This article is published as part of the *Dalton Transactions* themed issue entitled:

Pincers and other hemilabile ligands

Guest Editors Dr Bert Klein Gebbink and Gerard van Koten

Published in issue 35, 2011 of *Dalton Transactions*

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Cite this: *Dalton Trans.*, 2011, **40**, 9042

www.rsc.org/dalton

PAPER

Chiral palladacycles based on resorcinol monophosphite ligands: the role of the *meta*-hydroxyl in ligand C–H activation and catalysis†

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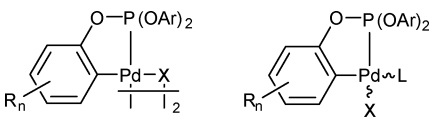
Received 2nd March 2011, Accepted 21st June 2011
DOI: 10.1039/c1dt10357a

The reactions of a range of chiral resorcinol monophosphite ligands with $[PdCl_2(NCMe)_2]$ was investigated in order to establish whether the *meta*-hydroxyl function was involved in the orthometallation processes. These ligands underwent facile orthopalladation at room temperature in the presence of Et_3N, whilst the equivalent hydroxyl-free analogues needed more forcing conditions to induce orthometallation. When the hydroxyl function was replaced by a similar sized methyl group no orthometallation occurred, even on heating. Furthermore the hydroxyl group influences both the structure and isomerism in the resultant palladacycles *via* hydrogen bonding to adjacent chloride ligands. Similarly, the hydroxyl function leads to higher enantiocontrol in the asymmetric allylation of benzaldehyde with allyl tributyltin. Representative examples of the ligands and the palladium complexes obtained were characterised by single crystal X-ray diffraction.

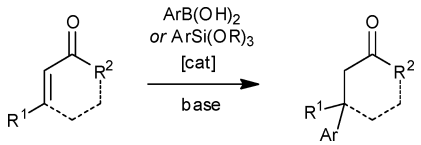
Introduction

Despite early reports on the preparation of triarylphosphite-based palladacycles, **1**,[1] until about 13 years ago, their catalytic activity was not examined in detail.[2] Since then phosphite-based palladacycles, **1**, and their phosphine and carbene adducts, **2**, have been shown to display excellent catalytic activity in a range of C–C and C-heteroatom bond-forming reactions.[3] This includes their application to Suzuki,[4] Stille,[4a,5] Heck[6] and Buchwald–Hartwig amination reactions,[7] catalytic C–P bond formation,[8] the alkoxy- and amido-carbonylation of aryl halides,[9] and the borylation of aryl halides.[10]

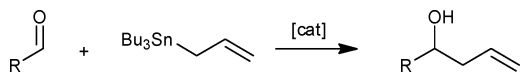


1 **2**

In most if not all of these cross-coupling reactions, where the mode of catalyst activation has been studied, the phosphite-palladacycles undergo reductive processes to liberate active palladium (0) species. By contrast Lewis-acid catalysed addition reactions do not require a reduction of the palladium(II) centre and thus the palladacycles are more likely to remain intact during the catalytic cycle. Accordingly, the use of catalysts of the types **1** and **2** in addition reactions has become the focus of recent research and they have been exploited in the conjugate addition of arylboronic acids and arylsiloxanes to enones (Scheme 1),[11] as well as the allylation of aldehydes with allyl tributyltin (Scheme 2).[12]



Scheme 1 Catalytic arylation of enones.



Scheme 2 Catalytic allylation of aldehydes.

Recently attention has focussed on the development of chiral versions of triarylphosphite-based palladacycles, not least because of the relative ease of synthesis of chiral phosphites. In particular, the BINOL-based ligand **3a**[13] has proved to be a particularly useful ligand for the facile production of palladacyclic and platinacyclic complexes (**4a** and **5**) and their phosphine, phosphite and carbene adducts.[14]

These complexes have been found to show good activity but poor enantioselectivity in the conjugate addition of arylboronic acids to enones and the allylation of aldehydes with allyl tin reagents (Schemes 1 and 2).[14b]

In the preceding paper we described the synthesis of chiral monophosphite ligands **6**, derived from 2,4-di-*tert*-butylresorcinol, which acted as intermediates in the formation of mixed phosphite-phosphinite pincer ligands.[15] These monophosphite ligands have the potential for secondary interactions arising from the *meta*-hydroxyl function which could play a

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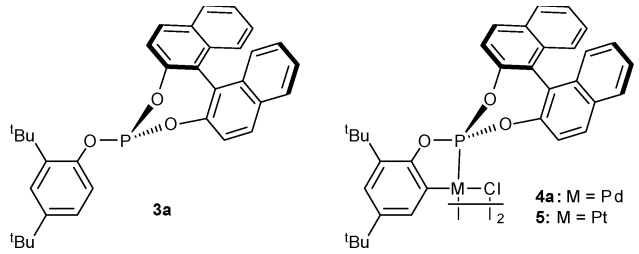
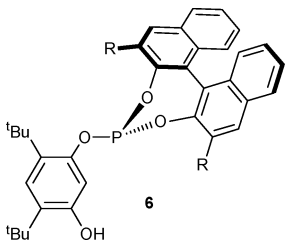
† CCDC reference numbers 815807–815810. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c1dt10357a



significant role in both the formation and structure of their complexes and also in the subsequent exploitation of the resultant complexes in catalytic reactions. Accordingly, we now turn our attention to the affect of the proximate hydroxyl function in both the formation of palladacycles and in asymmetric catalytic addition reactions.

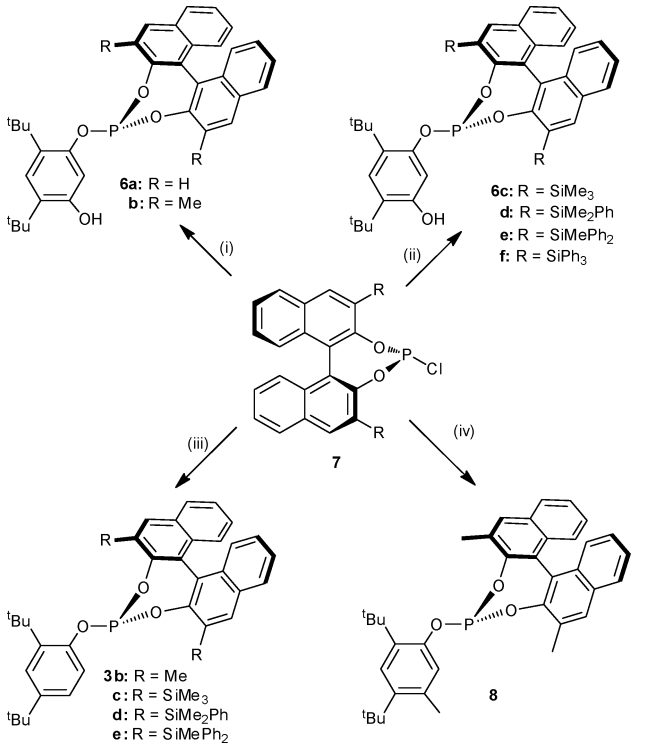


Results and discussion

Ligand synthesis

The lower steric profile monophosphite ligands **6a** and **b** (R = H and Me respectively) were synthesised from 2,4-di-*tert*-butylresorcinol by treating the latter with one equivalent of butyllithium followed by reaction of the resultant phenoxide with the appropriate *S*,*S*-chlorophosphite, **7**, in order to prevent formation of the bis(phosphite) pincer ligands (Scheme 3). By contrast, the bulkier monophosphite ligands **6c**, **e** and **f** were prepared as described in the preceding paper by reacting the resorcinol with the appropriate chlorophosphite **7** in the presence of triethylamine. This milder route is effective here because the formation of the bis(phosphite) ligands with these bulkier substituents is not possible under these or indeed more forcing conditions.[15] This latter methodology was extended to the synthesis of the 3,3′-dimethylphenylsilylated-BINOL derivative **6d**. For comparison purposes, in order to help delineate the role of the hydroxyl function in complex formation and catalysis, we also prepared the ligands **3b–e**, which lack the hydroxyl residue, and the analogue **8** in which the hydroxyl of **6b** was replaced by a similar sized methyl residue. The single crystal X-ray structure of one of the new ligands (**3b**) was determined and the molecule is shown in Fig. 1.

The ligands based on 3,3′-silylated BINOL phosphites showed a steady downfield shift in their ^{31}P NMR spectra as methyl groups were replaced with bulkier phenyl residues on the silicon for both ligands based on 2,4-di-*tert*-butylresorcinol, **6c–f** (δ 139.3 ppm for $SiMe_3$ to 148.8 ppm for $SiPh_3$) and 2,4-di-*tert*-butylphenol **3c–e** (δ 145.3 ppm for $SiMe_3$ to 149.5 ppm for $SiMePh_2$). It is tempting to conclude that this can be attributed to perturbations in the 7-membered ring caused by steric interactions with the silyl residues. However the ^{31}P NMR spectroscopic data for the unsubstituted ligand **6a** (δ 144.5 ppm) and the methyl substituted ligands **6b** and



Scheme 3 Ligand synthesis. Conditions: C_6H_2-2,4-^{t}Bu$_2$-1-(OH)-5-(OLi), toluene, 0 °C–r.t., 18 h. (ii) 2,4-di-*tert*-butylresorcinol, NEt_3, toluene, r.t., 24 h. (iii) 2,4-di-*tert*-butylphenol, NEt_3, toluene, r.t. 18 h. (For **3c**, 90 °C for 5 days). (iv) 2,4-di-*tert*-butyl-5-methylphenol, NEt_3, toluene, r.t. 18 h.

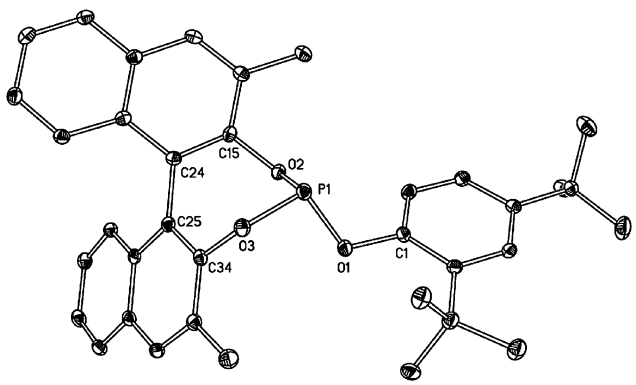


Fig. 1 X-ray structure of ligand **3b**. Thermal ellipsoids set at 30% probability.

3b (δ 141.0 and 142.9 ppm respectively) are not consistent with this simple analysis.

The ^{1}H NMR spectra of the ligands **6** showed broad singlets in the range δ 3.62–4.64 ppm for the OH peaks. These values are consistent with simple phenols in $CDCl_3$ solution.[16]

Complex synthesis

We previously reported that complex **4a** can be readily synthesised by the heating ligand **3a** with [$PdCl_2(NCMe)_2$] in toluene at reflux temperature for 20 h.[14b] Similar procedures led to the isolation of the new, bulkier palladacyclic complexes **4b–4d**. Complexes **4b–d** exist as a mixture of *cis* and *trans* isomers in solution as observed by ^{31}P and ^{1}H NMR spectroscopy, consistent with the

data obtained for **4a**[14b] and indeed most if not all previously reported triarylphosphite-based palladacycles.

In the solid state complex **4c** adopts the anticipated *trans*[17] geometry as determined by a single crystal X-ray diffraction study, the results of which are shown in Fig. 2. The square planar environments of the two palladium atoms are not co-planar: the angle α (defined by the two metal and two Cl atoms, Fig. 3) is 19.5(1)°. Of all 30 published crystal structures of square planar dimeric palladium and platinum phosphorus-based metallacycles of the form shown in Fig. 3,[18] only those twelve that are in space groups in which chiral molecules can crystallise have $\alpha > 0°$, with only two exceptions.[19] All others adopt a planar conformation (with $\alpha = 0°$), usually imposed by a crystallographic centre of inversion on the centroid of M···M, presumed to be the lowest energy conformation, but which is obviously unavailable to enantiomerically pure chiral compounds. Thus it is presumed that $\alpha > 0°$ is a consequence of the chiral nature of the ligands, with its value broadly dependent on the bulkiness of the substituents.

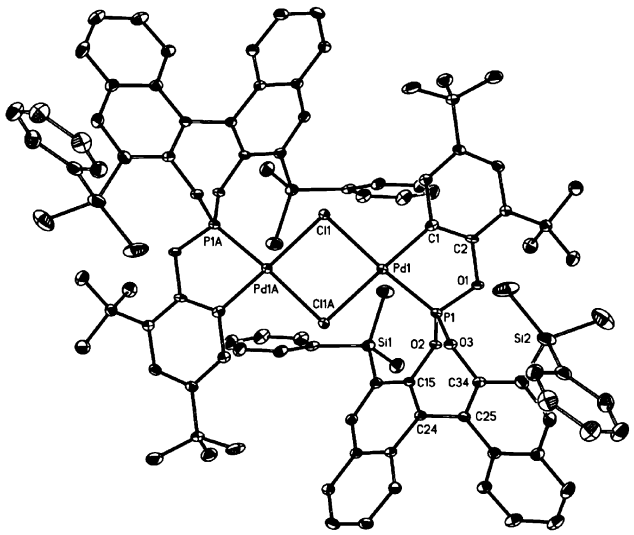


Fig. 2 X-ray structure of complex **4c**. Thermal ellipsoids set at 30% probability.

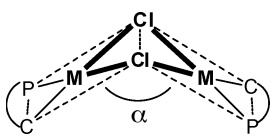
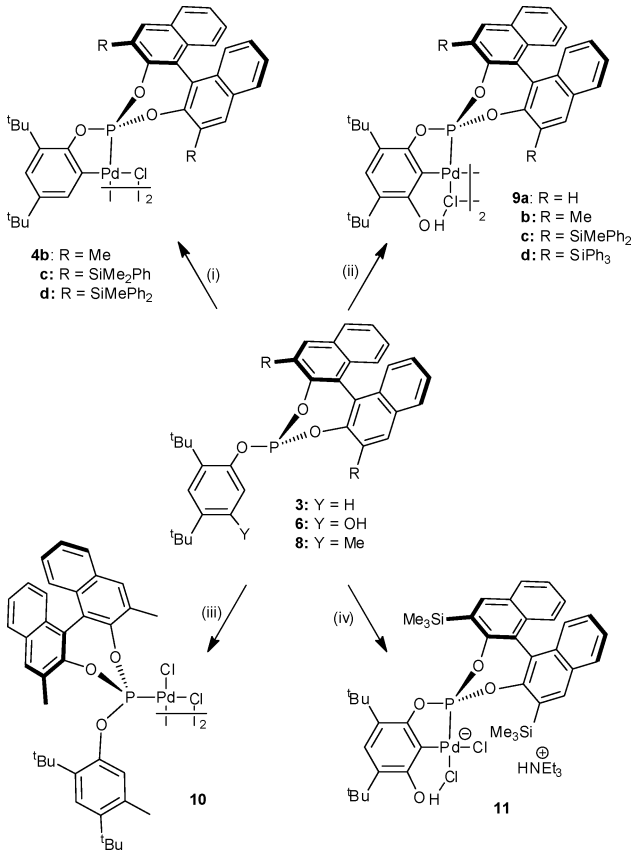


Fig. 3 Angle between square planes (α) in palladacyclic and platinacyclic dimers, defined by MCl_2 planes.

The palladacycles based on the resorcinol monophosphite ligands **6a, b, d–f**, complexes **9a–d** respectively, were readily formed at room temperature in 1,2-dichloroethane employing triethylamine as base. When the same conditions were applied to the reaction of ligand **3e** with $[PdCl_2(NCMe)_2]$ then a mixture of products was observed by ^{1}H NMR of which the dimer **4d** was a minor component. This suggests that the incorporation of the hydroxyl residue aids the orthometallation process. The role played by the hydroxyl group is unlikely to be due to steric considerations, indeed the similarly sized methyl-substituted ligand **8** does not undergo orthopalladation, even under heating, but rather generates the simple dimeric adduct, complex **10** (Scheme 4) as a mixture of *cis* and *trans* isomers. Therefore the role of the hydroxyl group in facilitating orthometallation is presumably an electronic one. The reactions are run in the presence of triethylamine as base, so the oxygen donor is likely to be deprotonated. The phenoxide formed may help direct C–H activation by coordination of the oxygen to the palladium centre and the oxygen anion could also act as an intramolecular base to facilitate the C–H deprotonation.[20]



Scheme 4 Synthesis of complexes. Conditions: (i) $[PdCl_2(NCMe)_2]$, toluene, 80–85 °C, 16–48 h. (ii) $[PdCl_2(NCMe)_2]$, NEt_3, DCE, r.t. 18–24 h. (iii) $[PdCl_2(NCMe)_2]$, toluene, 80 °C, 24 h. (iv) $[PdCl_2(NCMe)_2]$, NEt_3, DCE, r.t. 24 h.

The ^{1}H NMR spectra of complexes **9** in $CDCl_3$ show a substantial downfield shift of the hydroxyl protons to δ 8.4–10.0 ppm. This deshielding is consistent with hydrogen bonding to the phenolic OH.[16] Interestingly both ^{31}P and ^{1}H NMR spectra of complexes **9a–d** show only one isomer for the dimer, in contrast to all other triarphosphite-based palladacycles which, to the best of our knowledge, all show *cis–trans* isomerism in solution. The single crystal X-ray structure of complex **9d** (shown in Fig. 4) shows O···Cl separations of 2.974(9) and 2.997(8) Å, again consistent with a hydrogen bond, suggesting that this is the hydrogen bonding observed in solution.

As seen with complex **4c**, there is a deviation away from co-planarity of the two palladium square planes, although in this case it is far more pronounced (α = 48.4(1)°). The hydrogen-bonding motif may account for observation of only one isomer in solution for the complexes **9a–d**; the *trans* isomer would maximise the strength of the hydrogen bonds whereas the *cis* would lead to

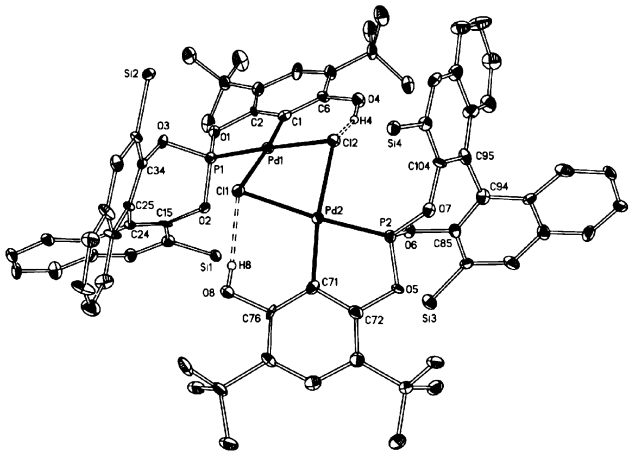


Fig. 4 X-ray structure of complex **9d**. Phenyl groups of $SiPh_3$ and pentane solvate omitted for clarity. Thermal ellipsoids set at 30% probability.

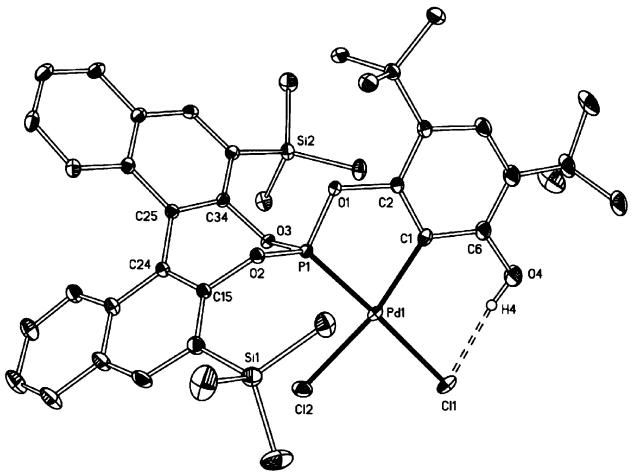


Fig. 5 X-ray structure of complex **11**, Et_3NH^+ counterion and solvate omitted for clarity. Thermal ellipsoids set at 30% probability.

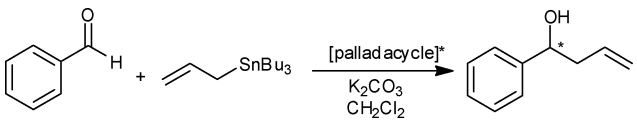
both hydroxyl residues competing for electron density from the same chloride.

The attempted synthesis of the palladacycle derived from ligand **6c** did not yield the expected dimeric complex; instead a monomeric palladacyclic 'ate' species with a triethylammonium counterion, complex **11**, was produced. Such palladacyclic 'ate' complexes have been prepared previously from dimeric palladacycles and ammonium chloride salts,[21] but we cannot account for why this is the sole instance where this occurs with ligands **6** in spite of the fact that all the palladacycles **9** are produced in the presence of triethylamine hydrochloride. The X-ray structure of complex **11** is shown in Fig. 5. Again the O···Cl (2.936(8) Å) separation is consistent with a hydrogen bonding interaction, which is supported by ^{1}H NMR spectroscopy which shows a downfield shift of the phenolic proton to δ 9.32 ppm in $CDCl_3$. The ^{31}P NMR spectrum of **11** shows a peak at δ 130.35 ppm. Interestingly solutions of complexes **9a–c** in $CDCl_3$ left to stand for 24 h show small amounts of a second product in their ^{31}P NMR spectra at δ 131.9, 129.5 and 125.8 ppm, consistent with 'ate' complex formation.

Catalysis

We have previously shown that chiral palladium-PCP pincer complexes based on BINOL-derived resorcinol bis(phosphites) show good activity and moderate enantioselectivity in the allylation of benzaldehye with allyl tributyltin.[22,15] By contrast, whilst complexes **4a** and **5** and various examples of their adducts show good to excellent activity in the same reaction, their stereoselectivity is poor (maximum 15% e.e.).[14b] We therefore chose the same reaction to study here as it would provide a clear indication as to whether or not the incorporation of a hydroxyl function and/or modified BINOL residues would improve enantiocontrol and the results from this study are summarised in Table 1.

Table 1 Palladacycle-catalysed allylation of benzaldehyde[a]



entry	palladacycle	K_2CO_3 (equiv.)	Temp., °C	Time, h	Spec. yield, %[b]	e.e., %[c]
1	**4b**	0	0	24	17	27
2		0.1	0	24	32	11
3	**4c**	0.1	0	24	32	13
4		0.1	R.T.	24	93	22
5	**4d**	0.1	R.T.	24	82	24
6		0.1	0	24	13	43
7		0	R.T.	24	71	37
8	**9b**	0.1	R.T.	24	48	24
9		0.1	0	24	12	46
10	**9c**	0	R.T.	24	54	24
11		0.1	R.T.	24	49	48
12		1.0	R.T.	24	58	46
13		0	0	70	15	29
14	**9d**	0.1	0	24	7	25
15		0.1	R.T.	24	47	17

[a] Conditions: 5 mol% Pd catalyst loading, CH_2Cl_2. [b] Determined by ^{1}H NMR spectroscopy (1,3,5-trimethoxybenzene internal standard). [c] Determined by chiral HPLC, *R*-isomer obtained in all cases.

Comparing entries 1 and 2 it can be seen that the addition of 10% K_2CO_3 to the reaction mixture increases the performance of palladacycles **4b** at the expense of stereoselectivity. Despite this, base was added to the rest of the reactions catalysed by complexes **4** (unless otherwise stated) in order to maximise turnover. Complex **4c** seems to show unusual behaviour in that lower e.e. is seen at lower temperature (compare entries 3 and 4, Table 1). This may well be as a result of base induced decomposition of the active catalyst to a more active but less selective species. Of the simple palladacyclic catalysts tested, complex **4d** showed the highest enantioselectivity, albeit at low conversion (entry 6, Table 1). With this catalyst, enantioselectivity was less strongly influenced by base than **4b** (entry 7, Table 1).

Comparing the hydroxyl-containing catalyst **9b** in the presence of 10 mol% base with the equivalent hydroxyl-free palladacycle **4b** under identical conditions (entries 9 and 2, Table 1) it appears that the introduction of the hydroxyl function led to a significant increase in enantioselectivity (from 11 to 46% ee). Unfortunately, in this case, the yield was lower. Running the reaction at room temperature led to an increase in yield but a drop in enantiocontrol (entry 8, Table 1). The best balance of enantioselectivity (46%) and activity (58%) was achieved using complex **9c** with 100 mol% K_2CO_3 at room temperature (entry 12, Table 1). Interestingly, when the reaction was performed in the absence of base then a similar conversion but a far lower enantioselectivity was observed (entry 10, Table 1). Here, unlike with hydroxyl-free palladacycles **4**, it seems that the addition of base is beneficial. It is possible that the deprotonated hydroxyl coordinates to the tin centre leading to greater enantiocontrol. This is an area that we are currently investigating further.

Conclusions

In summary we have demonstrated that the *meta*-hydroxyl function of chiral mono-phosphites based on 2,4-di-*tert*-butyl resorcinol can have a positive role on the ease of formation of palladacycles. Furthermore the structures of the resultant dimeric palladacycles feature hydrogen-bonding interactions between the hydroxyl group and proximate chloride ligands. These interactions influence both isomerism and the co-planarity of the metal coordination spheres in the dimers. In one instance a palladacyclic 'ate' complex was formed in preference to a dimeric species under the same reaction conditions, and again the complex contains a hydrogen-bonding motif between the OH and the adjacent chloride. Finally it was shown that the hydroxyl function can have a beneficial role on enantioselectivity in the asymmetric allylation of benzaldehyde with allyl tributyltin in the presence of base, giving the highest e.e. yet achieved in this reaction by chiral phosphite-based palladacycles, an effect that we are currently exploring further.

Experimental

General notes

All reactions were carried out under a nitrogen atmosphere in either a glove box or using standard Schlenk techniques. Dry N_2-saturated solvents were collected from a Grubbs solvent system.[23] All other chemicals were used as received unless otherwise stated. All NMR spectra were recorded using a Jeol GX270, Jeol GX400, Jeol ECP300 and Jeol Lambda 300 spectrometers. HPLC analysis was carried out using a Varian Prostar 210 solvent delivery module equipped with a Varian 320 UV/Vis detector fitted with a Chiralcel OD column (0.46 × 25 cm) and using STAR workstation software (v. 6.41). Compounds **7**,[24] **6c**, **e**, **f**,[15] were prepared according to literature methods. ESI and EI Mass spectra were recorded on VG Analytical Quattro and VG Analytical Autospec spectrometers respectively. Microanalyses were carried out by the Microanalytical Laboratory of the School of Chemistry at the University of Bristol.

Preparation of ligand 6a. To a solution of 2,4-di-*tert*-butyl resorcinol (0.271 g, 1.22 mmol) in toluene (10 ml) at 0 °C was added *n*-BuLi (1.5 M in hexane (titrated before use), 0.80 ml, 1.22 mmol) dropwise over 10 min. The resulting suspension was stirred at room temperature for 1 h then re-cooled to 0 °C. After a further 15 min at 0 °C, a solution of (*S*)-1,1′-binaphthalene-2,2′-dioxychlorophosphonite (0.259 g, 0.683 mmol) in toluene (10 ml) was added. The reaction mixture was left to warm to room temperature and stirred for 18 h. The reaction was quenched by addition of aqueous saturated NH_4Cl solution, then extracted into CH_2Cl_2. And the organic layer was washed with brine and then dried over $MgSO_4$, filtered and the solvent removed under reduced pressure. The product was purified by column chromatography (silica CH_2Cl_2 : hexane 3 : 2 eluent) to yield **6a** as a white solid. Yield: 0.246 g (37.5%). Anal. Calcd for $C_{34}H_{33}O_4P$: C, 76.10; H, 6.20%. Found: C, 76.48.; H, 7.08%. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 144.5 (s). ^1H NMR (300 MHz, $CDCl_3$): 1.38 (s, 9, $C(CH_3)_3$), 1.42 (s, 9, $C(CH_3)_3$), 4.64 (s, 1, O*H*), 6.66 (d, 1, Ar*H*), 7.26 (s, 1, Ar*H*), 7.27–7.34 (m, 2, Ar*H*), 7.41–7.50 (m, 5, Ar*H*), 7.59–7.61 (m, 1, Ar*H*), 7.89–7.98 (m, 3, Ar*H*), 8.02–8.04 (m, 1, Ar*H*). MS (ESI) *m*/*z*: 537.22 ($[M+H]^+$), 559.20 $(M+Na)^+$.

Preparation of ligand 6b. As for **6a** with 2,4-di-*tert*-butyl resorcinol (0.152 mg, 0.683 mmol) and (*S*)-3,3′-dimethyl-1,1′-binaphthalene-2,2′-dioxychlorophosphonite (0.259 g, 0.683 mmol). The product was purified by column chromatography (silica, CH_2Cl_2 : hexane 1 : 1 eluent) to yield **6b** as a white solid. Yield: 0.235 g (61.0%). Anal. Calcd for $C_{36}H_{37}O_4P$: C, 76.58; H, 6.60%. Found: C, 73.23; H, 6.64%. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 141.0 (s). ^1H NMR (300 MHz, $CDCl_3$): 1.29 (s, 9, $C(CH_3)_3$), 1.41 (s, 9, $C(CH_3)_3$), 2.49 (d, 3, Ar*Me*), 2.60 (d, 3, Ar*Me*), 4.53 (br, s, 1, O*H*), 6.58 (d, 1, Ar*H*), 7.19–7.24 (m, 3, Ar*H*), 7.30–7.33 (m, 2, Ar*H*), 7.39–7.45 (m, 2, Ar*H*), 7.77 (s, 1, Ar*H*), 7.84–7.88 (m, 3, Ar*H*). MS (ESI) *m*/*z*: 565.25 $(M+H)^+$.

Preparation of ligand 6d. A stirred solution of 2,4-di-*tert*-butylresorcinol (0.072 g, 0.32 mmol) and (*S*)-3,3′-bis-(dimethylphenylsilanyl)-1,1′-binaphthalene-2,2′-dioxychlorophosphonite (0.200 g, 0.32 mmol) in toluene (10 ml) at room temperature was treated with NEt_3 (0.32 ml, 2.26 mmol) dropwise. The reaction mixture was stirred for 1 day, the resultant mixture filtered through Celite and the volatiles removed under reduced pressure. Purification by column chromatography (silica, CH_2Cl_2 : hexane 1 : 1 eluent) to afforded **6d** as a white solid. Yield: 0.24 g (92.3%). Anal. Calcd for $C_{50}H_{53}O_4PSi_2$: C, 74.59; H, 6.64%. Found: C, 73.58; H, 6.89%. $^{31}P\{^1H$ NMR (121.5 MHz, $CDCl_3$): δ 143.5 (s). ^1H NMR (300 MHz, $CDCl_3$): 0.57–0.60 (m, 12, $SiMe_2Ph$), 1.04 (s, 9, $C(CH_3)_3$), 1.38 (s, 9, $C(CH_3)_3$), 3.95 (s, 1, O*H*), 5.80 (d, 1, Ar*H*),

7.11–7.24 (m, 7, Ar*H*), 7.29–7.40 (m, 6, Ar*H*), 7.46–7.48 (m, 2, Ar*H*), 7.54–7.56 (m, 2, Ar*H*), 7.79–7.88 (m, 3, Ar*H*), 8.103 (s, 1, Ar*H*). HRMS (ESI) *m/z*: 805.3270 $(M+H)^+$, 827.3080 $(M+Na)^+$.

Preparation of ligand 3b. A stirred solution of 2,4-di-*tert*-butyl phenol (0.12 g, 0.59 mmol) and (*S*)-3,3′-dimethyl-1,1′-binaphthalene-2,2′-dioxychlorophosphonite (0.222 g, 0.59 mmol) in toluene (20 ml) at room temperature was treated with NEt_3 (0.57 ml, 4.1 mmol) dropwise and the reaction mixture was then stirred for 18 h. Filtration through Celite and removal of the solvent gave the crude product which was purified by column chromatography (silica, CH_2Cl_2 : hexane 1 : 1 eluent) to afford **3b** as a white solid. Yield: 0.22 g (68.5%). Crystals suitable for X-ray analysis were grown from a concentrated diethyl ether solution. Anal. Calcd for $C_{36}H_{37}O_3P$: C, 78.81; H, 6.80%. Found: C, 78.97; H, 6.99%. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 142.9 (s). ^1H NMR (300 MHz, $CDCl_3$): 1.34 (s, 9, $C(CH_3)_3$), 1.36 (s, 9, $C(CH_3)_3$), 2.55 (s, 3, Ar*Me*), 2.61 (s, 3, Ar*Me*), 7.20–7.25 (m, 3, Ar*H*), 7.31–7.45 (m, 6, Ar*H*), 7.78 (s, 1, Ar*H*), 7.83–7.89 (m, 3, Ar*H*). MS (ESI) *m/z*: 549.25 $(M+H)^+$, 571.23 $(M+Na)^+$.

Preparation of ligand 3c. A stirred solution of 2,4-di-*tert*-butyl phenol (0.15 g, 0.73 mmol) and (*S*)-3,3′-bis(trimethylsilanyl)-1,1′-binaphthalene-2,2′-dioxychlorophosphonite (0.36 g, 0.73 mmol) in toluene (20 ml) at room temperature was treated dropwise with NEt_3 (0.71 ml, 5.1 mmol). The reaction mixture was heated at 90 °C for 5 days. Filtration through Celite and concentration under reduced pressure a light yellow solid which was purified by column chromatography (silica, CH_2Cl_2 : hexane 1 : 1 eluent) to afford **3c** as a white solid. Yield: 0.43 g (89%). Anal. Calcd for $C_{40}H_{49}O_3PSi_2$: C, 72.25; H, 7.43%. Found: C, 72.45; H, 7.65%. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 145.3 (s). ^1H NMR (300 MHz, $CDCl_3$): 0.36 (s, 9, SiMe_3), 0.39 (s, 9, SiMe_3), 1.10 (s, 9, $C(CH_3)_3$), 1.32 (s, 9, $C(CH_3)_3$), 7.09–7.15 (m, 2, Ar*H*), 7.18–7.28 (m, 4, Ar*H*), 7.33 (d, 1, Ar*H*), 7.41–7.4 (m, 2, Ar*H*), 7.93–7.96 (m, 2, Ar*H*), 8.09 (s, 2, Ar*H*). MS (ESI) *m/z*: 665.28 $(M+H)^+$, 687.26 $(M+Na)^+$.

Preparation of ligand 3d. As for **3c** using 2,4-di-*tert*-butyl phenol (0.077 g, 0.37 mmol) and (*S*)-3,3′-bis-(dimethyl-phenyl-silanyl)-1,1′-binaphthalene-2,2′-dioxychlorophosphonite (0.23 g, 0.37 mmol), the product was purified by column chromatography (silica, CH_2Cl_2 : hexane 1 : 3 eluent) to afford **3d** as a white solid. Yield: 0.20 g (69.1%). Anal. Calcd for $C_{50}H_{53}O_3PSi_2$: C, 76.10; H, 6.77%. Found: C, 76.14; H, 6.78%. $^{31}P\{^1H\}$ NMR (161.8 MHz, $CDCl_3$): δ 147.6 (s). ^1H NMR (400 MHz, $CDCl_3$): 0.61–0.63 (m, 12, SiMe_2Ph), 1.01 (s, 9, $C(CH_3)_3$), 1.36 (s, 9, $C(CH_3)_3$), 6.92–6.95 (m, 1, Ar*H*), 7.08–7.42 (m, 14, Ar*H*), 7.47–7.49 (m, 2, Ar*H*), 7.56–7.59 (m, 2, Ar*H*), 7.80–7.90 (m, 3, Ar*H*), 8.04 (s, 1, Ar*H*). HRMS (ESI) *m/z*: 789.3347 $(M+H)^+$, 811.3166 $(M+Na)^+$.

Preparation of ligand 3e. As for **3c** with 2,4-di-*tert*-butyl phenol (0.146 g, 0.71 mmol) and (*S*)-3,3′-bis-(diphenylmethyl-silanyl)-1,1′-binaphthalene-2,2′-dioxychlorophosphonite (0.53 g, 0.71 mmol). Purification by column chromatography (silica, CH_2Cl_2 : hexane 2 : 3 eluent) gave **3e** as a white solid. Yield: 0.50 g (77.5%). Anal. Calcd for $C_{60}H_{57}O_3PSi_2$: C, 78.91; H, 6.29%. Found: C, 78.72; H, 6.35%. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 149.5 (s). ^1H NMR (300 MHz, $CDCl_3$): 0.78 (s, 3, Si*Me*Ph_2), 0.88 (s, 3, Si*Me*Ph_2), 0.88 (s, 9, $C(CH_3)_3$), 1.33 (s, 9, $C(CH_3)_3$), 6.53 (dd, 1, Ar*H*), 6.95 (dd, 1, Ar*H*), 7.16–7.52 (m, 27, Ar*H*), 7.73–7.83 (m, 3, Ar*H*), 7.94 (s, 1, Ar*H*). MS (ESI) *m/z*: 913.36 $(M+H)^+$, 935.35 $(M+Na)^+$.

Preparation of ligand 8. As for **3b** with 2,4-di-*tert*-butyl-5-methylphenol (0.20 g, 0.91 mmol) and (*S*)-3,3′-dimethyl-1,1′-binaphthalene-2,2′-dioxychlorophosphonite (0.344 g, 0.91 mmol). White solid. Yield: 0.498 g (97.5%). Anal. Calcd for $C_{37}H_{39}O_3P$: C, 78.98; H, 6.99%. Found: C, 79.06; H, 7.02%. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 141.8 (s). ^1H NMR (300 MHz, $CDCl_3$): 1.57 (s, 9, $C(CH_3)_3$), 1.63 (s, 9, $C(CH_3)_3$), 2.64 (s, 3, Ar*Me*), 2.77 (s, 3, Ar*Me*), 2.81 (s, 3, Ar*Me*), 7.31 (s, 1, Ar*H*), 7.34–7.39 (m, 2, Ar*H*), 7.53–7.59 (m, 4, Ar*H*), 7.61 (s, 1, Ar*H*), 7.95 (s, 1, Ar*H*), 7.96–8.02 (m, 3, Ar*H*). HRMS (ESI) *m/z*: 563.2688 $(M+H)^+$, 585.2506 $(M+Na)^+$.

Preparation of complex 4b. A mixture of the ligand **3b** (0.100 g, 0.182 mmol) and $[PdCl_2(NCMe)_2]$ (0.047 g, 0.182 mmol) in toluene (5 ml) was heated at 80 °C for 2 days. The resulting mixture was filtered through Celite, the solvent was removed under reduced pressure and the product recrystallised from Et_2O to give **4b** as a yellow solid (0.086 g, 68.5%). Crystals suitable for X-ray analysis were grown by slow evaporation of an Et_2O/hexane solution under air. Anal. Calcd for $C_{72}H_{72}Cl_2O_6P_2Pd_2$: C, 62.71; H, 5.26%. Found: C, 62.84; H, 5.43%. HRMS (ESI) *m/z*: 1343.2589 $(M-Cl)^+$, 1401.2158 $(M+Na)^+$. Major isomer: $^{31}P\{^1H\}$ NMR (121.5 MHz, CDCl3): δ 136.4 (s). ^1H NMR (300 MHz, $CDCl_3$): 1.13 (s, 18, $C(CH_3)_3$), 1.23 (s, 18, $C(CH_3)_3$), 2.49 (s, 6, Ar*Me*), 2.96 (s, 6, Ar*Me*), 7.12–7.22 (m, 4, Ar*H*), 7.26–7.36 (m, 8, Ar*H*), 7.46–7.53 (m, 4, Ar*H*), 7.85–7.97 (m, 6, Ar*H*). Minor isomer: $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 139.0 (s). ^1H NMR (300 MHz, $CDCl_3$): 1.17 (s, 18, $C(CH_3)_3$), 1.40 (s, 18, $C(CH_3)_3$), 2.49 (s, 6, Ar*Me*), 2.58 (s, 6, Ar*Me*), all other peaks obscured.

Preparation of complex 4c. A mixture of the ligand **3d** (0.100 g, 0.127 mmol) and $[PdCl_2(NCMe)_2]$ (0.033 g, 0.127 mmol) in toluene (5 ml) was heated at 85 °C for 18 h. The resulting mixture was filtered through Celite, the solvent was removed under reduced pressure and the product recrystallised from Et_2O/hexane to give the **4c** as a yellow solid Yield: 0.066 g (56%). Anal. Calcd for $C_{100}H_{104}Cl_2O_6P_2Pd_2Si_4$: C, 64.58; H, 5.64%. Found: C, 64.27; H, 5.56%. Major isomer: $^{31}P\{^1H\}$ NMR (161.8 MHz, $CDCl_3$): δ 134.5 (s). ^1H NMR (400 MHz, $CDCl_3$): 0.51 (d, 6, SiMe_2Ph), 0.90 (s, 3, SiMe_2Ph), 1.06 (s, 3, SiMe_2Ph), 1.12 (s, 9, $C(CH_3)_3$), 1.16 (s, 9, $C(CH_3)_3$), 7.03–7.09 (m, 3, Ar*H*), 7.14–7.25 (m, 7, Ar*H*), 7.27–7.30 (m, 2, Ar*H*), 7.39–7.45 (m, 2, Ar*H*), 7.51–7.55 (m, 2, Ar*H*), 7.68–7.71 (m, 2, Ar*H*), 7.83–7.85 (m, 2, Ar*H*), 7.93 (s, 1, Ar*H*), 8.01 (s, 1, Ar*H*). Minor isomer: $^{31}P\{^1H\}$ NMR (161.8 MHz, $CDCl_3$): δ 134.8 (s). ^1H NMR (400 MHz, $CDCl_3$): all peaks obscured by major isomer. MS (ESI) *m/z*: 1825.20 $(M-Cl)^+$, 1883.15 $(M+Na)^+$.

Preparation of complex 4d. A mixture of the ligand **3e** (0.244 g, 0.267 mmol) and $[PdCl_2(NCMe)_2]$ (0.069 g, 0.267 mmol) in toluene (10 ml) was heated at 80 °C for 16 h. The resulting mixture was filtered through Celite, the solvent was removed under reduced pressure and the product purified by column chromatography (silica, EtOAc : hexane 1 : 3 eluent) to give **4d** as a white solid (0.23 g, 82%). Anal. Calcd for $C_{120}H_{112}Cl_2O_6P_2Pd_2Si_4$: C, 68.37; H, 5.35%. Found: C, 68.23; H, 5.50%. MS (ESI) *m/z*: 2073.46 $(M-Cl)^+$, 2132.43$(M+Na)^+$. Major isomer: $^{31}P\{^1H\}$ NMR (121.5 MHz, CDCl3): δ 135.7 (s). ^1H NMR (300 MHz, $CDCl_3$): 0.83 (d, 3, Si*Me*Ph_2), 1.19 (s, 9, $C(CH_3)_3$), 1.24 (s, 9, $C(CH_3)_3$), 1.52

(s, 3, Si*Me*Ph_2), 7.10–7.16 (m, 4, Ar*H*), 7.21–7.41 (m, 14, Ar*H*), 7.49–7.64 (m, 8, Ar*H*), 7.80 (dd, 2, Ar*H*), 7.91 (dd, 2, Ar*H*), 8.16 (d, 2, Ar*H*). Minor isomer: $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 136.2 (s). ^1H NMR (300 MHz, $CDCl_3$): all peaks obscured by major isomer.

Preparation of complex 9a. A mixture of the ligand **6a** (0.201 g, 0.37 mmol) and [$PdCl_2(NCMe)_2$] (0.097 g, 0.37 mmol) in 1,2-dichloroethane (10 ml) was stirred at room temperature for 1 h during which time the colour of the mixture changed from yellow to orange. The mixture was then treated with NEt_3 (0.05 ml, 0.354 mmol) and then stirred for 18 h. The resulting mixture was filtered through Celite, the solvent was removed under reduced pressure and the product purified by column chromatography (silica, THF : hexane 1 : 1 eluent) to afford **9a** as a yellow solid. Yield: 0.21 g (83%). Calcd for $C_{68}H_{64}Cl_2O_8P_2Pd_2$: C, 60.28; H, 4.76%. Found: C, 60.81; H, 5.06%. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 140.6 (s). ^1H NMR (300 MHz, $CDCl_3$): 1.13 (s, 9, C(CH_3)$_3$), 1.40 (s, 9, C(CH_3)$_3$), 7.03–7.04 (m, 1, Ar*H*), 7.14–7.18 (m, 3, Ar*H*), 7.28–7.38 (m, 4, Ar*H*), 7.44–7.54 (m, 4, Ar*H*), 7.97–8.03 (m, 2,Ar*H*), 9.81 (s, 1, OH). MS (ESI) *m*/*z*: 1319.15 $(M-Cl)^+$.

Preparation of complex 9b. As for **9a** with ligand **6b** (0.200 g, 0.354 mmol) and [$PdCl_2(NCMe)_2$] (0.092 g, 0.354 mmol) to give **9b** as a yellow solid. Yield: 0.222 g (89%). Anal. Calcd for $C_{72}H_{72}Cl_2O_8P_2Pd_2$: C, 61.29; H, 5.14%. Found: C, 60.97; H, 5.67%. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 138.1 (s). ^1H NMR (300 MHz, $CDCl_3$): 1.15 (s, 9, C(CH_3)$_3$), 1.49 (s, 9, C(CH_3)$_3$), 2.43 (s, 3, Ar*Me*), 2.48 (s, 3, Ar*Me*), 6.90–7.12 (m, 2, Ar*H*), 7.20–7.33 (m, 4, Ar*H*), 7.47–7.60 (m, 2, Ar*H*), 7.67–7.92 (m, 3, Ar*H*), 10.01 (s, 1, O*H*). MS (ESI) *m*/*z*: 1433.18 $(M+Na)^+$, 1397.21 $(M+Na-Cl)^+$, 1375.23 $(M-Cl)^+$.

Preparation of complex 9c. A solution of ligand **6e** (0.400 g, 0.43 mmol) and [$PdCl_2(NCMe)_2$] (0.112 g, 0.43 mmol) in 1,2-dichloroethane (10 ml) at room temperature was treated dropwise with NEt_3 (0.18 ml, 1.29 mmol) and the resultant mixture was stirred for 1 day. The resulting mixture was filtered through Celite, the solvent removed under reduced pressure and the product purified by column chromatography (silica, THF : hexane 3 : 2 eluent) to afford a **9c** as a yellow solid. Yield: 0.447 g (97%). Anal. Calcd for $C_{120}H_{112}Cl_2O_8P_2Pd_2Si_4$: C, 67.34; H, 5.27%. Found: C, 68.36; H, 5.77%. $^{31}P\{1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 132.9 (s). ^1H NMR (300 MHz, $CDCl_3$): 0.52 (s, 3, Si*Me*Ph_2), 1.08 (s, 3, Si*Me*Ph_2), 1.08 (s, 9, C(CH_3)$_3$), 1.51 (s, 9, C(CH_3)$_3$), 6.98–7.27 (m, 16, Ar*H*), 7.34–7.49 (m, 10, Ar*H*), 7.54–7.57 (m, 2, Ar*H*), 7.62 (s, 1, Ar*H*), 7.81–7.84 (m, 1, Ar*H*), 7.99 (s, 1, Ar*H*), 8.80 (s, 1, O*H*). MS (ESI) *m*/*z*: 2142.43 $(M+H)^+$, 2105.43 $(M-Cl)^+$, 2069.46 $(M-2Cl)^+$.

Preparation of complex 9d. As for **9c** with ligand **6f** (0.250 g, 0.24 mmol) and [$PdCl_2(NCMe)_2$] (0.062 g, 0.24 mmol), purified by column chromatography (silica, THF : hexane = 1 : 1) to afford **9d** as yellow solid. Yield: 0.249 g (88%). Crystals suitable for X-ray analysis were grown by slow evaporation of an Et_2O/pentane solution under air. Anal. Calcd for $C_{140}H_{120}Cl_2O_8P_2Pd_2Si_4$: C, 70.40; H, 5.06%. Found: C, 70.39; H, 5.31%. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 128.3 (s). ^1H NMR (300 MHz, $CDCl_3$): 0.98 (s, 9, C(CH_3)$_3$), 1.36 (s, 9, C(CH_3)$_3$), 6.71–6.85(m, 10, Ar*H*), 7.03(s, 1, ArH), 7.18–7.27 (m, 11, Ar*H*), 7.33–7.42 (m, 8, Ar*H*), 7.47–7.58 (m, 2, Ar*H*), 7.73–7.75 (m, 6, Ar*H*), 7.86–8.06 (m, 2, Ar*H*), 8.18 (s, 1, Ar*H*), 8.41 (s, 1, O*H*). MS (ESI) *m*/*z*: 2352.56 $(M-Cl)^+$.

Preparation of complex 10. A mixture of the ligand **8** (0.200 g, 0.355 mmol) and [$PdCl_2(NCMe)_2$] (0.092 g, 0.255 mmol) in toluene (8 ml) was heated at 80 °C for 1 day. The resulting mixture was filtered through Celite, the solvent was removed under reduced pressure and the product purified by column chromatography (silica, THF : hexane 1 : 2 eluent) followed by recrystallisation from Et_2O/hexane to afford **10** as an orange solid. Yield: 0.201 g, (76.5%). Anal. Calcd for $C_{74}H_{78}Cl_4O_6P_2Pd_2$: C, 60.05; H, 5.31%. Found: C, 60.35; H, 5.20%. MS (ESI) *m*/*z*: 1445.24 $(M-Cl)^+$, 1467.22 $(M-Cl+Na)^+$, 1503.20 $(M+Na)^+$. Major isomer: $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 74.70 (s). ^1H NMR (300 MHz, $CDCl_3$): 1.19 (s, 18, C(CH_3)$_3$), 1.43 (s, 18, C(CH_3)$_3$), 2.21 (s, 6, Ar*Me*), 2.38 (s, 6, Ar*Me*), 3.01 (s, 6, Ar*Me*), 7.10–7.24 (m, 8, Ar*H*), 7.32–7.51 (m, 6, Ar*H*), 7.63 (s, 4, Ar*H*), 7.77 (m, 2, Ar*H*), 7.95 (m, 2, Ar*H*), 8.01 (s, 2, Ar*H*). Minor isomer: $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 76.72 (s). ^1H NMR (300 MHz, $CDCl_3$): 1.21 (s, 18, C(CH_3)$_3$), 1.46 (s, 18, C(CH_3)$_3$), all other peaks obscured.

Preparation of complex 11. A solution of ligand **6c** (0.200 g, 0.29 mmol) and [$PdCl_2(NCMe)_2$] (0.076 g, 0.29 mmol) in 1,2-dichloroethane (10 ml) at room temperature was treated dropwise with NEt_3 (0.13 ml, 0.88 mmol) and the mixture stirred for 1 day. Filtration through Celite and removal of the solvent under reduced pressure gave the title compound as a brown solid (0.265 g, 94%). Crystals suitable for X-ray analysis were grown by slow evaporation of an Et_2O/pentane solution under argon. Anal. Calcd for $C_{46}H_{64}Cl_2NO_4PPdSi_2$: C, 57.58; H, 6.72%; N, 1.46. Found: C, 57.91; H, 7.02; N, 1.71%. MS (ESI) *m*/*z*: 924.28 $(M-Cl)^+$. $^{31}P\{^1H\}$ NMR (161.8 MHz, $CDCl_3$): δ 130.35 (s). ^1H NMR (400 MHz, $CDCl_3$): 0.41 (s, 9, SiMe_3), 0.48 (s, 9, SiMe_3), 0.97 (s, 9, C(CH_3)$_3$), 1.28 (t, 9, NCH_2Me), 1.40 (s, 9, C(CH_3)$_3$), 3.11 (dq, 6, NCH_2Me), 6.95 (d, 1, Ar*H*), 7.07–7.24 (m, 4, Ar*H*), 7.37–7.47 (m, 2, Ar*H*), 7.88–7.95 (m, 2, Ar*H*), 8.06 (s, 1, Ar*H*), 8.09 (s, 1, Ar*H*), 9.32 (s, 1, O*H*), 9.59 (br, s, 1, N*H*).

General method for the allylation of benzaldehyde

To a dried reaction tube, charged with a solution of the appropriate palladacycle (0.025 mmol Pd) in CH_2Cl_2 (0.5 ml), were added benzaldehyde (0.050 ml, 0.053 g, 0.5 mmol) and allyltributyl tin (0.200 ml, 0.212 g, 0.64 mmol). Additional CH_2Cl_2 (0.5 ml) was added to ensure all reagents were washed into the reaction mixture and the resulting solution was stirred at the appropriate temperature for 24–70 h (see Table 1 for details). The reaction mixture was quenched with water (10 ml), the product extracted with CH_2Cl_2 (3 × 10 ml), the combined organic phase dried ($MgSO_4$) and the solvent removed under reduced pressure. 1,3,5-Trimethoxybenzene (internal standard) was added and the spectroscopic yield was determined by ^1H NMR spectroscopy ($CDCl_3$, 300 MHz). The product was purified by column chromatography (silica, EtOAc : hexane 1 : 6 eluent) prior to determining optical purity by chiral HPLC.

X-ray crystallography

X-ray diffraction experiments on **9d** and **11** were carried out at 100 K on a Bruker APEX II diffractometer using Mo-Kα radiation (λ = 0.71073 Å). X-ray diffraction experiments on **3b** and **4c** were

Table 2 Crystallographic data

Compound	**3b**	**4c**	**9d**·C_5H_{12}	**11**
Colour, habit	colourless, plate	colourless, plate	yellow, cube	brown, shard
Size/mm	$0.08 \times 0.06 \times 0.04$	$0.05 \times 0.03 \times 0.02$	$0.07 \times 0.05 \times 0.05$	$0.68 \times 0.21 \times 0.10$
Empirical Formula	$C_{36}H_{37}O_3P$	$C_{100}H_{104}Cl_2O_6P_2Pd_2Si_4$	$C_{145}H_{132}Cl_2O_8P_2Pd_2Si_4$	$C_{46}H_{64}Cl_2NO_4PPdSi_2$
M	548.63	1859.83	2460.51	959.43
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\,2_1$	$C2$	$P\,2_1$	$C2$
a/Å	9.9688(11)	29.464(3)	14.4938(6)	27.1630(4)
b/Å	9.1502(10)	9.6174(9)	30.6692(13)	14.3800(2)
c/Å	16.0481(17)	22.049(2)	14.4991(5)	14.1182(2)
α (°)	90.00	90.00	90.00	90.00
β (°)	99.461(4)	132.779(3)	106.461(3)	105.286(1)
γ (°)	90.00	90.00	90.00	90.00
V/Å^3	1443.9(3)	4585.7(7)	6180.9(4)	5319.53(13)
Z	2	2	2	4
μ/mm^{-1}	1.115	4.946	0.458	0.561
T/K	100	100	100	100
$\theta_{min,max}$	2.79,60.85	2.73,65.11	2.20,27.58	1.50,30.60
Completeness	0.997 to $\theta = 60.85°$	0.994 to $\theta = 65.11°$	0.997 to $\theta = 27.58°$	0.994 to $\theta = 30.60°$
Reflections: total/independent	15287/4340	27683/7624	73461/27759	77077/16225
R_{int}	0.0414	0.0480	0.1448	0.0482
Final R_1 and wR_2	0.0310, 0.0783	0.0287, 0.0665	0.0919, 0.2009	0.0321, 0.0745
Largest peak, hole/eÅ^{-3}	0.281, –0.205	0.544, –0.443	1.523, –1.143	0.558, –0.281
ρ_c/g cm^{-3}	1.262	1.347	1.322	1.198
Flack parameter	0.056(16)	0.007(5)	0.01(3)	–0.013(11)

carried out at 100 K on a Bruker Microstar diffractometer using Cu-Kα radiation ($\lambda = 1.54178$ Å). Data collections were performed using a CCD area detector from a single crystal mounted on a glass fibre. Intensities were integrated[25] from several series of exposures measuring 0.5° in ω or ϕ. Absorption corrections were based on equivalent reflections using SADABS.[26] The structures were solved using SHELXS and refined against all F_o^2 data with hydrogen atoms riding in calculated positions using SHELXL.[27] Crystal structure and refinement data are given in Table 2.

The difference map of **11** contained residual electron density, likely to be disordered pentane, which could not be modelled satisfactorily. The data were modelled using the program SQUEEZE,[28] details of which may be found in the CIF.†

Acknowledgements

We thank and the CCDC for a studentship (CLM) and Johnson Matthey for the loan of palladium salts.

Notes and references

1 (*a*) N. Ahmad, E. W. Ainscough, T. A. James and S. D. Robinson, *J. Chem. Soc., Dalton Trans.*, 1973, 1151; (*b*) A. Albinati, S. Affolter and P. S. Pregosin, *Organometallics*, 1990, **9**, 379.
2 For an early report on their use in hydrogenation see: L. N. Lewis, *J. Am. Chem. Soc.*, 1986, **108**, 743.
3 Selected reviews: (*a*) J. Dupont and M. Pfeffer, (ed.), *Palladacycles: Synthesis Characterisation and Applications*, Wiley, New York, 2008; (*b*) J. Dupont, C. S. Consorti and J. Spencer, *Chem. Rev.*, 2005, **105**, 2527; (*c*) R. B. Bedford, C. S. J. Cazin and D. Holder, *Coord. Chem. Rev.*, 2004, **248**, 2283; (*d*) R. B. Bedford, *Chem. Commun.*, 2003, 1787.
4 (*a*) D. A. Albisson, R. B. Bedford, S. E. Lawrence and P. N. Scully, *Chem. Commun.*, 1998, 2095; (*b*) R. B. Bedford, S. L. Hazelwood and M. E. Limmert, *Chem. Commun.*, 2002, 2610; (*c*) R. B. Bedford, C. S. J. Cazin and S. L. Hazelwood, *Angew. Chem., Int. Ed.*, 2002, **41**, 4120; (*d*) R. B. Bedford, S. L. Hazelwood, M. E. Limmert, D. A. Albisson, S. M. Draper, P. N. Scully, S. J. Coles and M. B. Hursthouse, *Chem.–Eur. J.*, 2003, **9**, 3216; (*e*) R. B. Bedford, C. P. Butts, T. E. Hurstand and P. Lidström, *Adv. Synth. Catal.*, 2004, **346**, 1627; (*f*) R. B. Bedford, S. J. Coles, M. B. Hursthouse and V. J. M. Scordia, *Dalton Trans.*, 2005, 991; (*g*) R. B. Bedford, M. Betham, M. E. Blake, R. M. Frost, P. N. Horton, M. B. Hursthouse and R.-M. López-Nicolás, *Dalton Trans.*, 2005, 2774.
5 R. B. Bedford, C. S. J. Cazin and S. L. Hazelwood, *Chem. Commun.*, 2002, 2608.
6 (*a*) D. A. Albisson, R. B. Bedford and P. N. Scully, *Tetrahedron Lett.*, 1998, **39**, 9793; (*b*) 12 V. P. W. Böhm and W. A. Herrmann, *Chem.–Eur. J.*, 2000, **6**, 1017.
7 R. B. Bedford and M. E. Blake, *Adv. Synth. Catal.*, 2003, **345**, 1107.
8 J. Li, M. Lutz, A. L. Spek, G. P. M. van Klink, G. van Koten and R. J. M. Klein Gebbink, *J. Organomet. Chem.*, 2010, **695**, 2618.
9 I. J. S. Fairlamb, S. Grant, P. McCormack and J. Whittall, *Dalton Trans.*, 2007, 859.
10 W. Tang, S. Keshipeddy, Y. Zhang, X. Wei, J. Savoie, N. D. Patel, N. K. Yee and C. H. Senanayake, *Org. Lett.*, 2011, **13**, 1366.
11 (*a*) R. B. Bedford, M. Betham, J. P. H. Charmant, M. F. Haddow, A. G. Orpen and L. T. Pilarski, *Organometallics*, 2007, **26**, 6346; (*b*) P. He, Y. Lu, C. Guo-Dong and Q.-S. Hu, *Org. Lett.*, 2007, **9**, 343; (*c*) P. He, Y. Lu and Q.-S. Hu, *Tetrahedron Lett.*, 2007, **48**, 5283.
12 R. B. Bedford and L. T. Pilarski, *Tetrahedron Lett.*, 2008, **49**, 4216.
13 R. B. Bedford, M. Betham, M. E. Blake, A. Garces, S. L. Millar and S. Prashar, *Tetrahedron*, 2005, **61**, 9799.
14 (*a*) V. V. Dunina, P. A. Zykov, M. V. Livantsov, I. V. Glukhov, K. A. Kochetkov, I. P. Gloriozov and Y. K Grishin, *Organometallics*, 2009, **28**, 425; (*b*) R. B. Bedford, H. Dumycz, M. F. Haddow, L. T. Pilarski, A. G. Orpen, P. G. Pringle and R. L. Wingad, *Dalton Trans.*, 2009, 7796; (*c*) J. Li, M. A. Siegler, M. Lutz, A. L. Spek, R. J. M. Klein Gebbink and G. van Koten, *Organometallics*, 2009, **28**, 5323.
15 R. B. Bedford, Y.-N. Chang, M. F. Haddow and C. L. McMullin, *Dalton Trans.* , submitted.
16 R. J. Abraham and M. Mobli, *Magn. Reson. Chem.*, 2007, **45**, 865.
17 For a rare example of *cis* geometry observed in the solid state see: R. B. Bedford, M. Betham, S. J. Coles, P. N. Horton and M.-J. López-Sáez, *Polyhedron*, 2006, **25**, 1003.
18 Cambridge Structural Database V5.32, F. H. Allen, *Acta Crystallogr., Sect. B: Struct. Sci.*, 2002, **58**, 380.
19 In both of these complexes, the palladacyclic rings have significant steric hindrance orthogonal to the metallacyclic ring caused by the introduction of organometallic fragments into the palladacyclic ring. See: (*a*) Y.-H. Gan, J.-C. Lee and F.-E Hong, *Polyhedron*, 2006, **25**, 3555; (*b*) V. V. Dunina, O. N. Gorunova, M. V. Livantsov, Y. K. Grishin, L. G. Kuzmina, N. A. Kataeva and A. V. Churakov, *Tetrahedron: Asymmetry*, 2000, **11**, 3967.

20 For selected examples of base-assisted deprotonation mechanisms for C–H bond activation see: (*a*) D. L. Davies, S. M. A. Donald and S. A. Macgregor, *J. Am. Chem. Soc.*, 2005, **127**, 13754; (*b*) D. García-Cuadrado, P. de Mendoza, A. A. C. Braga, F. Maseras and A. M. Echavarren, *J. Am. Chem. Soc.*, 2007, **129**, 6880; (*c*) S. I. Gorelsky, D. Lapointe and K. Fagnou, *J. Am. Chem. Soc.*, 2008, **130**, 10848.
21 R. B. Bedford, M. Betham, C. P. Butts, S. J. Coles, M. B. Hursthouse, P. N. Scully, J. H. R. Tucker, J. Wilkie and Y. Willener, *Chem. Commun.*, 2008, 2429.
22 R. A. Baber, R. B. Bedford, M. Betham, M. E. Blake, S. J. Coles, M. F. Haddow, M. B. Hursthouse, A. G. Orpen, L. T. Pilarski, P. G. Pringle and R. L. Wingad, *Chem. Commun.*, 2006, 3880.
23 A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen and F. J. Timmers, *Organometallics*, 1996, **15**, 1518.
24 (*a*) A. H. M. de Vries, A. Meetsma Auke and B. L. Feringa, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 2374; (*b*) G. J. H. Buisman, L. A. van der Veen, A. Klootwijk, W. G. J. de Lange, P. C. J. Kamer, P. W. N. M van Leeuwen and D. Vogt, *Organometallics*, 1997, **16**, 2929.
25 Bruker-AXS SAINT, Madison, Wisconsin.
26 G. M. Sheldrick, *SADABS, Program for area detector adsorption correction*, Institute for Inorganic Chemistry, University of Göttingen, Germany, 1996.
27 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **64**, 112.
28 A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7.

