)], L = Hdpf (**2**) and *rac*-Hpfa (**4**). Similar reactions with the corresponding carboxylate salts (Kdpf and Kpfa) afford, respectively, an ill-defined polymer formulated tentatively [{Pd(η^3-CH$_2$C(Me)CH$_2$)(dpf)}$_n$] (**3**) and the molecular chelate complex [Pd(η^3-CH$_2$C(Me)CH$_2$)(pfa-κ^{2}O,P)] (**5**), which crystallizes as a monohydrate. All compounds were studied by spectral methods (IR and NMR) and the solid-state structures of **2**, **4**, and **5**·H$_2$O were determined by single-crystal X-ray diffraction.

Keywords: Palladium; Ferrocene; Phosphanylcarboxylic ligands; Allyl complexes; Crystal structure.

Phosphanylcarboxylic donors represent a specific class of hybrid ligands that have found manifold use as ligands in coordination compounds and as catalyst components[1]. The first ferrocene representative, 1′-(diphenylphosphanyl)ferrocene-1-carboxylic acid (Hdpf; Scheme 1), was reported in 1996[2]. Since then, we have studied coordination behaviour of this donor towards selected metals[3] and its further utilization in synthesis and catalysis[4]. More recently, we turned our attention also to coordination chemistry of the planarly chiral (*S*$_p$)-2-(diphenylphosphanyl)ferrocene-1-carboxylic acid (**I**)[5] and its homologous ligands, *rac*-[2-(diphenylphosphanyl)ferrocen-1-yl]acetic acid (*rac*-Hpfa)[6] and *rac*-2-[(diphenylphosphanyl)methyl]ferrocene-1-carboxylic acid (**II**)[7,8] (Scheme 1).

This contribution reports about (η^3-methallyl)palladium(II) complexes featuring Hdpf, *rac*-Hpfa and their respective carboxylates as the ligands,

describing their synthesis, spectral characterization and solid-state structures.
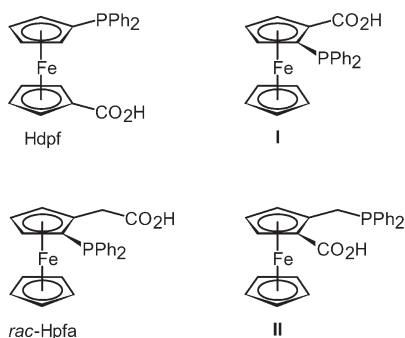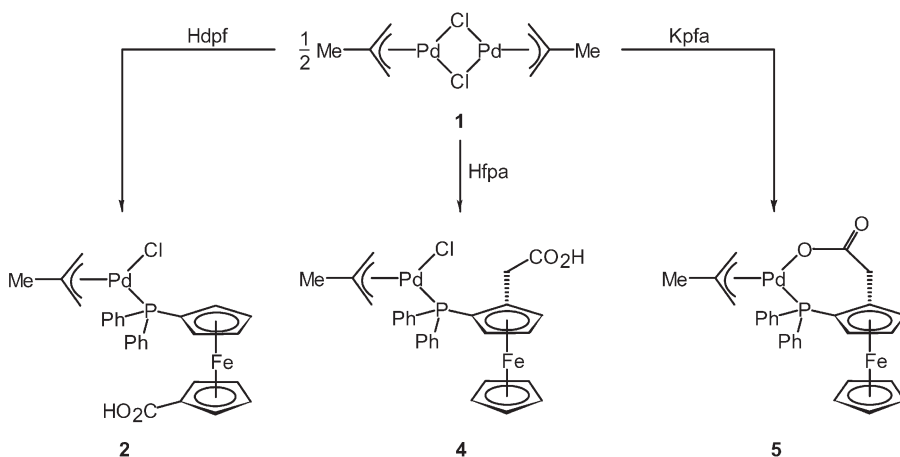

SCHEME 1

RESULTS AND DISCUSSION

Synthesis and Characterization

Reactions of the dinuclear chloro(η^3-methallyl)palladium complex **1** with the stoichiometric amounts of Hdpf and *rac*-Hpfa gave the expected bridge-cleavage products, **2** and **4**, respectively (Scheme 2). The corresponding carboxylate complexes were obtained similarly by metathesis reactions between **1** and the appropriate carboxylate salts generated in situ from the equimolar amounts of potassium *tert*-butoxide and the respective acid. Whereas the polymeric, insoluble (allyl)(dpf)palladium(II) complex **3** precipitates directly from the reaction mixture, its pfa$^-$ analogue was isolated as an orange, crystalline hydrate **5**·H_2O by crystallization of the crude product from dichloromethane–hexane (Scheme 2).

Compounds **2**, **4**, and **5**·H_2O are air-stable solids, showing characteristic carboxyl or carboxylate bands in their IR spectra (ν (in cm^{-1}) Hdpf: 1666, **2**: 1710/1674; *rac*-Hpfa 1712 (shoulder at 1695), **4**: 1727 (weak bands at 1761, 1686), and **5**·H_2O: 1608/1598). Once crystallized, complexes **4** and **5**·H_2O are only poorly soluble in common solvents including those used in synthesis, which makes a detailed NMR analysis difficult. The ^{1}H and ^{31}P\{^{1}H\} NMR spectra of complex **4** recorded in a $(CD_3)_2SO$ solution showed very broad proton resonances and two phosphorus signals at δ_P 7.6 and 8.0 (approximate ratio 1.6:1), respectively. Spectra of the better soluble **5** change with the solvent used: the spectra recorded in $(CD_3)_2SO$ exhibited markedly broadened proton signals and a single broad resonance at δ_P 16.9, whilst in

CDCl$_3$ two distinct signal sets from both the carboxyphosphane and methallyl ligands in ^{1}H and two signals in ^{31}P{^{1}H} NMR spectra (δ_P 16.4 and 17.8) were observed. Such behavior, indicating solvent-dependent dynamic processes, is consistent with the fluxionality of (η^3-allyl)palladium(II) complexes[9].

SCHEME 2

As mentioned above, the reaction of Kdpf with **1** produces an insoluble, ochre amorphous precipitate of the polymeric phosphanylcarboxylate **3**. Products obtained from repeated experiments have slightly different elemental analyses, indicating the materials to accommodate varying amounts of solvents used in the synthesis and work-up or other substances from the reaction medium (either chemically bonded or adsorbed). Nonetheless, the IR spectra of individual samples are perfectly reproducible and consistent with the presence of the dpf anion (ν (in cm^{-1}) 1612 and 1588; cf. ν_{as}(CO$_2$) for the simple salts Nadpf and M(dpf)$_2$, M = Ca, Sr and Ba (1540, ref.[10]), and the carboxylate complexes [Ni(dpf)$_2$] (1609, ref.[11]) and [Ti(dpf-κ^2O,O')] (1506, ref.[3f])). In addition, the spectra show bands typical for free and associated hydroxy groups, attributable to *tert*-BuOH (side-product) or ethanol (used in the work-up). In ESI mass spectra, compound **3** gives rise to ions at *m/z* 575 (most intense signal), corresponding to [Pd(η^3-CH$_2$C(Me)CH$_2$)(dpf) + H]$^+$. In summary, the spectral data allowed us to tentatively formulate **3** as a coordination polymer [{Pd(η^3-CH$_2$C(Me)CH$_2$)(dpf)}$_n$], where the dpf anion acts as a multidentate, bridging ligand. This compound is apparently formed in several steps, likely by salt metathesis followed by condensation, since the addition of Kdpf to **1** results in the formation of a clear solution,

which then rather slowly deposits the final product as a fine amorphous precipitate.

Crystal Structures

Structures of **2**, **4**, and the solvate **5**·H_2O have been determined by single-crystal X-ray diffraction. A view of the molecular structure of complex **2** is shown in Fig. 1 and the selected geometric parameters are given in Table I. As expected, the donors around the palladium atom in molecule of **2** are arranged in a pseudotrigonal manner. The η^3-bonded methallyl moiety is rotated with respect to the plane of the central and the remaining donor atoms: the {C(24),C(25),(26)} (allylic) and {Pd,P,Cl} planes intersect at an angle of 65.7(3)°. The methyl group attached to the *meso*-carbon of the methallyl ligand is inclined towards the metal centre, the perpendicular distance of the C(27) carbon atom from the allylic plane being 0.285(4) Å. Notably, the methallyl ligand is coordinated very symmetrically; the rela-
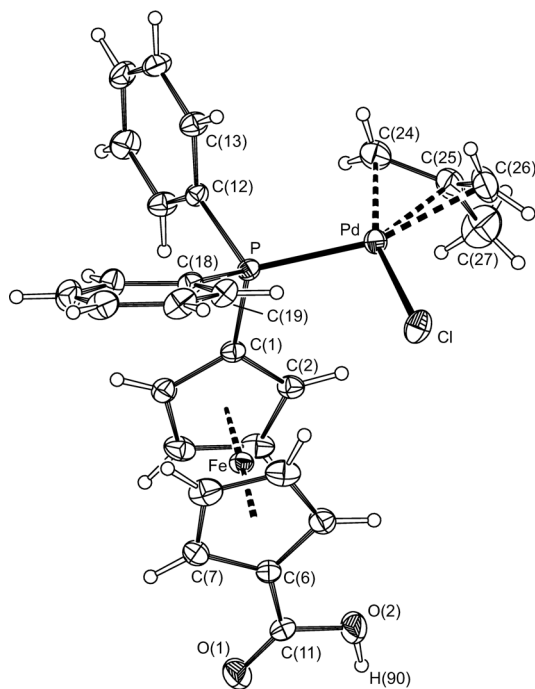

FIG. 1
Molecular structure of complex **2**. Displacement ellipsoids scaled to the 30% probability level

tive difference of the Pd–C bonds lengths is only ca. 4%. In addition, the {Pd,C(25),C(27)} plane practically bisects the methallyl group (cf. the perpendicular distances from this plane for C(24) and C(26) of 1.207(3) and 1.166(4) Å) as well as the Cl–Pd–P angle as evidenced by the angles subtended by the Pd–Cl and Pd–P vectors and the allylic plane of 54.2(3) and 49.9(3)°, respectively.

The Pd–donor bond distances in **2** are very similar to those in [PdCl(η^3-CH$_2$C(Me)CH$_2$)(PPh$_3$)][12]; however, the interligand angles in both compounds differ. In accordance with larger steric demands of Hdpf as compared with PPh$_3$, the Cl–Pd–P angle in **2** is more open while the X–Pd–C(24–26) (X = Cl an P) angles are more acute. The geometry of P-coordinated Hdpf differs only marginally from that of the uncoordinated carboxyphosphane[2]. The ferrocene moiety is nearly perpendicular to the {Pd,P,Cl} plane (dihedral angle of the Cp1 and {Pd,P,Cl} least-squares planes

TABLE I
Selected distances and angles for **2** (Å, °)[a]

Fe–Cg1	1.647(1)	∠Cp1,Cp2	2.5(2)
Fe–Cg2	1.650(1)		
Pd–Cl	2.3787(7)	Cl–Pd–P	104.08(2)
Pd–P	2.3132(6)	Cl–Pd–C(24)	160.92(9)
Pd–C(24)	2.101(3)	Cl–Pd–C(25)	123.89(8)
Pd–C(25)	2.180(3)	Cl–Pd–C(26)	93.8(1)
Pd–C(26)	2.196(3)	P–Pd–C(24)	95.00(8)
C(24)–C(25)	1.420(4)	P–Pd–C(25)	128.65(8)
C(25)–C(26)	1.380(5)	P–Pd–C(26)	161.8(1)
C(24)–C(27)	1.500(5)	C(24)–C(25)–C(26)	116.2(3)
P–C(1)	1.801(2)	C(1)–P–C(12)	103.91(9)
P–C(12)	1.827(2)	C(1)–P–C(18)	106.04(9)
P–C(18)	1.831(2)	C(12)–P–C(18)	101.17(9)
C(6)–C(11)	1.467(3)	O(1)–C(11)–O(2)	122.9(2)
C(11)–O(1)	1.197(3)	O(1)–C(11)–C(6)	125.0(2)
C(11)–O(2)	1.327(3)	O(2)–C(11)–C(6)	112.1(2)

[a] Plane definitions: Cp1: C(1–5), Cp2: C(6–10); Cg(1) and Cg(2) stand for the respective ring centroids.

is 86.4(1)°) and, as evidenced by the torsion angle $\tau(C(1)–Cg1–Cg2–C(6))$ = 161.6(2)° (see Table I for definitions), it adopts a conformation almost perfectly half-way between anti-staggered and anti-eclipsed (τ = 144 and 180°, respectively), similar to free Hdpf. The ligand carboxyl group, which is not involved in coordination, behaves as a hydrogen bond donor towards the chloro ligand in an adjacent molecule lying across the crystallographic inversion centre (and vice versa; Table II and Fig. 2a). Consequently, the complex molecules form centrosymmetric dimers joined by pairs of the $O(2)–H(90)\cdots Cl$ bonds. The crystal packing of these dimers is further supported by weak $C–H\cdots O$ interactions (Table II) and graphite-like stacking of the parallel ferrocene cyclopentadienyl rings ($C(1–5)$ or Cp1 ring; $Cg\cdots Cg$ distance 4.538(2) Å, interplanar separation: 3.95 Å, offset 2.23 Å; Cg stands for the ring centroid).

A survey in the Cambridge crystallographic database has shown that hydrogen bonding interactions between carboxyl groups and transition metal-bonded chloro ligands are not uncommon[13]. A correlation between $O\cdots Cl$ separations and angles at the carboxyl hydrogen atom clearly shows a distinct area of directional hydrogen bonds with $O\cdots Cl$ contacts between ca. 2.9–3.15 Å and angles at H of 150–177° (Fig. 2b). The number of entries falling into this region amounts to 26% of all retrieved hits (15 of 58 contacts in 41 structures, where the $O\cdots Cl$ distance range 2–4 Å, the $O–H\cdots Cl$ angles 100–180°, and the R-values are below 10%; see ref.[13]).
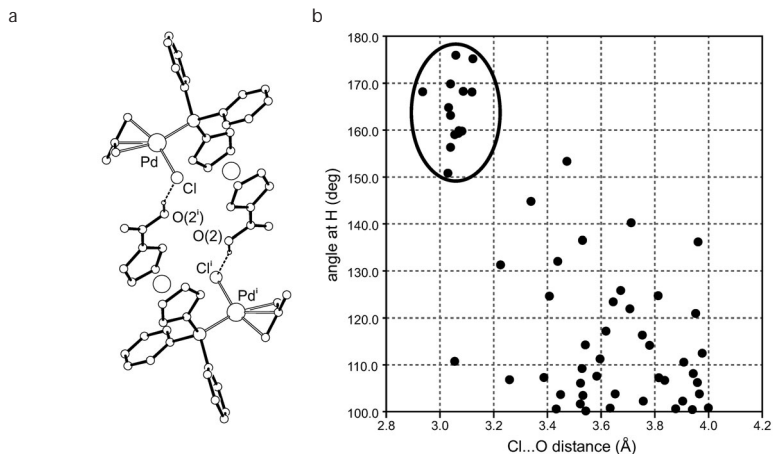

FIG. 2
a: A view of the hydrogen-bonded dimers in the structure of **2** (prime labeled atoms are generated by crystallographic inversion operation). b: Scatter plot for the CSD survey showing the correlation between the $Cl\cdots O$ distances and $O–H\cdots Cl$ angles. The area of relatively short, directional hydrogen bonds is indicated with an ellipse

The molecular structures of **4** and **5**·H_2O are shown in Figs 3 and 4, and the selected geometric data are summarized in Table III. The coordination sphere around palladium in complex **4** compares favourably to that in **2**, particularly in the Pd–donor bond lengths. Likewise, the arrangement of the (η^3-methallyl)palladium fragment in **4** is similar to that in **2**, exerting similar dihedral angles between the allylic ({C(25),C(26),C(27)}) and {Pd,P,Cl} planes (66.0(2)°). However, in accordance with increased steric crowding around the coordinated phosphorus atom in Hpfa, resulting from the presence of the carboxymethyl arm in the vicinal position, the Cl–Pd–P angle in **4** is more acute (by 5.5°) and the remaining interdonor angles are slightly more open (by ca. 2–3°) than those in **2**.

The Hpfa ligand in **4** is simply P-coordinated and its carboxyl group adopts a position practically perpendicular to the Cp1 plane, pointing towards the methallyl moiety on its *anti* side (see Table III for definitions; the dihedral angle of the respective least-squares planes is 87.6(3)°). Similarly to the structure of complex **2**, the ligand carboxyl group in **4** acts as

TABLE II
Hydrogen bond parameters for **1**, **4**, and **5**·H_2O (Å, °)[a]

D–H···A	D···A	D–H	H···A	angle at H
Complex 1				
O(2)–H(90)···Cl[i]	3.082(2)	0.94	2.18	160
C(10)–H(10)···O(2)[i]	3.315(3)	0.93	2.57	138
Complex 4				
O(2)–H(90)···Cl[ii]	3.054(2)	0.79(3)	2.27(3)	172(3)
C(5)–H(5)···O(2)[iii]	3.448(3)	0.93	2.57	158
C(27)–H(27B)···O(1)[iv]	3.667(2)	0.97	2.71	167
C(28)–H(28A)···O(1)[v]	3.472(4)	0.96	2.51	178
Complex 5·H_2O				
O(3)–H(91)···O(2)	2.822(2)	0.98(4)	1.87(4)	166(3)
O(3)–H(92)···O(1)[vi]	2.895(2)	0.92(4)	1.99(4)	166(3)
C(28)–H(28A)···O(1)[vi]	3.460(3)	0.96	2.52	165

[a] D, donor; A, acceptor. Parameters involving atoms in constrained positions are given without estimated standard deviations. Symmetry codes: i. (–1 – *x*, –*y*, 1 – *z*), ii. (1 – *x*, 1/2 + *y*, 1/2 – *z*), iii. (1 – *x*, 1 – *y*, 1 – *z*), iv. (1 – *x*, –1/2 + *y*, 1/2 – *z*), v. (*x*, 3/2 – *y*, –1/2 + *z*), vi. (2 – *x*, 1/2 + *y*, 1/2 – *z*).
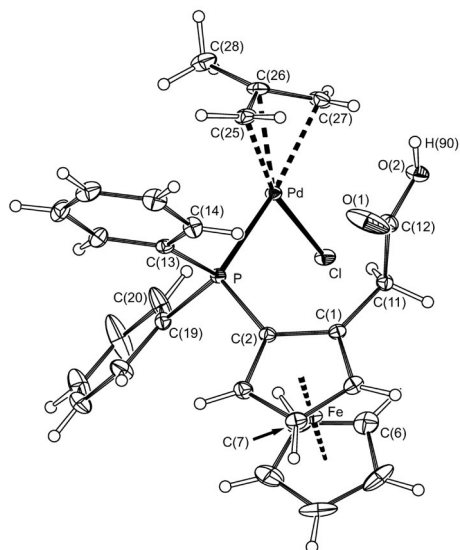
F_{IG.} 3

Molecular structure of complex **4**. Displacement ellipsoids are drawn with 30% probability
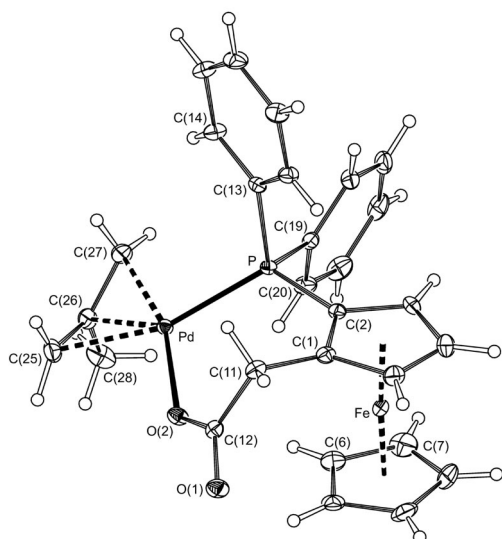

F_{IG.} 4

The structure of complex **5** in the crystallographically characterized hydrate **5**·H_2O. Displacement ellipsoids are scaled to 30% probability

Selected geometric data for **4** and **5**·H_2O (Å, °)[a]

Parametr	**4** (X = Cl)	**5**·H_2O[b] (X = O(2))
Fe–Cg1	1.637(1)	1.644(1)
Fe–Cg2	1.649(1)	1.656(1)
∠Cp1,Cp2	0.9(1)	5.3(1)
Bond angle		
Pd–X	2.4027(4)	2.103(1)
Pd–P	2.3127(5)	2.2792(5)
Pd–C(25)	2.108(2)	2.249(2)
Pd–C(26)	2.176(2)	2.181(2)
Pd–C(27)	2.207(3)	2.074(2)
C(25)–C(26)	1.421(3)	1.381(4)
C(26)–C(27)	1.390(3)	1.427(3)
C(26)–C(28)	1.508(3)	1.487(4)
P–C(2)	1.813(2)	1.785(2)
P–C(13)	1.831(2)	1.829(2)
P–C(19)	1.829(2)	1.824(2)
C(1)–C(11)	1.496(3)	1.508(3)
C(11)–(12)	1.512(3)	1.525(3)
C(12)–O(1)	1.185(3)	1.236(2)
C(12)–O(2)	1.324(3)	1.285(2)
Angle		
X–Pd–P	98.57(2)	104.29(4)
X–Pd–C(25)	163.82(7)	95.21(8)
X–Pd–C(26)	127.33(6)	124.10(7)
X–Pd–C(27)	96.95(6)	161.86(8)
P–Pd–C(25)	97.47(7)	160.16(7)
P–Pd–C(26)	130.81(6)	128.02(7)
P–Pd–C(27)	163.91(6)	93.86(7)
C(25)–C(26)–C(27)	115.7(2)	116.0(2)
C(1)–C(1)–C(12)	111.9(2)	114.3(2)
O(1)–C(12)–O(2)	123.4(2)	122.8(2)
C(11)–C(1)–C(2)–P	–4.1(3)	–0.9(3)

[a] Plane definitions: Cp1: C(1–5), Cp2: C(6–10); Cg(1) and Cg(2) denote the respective ring centroids. [b] Data for the solvating water molecule: O(3)–H(91) 0.98(4), O(3)–H(92) 0.92(4) Å; H(91)–O(3)–H(92) 106(3)°.

the hydrogen bond donor via its OH group towards chloride in a neighbouring molecule. However, unlike complex **2**, the molecules of **4** associate into infinite twisted chains running parallel to the crystallographic *b* axis (Table II). This solid-state assembly is further aided by intermolecular CH···O hydrogen bonds (Table II) and π···π stacking interactions of the aromatic rings (C(19–24) benzene ring and its centrosymmetric image: Cg···Cg 4.360(2) Å, interplanar distance 3.77 Å, offset of the rings 2.2 Å).

On going from **4** to **5**, the formal replacement of the chloro ligand with carboxylate results in an opening of the P–Pd–O(2) and closure of the other interligand angles so that the arrangement around palladium atom in **5** is closer to that in **2** than to the coordination geometry observed for **4** – though with slightly more diverse Pd–C bonds lengths (see data in Table III; the dihedral angle between the allylic and {Pd,P,O(2)} planes is 67.8(2)°). In contrast to Hpfa in **4**, the pfa anion in **5** exhibits nearly balanced carboxylate C–O bond lengths and a different orientation of the carboxylate arm. The carboxyl group is rotated into a position that allows for its efficient bonding to the palladium atom, the dihedral angle subtended by the carboxylate {C(11),O(1),O(2)} and Cp1 planes in **5** being 60.6(2)°. It is noteworthy that the angles between the C(11)–C(12) bond and Cp1 plane do not differ much in both (H)pfa complexes (68.5(1) and 60.2(2)° in **4** and **5**, respectively). However, the orientations of the $CH_2CO_2(H)$ group are just the opposite: in **4**, the carboxymethyl arm is directed outwards the ferrocene unit while in **5** it points to the iron atom. Hence, the $CH_2CO_2(H)$ groups appear mutually rotated along the C(1)–C(11) bond by the straight angle.
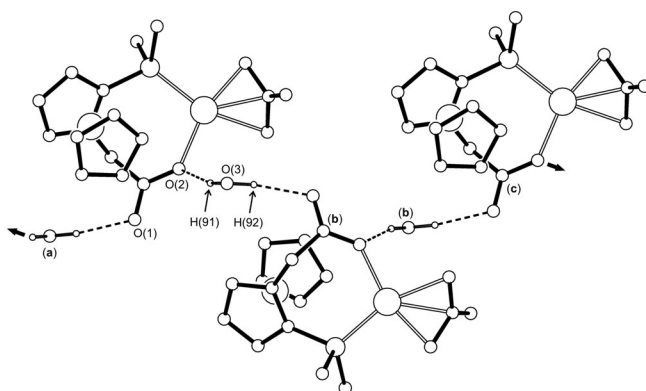

Fig. 5

Arrangement of hydrogen-bonded chains in the structure of **5**·H_2O. For clarity, only the pivot atoms from the benzene rings are shown. The arrows indicate the propagation of the chain. Symmetry operations: (**a**) (2 – *x*, *y* – 1/2, 1/2 – *z*), (**b**) (2 – *x*, *y* + 1/2, 1/2 – *z*), and (**c**) (*x*, 1 + *y*, *z*)

As mentioned earlier, complex **5** was isolated as a monohydrate. In crystal, the solvating water molecules form hydrogen bridges to the carboxylate oxygen atoms O(1) and O(2) located in two adjacent molecules of the complex, thus resulting in the formation of infinite hydrogen-bonded, helical chains oriented parallel to the (0 1 0) vector (Fig. 5, Table II). No further significant intermolecular interactions were detected in the structure, the exception being some weak CH⋯O hydrogen bonds (Table II) and contacts at the van der Waals level.

CONCLUSIONS

Reactions of **1** with phosphanylferrocenecarboxylic acids Hdpf and *rac*-Hpfa give the discrete (η^3-methallyl)palladium(II) complexes with P-monodentate ligands while the respective potassium carboxylates afford either the molecular complex with O,P-chelating phosphanylcarboxylate from K[*rac*-pfa] or an ill-defined coordination polymer featuring multidentate bridging dpf anions from Kdpf. The formation of the polymeric material seems to reflect steric properties of the {Ph$_2$PfcC(O)O} moiety (fc = ferrocene-1,1′-diyl), not favourable for the formation of chelate complexes with palladium. This is in accordance with the previous observation that metathesis reaction of NiCl$_2$ with Kdpf produces polymeric carboxylate complex [Ni(dpf)$_2$] (ref.[11]) and the fact that the respective esters, Medpf and *rac*-Mepfa, react with the same palladium(II) precursor, [Pd{C$_6$H$_4$(CH$_2$NMe$_2$-2)-$\kappa^2 C^1$,N}(MeCN)$_2$]ClO$_4$, to give complexes with P-monodentate[4b] and O,P-chelating ligands[6a], respectively.

EXPERIMENTAL

Materials and Methods

Dichloromethane and chloroform were dried over potassium carbonate. Hexane for crystallizations was used without purification. Di-µ-chlorobis{(η^3-methallyl)palladium(II)} (**1**) was prepared similarly to its η^3-allyl analogue[14]. The ligands Hdpf (ref.[2]) and *rac*-Hpfa (ref.[6a]) were synthesized by the literature procedures. Potassium *tert*-butoxide was used as received (Fluka).

NMR spectra were recorded on a Varian Unity Inova 400 spectrometer (^{1}H, 399.95; ^{31}P, 161.90 MHz) at 25 °C. Chemical shifts (δ, ppm) are given relative to internal tetramethylsilane (^{1}H) and to external 85% aqueous H$_3$PO$_4$ (^{31}P), coupling constants (J) are given in Hz. IR spectra were measured on an FT IR Nicolet Magna 650 instrument in the range of 400–4000 cm^{-1}. Electrospray mass spectra were obtained on a Q-TOF (Micromass) instrument. The sample was dissolved in aqueous acetonitrile.

Syntheses

Chloro[1′-(diphenylphosphanyl)ferrocene-1-carboxylic acid-κP](η³-methallyl)palladium(II) (**2**).
A solution of dimer **1** (197 mg, 0.50 mmol) in dichloromethane (5 ml) was mixed with a
warm solution of Hdpf (414 mg, 1.0 mmol) in the same solvent (10 ml). After standing at
room temperature for 1 h, the clear reaction mixture was evaporated under reduced pres-
sure, the residue washed well with hexane and dried in vacuo to give **2** as orange flakes
(59 mg, 98%). ^{1}H NMR (CD$_2$Cl$_2$): 2.02 (s, 3 H, Me), 2.77 (s, 1 H, allyl C**H**^{Cl}), 2.97 (s, 1 H,
allyl C**H**^{Cl}), 3.65 (d, $^3J_{PH}$ = 10.2, 1 H, allyl C**H**^{P}), 4.45, 4.48 (2 × s, 1 H, CH of fc); 4.52 (dd,
J = 6.9 and 2.4, 1 H, allyl C**H**^{P}), 4.56 (s, 2 H, CH of fc), 4.59 (apparent qi, 2 H, CH of fc),
4.89, 4.92 (2 × s, 1 H, CH of fc); 6.87 (br s, 1 H, CO$_2$H), 7.37–7.57 (m, 10 H, PPh$_2$). ^{31}P{^{1}H}
NMR (CD$_2$Cl$_2$): 15.9 (s). IR (Nujol): ν(C=O) 1710 s, 1674 s; 1294 m, 1167 m, 1138 m, 1097 m,
1028 m, 836 m, 746 m, 696 s, 468–536 m, composite band. For C$_{27}$H$_{26}$ClFeO$_2$PPd calcu-
lated: 53.06% C, 4.29% H; found: 52.68% C, 4.29% H.

*Reaction of **1** with Kdpf.* Hdpf (83 mg, 0.20 mmol) and potassium *tert*-butoxide (23 mg,
0.21 mmol) were suspended in dichloromethane (8 ml) and the mixture was stirred at room
temperature. The solids rapidly and almost completely dissolved – but, within few minutes,
a fine yellow-orange precipitate separated (most likely Kdpf). After stirring for 30 min, a so-
lution of **1** (39.5 mg, 0.10 mmol) in dichloromethane (2 ml) was added to the formed salt,
causing an immediate dissolution of the precipitate and, shortly afterwards, precipitation of
a yellow solid. The mixture was stirred for another 20 h, the precipitate was filtered off,
washed with ethanol, water, ethanol and diethyl ether (2 × 1.5 ml each), and dried under
vacuum over phosphorus pentoxide to afford **3** as an ochre solid. Yield 85 mg. IR (Nujol):
3653 m, ca. 3325 br m, 3213 br w; ν(CO$_2$) 1612 s, 1588 s; 1182 m, 1166 m, 1099 m, 1029 m,
895 w, 834 m + sh, 798 m + sh, 751 m, 696 m, 629 m, 521 m, 507 s, 469 m. ESI (aceto-
nitrile–water 1:1), *m/z* (rel.%): 575 (100), 597 (28), 613 (19), 1178 (18). HR ESI(+)/MS calcu-
lated for C$_{27}$H$_{26}$FeO$_2$PPd ([Pd(η³-CH$_2$C(Me)CH$_2$)(dpf) + H]$^+$): 575.0055, found: 574.9881.
Experimentally determined isotopic peak distribution matches the calculated one.

rac-Chloro{[2-(diphenylphosphanyl-κP)ferrocen-1-yl]acetic acid}(η³-methallyl)palladium(II) (**4**).
Complex **1** (39.5 mg, 0.10 mmol) and *rac*-Hpfa (90 mg, 0.21 mmol) were dissolved in
dichloromethane (3 ml) and the solution was allowed to stand for 30 min. Then, it was
layered with hexane (ca. 10 ml) and the mixture allowed to crystallize by diffusion for sev-
eral days. The formed solid was filtered off, washed with diethyl ether and dried under vac-
uum to afford **4** (84 mg, 67%) as yellow-orange crystals. (Note: diethyl ether can be used for
crystallization instead of hexane without lowering the yield.) IR (Nujol): ν(C=O) 1761 w,
1727 vs, 1686 w; 1246 m, 1170 vs, 1098 m, 1049 m, 1029 m, 999 m, 923 m, 846 s, 833 s,
806 s, 742 s, 693 s, 651 m, 625 m, 519 vs, 492 vs, 471 s, 441 m. For C$_{28}$H$_{28}$ClFeO$_2$PPd calcu-
lated: 53.79% C, 4.51% H; found: 53.49% C, 4.43% H.

rac-{[2-(Diphenylphosphanyl)ferrocen-1-yl]acetato-κ²O,P}(η³-methallyl)palladium(II) *mono-
hydrate (**5**·H$_2$O).* The preparation was performed similarly to the synthesis of **3**. *rac*-Hpfa
(90 mg, 0.21 mmol) and potassium *tert*-butoxide (23 mg, 0.21 mmol) were dissolved in
dichloromethane (8 ml). The solids dissolved very quickly but a fine yellow precipitate sepa-
rated from the solution formed after few minutes (*rac*-Kpfa). After stirring for 30 min, a solu-
tion of **1** (39.5 mg, 0.10 mmol) in dichloromethane (2 ml) was introduced to the formed
salt and the resulting clear orange solution was stirred for another 20 h. Then, hexane
(20 ml) was added to precipitate KCl, the mixture was allowed to stand for 1 h and filtered.
The orange filtrate was evaporated to dryness and the residue redissolved in dichloro-

methane (3 ml). Addition of hexane (10 ml) and water (ca. 10 mg) followed by crystallization at –18 °C for several days gave **5**·H_2O as an orange crystalline solid, which was filtered off, washed with diethyl ether and dried under reduced pressure. Yield 105 mg (89 %). IR (Nujol): ν(OH) 3446 br, m, 3405 sh; $\nu(CO_2)$ 1608 vs, 1598 vs; 1185 s, 1097 s, 1073 m, 1034 m, 842 br s, 820 m, 752 s, 735 m, 715 m, 699 vs, 637 w, 590 br m, 525 vs, 500 vs, 484 w, 467 s, 451 w. For $C_{28}H_{27}ClFeO_2PPd$·H_2O·1/2CH_2Cl_2 calculated: 54.30% C, 4.75% H; found: 54.19% C, 4.75% H.

X-ray Crystallography

Single crystals suitable for X-ray diffraction analysis have been selected from the reaction batch (**4**: orange block, $0.20 \times 0.43 \times 0.45$ mm^3; **5**·H_2O: orange prism, $0.23 \times 0.23 \times 0.28$ mm^3) or obtained by recrystallization from dichloromethane–heptane (**2**: orange plate, $0.08 \times 0.17 \times 0.50$ mm^3). The crystals were mounted onto glass fibres with epoxy cement or wax and transferred to diffractometer.

The diffraction data for **2** were collected on an Enraf–Nonius CAD 4-MACH III four-circle diffractometer using graphite-monochromatized MoKα radiation (λ = 0.71073 Å) and θ–2θ scan. The cell parameters were determined by least-squares refinement from 25 automatically centered diffractions with $13 \le \theta \le 14°$. The absorption was neglected because the ψ-scan for selected diffractions showed no significant angular dependence for their intensities. The data were corrected for the Lorentz-polarization effects and for linear decay (three standard diffractions monitored every hour showed an intensity variation of only 2.8%).

Full-set diffraction data ($\pm h$, $\pm k$, $\pm l$) for **4** and **5**·H_2O were collected on a Nonius KappaCCD diffractometer equipped with Cryostream Cooler (Oxford Cryosystems) using graphite-monochromatized MoKα radiation (λ = 0.71073 Å) and analyzed with HKL program package[15]. The data for **4** and **5**·H_2O have been corrected for absorption by empirical methods included in diffactometer software (SORTAV routine[16]) and in Platon program[17], respectively.

The structures were solved by direct methods (SIR92 [18]) and refined by weighted full-matrix least squares on F^2 (SHELXL97 [19]). All non-hydrogen atoms were refined with anisotropic thermal motion parameters. For **2**, hydrogen atoms at the methylene groups of the methallyl ligand were identified on the difference electron density maps and isotropically refined. The carboxylic hydrogen atom, H(90), was located similarly and fixed in the position revealed by the difference electron density map. All other hydrogen atoms were included in calculated positions and assigned U_{iso}(H) = 1.2U_{eq}(C) (aromatic and methylene) or 1.5U_{eq}(C) (methyl). Hydrogen atoms in **4** and **5**·H_2O were treated analogously except that the hydrogen atoms at the carboxyl group in **4** and at the water molecule in **5**·H_2O were refined isotropically without any constraints applied.

Relevant crystallographic data for all compounds are given in Table IV. (Note: The final geometric calculations were carried out with a recent version of Platon program and may thus slightly differ from the values calculated with SHELXL97 program.) CCDC 278662 (**2**), 278663 (**4**), and 278664 (**5**·H_2O) 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).

Crystallographic data and structure refinement parameters for **2**, **4**, and **5**·H_2O

Parameter	**2**	**4**	**5**·H_2O
Formula	$C_{27}H_{26}ClFeO_2PPd$	$C_{28}H_{28}ClFeO_2PPd$	$C_{28}H_{29}FeO_3PPd$
M	611.15	625.17	606.73
Crystal system	triclinic	monoclinic	monoclinic
Space group	P-1 (No. 2)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
a, Å	9.5950(8)	14.9851(2)	8.8226(1)
b, Å	10.4363(9)	10.5251(1)	11.7837(1)
c, Å	13.771(1)	17.0709(2)	23.9582(2)
α, °	76.547(7)		
β, °	81.014(7)	108.1159(7)	100.4950(5)
γ, °	69.198(7)		
V, Å^3	1249.6(2)	2558.95(5)	2449.09(4)
Z	2	4	4
D, g ml^{-1}	1.624	1.623	1.646
T, °C	23(2)	–123(2)	–123(2)
μ(MoKα), mm^{-1}	1.493	1.460	1.421
T ^{a}	not corrected	0.690–0.753	0.610–0.655
θ_{max}, °	25.0	27.5	27.5
Diffractions total	4399	37212	44976
Unique/obsd^b diffrns	4399/3873	5852/5380	5621/5005
R_{int}, %^{c}	–	3.53	4.55
No. of parameters	316	328	332
R obsd diffrns, %^{d}	1.95	2.56	2.66
R, wR all data, %^{d}	2.71, 5.27	2.87, 6.58	3.30, 6.11
$\Delta\rho$, eÅ^{-3}	0.33, –0.37	0.60, –0.83	0.60, –0.88

^{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} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma\ w(F_o^2)^2]^{1/2}$.

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