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Chelating behaviour of a phosphinoalcohol leading to a stable alcohol palladium complex

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Dedicated to Professor H. Brunner on the occasion of his 65th birthday, with our best wishes and most sincere congratulations

Abstract

Using the enantiopure phosphinoalcohol ligand (P,OH) (**1**) [(P,OH) = [(1*S*),(2*S*),(4*R*)-1-OH-1-Me-2-PPh$_2$-4-C(Me)=CH$_2$-*c*-C$_6$H$_7$], the stable Pd(II) complexes [(dmba)Pd(*P*,OH)Cl] (**2**) (dmba = *o*-C$_6$H$_4$CH$_2$NMe$_2$), [(dmba)Pd(*P*,*O*H)]PF$_6$ (**3**) and [(dmba)Pd(*P*,*O*)] (**4**) have been prepared. Conductivity and NMR measurements showed that complex **2** gives rise to a solvent-dependent equilibrium in solution between the neutral and the cationic species [(dmba)Pd(*P*,OH)Cl] (**2a**) and [(dmba)Pd(*P*,*O*H)]Cl (**2b**), respectively. The crystal structures of **2b** and [(dmba)Pd(*P*,*O*H)]PF$_6$ (**3**) have been determined by X-ray diffraction. In the solid state, both cationic complexes display chelating behaviour for the P,OH ligand. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Synthesis; Chiral ligands; Ditopic ligands; Functional phosphines; Palladium; X-ray structures

1. Introduction

Palladium and platinum alkoxide complexes have aroused special interest because they offer a rich chemistry with versatile reactivity [1]. They undergo for instance insertion reactions of carbon monoxide, carbon dioxide and olefins into the metal–oxygen bond and are assumed to be intermediates in several catalytic and stoichiometric reactions [2]. The difficulties often encountered in isolating them are mainly due to their sensitivity towards β-hydride elimination reactions [1]. However, an appropriate choice of ligands has recently allowed the preparation of several palladium and platinum alkoxide complexes [1]. One possible approach in this context is the use of chelating P, O ligands [3].

In the course of current studies with phosphinoalcohols, we discovered the advantages of the easily accessible limonene-based ligand **1** [4]. The tertiary character of its alcohol function prevents β-hydride elimination and enabled us to obtain the stable palladium alkoxide **4**. It was prepared in a stepwise approach: first the phosphinoalcohol ligand **1** was introduced by coordination of the phosphine moiety to the metal centre, then the Pd–O bond is created by reaction with a base [3c–f]. The intermediate phosphinoalcohol palladium complex **2** could also be isolated. An interesting feature of this complex is the strong tendency for chelation displayed by the ligand which leads after dissociation of the chloride ion to the formation of a cationic complex in the solid state. This structure is partly retained in solution.

2. Results and discussion

2.1. Synthesis

Using a modified literature method we prepared the phosphinoalcohol ligand (1*S*)-*trans*-(+)-1-hydroxy-1-methyl-2-diphenylphosphino-4-isopropene-cyclohexane (**1**), (abbreviated P,OH in the following), which is derived from *trans*-(+)-limonene oxide [4]. Reaction of **1** with [(dmba)Pd(μ-Cl)]$_2$ (dmba = *o*-C$_6$H$_4$CH$_2$NMe$_2$) in the ratio 2:1 in dichloromethane at room temperature led to the formation of an air-stable complex **2a** in 93% yield (see Scheme 1).

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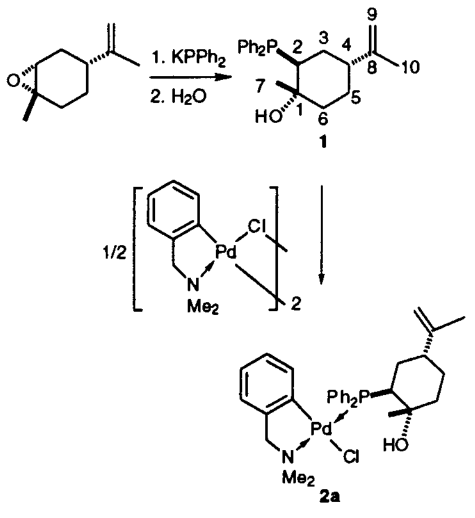
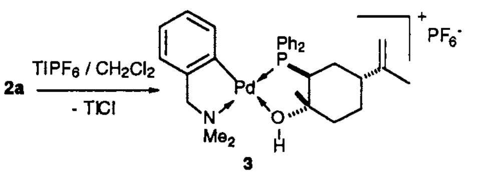


2a

Scheme 1.

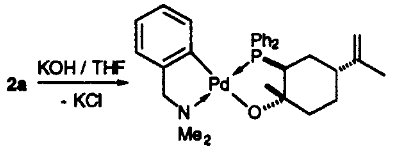
The related cationic complex [(dmba)Pd(*P*,*O*H)]PF_6 (**3**) was readily prepared in 80% yield by reaction of **2a** with $TlPF_6$ (Eq. (1)). This complex forms colourless needles from dichloromethane–*n*-hexane.



3

(1)

The neutral complex [(dmba)Pd(*P*,*O*)] (**4**) was obtained in 69% yield by treatment of **2a** with potassium hydride. The deprotonated P,O ligand now acts as a three-electron donor chelate (Eq. (2)).



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(2)

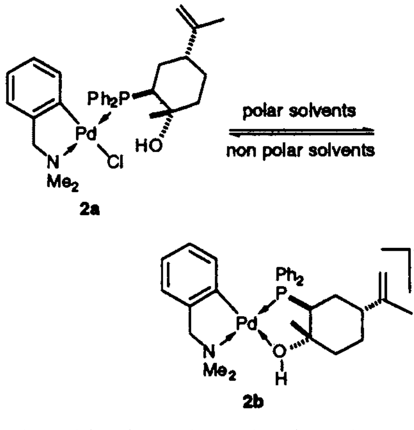
Table 1
Selected $^{31}P\{^{1}H\}$- and ^{13}C-NMR data of **2**, **3** and **4** (δ in ppm)

	$^{31}P\{^{1}H\}$		^{13}C C(1)	C(2)	C(7)
1	$CDCl_3$	11.2	72.9	42.7 (d, 13.8 Hz)	29.4
2	$CDCl_3$	49.5	79.0	48.5 (d, 24.2 Hz)	22.2
	$CDCl_3$ [a]	49.3			
	C_6D_6	43.8	77.3	48.2 (d, 24.4 Hz)	22.0
	CD_3OD	48.7	80.7	not found	22.8
3	$CDCl_3$	48.7	80.1	48.3 (d, 24.4 Hz)	22.0
	C_6D_6	48.5			
4	$CDCl_3$	58.8	75.5	54.6 (d, 13.5 Hz)	26.9
	C_6D_6	59.4	76.2	57.6 (d, 25.5 Hz)	27.6

[a] At −60°C.

2.2. NMR investigations

In order to obtain information about the structure of **2**, a comparison of the $^{31}P\{^{1}H\}$-NMR data of **2**, **3** and **4** recorded in different solvents was most revealing (Table 1). The signal for the neutral alkoxide complex **4** appears in $CDCl_3$ at δ 58.8 ppm. No significant shift is observed in C_6D_6 (δ 59.4 ppm). The signal for the cationic **3** appears at δ 48.7 ppm in $CDCl_3$ and at δ 48.5 ppm in C_6D_6. However, the situation changes dramatically for **2**: whereas in the polar solvents $CDCl_3$ or CD_3OD the resonance appears at δ 49.5 ppm, a highfield shift of about 6 ppm is observed in C_6D_6. The similarity of the chemical shifts between **2** in polar solvents and **3** indicates that chloride dissociation readily occurs in such a medium. This situation corresponds to the solid state structure determined for **2b** (vide infra). Taking into account the high field shift of the signals on going from **4**, where the oxygen is strongly covalently bonded to palladium, to **3** (and **2** in polar solvents), where the oxygen is less strongly bonded, the further highfield shift for **2** in apolar C_6D_6 suggests a structure with less strong O → Pd or no oxygen bonding at all. We assume an equilibrium between the neutral and the cationic form for **2** in solution (Eq. (3)). The $^{31}P\{^{1}H\}$-NMR shifts are consistent with those observed for the related neutral and cationic ketophosphine complexes [(dmba)PdCl{$Ph_2PCH_2C(O)Ph$}] (δ 29.5 ppm) and [(dmba)Pd{$Ph_2PCH_2C(O)Ph$}]CF_3SO_3 (δ 34.8 ppm), respectively [5]. Clearly, polar solvents lead **1** to bind in a chelating mode by dissociation of the palladium–chloride bond and form **2b** is stabilized whereas in non-polar solvents, the neutral form **2a** of this complex is preferred, and the phosphinoalcohol ligand is only bound via the phosphorus atom and the chloride ligand remains bonded to the palladium.



(3)

With the objective of confirming the equilibrium of Eq. (3) using ^{13}C- and ^{1}H-NMR spectroscopy, we observed a shift of the C(1) resonance to lower field when compared to the free ligand (Tables 1 and 2). But all signals of **2** and **3** are very close to each other, and we were unable to detect significant differences between

Table 2
Selected ^{1}H-NMR data of **2**, **3** and **4** (δ in ppm)

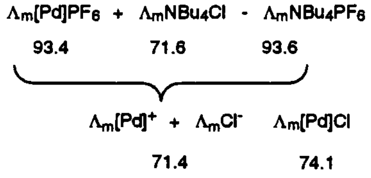
		Me	Me	NMe$_2$	NCH$_2$	C(9)H*H*	C(9)*H*H	OH
1	CDCl$_3$	1.09	1.42			4.57	4.62	n.f.
2	CDCl$_3$	1.13	1.54	3.01 (d, 2.2 Hz), 3.11 (d, 2.5 Hz)	3.96	4.66	4.97	9.62
	C$_6$D$_6$	0.86	1.53	2.60	3.04 (dd, 2.5, 13.8 Hz), 3.72 (d, 13.5 Hz)	5.02	5.16	9.49(br)
	C$_6$D$_6$ [a]	0.89	1.52	2.60, 2.67	3.09 (dd, 2.9, 13.7 Hz), 3.68 (d, 13.7 Hz)	4.98	5.14	9.72(br)
	CD$_3$OD	1.17	1.53	2.85 (d, 2.1 Hz), 2.91 (d, 2.0 Hz)	4.01 (d, 14.2 Hz), 4.15 (d, 14.1 Hz)	4.64	4.94	n.f.
3	CDCl$_3$	1.14	1.51	2.92	3.97	4.61	4.95	5.01
	C$_6$D$_6$	0.96	1.46	2.42 (d, 2.3 Hz), 2.61 (d, 2.5 Hz)	3.24	4.65	5.12	5.90
4	CDCl$_3$	1.12	1.62	2.90 (d, 2.5 Hz), 2.94 (d, 1.3 Hz)	3.85 (dd, 3.0, 13.8 Hz), 4.1 (d, 14.1 Hz)	4.68	4.84	
	C$_6$D$_6$	1.26	1.53	2.73 (d, 2.2 Hz), 2.74 (d, 2.2 Hz)	3.44 (d, 15 Hz), 3.61 (d, 12 Hz)	4.84	4.96	
	C$_6$D$_6$ [a]	1.29	1.52	2.71 (d, 2.2 Hz), 2.75 (d, 1.8 Hz)	3.55 (d, 1.8 Hz)	4.84	4.92	

[a] At higher concentration (20 mg dissolved in 1 ml benzene).

polar and non-polar solvents, neither for C(1) nor for the aromatic *ipso* carbon which is in *trans* position to oxygen when the alcohol moiety coordinates to palladium. An interesting feature was noticed in the ^{1}H-NMR spectrum in benzene: depending on the concentration of **2** or **4** we observe differences for the signals of N*Me*$_2$ and NC*H*$_2$ (a dependence on the concentration of **3** in benzene could not be studied owing to the poor solubility of this complex). Whereas at low concentration of **2** the N*Me*$_2$ signal appears as a singlet, at higher concentration two singlets were observed. Concentrating a benzene solution of **4** led to a slightly larger splitting for the N*Me*$_2$ group, while in contrast, the NC*H*$_2$ signal changes from two doublets to only one doublet (we also found in the ^{31}P-NMR spectra a slight dependence on the concentration: at higher concentration the signal shifts up to 1.5 ppm to higher field). These observations point to the occurrence of intermolecular phenomena which have not been further investigated.

2.3. Conductivity investigations

Conductivity measurements were carried out in methanol at room temperature. Complex **2** behaves like a 1:1 electrolyte with a molar conductivity of $\Lambda_m = 74.1$ S cm^2 mol^{-1}, which is similar to the value found by Pringle et al. for the palladium complex [PdCl$_2$(PPh$_2$CH$_2$CMe$_2$OH)$_2$] ($\Lambda_m = 78$ S cm^2 mol^{-1}) [3f]. Since we were not only interested in the value of the molar conductivity Λ_m but also in the degree of dissociation of **2** in methanol, we compared its value Λ_m[Pd]Cl with the sum of Λ_m[Pd$^+$] and Λ_mCl$^-$. The latter were determined by subtracting the values Λ_m of complexes fully dissociated into ions (see Scheme 2). Within experimental error, these values are almost the same (Λ_m[Pd]Cl = 74.1 S cm^2 mol^{-1}, Λ_m[(Pd$^+$) + (Cl$^-$)] = 71.4 S cm^2 mol^{-1}). This indicates that **2** is completely dissociated in methanol and is present as **2b**.



Scheme 2. All values Λ_m in S cm^2 mol^{-1}.

2.4. Crystal structure of *2b* and *3*

Crystals of **2b** suitable for X-ray determination were obtained from dichloromethane–*n*-hexane. They contain one molecule of dichloromethane per formula unit. In the solid state, a cationic palladium complex is separated from the chloride anion (Fig. 1). The ligand arrangement around the metal is square planar. The palladium is chelated by the dmba moiety and coordination of the phosphorus occurs in *cis* position to the aryl group, in agreement with the antisymbiotic effect. The coordination environment around the palladium centre is completed by the oxygen atom of the P,OH ligand. Although the proton of the hydroxy group could not be located, the Pd–O bond distance (2.174(3) Å) clearly indicates a dative interaction. In the related complexes with a negatively charged oxygen donor atom [(dmba)Pd{Ph$_2$PCH$_2$C(O)O}], [(dmba)-Pd{Ph$_2$PCH···C(···O)OEt}] and [(dmba)-Pd[Ph$_2$PC{C(O)NHPh}C(Ph)O], the Pd–O bond distance is shorter than in **2b** (2.105(3), 2.117(5)

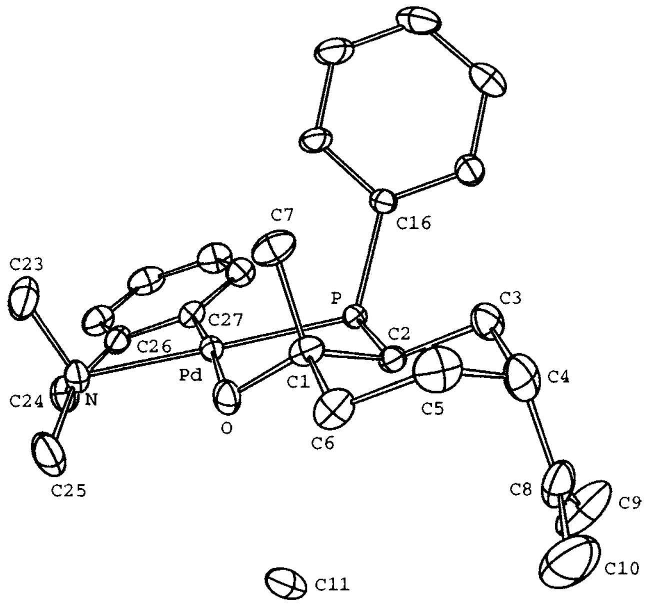


Fig. 1. ORTEP view of the molecular structure of [(dmba)Pd(*P*,*O*H)]Cl (**2b**). The second phenyl substituent at P is not shown for clarity. Thermal ellipsoids are drawn at the 30% probability level.

Table 3
Selected bond lengths (Å) and angles (°) for **2b** with estimated standard deviations in parentheses

Pd–P	2.241(1)	P–Pd–O	84.5(1)
Pd–O	2.174(3)	P–Pd–C(27)	99.7(2)
Pd–N	2.115(5)	O–Pd–N	93.3(2)
Pd–C(27)	1.984(5)	N–Pd–C(27)	82.6(2)
Pd–Cl	3.853	Pd–O–Cl	97.4
O–Cl	2.913	P–O–Cl	92.7

and 2.096(3) Å, respectively) [6]. The same holds true for the cationic palladium alcohol complex $[Me_2NCH_2CH_2NMe_2)Pd(o\text{-}C_6H_4CH_2CH_2OH)]NO_3$ (Pd–O 2.076(4) Å) [7], and even for the neutral palladium alcohol compounds $[Pd\{OC(NMe_2)CH_2(Me_2)OH\}Cl(NO_2)]$, $[PdNCH_2CH_2NH_2)$ $\{cyclo\text{-}CHCH_2C(O)HC(Me)HCH_2N(CH_2CH_2OH)\}]$ and $[Pd\{PPh_2CH_2S(O)Me\}Cl_2(MeOH)]$ (Pd–O 2.059(4), 2.045(6), 2.148(2) Å) [8]. The bond distances and angles around the dmba moiety and around the phosphorus atom are all in the expected range (Table 3). The chloride ion is located below the palladium coordination plane, rather close and almost at the vertical of the oxygen atom (bond angles Pd–O–Cl and P–O–Cl of 97.4 and 92.7°, respectively). Whereas the value of the Pd–Cl distance (3.853 Å) excludes any interaction, the O–Cl distance of 2.913 Å is indicative of a short hydrogen bridge (with an estimated O–H bond length of 0.9 Å, the H–Cl bond distance is calculated to be ca. 2.2–2.4 Å, which is less than the H–Cl bond distances typically considered as short ≤ 2.52 Å) [9]. Interactions with the dichloromethane molecule are not observed. Several solid-state structures of palladium complexes with phosphino alcohols have been reported. Two examples contain the 2-diphenylphosphino cyclohexanol, a ligand very similar to **1**. However, in all these structures, the ligand coordinates only in a monodentate fashion via the phosphorus atom and no dissociation of the chloride coligand occurs [10]. This indicates that very slight differences in electronic and steric properties may be sufficient to control the mono- or bidentate coordination mode of the phosphino alcohols.

In the crystal structure of **3**, determined for comparative purposes, we observe the expected ligand arrangement with the chelating P,OH ligand (Fig. 2). Like in the crystal structure of **2b** there is a molecule of dichloromethane of solvation in the unit cell. The proton of the hydroxy group could not be located. All

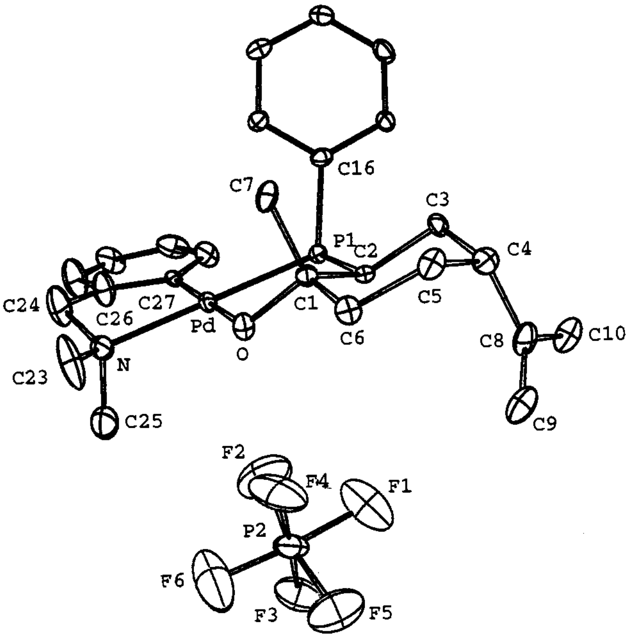


Fig. 2. ORTEP view of the molecular structure of [(dmba)Pd(*P*,*O*H)]PF_6 (**3**). The second phenyl substituent at P is not shown for clarity. Thermal ellipsoids are drawn at the 30% probability level.

Table 4
Selected bond lengths (Å) and angles (°) for **3** with estimated standard deviations in parentheses

Pd–P	2.251(2)	O–F(1)	3.060
Pd–O	2.206(5)	O–F(2)	2.977
Pd–N	2.119(7)	P–Pd–O	84.6(1)
Pd–C(13)	1.968(7)	P–Pd–C(27)	97.6(2)
Pd–F(1)	3.406	O–Pd–N	95.7(2)
Pd–F(2)	4.52	N–Pd–C(27)	82.1(3)

bond distances and angles are similar to those in **2b** (Table 4), except for the longer Pd–O bond distance (2.206(5) Å). This lengthening may be due to the presence of stronger hydrogen bonding: a bifurcated H-bonding occurs between the OH proton and two fluor atoms of the PF_6 anion (O–F: 2.977 and 3.060 Å).

3. Conclusion

We have synthesized the very stable, chiral palladium phosphinoalcohol complex **2** whose solid-state structure shows that the ligand coordinates in a chelating mode by displacement of a chloride ligand. The bonding behaviour of phosphinoalcohols depends critically on small steric and electronic factors, as evidenced by the fact that ligands similar to **1** gave palladium complexes with only monodentate coordination via phosphorus. In solution, complex **2** gives rise to an equilibrium between the cationic (polar solvents) and the neutral species (apolar solvents). Its deprotonation afforded the neutral complex [(dmba)Pd(*P*,*O*)] (**4**) with a chiral, chelating phenolate ligand. Nickel phosphino phenolates have been recently shown to catalyse the oligomerization of ethylene into linear α-olefins [11] and early transition metal complexes with chelating phenolate ligand continue to attract attention as catalyst precursors in α-olefin polymerization [12].

4. Experimental

4.1. General procedures

All manipulations were carried out under an atmosphere of dry oxygen-free nitrogen with standard Schlenk techniques. Solvents were dried and degassed by refluxing over suitable reagents before use.

4.2. Synthesis of the ligand P,OH (1)

The literature method [4] was modified. To a mixture of (+) *cis*/*trans* limonene oxides (8.6 ml, 26.2 mmol *trans* oxide) in 30 ml THF at −80°C was slowly added a 0.5 M solution of $KPPh_2$ in THF (52.4 ml, 26.2 mmol). After the mixture was stirred for 2 h, it was slowly warmed up to room temperature (r.t.). Addition of 60 ml of a degassed NH_4Cl solution (10%) in water was followed by separation of the layers and extraction of the water phase with THF (2 × 20 ml). The combined THF extracts were dried over sodium sulfate. The filtered colourless solution was concentrated to 25 ml and *n*-pentane (150 ml) was added. At −80°C, 6.8 g (20.1 mmol, 77%) of the white product crystallized. Anal. Calc. for $C_{22}H_{27}OP$: C, 78.08; H, 8.04. Found: C, 77.6; H, 8.3%.

4.3. Synthesis of complex 2

To a solution of **1** (0.95 g, 2.8 mmol) in dichloromethane (20 ml) [(dmba)Pd(μ-Cl)]$_2$ (0.78 g, 1.4 mmol) was added at room temperature. After the solution was stirred for 30 min, it was filtered and concentrated to 8 ml and then *n*-hexane (50 ml) was added. At −30°C 1.60 g (2.6 mmol, 93%) of the off-white product crystallized. Anal. Calc. for $C_{31}H_{39}ClNOPPd$: C, 60.59; H, 6.40. Found: C, 60.96; H, 6.55%.

4.4. Synthesis of complex 3

Solid $TlPF_6$ (0.41 g, 1.2 mmol) was added to a solution of **2** (0.36 g, 0.59 mmol) in dichloromethane (15 ml). After the mixture was stirred overnight, it was filtered and concentrated to 3 ml and then *n*-hexane (20 ml) was added. At −30°C, 0.34 g (0.47 mmol, 80%) of the white product crystallized. Anal. Calc. for $C_{31}H_{39}F_6NOP_2Pd$: C, 51.43; H, 5.43. Found: C, 51.03; H, 5.90%.

4.5. Synthesis of complex 4

To a solution of **2** (0.57 g, 0.93 mmol) in THF (20 ml) potassium hydride (0.2 g, 5 mmol) was added at 0°C. After the mixture was stirred overnight at r.t, it was filtered and concentrated to 5 ml and then *n*-hexane (30 ml) was added. At −30°C, 0.37 g (0.64 mmol, 69%) of the beige product crystallized. Anal. Calc. for $C_{31}H_{38}NOPPd$: C, 64.41; H, 6.63; N, 2.42. Found: C, 64.42; H, 6.73; N, 2.46%.

4.6. X-ray crystal structure determinations of 2b and 3

The X-ray data for both structures were collected on a Kappa CCD diffractometer. The structures were solved using direct methods and refined against $|F|$. Absorption corrections were computed from the psi scans of four reflections. For all computations the Nonius MOLEN package was used [13]. The hydrogen atoms were introduced as fixed contributors ((d_{C-H} = 0.95 Å, $B_H = 1.3B_{equiv}(C)$ Å^2).

Crystal data for **2b**. Colourless crystals from dichloromethane–*n*-hexane. Crystal data: $C_{31}H_{38}ClNOPPd\cdot CH_2Cl_2$, $M = 698.41$; orthorhombic; space group $P2_12_12_1$; $a = 9.3780(3)$, $b = 16.4500(6)$, $c = 21.4210(4)$ Å, $U = 3304.6(3)$ Å^3, $Z = 4$, $D_{calc} = 1.40$ g cm^{-3}, $T = 294$ K, $\mu(\lambda(\text{Mo}-K_\alpha) = 0.71073$ Å$) = 0.877$ mm^{-1}. Number of data with $I > 3\sigma(I)$ 2986; weighting scheme $4F_o^2/(\sigma^2(F_o^2) + 0.0004F_o^4)$; number of variables 352; $R = 0.030$, $R_w = 0.034$.

Crystal data for **3**. Colourless crystals from dichloromethane–*n*-hexane. Crystal data: $C_{31}H_{38}F_6NOP_2Pd\cdot CH_2Cl_2$, $M = 807.93$; orthorhombic; space group $P2_12_12_1$; $a = 9.3752(4)$, $b = 18.5773(8)$, $c =$

20.3704(8) Å, $U = 3547.8(4)$ Å^3, $Z = 4$, $D_{\text{calc}} = 1.51$ g cm^{-3}, $T = 173$ K, $\mu(\lambda(\text{Mo–K}_\alpha) = 0.71073$ Å$) = 0.822$ mm^{-1}. Number of data with $I > 3\sigma(I)$ 4194; weighting scheme $4F_o^2/(\sigma^2(F_o^2) + 0.0064F_o^4)$; number of variables 406; $R = 0.050$, $R_w = 0.064$.

5. Supplementary material

Crystallographic data for the structures of **2b** and **3** have been deposited in cif format with the Cambridge Crystallographic Data Centre, CCDC Nos 148987 and 148988, respectively. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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