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Novel unsymmetrical PCP′ pincer ligands and their palladium(II) complexes

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Abstract

Synthetic routes towards novel PCP′ pincer ligands were devised. Ligand 1-($Pr^i_2POCH_2$)-3-($Bu^t_2PCH_2$)(C_6H_4) is prepared in a three step synthesis from 1,3-benzenedimethanol and 1-(Pr^i_2PO)-3-($Bu^t_2PCH_2$)(C_6H_4) is accessible in three steps from 3-hydroxybenzylalcohol. Both their palladium(II) complexes are prepared in good yields but are distinctly different since [PdCl{(C_6H_3)($OPPr^i_2$)-2-($CH_2PBu^t_2$)-6}] possesses two five-membered palladacycles, whereas [PdCl{(C_6H_3)($CH_2PBu^t_2$)-2-($CH_2OPPr^i_2$)-6}] is unusual for a pincer complex in that it contains both five- and six-membered palladacycles. Both compounds also represent the first examples of pincer complexes where one donor is a phosphinite and the other is a phosphine. The X-ray structures of these complexes were solved and are discussed. The data reveal that an increase in the metallacycle ring-size leads to changes in bond lengths, but more importantly to significant increases in the bond angles.

Keywords: Pincer; Phosphorus; Palladium; Unsymmetrical; Complexes

1. Introduction

A wide variety of PCP pincer ligands have been prepared in the last 30 years and are based on the generic structure shown in Fig. 1. Several reviews on pincer complexes and their chemistry have been published [1].

Steric and electronic properties of PCP pincer ligands can be modified by varying the substituents on the phosphorus (R^1 and R^2), the atom-linkage X and Y between phosphorus and aryl-ring carbon, and the ring-substituent R^3. Consequently, many examples of phosphines [2] ($X = Y = CH_2$, $R^1 = R^2 =$ alkyl or aryl), phosphinites [3] ($X = Y = O$, $R^1 = R^2 =$ alkyl or aryl) and phosphites [4] ($X = Y = O$, $R^1 = R^2 =$ O-alkyl or O-aryl), as well as ligands where $R^3 \neq H$ [5], have been synthesised. However, to the best of our knowledge there are no synthetic procedures available for PCP′ pincer ligands where $R^1 \neq R^2$ and/or $X \neq Y$. Such ligands are however of great interest since this would allow greater control over steric and electronic properties and may, for example, influence the activity of complexes in homogeneous catalysis. Many unsymmetrical diphosphines are known [6] and some of their complexes have proven to be valuable in homogeneous catalysis [6g,6h].

We have now developed such ligands where $R^1 \neq R^2$ and $X \neq Y$ and prepared their palladium(II) complexes. In this article we would like to describe the synthesis of 1-($Pr^i_2POCH_2$)-3-($Bu^t_2PCH_2$)(C_6H_4) and 1-(Pr^i_2PO)-3-($Bu^t_2PCH_2$)(C_6H_4), as well as [PdCl{(C_6H_3)($CH_2PBu^t_2$)-2-($CH_2OPPr^i_2$)-6}] and [PdCl{(C_6H_3)($OPPr^i_2$)-2-($CH_2PBu^t_2$)-6}]. The X-ray crystallographic structures for both complexes are described and compared.

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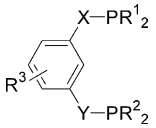


Fig. 1. Design of PCP pincer ligands.

2. Results and discussion

2.1. Ligand and complex synthesis

Mixed phosphino–phosphinito pincer ligand **3** was synthesised via a three step synthesis from 3-hydroxybenzylalcohol **1** (Scheme 1). Reaction of **1** with PBr_3 gives 3-hydroxybenzylbromide according to a published procedure [7], which after reaction with $HPBu^t_2$ in acetone leads to compound **2** in quantitative yield. Addition of $ClPPr^i_2$ in THF in the presence of DMAP yields the air-sensitive pincer ligand **3** in 81% yield. Refluxing a suspension of $[PdCl_2(cod)]$ and ligand **3** in toluene furnishes complex **4** in 44% yield as a pale yellow solid. The $^{31}P\{^1H\}$ spectrum of **4** is characterised by a large *trans*-coupling between the inequivalent phosphorus nuclei with $^2J(P,P')$ 429 Hz.

Complex **4** formed suitable crystals for X-ray diffraction by slow diffusion of pentane into a saturated solution of **4** in CH_2Cl_2. The molecular structure is shown in Fig. 2.

The bond lengths are within the typical range. Note that Pd(1)–P(1) is slightly longer than Pd(1)–P(2) [2.3198(6) Å vs. 2.2495(7) Å]. The structure is distorted square-planar with the five-membered palladacycles showing two envelope conformations.

1,3-Benzenedimethanol **5** is a suitable starting material for the synthesis of unsymmetrical ligand **7** and complex **8** (Scheme 2). Reaction of **5** with one equivalent of $SOCl_2$ in the presence of one equivalent pyridine gives 1-$(HOCH_2)$-3-$(ClCH_2)(C_6H_4)$ in 44% yield. However, this compound is unreactive towards $HPBu^t_2$ in acetone under reflux. Addition of NaI facilitates nucleophilic attack of the secondary phosphine furnishing **6** (89% yield) after addition of NEt_3. Reaction of $ClPPr^i_2$ in THF in the presence of DMAP yields the air- and moisture-sensitive unsymmetrical pincer ligand **7** in 56% yield. Complex **8** is formed from the reaction of $[PdCl_2(cod)]$ with **7** in refluxing toluene (72% yield). Again, two doublets with a typical large coupling of $^2J(P,P')$ 388 Hz are observed for *trans*-co-ordinated phosphorus atoms.

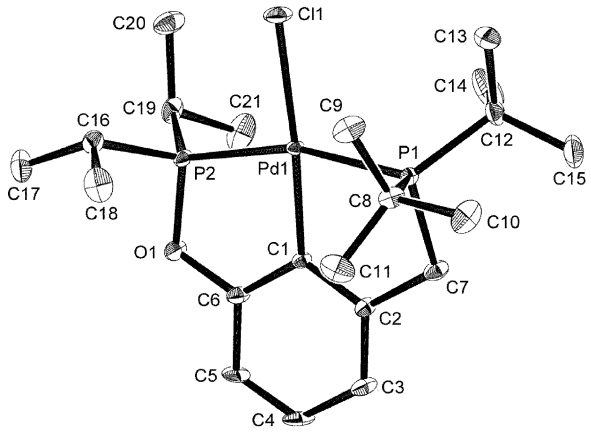


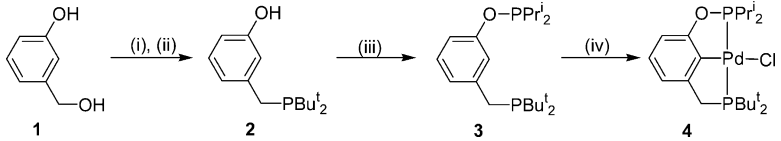
Fig. 2. Displacement ellipsoid plot (50% probability level) of **4**. Hydrogen atoms have been omitted for clarity. Pertinent bond lengths (Å) and angles (°): Pd(1)–Cl(1) 2.3938(6); Pd(1)–P(1) 2.3198(6); Pd(1)–P(2) 2.2495(7); Pd(1)–C(1) 2.008(2); Cl(1)–Pd(1)–P(1) 101.17(2); Cl(1)–Pd(1)–P(2) 95.16(2); Cl(1)–Pd(1)–C(1) 175.82(7); P(1)–Pd(1)–P(2) 163.03(2); P(1)–Pd(1)–C(1) 82.60(7); P(2)–Pd(1)–C(1) 80.95(7).

Compound **8** is unusual in that it contains both five- and six-membered metallacycles. 'Classical' pincer complexes such as **4** possess two five-membered metallacycles. We recently reported on the synthesis of $[PdCl\{(C_6H_3)(OPPr^i_2)$-2-$(CH_2OPPr^i_2)-6\}]$, the first pincer complex containing both five- and six-membered metallacycles [8]. Venanzi et al. synthesised $[MBr\{(C_6H_3)((CH_2)_2PPh_2)_2$-2,6$\}]$ (M = Pd, Pt), the only example of a PCP pincer complex with two six-membered metallacycles [9]. Complexes **4** and **8** are both stable to heat, air and moisture in the solid state, as well as in solution. No ligand dissociation is observed in solution at room temperature, as well as up to 180 °C.

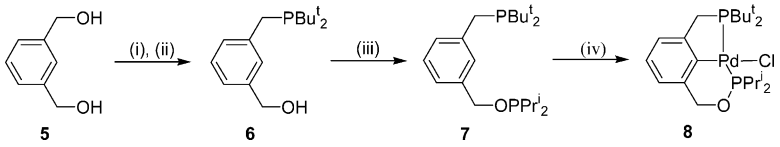
The crystal structure of complex **8** is shown in Fig. 3.

All bond lengths are within the typical range. Pd(1)–P(1) is slightly longer than Pd(1)–P(2) (2.3123(9) vs. 2.282(1) Å). Increasing the ring-size of one of the palladacycles in **8**, compared to **4**, leads to a lengthening of Pd(1)–P(2) with 2.282(1) Å for **8** and 2.2495(7) for **4**, whilst Pd(1)–P(1) does not change in both complexes (2.3198(6) for **4** and 2.3123(9) Å for **8**). The distorted square-planar structure shows the five-membered metallacycle in the expected distorted envelope conformation, whereas the six-membered metallacycle reveals a boat-conformation.

Most notably, when comparing the data of complex **4** with complex **8**, increasing the ring-size of one of the



Scheme 1. Reagents and conditions: (i) PBr_3, $CHCl_3$; (ii) $HPBu^t_2$, acetone, reflux, then NEt_3, Et_2O; (iii) $ClPPr^i_2$, DMAP, THF, rt; (iv) $[PdCl_2(cod)]$, toluene, reflux.



Scheme 2. Reagents and conditions: (i) one equivalent $SOCl_2$, one equivalent pyridine, CH_2Cl_2; (ii) $HPBu^t_2$, NaI, acetone, reflux, then NEt_3, Et_2O; (iii) $ClPPr^i_2$, DMAP, THF, rt; (iv) $[PdCl_2(cod)]$, toluene, reflux.

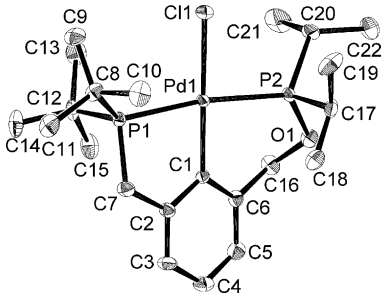


Fig. 3. Displacement ellipsoid plot (50% probability level) of **8**. Hydrogen atoms have been omitted for clarity. Pertinent bond lengths (Å) and angles (°): Pd(1)–Cl(1) 2.396(1); Pd(1)–P(1) 2.3123(9); Pd(1)–P(2) 2.282(1); Pd(1)–C(1) 2.043(4); Cl(1)–Pd(1)–P(1) 97.40(4); Cl(1)–Pd(1)–P(2) 89.83(4); Cl(1)–Pd(1)–C(1) 177.7(1); P(1)–Pd(1)–P(2) 171.04(4); P(1)–Pd(1)–C(1) 82.5(1); P(2)–Pd(1)–C(1) 90.1(1).

metallacycles of these two related pincer complexes leads to a 'relaxation' of the structure. For example, the P(1)–Pd(1)–P(2) angle increases significantly from 163.03(2)° in **4** to 171.04(4)° in **8**; the Cl(1)–Pd(1)–P(2) angle decreases from 95.16(2)° in **4** to 89.83(4)° in **8**, and the P(2)–Pd(1)–C(1) angle of **4** increases from 80.95(7) to 90.1(1)° in **8** (Table 1).

3. Conclusion

In conclusion, we have prepared the first examples of mixed phosphino–phosphinito pincer ligands. A series of palladium(II) complexes derived from these ligands were prepared. Both structures are related by virtue of one additional methylene-group in **8** compared to **4**. This has important structural consequences, leading to a significant increase in bond angles in **8** compared to **4**. The synthetic methodologies described in this article will be useful in expanding the family of pincer complexes. For example, one can envisage structures with only one chiral side-arm.

4. Experimental

4.1. General procedure

All manipulations were carried out using standard Schlenk procedures under nitrogen. Solvents (CH_2Cl_2, toluene, THF, Et_2O) were freshly distilled from either CaH_2 or K/benzophenone under nitrogen. 3-Hydroxybenzylalcohol, 1,3-benzenedimethanol, 4-dimethylaminopyridine DMAP, chlorodiisopropylphosphine, di-*tert*-butylphosphine and Py were purchased from Aldrich and used without further purification. Silica gel (100–200 mesh), alumina, celite and magnesium sulfate were purchased from Fisher Scientific. $[PdCl_2(cod)]$ was prepared according to a previously published method [10].

^1H-, $^{13}C\{^1H\}$- and $^{31}P\{^1H\}$-NMR spectra were recorded on a Varian Unity Inova 300 Spectrometer at ambient temperature of the probe using the deuterated solvent to provide the field/frequency lock. Chemical shifts are reported in ppm relative to high frequency of Me_4Si for ^1H and $^{13}C\{^1H\}$ and relative to high frequency of 85% H_3PO_4 for $^{31}P\{^1H\}$—Elemental analysis were performed by Oneida Research Services.

Table 1
Crystallographic data

Compound	**4**	**8**
Empirical formula	$C_{21}H_{37}ClOP_2Pd$	$C_{22}H_{39}ClOP_2Pd$
M	509.32	523.35
T (K)	200	200
Colour	Yellow	yellow
Crystal system	Monoclinic	Orthorhombic
Space group [a]	$P2_1/n$	$P2_12_12_1$
a (Å)	15.1500(1)	11.2560(2)
b (Å)	10.8770(2)	14.0230(2)
c (Å)	15.9130(3)	16.1210(3)
$\alpha = \gamma$ (°)	90	90
β (°)	112.587(1)	90
U (Å^3)	2421.11(7)	2544.59(7)
Z	4	4
μ Mo–K$_\alpha$ (cm^{-1})	1.017	0.970
Crystal dimensions (mm)	0.400 × 0.350 × 0.250	0.350 × 0.300 × 0.250
θ Range (°)	12.6–27.9	12.6–27.9
Data/restraints/parameters	3862/0/235	3361/0/244
Reflections observed	3977	3399
Final R_2 and wR_2 indices [b]	0.0297, 0.0723	0.0321, 0.0656
Conventional R index $[F^2 > 3\sigma(F^2)]$ [b]	0.0297	0.0321
Reflections with $F^2 > 3\sigma(F^2)$	3862	3361
Goodness-of-fit	1.056	1.063

[a] A chirality test of the crystal of compound **8** was not performed.
[b] $w = 1/[\sigma^2(F_o) + 0.0856(F_o)^2]$.

4.1.1. Ligand and complex synthesis

4.1.1.1. 1-(HO)-3-($Bu^t_2PCH_2$)(C_6H_4) (**2**). $HPBu^t_2$ (0.749 g, 0.95 ml, 5.12 mmol) was added dropwise to a stirred solution of 1-(HO)-3-($BrCH_2$)(C_6H_4) [7] (0.953 g, 5.12 mmol) in degassed acetone (40 ml). The mixture was heated to reflux for 6 h and then cooled to room temperature (r.t.); the solvent was removed, the colorless residue washed with Et_2O and dried in vacuum. It was then suspended in Et_2O and NEt_3 (0.758 g, 1.05 ml, 7.5 mmol) was added dropwise. After stirring for 30 min the suspension was filtered through alumina and the filtrate was concentrated in vacuum to give **2** (1.35 g, 5.07 mmol, 99%) as a clear oil. ^{1}H-NMR (300 MHz, CD_2Cl_2): $\delta = 1.15$ (d, $J = 10.8$ Hz, 18H, $C(CH_3)_3$), 2.82 (s, 2H, CH_2P), 6.59–7.16 (m, 4H, Ar*H*). $^{13}C\{^1H\}$-NMR (75 MHz, CD_2Cl_2): $\delta = 28.5$ (d, $J = 23$ Hz), 29.6 (d, $J = 13$ Hz), 31.7 (d, $J = 21$ Hz), 112.7, 116.8 (d, $J = 9$ Hz), 121.6 (d, $J = 8$ Hz), 129.2, 143.6 (d, $J = 13$ Hz), 156.1. $^{31}P\{^1H\}$-NMR (121 MHz, CD_2Cl_2): $\delta =$ 35.4.

4.1.1.2. 1-(Pr^i_2PO)-3-($Bu^t_2PCH_2$)(C_6H_4) (**3**). $ClPPr^i_2$ (0.153 g, 0.160 ml, 1 mmol) was added dropwise to a stirred solution of **2** (0.252 g, 1 mmol) and DMAP (0.122 g, 1 mmol) in THF (10 ml) at r.t. A precipitate formed immediately and the mixture was stirred overnight. The solvent was removed in vacuum and the residue extracted repeatedly with toluene. The toluene extracts were filtered over celite and the filtrate was concentrated in vacuum to give **3** (0.275 g, 0.81 mmol, 81%) as an oil. ^{1}H-NMR (300 MHz, CD_2Cl_2): $\delta = 1.02$ (d, $J = 10.8$ Hz, 18H, $C(CH_3)_3$), 1.78–1.83 (m, 2H, $CH(CH_3)_2$), 2.71 (d, $J = 2.7$ Hz, 2H, CH_2P), 6.77–7.15 (m, 4H, Ar*H*). $^{13}C\{^1H\}$-NMR (75 MHz, CD_2Cl_2): $\delta =$ 17.0 (d, $J = 8.2$ Hz), 17.8 (d, $J = 19.8$ Hz), 28.4, 28.5, 28.6, 28.8, 29.7 (d, $J = 13.5$ Hz), 31.8 (d, $J = 22.7$ Hz), 115.7 (d, $J = 10.1$ Hz), 119.95, 120.08, 120.19, 123.1 (d, $J = 8.1$ Hz), 129.0, 143.7 (d, $J = 12.6$ Hz), 159.5 (d, $J =$ 8.7 Hz). $^{31}P\{^1H\}$-NMR (121 MHz, CD_2Cl_2): $\delta = 35.7$ (P^tBu_2), 150.0 (OP^iPr_2).

4.1.1.3. [PdCl{(C_6H_3)-2-($OPPr^i_2$)-6-($CH_2PBu^t_2$)}] (**4**). A solution of **3** (0.275 g, 0.81 mmol) in toluene (10 ml) was added dropwise to a stirred suspension of [$PdCl_2$(cod)] (0.231 g, 0.81 mmol) in toluene (10 ml). The suspension was refluxed for 4 h during which time a clear yellow solution formed. The solvent was removed in vacuum and the solid was dissolved in CH_2Cl_2 and filtered over a short silica pad to give **4** (2.76 g, 17.6 mmol, 44%) as a yellow solid. Single crystals were grown from CH_2Cl_2–pentane. ^{1}H-NMR (300 MHz, $CDCl_3$): $\delta = 1.20$–1.60 (m, 30H, $C(CH_3)_3$ and $CH(CH_3)_2$), 2.21–2.43 (m, 2H, $CH(CH_3)_2$), 3.23 (d, $J = 9.3$ Hz, 2H, CH_2P), 6.60–7.00 (m, 3H, Ar*H*). $^{13}C\{^1H\}$-NMR (75 MHz, $CDCl_3$): $\delta =$ 17.0, 17.7, 17.8, 28.6, 28.6, 28.8, 28.9, 29.4, 29.5, 29.9, 30.5, 34.0, 34.3, 35.43, 35.6, 109.6 (d, $J = 15.5$ Hz), 118.7 (d, $J = 19.8$ Hz), 126.7, 144.0, 152.1 (d, $J = 18.4$ Hz), 166.4 (d, $J = 13.1$ Hz). $^{31}P\{^1H\}$-NMR (121 MHz, CD_2Cl_2): $\delta = 73.6$ (d, $J = 388$ Hz, P^tBu_2), 187.1 (d, $J = 388$ Hz, OP^iPr_2). $C_{21}H_{37}ClOP_2Pd$ (509.34): Anal. Calc. C, 49.52; H, 7.32. Found: C, 49.36; H, 7.02%.

4.1.1.4. 1-($HOCH_2$)-3-($ClCH_2$)(C_6H_4). Thionyl chloride (4.82 g, 2.96 ml, 40.5 mmol) was added dropwise to a stirred solution of 1,3-benzenedimethanol **5** (5.52 g, 40 mmol) and Py (3.19 g, 3.27 ml, 40.3 mmol) in CH_2Cl_2 (40 ml) at 0 °C. The mixture was stirred overnight at r.t. and then poured into ice-water (100 ml), extracted with CH_2Cl_2, washed with a saturated $NaHCO_3$ solution and water, dried over $MgSO_4$ and concentrated in vacuum. The crude product was purified via column chromatography on silica. The impurities are first eluted with hexanes and the product with CH_2Cl_2 to give 1-($HOCH_2$)-3-($ClCH_2$)(C_6H_4) (2.76 g, 17.6 mmol, 44%) as a colorless liquid. ^{1}H-NMR (300 MHz, CD_2Cl_2): $\delta =$ 2.25 (s, 1H, O*H*), 4.62 (s, 2H, CH_2Cl), 4.66 (s, 2H, CH_2O), 7.41–7.28 (m, 4H, Ar*H*). $^{13}C\{^1H\}$-NMR (75 MHz, CD_2Cl_2): $\delta = 46.6$, 64.8, 127.1, 127.3, 127.9, 129.1, 138.1, 142.1.

4.1.1.5. 1-($HOCH_2$)-3-($Bu^t_2PCH_2$)(C_6H_4) (**6**). $HPBu^t_2$ (1.75 g, 2.22 ml, 12 mmol) was added dropwise to a stirred solution of 1-($HOCH_2$)-3-($ClCH_2$)(C_6H_4) (1.879 g, 12 mmol) and NaI (2.25 g, 15 mmol) in degassed acetone at r.t. The mixture was heated to reflux for 5 h and then cooled to r.t., the solvent was removed and the residue washed three times with Et_2O (15 ml each). It was then suspended in Et_2O (30 ml) and NEt_3 (1.82 g, 2.51 ml, 18 mmol) was added dropwise. After stirring for 30 min the suspension was filtered through alumina and the filtrate was concentrated in vacuum to give pure **6** (2.83 g, 10.6 mmol, 89%) as a clear oil. ^{1}H-NMR (300 MHz, CD_2Cl_2): $\delta = 1.14$ (d, 18H, $J = 10.8$ Hz, $C(CH_3)_3$), 2.86 (d, 2H, $J = 2.7$ Hz, CH_2P), 4.63 (s, 2H, CH_2OH), 7.09–7.39 (m, 4H, Ar*H*). $^{13}C\{^1H\}$-NMR (75 MHz, CD_2Cl_2): $\delta = 28.4$ (d, $J = 24$ Hz), 29.6 (d, $J = 13$ Hz), 31.7 (d, $J = 23$ Hz), 65.0, 123.9, 128.1, 128.2, 128.7 (d, $J = 8$ Hz), 141.2, 142.4 (d, $J = 13$ Hz). $^{31}P\{^1H\}$-NMR (120 MHz): $\delta = 36.2$.

4.1.1.6. 1-($Pr^i_2POCH_2$)-3-($Bu^t_2PCH_2$)(C_6H_4) (**7**). $ClPPr^i_2$ (1.62 g, 1.69 ml, 10.6 mmol) was added dropwise to a stirred solution of **6** (2.83 g, 10.6 mmol) and DMAP (1.30 g, 10.6 mmol) in THF at r.t. A precipitate formed immediately and the mixture was stirred overnight. The solvent was removed in vacuum and the residue extracted repeatedly with toluene. The toluene extracts were filtered over celite and the filtrate was concentrated in vacuum to give **7** (2.27 g, 6.0 mmol, 56%) as an oil. ^{1}H-NMR (300 MHz, $CDCl_3$): $\delta = 0.96$–1.16 (dd and d, 30H, $CH(CH_3)_2$ and $C(CH_3)_3$, overlapping signals),

1.78 (m, 2H, C*H*(CH_3)$_2$), 2.82 (d, $J = 2.7$ Hz, 2H, CH_2P), 4.75 (d, $J = 22.2$ Hz, 2H, CH_2O), 7.10–7.31 (m, 4H, Ar*H*). $^{13}C\{^1H\}$-NMR (75 MHz, $CDCl_3$): $\delta =$ 17.3 (d, $J = 8.2$ Hz), 18.2 (d, $J = 20.3$ Hz), 28.2, 28.4, 28.8, 30.0 (d, $J = 13.0$ Hz), 32.0 (d, $J = 21.7$ Hz), 74.5 (d, $J = 20.8$ Hz), 124.7, 128.4, 128.9, 129.0, 129.1, 139.6 (d, $J = 6.8$ Hz), 141.9 (d, $J = 12.1$ Hz). $^{31}P\{^1H\}$-NMR (121 MHz, $CDCl_3$): $\delta = 36.0$ (P^{t}Bu$_2$), 155.6 (OP^{i}Pr$_2$).

4.1.1.7. [PdCl{(C_6H_3)-2-($CH_2OPPr^i_2$)-6-($CH_2PBu^t_2$)] (***8***). A solution of **7** (0.382 g, 1 mmol) in toluene (10 ml) was added dropwise to a suspension of [$PdCl_2$(cod)] (0.285 g, 1 mmol) in toluene (10 ml). The suspension was refluxed for 4 h during which time a clear yellow solution formed. The solvent was removed in vacuum and the solid was dissolved in CH_2Cl_2 and the solution filtered over a short silica pad to give **8** (0.378 g, 0.72 mmol, 72%) as a yellow solid. Single crystals were grown from CH_2Cl_2–pentane. ^{1}H-NMR (300 MHz, CD_2Cl_2): $\delta = 1.02$ (dd, 6H, $^1J = 14.1$ Hz, $^2J = 7.2$ Hz, CH(CH_3)$_2$), 1.30–1.44 (dd and d, 24H, C*H*(CH_3)$_2$ and C(CH_3)$_3$, overlapping signals), 2.42–2.62 (m, 2H, C*H*(CH_3)$_2$), 3.26 (d, 2H, $J = 8.7$ Hz, CH_2P), 4.74 (d, 2H, $J = 19.5$ Hz, CH_2O), 6.82–7.22 (m, 3H, Ar*H*). $^{13}C\{^1H\}$-NMR (75 MHz, CD_2Cl_2): $\delta = 16.9$, 18.0 (d, $J = 6.3$ Hz), 26.6 (d, $J = 4.4$ Hz), 26.9 (d, $J = 4.8$ Hz), 29.5 (d, $J = 3.4$ Hz), 33.8 (d, $J = 20.3$ Hz), 35.39, 35.45, 35.54, 35.61, 79.3 (d, $J = 5$ Hz, CH_2O), 124.5 (d, $J = 18$ Hz), 125.0 (d, $J = 20$ Hz), 138.8 (d, $J = 12$ Hz), 150.3, 152.1 (d, $J = 21$ Hz). $^{31}P\{^1H\}$-NMR (121 MHz, CD_2Cl_2): $\delta = 82.2$ (d, $J = 405$ Hz, P^{t}Bu$_2$), 150.9 (d, $J = 405$ Hz, OP^{i}Pr$_2$). $C_{22}H_{39}ClOP_2Pd$ (523.36): Anal. Calc. C, 50.49; H, 7.51. Found: C, 50.51; H, 7.06%.

*4.2. X-ray data collection and structure determination for complexes **4** and **8***

Crystals of **4** suitable for X-ray analysis were obtained from slow diffusion of pentane into a saturated solution of **4** in CH_2Cl_2. Crystals of **8** suitable for X-ray analysis were obtained from slow diffusion of pentane into a saturated solution of **8** in CH_2Cl_2. Intensity data were collected at 200 K on a Mac Science DIP2030 imaging plate equipped with graphite-monochromated Mo–K_α radiation ($\lambda = 0.71073$ Å). Unit cell parameters were determined by autoindexing several images in each data set separately with program DENZO. For each data set, rotation images were collected in 3° increments with a total rotation of 180° about ϕ. Data were processed by using SCALEPACK. The structure was solved using the TEXSAN system and refined by full-matrix least-squares.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 210823 and 210824 for compounds **4** and **8**. Copies of this information may be obtained free of charge from 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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