Novel palladium complexes employing mixed phosphine phosphonates and phosphine phosphinates as anionic chelating [P,O] ligands†

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Received 13th September 2006, Accepted 30th October 2006
First published as an Advance Article on the web 14th November 2006
DOI: 10.1039/b612694d

A route to various substituted phosphine phosphonic acid compounds of the general form $Ar_2PC_6H_4PO(OH)_2$ (Ar = Ph, *o*-MeC_6H_4, *o*-$MeOC_6H_4$) has been investigated. These compounds were employed as bidentate anionic [P,O] ligands in neutral palladium complexes. The [P,O] chelating coordination was determined by X-ray crystallography of a representative palladium complex. Furthermore, the bifunctional ligand $Ph_2PC_6H_4PO(OH)Ph$ represents the first example of a chelating anionic [P,O] ligand resulting from the combination of a phosphine and a phosphinate moiety.

Introduction

In the early 1980s, nickel complexes bearing anionic chelating [P,O] ligands were already being successfully applied as catalysts in the Shell Higher Olefin Process (SHOP).[1] Nevertheless, research activities concerning the use of late transition metal catalysts, especially in polymerisation reactions, increased slowly.[2] By employing anionic ligands, the generally low oxophilicity of late transition metal systems can be further decreased. This may lead to catalyst systems with enhanced functional group tolerance, thereby offering the attractive possibility of being able to copolymerise ethylene with polar comonomers,[3] or even to run reactions in aqueous solution.[4]

So far, the most commonly employed anionic ligands are bidentate [P,O] and [N,O] compounds. However, there are notable examples, in which other types of chelating anionic ligands, *e.g.* [N,N] or [P,N], have been used.[3a]

In 2002, Drent *et al*. reported the use of alkoxyarylphosphine ligands bearing sulfonic acid groups that, when combined *in situ* with palladium acetate or $Pd_2(dba)_3$, were able to promote the formation of non-alternating polyketones from carbon monoxide and ethylene. In the copolymerisation of ethylene and methyl acrylate, copolymers with the acrylate units statistically built into the linear polyethylene chain were produced.[5] In fact, this was the first reported example of transition metal catalysis providing a low-temperature/low-pressure route to this particular subclass of copolymers.

To gain a deeper insight into the structure of the catalytically active palladium species, recent work in our group was focused on the development of defined single-site catalysts containing bisarylphosphinobenzene sulfonic acids in deprotonated form as anionic bidentate [P,O] ligands. In the copolymerisation of carbon monoxide and ethylene, these single-site catalysts proved to be superior compared to the palladium species formed *in situ*. Higher percentages of additional ethylene incorporation were observed, as well as higher turnover numbers.[6]

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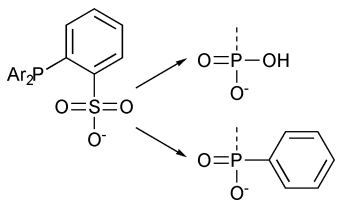
† Dedicated to Professor Heinz Berke on the occasion of his 60th birthday.

In view of the interesting properties of the single-site palladium catalysts based on phosphine sulfonate ligands, we designed a new class of chelating anionic [P,O] ligands by replacing the sulfonate moiety by the related phosphonate or phosphinate group (Scheme 1). Similar tertiary phosphines containing phosphate or phosphonate ester functionalities have recently attracted attention as neutral [P,O] ligands owing to their well investigated hemilabile behaviour in transition metal complexes.[7] Furthermore, the improvement in water-solubility of phosphine ligands due to included phosphonate groups has also been demonstrated.[8]



Scheme 1 Phosphine phosphonate and phosphine phosphinate ligands analogue to Drent's phosphine sulfonate ligands.

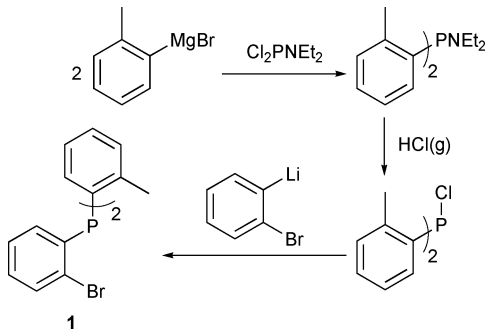
In this paper, we report the synthesis and characterisation of various mixed phosphine phosphonate and phosphine phosphinate ligands. In addition, we focus on their use as novel anionic chelating [P,O] ligands in palladium complexes.

Results and discussion

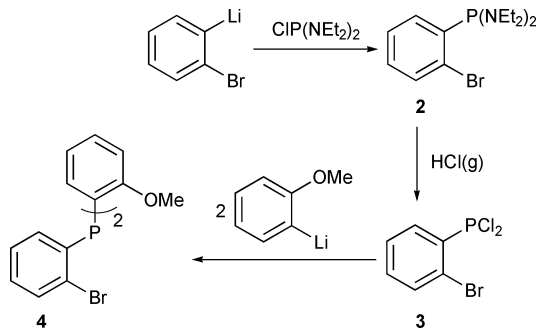
Preparation of 2-diphenylphosphinophenylphosphonic acid was carried out according to the procedure reported by Knight and co-workers.[8a] In a similar manner, the *ortho*-substituted derivatives $Ar_2PC_6H_4PO(OH)_2$ (Ar = Me, OMe) were obtained.

Initially, we prepared *ortho*-substituted bromo-bisarylphosphinobenzenes by two different strategies (Schemes 2 and 3), followed by the conversion into the corresponding phosphine-diethylphosphonates (Scheme 4). Afterwards, the phosphine phosphonic acids (**7–9**) were obtained by cleavage of the ester groups.

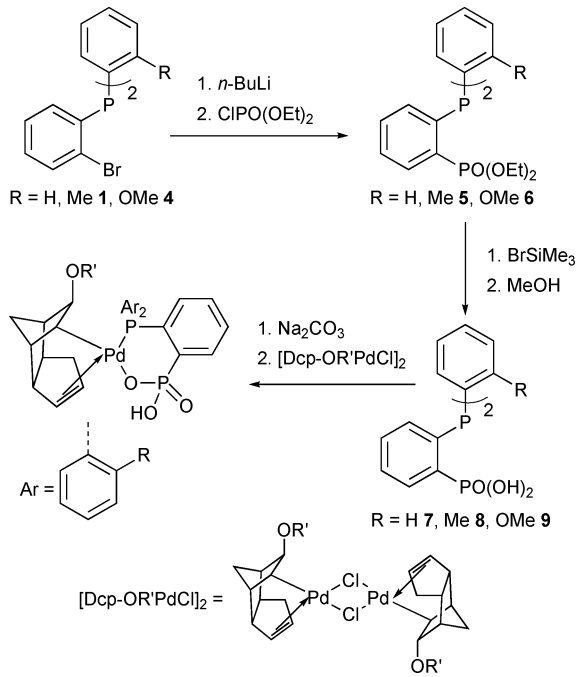
After deprotonation of the phosphonic acid moiety by Na_2CO_3, the phosphine phosphonates were employed as anionic ligands,



Scheme 2 Synthesis of 1-bromo-2-bis(2-methylphenyl)phosphinobenzene (**1**).



Scheme 3 Synthesis of 1-bromo-2-bis(2-methoxyphenyl)phosphinobenzene (**4**).



Scheme 4 Synthesis of phosphine phosphonate ligands **7–9** and the corresponding palladium complexes **10–13** (R = H, R′ = Me **10**, R = H, R′ = Et **11**, R = Me, R′ = Et **12**, R = OMe, R′ = Me **13**).

generating neutral palladium complexes (Scheme 4). The structure of complex **10** was tentatively assigned based on NMR spectroscopy, mass spectrometry and elemental analysis, and

Table 1 Selected bond lengths (Å) and bond angles (°) for complex **10**

Pd(1)–O(1)	1.508(7)	P(1)–O(2)	1.542(6)
Pd(1)–P(2)	2.280(2)	P(1)–O(3)	1.508(6)
Pd(1)–C(19)	2.269(10)	P(1)–C(1)	1.805(7)
Pd(1)–C(20)	2.395(13)	P(2)–C(6)	1.836(9)
Pd(1)–C(24)	2.039(9)	P(2)–C(7)	1.816(8)
P(1)–O(1)	1.508(7)	P(2)–C(13)	1.815(8)
O(1)–Pd(1)–P(2)	94.28(17)	O(1)–P(1)–C(1)	106.6(3)
P(2)–Pd(1)–C(24)	91.3(3)	O(2)–P(1)–O(3)	112.3(3)
C(24)–Pd(1)–C(19)	81.5(4)	O(2)–P(1)–C(1)	106.6(3)
C(24)–Pd(1)–C(20)	94.6(5)	O(3)–P(1)–C(1)	107.2(4)
C(19)–Pd(1)–C(20)	34.6(5)	C(6)–P(2)–Pd(1)	112.0(2)
C(19)–Pd(1)–O(1)	95.5(4)	C(6)–P(2)–C(7)	105.5(4)
C(20)–Pd(1)–O(1)	79.8(4)	C(6)–P(2)–C(13)	103.2(4)
P(1)–O(1)–Pd(1)	120.8(4)	C(7)–P(2)–Pd(1)	118.7(3)
O(1)–P(1)–O(2)	110.3(4)	C(7)–P(2)–C(13)	102.8(4)
O(1)–P(1)–O(3)	113.3(3)	C(13)–P(2)–Pd(1)	113.0(3)

confirmed by single-crystal X-ray diffraction studies. The solid-state structure clearly provides evidence for the phosphine phosphonate ligand binding as an anionic bidentate [P,O] ligand to the palladium centre (Fig. 1). It is interesting to note that in previous reports it was claimed that such ligands are unable to coordinate in a chelating manner.[8a]

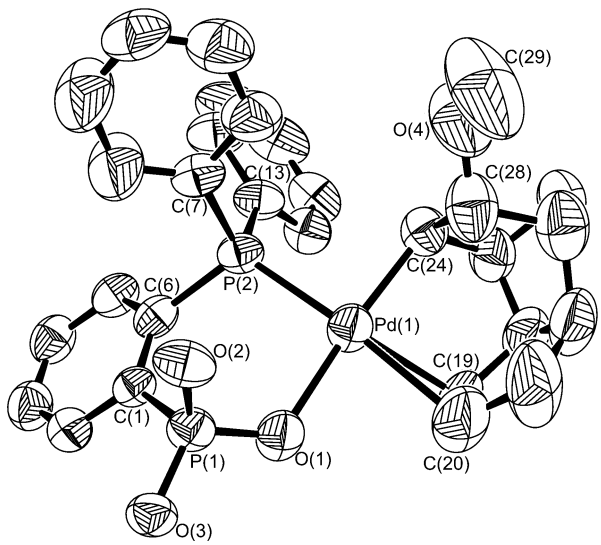


Fig. 1 ORTEP plot of the solid-state structure of complex **10** (ellipsoids with 50% probability; hydrogen atoms are omitted for clarity).

In the solid state, the second hydroxyl group of the phosphonic acid moiety, which remains free after coordination, is involved in an intermolecular hydrogen bonding system building up dimeric structures of high symmetry (Fig. 2). A similar behaviour is already known to exist in the phenylphosphonic acid skeleton.[9]

Variable-temperature NMR studies of the palladium complex **11** in solution indicated a dynamic coordination mode of the phosphine phosphonate ligand.

In Fig. 3, the ^{31}P NMR spectra of complex **11** within a temperature range from 20 to −20 °C are shown. During the cooling and heating process, the phosphorus signal of the phosphine moiety underwent remarkable changes in shape. The well defined doublet became a broad singlet by lowering the temperature from 20 to

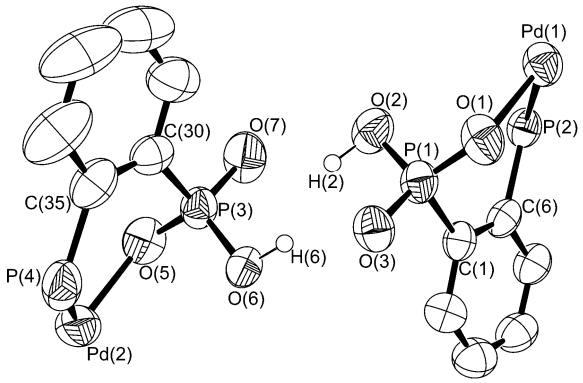
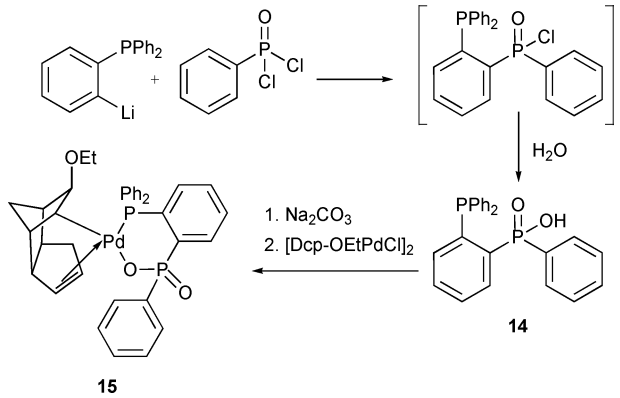


Fig. 2 Excerpt from the structure of complex **10**: intermolecular hydrogen bonding between two molecules of the asymmetric unit.



Scheme 5 Synthesis of phosphine phosphinate ligand **14** and the corresponding palladium complex **15**.

10 °C. At 0 °C, the signal appeared as a quasi-triplet. On closer inspection, the signal shape can be explained by the partial overlap of two separate doublets, which can be recognised by the significant hump in the triplet structure at −10 °C. This reveals that there are two slightly different complex structures existing in a dynamic equilibrium. Either the second hydroxyl group (P–OH) or the doubly-bonded oxygen (P=O) could, to some extent, be involved in bonding to the palladium centre.

In one step, 2-diphenylphosphinophenylphosphinic acid was prepared from 1-bromo-2-diphenylphosphinobenzene and dichlorophenylphosphine oxide (Scheme 5). After deprotonation of the phosphinic acid moiety by Na_2CO_3, the phosphine phosphinate could be introduced as an anionic chelating [P,O] ligand in a palladium complex.

Compared to complex **11**, complex **15** showed a reduced dynamic behaviour in the variable-temperature NMR spectra. This difference may be attributed to the lack of a second, free hydroxyl group in the case of the phosphinate instead of the phosphonate moiety.

Conclusion

In summary, we have prepared three different phosphine phosphonate ligands and the corresponding neutral palladium complexes. For the first time, the chelating coordination mode of this class of anionic [P,O] ligands has been clearly confirmed by a solid-state structure of one representative palladium complex. In addition, we report the synthesis of the first bidentate [P,O] ligand combining a phosphine moiety and a phosphinic acid functionality. Studies concerning the use of the neutral palladium complexes as single-site catalysts in different polymerisation reactions are currently under way.

Experimental

General considerations

All reactions were carried out under a dry argon atmosphere using standard Schlenk line techniques. Solvents were obtained from commercial sources, dried (as appropriate, *tert*-butyl methyl ether, diethyl ether, hexane, pentane, tetrahydrofuran over sodium (benzophenone) and dichloromethane over calcium hydride) and deoxygenated prior to use. Deuterated solvents were dried over the appropriate drying agents (chloroform-d_1 and dichloromethane-d_2 over calcium hydride). The NMR solvents were deoxygenated using three freeze–thaw pump cycles and transferred using a high vacuum line. *N*,*N*-Diethylaminodichlorophosphine, 1-bromo-2-diphenylphosphinobenzene, bis(2-methylphenyl)chlorophosphine and 1-diethylphosphonato-2-diphenylphosphinobenzene were prepared according to literature procedures,[7c,8a,10] [(Dcp-OR′)PdCl]$_2$ (R′ = Me, Et) was prepared as previously reported.[6] Other chemicals were purchased from commercial sources and used without further purification. ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR

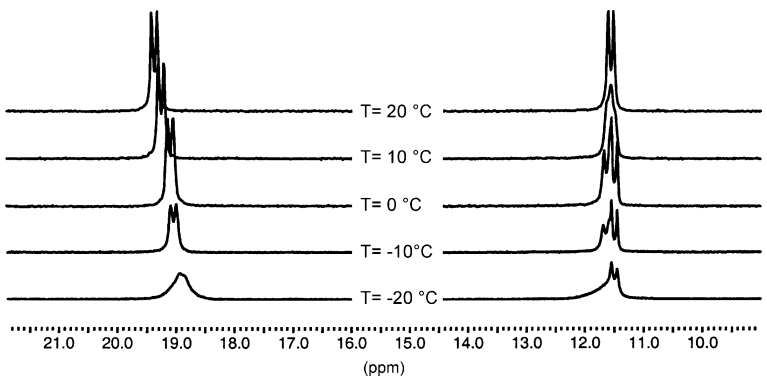


Fig. 3 Variable-temperature NMR study of the palladium complex **11** in CD_2Cl_2 solution within the temperature range from 20 to −20 °C.

spectra were recorded on a Bruker Avance 400 MHz spectrometer. Values of coupling constants are given in Hz. Shift references are $CHCl_3$ or CH_2Cl_2 as internal standards in ^1H and ^{13}C NMR and H_3PO_4 (85%) as external standard in ^{31}P NMR spectra. Elemental analyses were performed on a VARIO EL by the analytical department, University of Ulm. Mass spectra were recorded on a Finnigan MAT, SSQ-7000 and TSQ-7000 or a Bruker Daltonics REFLEX III spectrometer.

Bis(*N*,*N*-diethylamino)chlorophosphine

A 1 L Schlenk flask was charged with diethyl ether (300 mL) and PCl_3 (68.0 g, 0.50 mol) and cooled to −50 °C. Diethylamine (138 g, 1.88 mol) in 150 mL diethyl ether was added dropwise over a period of 2 h with vigorous stirring. The reaction mixture was allowed to warm to room temperature and stirred for an additional hour. Diethyl ether was removed by distillation under argon at normal pressure and the product was distilled *in vacuo* from the inorganic salts. The crude product was purified by fractional distillation (49 °C, 10^{-2} mbar) and bis(*N*,*N*-diethylamino)chlorophosphine was obtained as a colourless liquid (39.5 g, 38%). δ_H(400 MHz; $CDCl_3$; $CHCl_3$) 1.12 (12 H, t, *J* 7.2, 4 × CH_3), 3.11–3.19 (8 H, m, 4 × CH_2), δ_C (100 MHz; $CDCl_3$) 13.7 (2 × d, *J* 5.1), 41.0 (2 × d, *J* 17.6), δ_P (162 MHz; $CDCl_3$; H_3PO_4) 160.0 (s). **CAUTION**: the solid residue is pyrophoric and should be destroyed carefully by slow addition of water.

1-Bromo-2-bis(2-methylphenyl)phosphinobenzene (1). 1,2-Dibromobenzene (1.99 g, 8.44 mmol) was dissolved in a mixture of diethyl ether and THF (30 mL–30 mL). At −110 °C, *n*-BuLi (5.0 mL, 8.00 mmol, 1.6 M solution in hexanes) was added over a period of 40 min. The resulting mixture was stirred for further 30 min at −110 °C followed by the dropwise addition of bis(2-methylphenyl)chlorophosphine (2.00 g, 8.04 mmol) dissolved in diethyl ether–THF (10 mL–10 mL). The reaction mixture was then allowed to warm to room temperature over 20 h. After hydrolysis with saturated NH_4Cl solution (80 mL), the aqueous phase was extracted with diethyl ether (2 × 25 mL). The combined organic phases were washed with water (2 × 25 mL), dried (Na_2SO_4) and evaporated. The crude product was dissolved in dichloromethane (30 mL) and filtered over a small pad of silica. Then the filtrate was evaporated to dryness and the residue washed with small amounts of pentane (5 × 5 mL) to yield compound **1** (1.72 g, 59%) as a white solid (Found: C, 64.9; H, 4.9. $C_{20}H_{18}BrP$ requires C, 65.1; H, 4.9%); δ_H (400 MHz; $CDCl_3$; $CHCl_3$) 2.48 (6 H, s, 2 × CH_3), 6.79–6.82 (3 H, m), 7.13–7.16 (2 H, m), 7.22–7.27 (2 H, m) 7.28–7.36 (4 H, m), 7.64–7.69 (1 H, m); δ_C (100 MHz; $CDCl_3$) 21.2 (2 × d, *J* 22.0), 126.2 (2 × s), 127.5, 129.0 (2 × s), 130.1, 130.2 (2 × d, *J* 5.1), 130.5 (d, *J* 32.2), 133.0 (d, *J* 2.2), 133.2 (2 × s), 134.0 (2 × d, *J* 11.7), 134.6 (d, *J* 1.5), 137.7 (d, *J* 11.0), 142.8 (2 × d, *J* 27.1); δ_P (162 MHz; $CDCl_3$; H_3PO_4) −19.0 (s); *m*/*z* (CI) 370 (MH^+, 100%), 371 (66), 369 (67), 368 (99), 289 (94, M^+ − Br).

1-Bromo-2-bis(diethylamino)phosphinobenzene (2). To a solution of 1,2-dibromobenzene (15.0 g, 63.3 mmol) in a mixture of diethyl ether and THF (120 mL–120 mL) at −110 °C *n*-BuLi (39.7 mL, 63.6 mmol, 1.6 M solution in hexanes) was added over a period of 4 h. Afterwards, the reaction mixture was stirred for further 45 min at −110 °C, before bis(*N*,*N*-diethylamino)-chlorophosphine (13.4 g, 63.6 mmol) was added dropwise at the same temperature. The resulting mixture was allowed to warm to room temperature and stirred for a further 16 h. After hydrolysis with water (200 mL), the aqueous phase was extracted with diethyl ether (2 × 25 mL), the combined organic phases were washed with water (2 × 25 mL), dried (Na_2SO_4) and evaporated. Pure compound **2** was isolated as a colourless oil (17.4 g, 83%) after distillation (110 °C, 10^{-2} mbar) of the crude product (Found: C, 50.6; H, 7.2; N, 8.9. $C_{14}H_{24}BrN_2P$ requires C, 50.8; H, 7.3; N, 8.5%); δ_H (400 MHz; $CDCl_3$; $CHCl_3$) 1.13 (12 H, t, *J* 7.1, 2 × CH_3), 3.03–3.19 (8 H, m, 2 × CH_2), 7.11–7.15 (1 H, m), 7.30–7.33 (1 H, m), 7.47–7.50 (1 H, m), 7.53–7.56 (1 H, m); δ_C (100 MHz; $CDCl_3$) 14.9 (d, *J* 3.7), 43.6 (d, *J* 18.3), 126.7, 126.9 (d, *J* 30.0), 129.0 (d, *J* 1.5), 132.3 (d, *J* 5.9), 133.4, 142.5 (d, *J* 11.7); δ_P (162 MHz; $CDCl_3$; H_3PO_4) 96.4 (s).

1-Bromo-2-dichlorophosphinobenzene (3). Compound **2** (9.59 g, 28.95 mmol) was dissolved in diethyl ether (400 mL). Dry HCl (g) was passed through this solution for 30 min. The HCl-saturated solution was stirred for a further 2.5 h, and then the solvent was removed *in vacuo*. The residue was taken up in diethyl ether (300 mL) and the resulting suspension filtered to separate the insoluble diethylamine hydrochloride. After concentration of the filtrate *in vacuo*, the resulting crude oil was purified by distillation (65 °C, 10^{-2} mbar) to yield compound **3** (6.25 g, 84%) as a colourless liquid (Found: C, 28.1; H, 1.7. $C_6H_4BrCl_2P$ requires C, 27.9; H, 1.6%); δ_H (400 MHz; $CDCl_3$; $CHCl_3$) 7.40–7.44 (1 H, m), 7.54–7.57 (1 H, m), 7.61–7.65 (1 H, m), 8.13–8.15 (1 H, m); δ_C (100 MHz; $CDCl_3$) 126.4 (d, *J* 46.1), 128.4, 131.8 (d, *J* 4.4), 132.9, 133.7, 139.5 (d, *J* 56.4); δ_P (162 MHz; $CDCl_3$; H_3PO_4) 154.6 (s); *m*/*z* (CI) 221 (M^+ − Cl, 100%), 223 (94).

1-Bromo-2-bis(2-methoxyphenyl)phosphinobenzene (4). To a solution of anisole (2.10 g, 19.39 mmol) and TMEDA (200 mg, 1.72 mmol) in *tert*-butyl methyl ether (120 mL) at 0 °C was added *n*-BuLi (10.7 mL, 17.2 mmol, 1.6 M solution in hexanes) dropwise. Upon completion of the addition, the resulting mixture was refluxed for 24 h. The reaction was then cooled to 0 °C and a solution of compound **3** (2.00 g, 7.76 mmol) in *tert*-butyl methyl ether (25 mL) was added over the period of 1 h. The reaction mixture was stirred for 1 h at room temperature and then for a further 24 h under reflux conditions. After hydrolysis with water (120 mL) at room temperature, the suspension was filtered and the resulting solid dissolved in dichloromethane (100 mL). The organic phase was washed with water (2 × 50 mL), dried (Na_2SO_4) and evaporated to yield compound **4** (2.19 g, 62%) as a white solid (Found: C, 59.5; H, 4.6. $C_{20}H_{18}BrO_2P$ requires C, 59.9; H, 4.5%); δ_H (400 MHz; $CDCl_3$; $CHCl_3$) 3.78 (6 H, s, 2 × OCH_3), 6.71–6.75 (2 H, m), 6.83–6.86 (1 H, m), 6.88–6.91 (2 H, m), 6.93–6.96 (2 H, m), 7.18–7.23 (2 H, m), 7.37–7.41 (2 H, m), 7.59–7.64 (1 H, m); δ_C (100 MHz; $CDCl_3$) 55.7 (2 × s), 110.4 (2 × d, *J* 1.5), 121.1 (2 × s), 123.9 (2 × d, *J* 13.2), 127.1, 129.8, 130.3 (d, *J* 33.7), 130.4 (2 × s), 132.7 (d, *J* 2.9), 134.0 (2 × d, *J* 1.5), 134.6, 138.2 (d, *J* 12.4), 161.6 (2 × d, *J* 16.8); δ_P (162 MHz; $CDCl_3$; H_3PO_4) −25.4 (s); *m*/*z* (CI) 402 (MH^+, 100%), 404 (16), 403 (86), 401 (96), 400 (87), 321 (42, M^+ − Br).

1-Diethylphosphonato-2-bis(2-methylphenyl)phosphinobenzene (5). To a solution of compound **1** (1.20 g, 3.25 mmol) in THF (75 mL) was added *n*-BuLi (2.1 mL, 3.25 mmol, 1.6 M solution

in hexanes) dropwise at −78 °C. The resulting solution was stirred for 1 h, before diethylchlorophosphate (0.5 mL, 560 mg, 3.25 mmol) was added dropwise at the same temperature. The reaction was allowed to warm to room temperature and stirred for an additional 16 h. After concentrating under reduced pressure, the residue was dissolved in diethyl ether (40 mL) and hydrolysed with water (40 mL). The aqueous phase was extracted with diethyl ether (2 × 30 mL). The combined organic phases were washed with water (2 × 50 mL), dried (Na_2SO_4) and evaporated. The crude product was washed with pentane (5 × 7 mL) to yield compound **5** (1.31 g, 95%) as a white solid (Found: C, 67.3; H, 6.6. $C_{24}H_{28}O_3P_2$ requires C, 67.6; H, 6.6%); δ_H (400 MHz; $CDCl_3$; $CHCl_3$) 1.11 (6 H, t, *J* 6.8, 2 × OCH_2CH_3), 2.39 (6 H, s, 2 × CH_3), 3.85–3.93 (2 H, m, C*H*H), 4.07–4.16 (2 H, m, CH*H*), 6.66–6.69 (2 H, m), 7.05–7.11 (3 H, m), 7.20–7.28 (4 H, m), 7.39–7.42 (2 H, m), 8.17–8.23 (1 H, m); δ_C (100 MHz; $CDCl_3$) 15.9 (2 × d, *J* 7.3), 21.1 (2 × d, *J* 22.0), 62.0 (2 × dd, *J* 5.9 and 2.2), 125.9 (2 × s), 128.4 (d, *J* 14.6), 128.5 (2 × s), 130.0 (2 × d, *J* 4.4), 132.1 (d, *J* 2.9), 133.0 (2 × s), 133.7 (d, *J* 32.9), 134.8 (dd, *J* 11.0 and 8.1), 135.6 (2 × d, *J* 13.2), 135.9 (dd, *J* 15.4 and 1.5), 140.4 (dd, *J* 23.4 and 12.4), 142.2 (2 × d, *J* 27.1); δ_P (162 MHz; $CDCl_3$; H_3PO_4) −22.5 (s, P), 18.7 (s, PO); *m*/*z* (CI) 427 (MH^+, 100%), 428 (25), 426 (26).

1-Diethylphosphonato-2-bis(2-methoxyphenyl)phosphinobenzene (6). To a solution of compound **4** (1.31 g, 3.25 mmol) in THF (75 mL) was added *n*-BuLi (2.1 mL, 3.25 mmol, 1.6 M solution in hexanes) dropwise at −78 °C. The resulting solution was stirred for 1 h, before diethylchlorophosphate (0.5 mL, 560 mg, 3.25 mmol) was added dropwise at the same temperature. The reaction was allowed to warm to room temperature and then stirred for 16 h. After concentrating *in vacuo*, the residue was dissolved in dichloromethane (80 mL) and hydrolysed with water (80 mL). The aqueous phase was extracted with dichloromethane (2 × 20 mL). The combined organic phases were washed with water (2 × 20 mL), dried (Na_2SO_4) and evaporated. Compound **6** was obtained as a white solid (1.20 g, 80%) from the crude oil by the addition of diethyl ether (10 mL) (Found: C, 62.9; H, 6.1. $C_{24}H_{28}O_5P_2$ requires C, 62.9; H, 6.2%); δ_H (400 MHz; $CDCl_3$; $CHCl_3$) 1.10 (6 H, t, *J* 7.0, 2 × OCH_2CH_3), 3.71 (6 H, s, 2 × OCH_3), 3.93–4.03 (2 H, m, C*H*H), 4.08–4.17 (2 H, m, CH*H*), 6.58–6.62 (2 H, m), 6.82–6.86 (2 H, m), 6.87–6.91 (2 H, m), 7.08–7.12 (1 H, m), 7.31–7.35 (2 H, m), 7.38–7.42 (1 H, m), 7.44–7.48 (1 H, m), 8.20–8.26 (1 H, m); δ_C (100 MHz; $CDCl_3$) 15.9 (2 × d, *J* 7.3), 55.5 (2 × s), 61.9 (2 × dd, *J* 5.9 and 2.2), 110.1 (2 × d, *J* 1.5), 120.8 (2 × s), 125.6 (2 × d, *J* 15.4), 128.1 (d, *J* 14.6), 129.9 (2 × s), 131.8 (d, *J* 2.9), 133.9 (2 × s), 134.9 (dd, *J* 11.0 and 8.1), 135.1 (d, *J* 32.9), 135.3 (dd, *J* 16.1 and 1.5), 141.7 (dd, *J* 24.9 and 12.4), 161.0 (2 × d, *J* 16.1); δ_P (162 MHz; $CDCl_3$; H_3PO_4) −26.9 (s, P), 19.1 (s, PO); *m*/*z* (CI) 459 (MH^+, 100%), 460 (34), 458 (34).

2-Diphenylphosphinophenylphosphonic acid (7). In a Schlenk flask, 1-diethylphosphonato-2-diphenylphosphinobenzene (5.12 g, 12.8 mmol) was dissolved in dichloromethane (100 mL) and bromotrimethylsilane (5.9 mL, 44.8 mmol, 3.5 equiv.) was added dropwise at room temperature. After stirring for 24 h, dichloromethane and the excess bromotrimethylsilane was removed *in vacuo*. The residue was dissolved in methanol (100 mL) to hydrolyse the silyl esters formed and stirred for further 4 h before evaporating. The crude product was recrystallised from ether/pentane to obtain compound **7** (4.04 g, 92%) as a white solid; δ_H (400 MHz; $CDCl_3$; $CHCl_3$) 7.22–7.27 (1 H, m), 7.33–7.39 (4 H, m), 7.42–7.50 (7 H, m), 7.53–7.56 (1 H, m), 8.05–8.11 (1 H, m), 9.12 (2 H, br s, 2 × OH); δ_C (100 MHz; $CDCl_3$) 126.9 (d, *J* 42.4), 129.2 (4 × d, *J* 10.3), 131.6 (2 × s), 131.8, 131.9 (dd, *J* 24.2 and 2.9), 133.7 (4 × d, *J* 14.6), 134.1 (dd, *J* 9.5 and 9.5), 135.6 (dd, *J* 13.9 and 5.1), 137.1 (d, *J* 21.2), 138.9 (2 × d, *J* 21.2); δ_P (162 MHz; $CDCl_3$; H_3PO_4) −3.3 (s, P), 14.6 (s, PO); *m*/*z* (CI) 341 (MH^+, 100%), 343 (51), 342 (23), 340 (8), 339 (23), 325 (60, M − H_2O), 311 (50).

2-Bis(2-methylphenyl)phosphinophenylphosphonic acid (8). This ligand was obtained as a white solid (623 mg, 68%), in a manner similar to ligand **7** from compound **5** (1.06 g, 2.47 mmol) and bromotrimethylsilane (1.2 mL, 8.65 mmol, 3.5 equiv.); δ_H (400 MHz; $CDCl_3$; $CHCl_3$) 2.47 (6 H, s, 2 × CH_3), 6.99–7.05 (2 H, m), 7.18–7.22 (1 H, m), 7.31–7.34 (2 H, m), 7.41–7.44 (2 H, m), 7.59–7.67 (3 H, m), 7.83–7.86 (1 H, m), 8.15–8.21 (1 H, m), 9.88 (2 H, br s, 2 × OH); δ_C (100 MHz; $CDCl_3$) 21.2 (2 × d, *J* 19.0), 117.2 (2 × d, *J* 18.9), 126.0 (2 × d, *J* 2.9), 129.4 (2 × s), 129.7, 130.4 (2 × d, *J* 5.9), 131.6, 132.9 (2 × d, *J* 2.9), 133.8 (dd, *J* 9.5 and 9.5), 136.1 (d, *J* 15.4), 136.9 (dd, *J* 193.2 and 29.8), 138.0 (dd, *J* 176.4 and 9.5), 142.5 (2 × d, *J* 23.4); δ_P (162 MHz; $CDCl_3$; H_3PO_4) −8.4 (d, *J* 15.1, P), 11.7 (d, *J* 15.1, PO); *m*/*z* (CI) 371 (MH^+, 100%), 372 (21), 370 (17).

2-Bis(2-methoxyphenyl)phosphinophenylphosphonic acid (9). This ligand was obtained as a white solid (649 mg, 93%), in a manner similar to ligand **7** from compound **6** (795 mg, 1.73 mmol) and bromotrimethylsilane (0.8 mL, 6.06 mmol, 3.5 equiv.); δ_H (400 MHz; $CDCl_3$; $CHCl_3$) 3.85 (6 H, s, 2 × OCH_3), 7.11–7.19 (6 H, m), 7.27–7.34 (1 H, m), 7.61–7.64 (1 H, m), 7.73–7.77 (2 H, m), 7.82–7.85 (1 H, m), 8.27–8.33 (1 H, m), 9.25 (2 H, br s, 2 × OH); δ_C (100 MHz; $CDCl_3$) 56.9 (2 × s), 104.8 (2 × d, *J* 95.1), 112.3 (2 × d, *J* 5.8), 118.3 (dd, *J* 103.9 and 11.0), 122.1 (2 × d, *J* 13.2), 131.8 (dd, *J* 13.2 and 2.2), 134.1–134.4 (2 × m), 134.7 (2 × d, *J* 8.8), 135.0 (dd, *J* 9.5 and 9.5), 137.2 (2 × s), 137.3 (dd, *J* 186.6 and 11.0), 161.4 (2 × d, *J* 2.2); δ_P (162 MHz; $CDCl_3$; H_3PO_4) −9.9 (br s, P), 11.8 (d, *J* 6.8, PO); *m*/*z* (CI) 95 ($C_6H_7O^+$, 100%), 403 (38, MH^+), 402 (6), 401 (9), 385 (49, M − H_2O).

Complex 10. In a Schlenk flask, a solution of **7** (500 mg, 1.46 mmol) and Na_2CO_3 (170 mg, 1.61 mmol, 1.1 equiv.) in dichloromethane (20 mL) was stirred for 20 h. During this time, the white monosodium salt of **7** precipitated and $[(Dcp\text{-}OMe)PdCl]_2$ (446 mg, 0.73 mmol) was added with stirring at −18 °C. The resulting solution was allowed to stir for further 6 h at room temperature. Before concentrating *in vacuo*, the complex solution was filtered to separate the NaCl formed during the reaction. The crude product obtained was washed with small amounts of diethyl ether (5 × 7 mL) to yield complex **10** (698 mg, 78%) as a pure pale yellow solid (Found: C, 56.7; H, 5.2. $C_{29}H_{30}O_4P_2Pd$ requires C, 57.0; H, 5.0%); δ_H (400 MHz; CD_2Cl_2; CH_2Cl_2) 1.07 (1 H, d, *J* 9.9, C*H*H), 1.26 (1 H, d, *J* 9.6, CH*H*), 2.09 (1 H, dd, *J* 14.0 and 3.9, CH), 2.32–2.35 (2 H, m, CH, C*H*H), 2.61–2.72 (2 H, m, CH, CH*H*), 2.79–2.83 (1 H, m, CH), 2.91–2.97 (1 H, m, CH), 3.01 (3 H, s, OCH_3), 3.47–3.49 (1 H, m, CH), 6.46 (1 H, br s, CH), 6.89–6.95 (1 H, m, CH), 7.21–7.25 (1 H, m, CH), 7.28–7.34 (1 H, m, CH), 7.37–7.40 (1 H, br s, CH), 7.41–7.59 (10 H, m, CH), 7.95–8.00 (1 H, m, CH), 8.60 (1 H, br s, OH); δ_C (100 MHz; CD_2Cl_2) 31.8, 35.7,

39.2, 40.9, 51.5, 53.9, 55.9, 57.4, 82.6, 127.3 (d, *J* 6.6), 128.6 (2 × d, *J* 11.0), 128.7 (2 × d, *J* 11.0), 129.2 (d, *J* 5.1), 129.7 (d, *J* 8.8), 130.2 (2 × d, *J* 46.8), 130.3 (dd, *J* 11.3 and 1.1), 130.6 (d, *J* 2.2), 130.9 (d, *J* 2.2), 131.1 (d, *J* 49.8), 131.5 (dd, *J* 45.0 and 8.0), 133.2 (dd, *J* 10.2 and 8.8), 133.9 (2 × d, *J* 12.4), 134.2 (2 × d, *J* 12.4), 134.5 (dd, *J* 11.0 and 2.2); δ_P (162 MHz; CD_2Cl_2; H_3PO_4) 11.6 (d, *J* 13.7, P), 19.9 (d, *J* 13.7, PO); *m*/*z* (MALDI): found: 610.5. $C_{29}H_{30}O_4P_2Pd$ requires 610.1 (M^+).

Complex 11. This complex was obtained as a pale yellow solid (343 mg, 63%), in a manner similar to complex **10** from **7** (300 mg, 0.79 mmol), Na_2CO_3 (112 mg, 1.06 mmol, 1.1 equiv.) and [(Dcp-OEt)PdCl]$_2$ (280 mg, 0.38 mmol); δ_H (400 MHz; CD_2Cl_2; CH_2Cl_2) 1.00 (3 H, t, *J* 7.0, CH_2CH_3), 1.09 (1 H, d, *J* 9.8, C*H*H), 1.32 (1 H, d, *J* 9.8, CH*H*), 1.76–1.77 (1 H, m, CH), 2.33–2.34 (2 H, m, CH, C*H*H), 2.67–2.72 (2 H, m, CH, CH*H*), 2.82–2.83 (1 H, m, CH), 2.96–3.02 (1 H, m, CH), 3.10–3.17 (1 H, m, C*H*HCH$_3$), 3.32–3.40 (1 H, m, CH*H*CH$_3$), 3.64–3.67 (1 H, m, CH), 6.46 (1 H, br s, CH), 6.85–6.91 (1 H, m, CH), 7.22–7.26 (1 H, m, CH), 7.34–7.37 (1 H, m, CH), 7.41–7.45 (2 H, m, CH), 7.46–7.47 (1 H, m, CH), 7.48–7.55 (8 H, m, CH), 8.00–8.03 (1 H, m, CH), 12.31 (1 H, br s, OH); δ_C (100 MHz; CD_2Cl_2) 15.6, 31.8, 35.8, 39.3, 41.8, 52.4, 53.9, 57.4, 63.6, 80.7, 127.5 (d, *J* 7.3), 128.6 (2 × d, *J* 11.0), 128.8 (2 × d, *J* 11.0), 129.2–129.4 (2 × m), 130.2 (2 × d, *J* 46.8), 130.3 (dd, *J* 11.7 and 2.2), 130.7 (d, *J* 2.2), 130.8 (d, *J* 2.2), 131.3 (d, *J* 49.8), 131.5 (dd, *J* 45.0 and 8.1), 133.2 (dd, *J* 11.0 and 8.8), 134.0 (2 × d, *J* 12.4), 134.1 (2 × d, *J* 12.4), 134.5 (dd, *J* 11.0 and 2.9); δ_P (162 MHz; CD_2Cl_2; H_3PO_4) 11.6 (d, *J* 13.7, P), 20.0 (d, *J* 13.7, PO); *m*/*z* (MALDI): found: 623.1. $C_{30}H_{32}O_4P_2Pd$ requires 624.1 (M^+).

Complex 12. This complex was obtained as a pale yellow solid (246 mg, 55%), in a manner similar to complex **10** from **8** (250 mg, 0.68 mmol), Na_2CO_3 (80 mg, 0.75 mmol, 1.1 equiv.) and [(Dcp-OEt)PdCl]$_2$ (205 mg, 0.34 mmol); δ_H (400 MHz; CD_2Cl_2; CH_2Cl_2) 0.91 (3 H, t, *J* 6.9, CH_2CH_3), 1.06 (1 H, d, *J* 9.9, C*H*H), 1.35 (1 H, d, *J* 9.6, CH*H*), 1.35–1.37 (1 H, m, CH), 2.23–2.34 (2 H, m, CH, C*H*H), 2.52 (3 H, s, CH_3), 2.65–2.70 (5 H, m, CH, CH*H*, CH_3), 2.87–2.89 (1 H, m, CH), 2.91–2.94 (1 H, m, CH), 2.97–3.03 (1 H, m, C*H*HCH$_3$), 3.32–3.36 (1 H, m, CH*H*CH$_3$), 3.54–3.55 (1 H, m, CH), 6.40 (1 H, br s, CH), 6.85–6.92 (3 H, m, CH), 7.13–7.19 (2 H, m, CH), 7.24–7.28 (1 H, m, CH), 7.34–7.37 (2 H, m, CH), 7.40–7.46 (3 H, m, CH), 7.49–7.55 (1 H, m, CH), 8.17–8.19 (1 H, m, CH), 10.41 (1 H, br s, OH); δ_C (100 MHz; CD_2Cl_2) 15.5, 22.9, 23.1, 31.7, 35.9, 39.3, 41.3, 54.3, 58.3, 63.2, 81.7, 126.3 (2 × d, *J* 8.8), 126.4 (2 × d, *J* 8.8), 129.4–129.5 (2 × m), 130.7 (d, *J* 10.3), 131.0 (2 × s), 131.5 (dd, *J* 6.6 and 1.5), 131.7 (2 × d, *J* 10.3), 133.42 (m), 133.7 (2 × d, *J* 7.3), 134.5–134.7 (2 × m), 142.4 (d, *J* 11.7), 142.9 (d, *J* 12.4); δ_P (162 MHz; CD_2Cl_2; H_3PO_4) 12.7 (br s, P, PO); *m*/*z* (MALDI): found: 651.7. $C_{32}H_{36}O_4P_2Pd$ requires 652.1 (M^+).

Complex 13. This complex was obtained as a pale yellow solid (327 mg, 78%), in a manner similar to complex **10** from **9** (250 mg, 0.62 mmol), Na_2CO_3 (72 mg, 0.68 mmol, 1.1 equiv.) and [(Dcp-OMe)PdCl]$_2$ (189 mg, 0.31 mmol), (Found: C, 55.0; H, 5.2. $C_{31}H_{34}O_6P_2Pd$ requires C, 55.5; H, 5.1%); δ_H (400 MHz; CD_2Cl_2; CH_2Cl_2) 1.03 (1 H, m, C*H*H), 1.21 (1 H, m, CH*H*), 1.41–1.59 (1 H, m, CH), 2.20–2.35 (2 H, m, CH, C*H*H), 2.61–2.79 (2 H, m, CH, CH*H*), 2.72 (3 H, s, OCH_3), 3.28 (1 H, s, CH), 3.36–3.56 (2 H, m, CH), 3.62 (3 H, s, OCH_3), 3.68 (3 H, s, OCH_3), 6.35 (1H, s, CH), 6.93–6.96 (4 H, m, CH), 7.08 (1 H, m, CH), 7.16 (1 H, m, CH), 7.28 (3 H, br s, CH), 7.36–7.38 (1 H, m, CH), 7.49 (2 H, m, CH), 7.93–8.00 (1 H, br s, CH), 11.18 (1 H, br s, OH); δ_C (100 MHz; CD_2Cl_2) 32.1, 36.2, 39.7, 40.1, 41.9, 43.5, 55.2, 55.0, 55.7, 55.9, 83.1, 111.8 (d, *J* 54.8), 121.1 (d, *J* 11.0), 125.5 (d, *J* 7.3), 125.9 (d, *J* 8.7), 128.8, 129.9 (d, *J* 13.1), 133.3 (d, *J* 14.6), 137.3, 161.1 (d, *J* 51.3); δ_P (162 MHz; CD_2Cl_2; H_3PO_4) 12.3 (br s, P), 12.7 (br s, PO); *m*/*z* (MALDI): found: 669.4. $C_{31}H_{34}O_6P_2Pd$ requires 670.9 (M^+).

2-Diphenylphosphinophenylphosphinic acid (14). In a Schlenk flask, 1-bromo-2-diphenylphosphinobenzene (1.00 g, 2.93 mmol) was dissolved in THF (40 mL). At −78 °C, *n*-BuLi (1.8 mL, 2.93 mmol, 1.6 M solution in hexanes) was added dropwise with stirring over a period of 40 min. The resulting solution was slowly transferred *via* cannula to a stirred solution of dichlorophenylphosphonate (0.63 g, 3.22 mmol, 1.1 equiv.) in THF (50 mL) at −78 °C. After completion of the addition, the solution was stirred for a further 18 h and allowed to warm to room temperature. Then, the solvent was removed *in vacuo* and the residue dissolved in diethyl ether (100 mL). Water (100 mL) was added to hydrolyse the monochlorophosphonate formed. The phases were separated and the aqueous phase was extracted with diethyl ether (2 × 50 mL). The combined organic phases were washed with water (50 mL), dried (Na_2SO_4) and evaporated. The crude product was purified by recrystallisation from dichloromethane/pentane to obtain the desired compound **14** (246 mg, 21%) as a white solid (Found: C, 71.2; H, 5.2. $C_{24}H_{20}O_2P_2$ requires C, 71.6; H, 5.0%); δ_H (400 MHz; $CDCl_3$; $CHCl_3$) 7.03–7.06 (4 H, m), 7.18–7.27 (9 H, m), 7.31–7.35 (1 H, m), 7.37–7.40 (2 H, m), 7.67–7.72 (2 H, m), 8.13–8.19 (1 H, m), 11.01 (1 H, br s, OH); δ_C (100 MHz; $CDCl_3$) 127.7 (2 × d, *J* 13.9), 128.1 (4 × d, *J* 2.9), 128.2 (2 × s), 128.6 (dd, *J* 17.6 and 12.4), 131.5 (dd, *J* 56.0 and 2.6), 131.6 (2 × dd, *J* 11.0 and 3.7), 132.1 (d, *J* 10.2), 133.3 (4 × d, *J* 19.8), 133.6 (dd, *J* 9.5 and 9.5), 136.3 (dd, *J* 13.2 and 1.5), 137.3 (2 × d, *J* 13.2), 138.0 (d, *J* 32.9), 139.3 (d, *J* 32.9), 141.3 (dd, *J* 23.4 and 14.6); δ_P (162 MHz; $CDCl_3$; H_3PO_4) −12.2 (d, *J* 9.1, P), 34.7 (d, *J* 9.1, PO); *m*/*z* (CI) 403 (MH^+, 100%), 404 (25), 402 (12).

Complex 15. In a Schlenk flask, a solution of **14** (179 mg, 0.45 mmol) and Na_2CO_3 (57 mg, 0.53 mmol, 1.1 equiv.) in dichloromethane (10 mL) was stirred for 40 h. During this time, the white sodium salt of **14** precipitated and [(Dcp-OEt)PdCl]$_2$ (142 mg, 0.22 mmol) was added with stirring at −18 °C. The resulting solution was allowed to stir for further 20 h at room temperature. Before concentrating *in vacuo*, the complex solution was filtered to separate the NaCl formed during the reaction. The crude product obtained was washed with small amounts of diethyl ether (5 × 5 mL) to yield complex **15** (170 mg, 61%) as a pure yellow solid; δ_H (400 MHz; CD_2Cl_2; CH_2Cl_2) 0.97 (3 H, t, *J* 7.0, CH_3), 1.10 (1 H, d, *J* 9.9, C*H*H), 1.31 (1 H, d, *J* 9.9, CH*H*), 1.71 (1 H, dd, *J* 13.6 and 4.8, CH), 2.29–2.39 (2 H, m, CH, C*H*H), 2.70–2.74 (2 H, m, CH, CH*H*), 2.82–2.83 (1 H, m, CH), 2.97–3.02 (1 H, m, CH), 3.07–3.14 (1 H, m, C*H*H), 3.32–3.39 (1 H, m, CH*H*), 3.75–3.76 (1 H, m, CH), 6.46–6.48 (1 H, br s, CH), 6.89–6.94 (1 H, m, CH), 7.11–7.15 (2 H, m, CH), 7.21–7.26 (2 H, m, CH), 7.27–7.29 (1 H, m, CH), 7.36–7.45 (11 H, m, CH), 7.47–7.52 (2 H, m, CH), 7.82–7.89 (1 H, m, CH); δ_C (100 MHz; CD_2Cl_2) 15.5, 31.9, 35.9, 39.3, 42.2, 54.0, 57.6, 63.7, 80.9, 126.9 (d, *J* 57.1), 127.6 (2 × d,

Table 2 Selected crystallographic data for complex **10**·2/3C_7H_8

Empirical formula	$3(C_{29}H_{30}O_4P_2Pd)\cdot 2(C_7H_8)$
M_r	2016.88
Crystal system	Monoclinic
Space group	$P2_1/c$ (no. 14)
a/Å	16.955(3)
b/Å	33.696(7)
c/Å	18.155(4)
β/°	116.24(3)
V/Å^3	9303(3)
T/K	193(2)
Z	4
μ(Mo-Kα)/mm^{-1}	0.738
Total reflections	72578
Independent reflections	17313
R_{int}	0.0882
R_1, wR_2 [$I > 2\sigma(I)$]	0.0909, 0.2620

J 12.4), 128.8 (2 × d, *J* 9.5), 128.9 (2 × d, *J* 11.0), 129.5 (2 × d, *J* 46.8), 129.6 (dd, *J* 7.3 and 2.2), 129.9 (d, *J* 2.9), 130.4 (d, *J* 2.2), 130.5 (d, *J* 2.2), 130.6 (d, *J* 44.6), 130.9 (2 × m), 131.3 (2 × d, *J* 9.5), 131.7 (m), 133.9 (2 × d, *J* 12.4), 134.3 (2 × d, *J* 12.4), 134.5 (dd, *J* 9.1 and 3.3), 135.1 (dd, *J* 10.3 and 10.3); δ_P (162 MHz; CD_2Cl_2; H_3PO_4) 19.1 (br s, P), 23.2 (d, *J* 11.4, PO); *m*/*z* (MALDI): found: 683.3. $C_{36}H_{36}O_3P_2Pd$ requires 684.1 (M^+).

X-Ray crystallography

Single crystals of complex **10** were recrystallised from toluene. Data of complex **10** was collected on a STOE-IPDS diffractometer using graphite-monochromated Mo-Kα radiation. Table 2 summarises the crystallographic data of complex **10**. The structure was solved by direct methods with the program SHELXS-97 [Sheldrick, 1997][11] and refined by full-matrix least-squares based on F^2 using SHELXL-97[12] to give a final $R1 = 0.0872$ for 10260 reflections with $I > 2\sigma(I)$. All hydrogen atoms were placed in calculated positions with the following parameters: $d(C_{ar}–H) = 0.95$ Å, $U(H) = 1.2U_{eq}(C)$; $d(C_{methylene}–H) = 0.99$ Å, $U(H) = 1.2U_{eq}(C)$; $d(C_{methyl}–H) = 0.98$ Å, $U(H) = 1.5U_{eq}(C)$; $d(O–H) = 0.84$ Å, $U(H) = 1.5U_{eq}(O)$. For atoms C(48)–C(58) (corresponding to the dicyclopentadienyl ligand in coordination unit 2), we had to fix the individual bond distances for individual bonds using a set of DFIX instructions. The electron density in this region of the asymmetric unit is not sharply defined to allow an unrestrained refinement of atomic positions. We have to point out that the absolute configuration of the coordinated dicyclopentadienyl ligand in this coordination unit therefore is uncertain. However, the refinement of a split model placing both stereoisomers at the palladium centre (Pd(2)) gave rise to an unstable refinement. This refinement strategy does not influence the absolute ratio of chiral isomers in the crystal lattice, since the centrosymmetric space group warrants an even distribution. The compound crystallises as the (non-chiral) racemate.

CCDC reference number 616052.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b612694d

Acknowledgements

We would like to thank Deutsche Forschungs Gemeinschaft (DFG) and Fond der Chemischen Industrie for funding. C. R. and R. N. would like to express thanks to Mr B. Müller for X-ray data collection and Mr U. Ziegler for NMR measurements.

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