A series of enantiopure MOP-phosphonite ligands, with tailored steric profiles, have been synthesised and are proven to be very successful in high-yielding, regio- and enantioselective catalytic hydrosilylation reactions of substituted styrenes, affording important chiral secondary alcohols.

Chiral mono- and bidentate phosphorus ligands have achieved considerable acclaim in a variety of transition metal-catalysed asymmetric transformations. Atropisomeric monophosphines with a binaphthyl backbone have been reported to be particularly successful in high-yielding chiral alkenes.

We recently reported a new class of MOP-phosphonite ligands (Ia and Ib), based on a MOP/XuPhos-type hybrid (Chart 1). Chiral phosphonites are ligands with good π-acceptor properties and are effective in a range of asymmetric hydrocyanations, hydroformylations and hydrogenations. Ligands Ia and Ib possess a phosphorus donor bound directly to a binaphthyl backbone – the a series has a hydrogen in the 2′ position of the lower naphthyl ring whilst a methoxy group occupies the site of the b series (Chart 1). This difference has profound implications for the catalytic performance of the parent (S)-H-MOP and (R)-MeO-MOP ligands, and we wished to examine this effect for phosphonite derivatives. Importantly, we also wanted to examine the effect of incorporating a second chiral moiety, which we achieved by appending either (R) or (S)-binol to isolate the diastereomeric pairs (R,Rb)-Ia, (S,Sb)-Ia and (R,Rb)-Ib, (S,Sb)-Ib. By investigating the coordination chemistry and catalytic performance of the four ligand pairs, we were able to demonstrate that subtle differences in the position of the palladium atom relative to the lower naphthyl ring in these complexes appears to have important consequences for chiral induction in the catalytic hydrosilylation of styrene. These results led us to question whether the large chiral binol group was in fact necessary for effective asymmetric catalysis.

In this study we sought to investigate the effect of replacing the binol moiety of Ia and Ib with achiral ancillary arylxides, in order to establish if the enantioselectivities remain high by virtue of the phosphorus-bonded binaphthyl backbone, and thus eliminate the requirement for a second chiral centre. To the best of our knowledge this has not been demonstrated for MOP phosphonites, which are likely to effectively catalyse alternate substrates than their phosphine cousins, by virtue of their differing electronic properties. Herein we describe the synthesis of the phenoxy derivatives (S)-3a and (R)-3b, which allowed us to probe the effect of removing the chelating element of the added arylxide, before describing how the sensitivity of these ligands to hydrolysis demanded the design of next generation biphenoxo-based MOP-phosphonites (S)-4a and (R)-4b, which were further improved upon to yield the user-friendly, chiral phosphonites (S)-5a and (R)-5b, that perform better than the corresponding MOP phosphines in the hydrosilylation of functionalised styrenes (Chart 2 and Table 2).

The six new MOP-phosphonite ligands were synthesised following a procedure we have developed, starting with the air-stable, chiral primary phosphine precursors (S)-1a and (R)-1b. In a two-step, one-pot reaction, the primary phosphine was treated with phosphorus pentachloride, quantitatively yielding the dichlorophosphines (S)-2a and (R)-2b (Scheme 1). Our initial targets (S)-3a and (R)-3b were synthesised by employing...
two equivalents of phenol, however both syntheses proved to be temperamental as a result of their sensitivity to hydrolysis, with (S)-3a particularly low-yielding. Therefore we sought to replace the two phenol groups with the achiral, chelating 2,2'-biphenol, in order to ascertain whether we could inhibit this decomposition. This approach led to the successful preparation of the enantiopure compounds (S)-4a and (R)-4b; the ligands can be stored under nitrogen for a period of weeks with only minimal decomposition. However, during our initial investigations into the coordination chemistry of these ligands, we noticed slow decomposition in solution and their performance in catalytic hydrosilylation required improvement (vide infra). Thus, in order to push the design concept still further and optimise both ligand stability and catalytic capability, we synthesised the bulky ortho-methyl substituted starting material 2,2'-dihydroxy-3,3'-dimethyl-1,1'-biphenyl (ESI†), and used it to prepare the ligands (S)-5a and (R)-5b which possess a more imposing steric profile. Both phosphonites were isolated in high yield, and are purified by passing through a plug of alumina in air. They can be stored under nitrogen without decomposition over several months, and their coordination complexes also exhibit better stability.

The phosphonites were fully characterised by multinuclear NMR spectroscopy and High Resolution Mass Spectrometry. Their 31P{1H} spectra show characteristic singlet peaks; δ (ppm) = (S)-3a (154.8), (R)-3b (155.6), (S)-4a (177.7), (R)-4b (180.0), (S)-5a (172.4) and (R)-5b (174.2). The resonances for the phenoxyl-derived phosphonites have a notable upfield shift compared to the biphenoxyl analogues. Single crystals of (R)-3b and (R)-4b suitable for X-ray crystallographic analysis were obtained (Fig. 1 and 2); there are two crystallographically independent molecules in the asymmetric unit of (R)-3b. Density Functional Theory calculations at the B3LYP/6-31G* level of theory (ESI†) revealed that the phosphonites have lower HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital) energies than their aryl counterparts, and have a lower phosphorus contribution to the HOMO, implying the phosphonites are weaker P-ligand σ-donors. To study the coordination chemistry of our ligands with Pd(n), we reacted them with [Pd(η3–C5H5)Cl]2 in a 1 : 1, P : Pd ratio, to quantitatively synthesise the complexes [{η3–C5H5}PdCl(L)]2.

Single crystals of [{η3–C5H5}PdCl(S)-4a] [(S)-6a] and [{η3–C5H5}PdCl((S)+5a)] [(S)-7a] suitable for X-ray analysis were grown (Fig. 3 and 4); the asymmetric unit of (S)-7a comprises two molecules in different conformations (the second structure and an overlay is provided in the ESI†) and there is twofold disorder of the methallyl ligand and the palladium atom in one of these independants. The phosphonites show monodentate coordination through the phosphorus, and there is a pseudo-square-planar geometry around the palladium.

The allyl carbons trans to phosphorus exhibit a longer Pd–C bond length (2.195, 2.206 Å) than the allyl carbons cis to the phosphorus (2.096, 2.095 Å), which is consistent with the
stronger trans influence of the phosphonite compared to the chloride ligand. In (S)-6a the lower naphthyl fragment of the binaphthyl backbone is face-to-face with the palladium centre (Fig. 3). Neither of the two independents of (S)-7a display this feature, with the lower naphthyl group being orientated away from the palladium centre and facing the biphenyl moiety (Fig. 4 and ESI†). In the two independents of (S)-7a the torsion angle of the dimethyl substituted biphenyl moiety is of opposite sign, and also when comparing the biphenyl moiety in (R)-4b and (S)-6a (Fig. 2 and 3), implying no restriction to rotation about the C11–C11’ bond.

The $^{31}$P($^1$H) NMR peaks of (S)-6a and (S)-7a experience slight shifts compared to the free ligands, and show the presence of two independent resonances due to the two isomers formed; $\delta$ (ppm) = (S)-6a (172.0 and 173.6) and (S)-7a (172.9 and 177.6). The isomers are a result of the rotation of the allyl moiety, via a selective syn/anti exchange of the allyl protons cis to the phosphorus, by a $\eta^3$-$\eta^1$-$\eta^3$ mechanism, due to the stronger trans effect of the phosphonite donor ligand.4,9 The rapid exchange process resulted in broadened peaks in the NMR spectra at room temperature; cooling of CD$_2$Cl$_2$ solutions of the complexes to ~20 °C sharpened the resonances and allowed for full characterisation of the methallyl ligands in both isomers (ESI†). Reaction of (S)-7a with NaBARF resulted in loss of NaCl and the formation of [[$\eta^3$-C$_3$H$_7$]Pd(S)-5a]BARF ([(S)-8a]), where (S)-5a acts as a chelating P,C-$\pi$-donor. The upfield $^{13}$C($^1$H) NMR coordination chemical shifts for both C1’ and C2’ suggest a $\eta^3$-binding mode (Fig. 5), which is in agreement with the results of an NMR study reported by Pregosin and co-workers.9

As discussed, MOP phosphine ligands are known to give high enantioselectivity in the palladium-catalysed asymmetric hydrosilylation of alkenes, particularly styrene, to give chiral secondary alcohols (Scheme 2). To gain an insight into how the different stereoelectronic profiles of our phosphonites impacts upon their catalytic activity in the same transformation, we prepared catalysts by reacting each phosphonite with [Pd($\eta^3$-C$_3$H$_7$)Cl]$_2$ (Table 1). We chose to test our phosphonites against the well-known H-MOP and MeO-MOP phosphines (the latter is a commercial compound), employing P: Pd ratios of 1:1 and 2:1 at room temperature — full conversion was obtained in all cases. We noted a general increase in enantioselectivity and reaction rate in the order (S)-5a/(R)-5b/(S)-4a/(R)-4b/(S)-3a/(R)-3b, with the introduction of the biphenyl moiety, and subsequently the methyl groups, markedly improving the ligand performance. Phosphonite (S)-5a gave excellent enantioselectivity for (R)-1-phenylethanol (Table 1, 93%, entry 18), which is slightly higher than that for the (S)-H-MOP phosphine (Table 1, 94%, entry 4), although the latter reaction reached conversion more quickly. We also tested the H-MOP phosphonite ligands [(S,R)$_3$]-1a and [(S,S)$_3$]-1a at 0 °C, these ligands are far less selective than (S)-5a.4

Interestingly, although the methoxy-substituted ligands (R)-MeO-MOP phosphine and (R)-5b performed poorly compared
to their H-substituted counterparts – an established trend for this ligand family\textsuperscript{10} – the phosphonite ligand gave much higher enantioselectivities than the corresponding phospine (51\% versus 20\%, Table 1, entries 20 and 6), demonstrating further the potential these derivatives have to improve existing tools.

It is notable that at room temperature, the hydrosilylation occurs as a highly exothermic, quite violent reaction which is accompanied by a spontaneous colour change to deep black; similar observations with arylmonophosphinoferrocenes have also been made.\textsuperscript{11} When a 2 : 1, P : Pd ratio was used there was often a significant delay in the time taken to observe this phenomenon (from 1-8 h, Table 1). However these exothermic colour changes were not observed when the external temperature of the flask was kept at 0 °C. Consequently, the catalysis performed at 0 °C using both (S)-H-MOP and the sterically bulky (S)-5a resulted in longer reaction times, however this was offset by an increased ee of the product – phosphonite (S)-5a gave the best ee with a value of 95\%.

The final objective in this study was to extend our styrene screening regimen to substrates that MOP phosphines struggle to catalyse, or confer only low or moderate enantioselectivity in the product, with the aim that the unique stereoelectronic properties of the phosphonites would allow for improvements to be made. As such we extended our screening with (S)-5a to include the para-substituted styrenes listed in Table 2. Intro-

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**Table 1** Catalytic results from the asymmetric hydrosilylation of styrenes\textsuperscript{a}

| L | P : Pd | T | Time\textsuperscript{b} | Conv.\textsuperscript{c} | ee\textsuperscript{d} |
|---|---|---|---|---|---|
| 1 | (S)-H-MOP | 1 : 1 | rt | 1 min | >99\% | 74 (R) |
| 2 | (S)-H-MOP | 1 : 1 | 0 °C | 4 h | >99\% | 93 (R) |
| 3 | (S)-H-MOP | 2 : 1 | rt | 1 h | >99\% | 75 (R) |
| 4 | (S)-H-MOP | 2 : 1 | 0 °C | 12 h | >99\% | 94 (R) |
| 5 | (R)-MeO-MOP | 1 : 1 | rt | 10 min | >99\% | 22 (R) |
| 6 | (R)-MeO-MOP | 2 : 1 | rt | 1 h | >99\% | 20 (R) |
| 7 | (S)-3a | 1 : 1 | rt | 24 h | >99\% | 63 (R) |
| 8 | (S)-3a | 2 : 1 | rt | 24 h | >99\% | 73 (S) |
| 9 | (R)-3b | 1 : 1 | rt | 24 h | >99\% | 7 (S) |
| 10 | (R)-3b | 2 : 1 | rt | 24 h | >99\% | 1 (S) |
| 11 | (S)-4a | 1 : 1 | rt | 6 min | >99\% | 73 (R) |
| 12 | (S)-4a | 2 : 1 | rt | 1 h | >99\% | 79 (R) |
| 13 | (R)-4b | 2 : 1 | rt | 10 min | >99\% | 23 (R) |
| 14 | (R)-4b | 2 : 1 | rt | 1 h | >99\% | 27 (R) |
| 15 | (S)-5a | 1 : 1 | rt | 2 min | >99\% | 79 (R) |
| 16 | (S)-5a | 1 : 1 | 0 °C | 5 h | >99\% | 92 (R) |
| 17 | (S)-5a | 2 : 1 | rt | 2 h | >99\% | 80 (R) |
| 18 | (S)-5a | 2 : 1 | rt | 72 h | >99\% | 95 (R) |
| 19 | (R)-5b | 1 : 1 | rt | 1 h | >99\% | 45 (R) |
| 20 | (R)-5b | 2 : 1 | rt | 70 min | >99\% | 51 (R) |
| 21 | (S,R\textsubscript{o})-la | 1 : 1 | 0 °C | 168 h | 88\% | 4 (S) |
| 22 | (S,R\textsubscript{o})-la | 2 : 1 | 0 °C | 168 h | >99\% | 60 (R) |
| 23 | (S,S\textsubscript{o})-la | 1 : 1 | 0 °C | 72 h | >99\% | 59 (R) |
| 24 | (S,S\textsubscript{o})-la | 2 : 1 | 0 °C | 168 h | 22\% | 77 (R) |

\textsuperscript{a}The catalyst was generated in situ from the ligand (0.50 mol\%) and [Pd(η\textsubscript{3}-C\textsubscript{3}H\textsubscript{5})Cl\textsubscript{2} (0.125 mol\%), and reacted with styrene (10 mmol) and trichlorosilane (12 mmol). \textsuperscript{b}Time taken for reaction to reach completion. \textsuperscript{c}Determined by \textsuperscript{1}H NMR spectroscopy. \textsuperscript{d}ee determined by chiral GC; absolute configuration assigned by comparison of the sign of optical rotation to literature (ESI). \textsuperscript{e}Reaction stopped.

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**Table 2** Asymmetric hydrosilylation of heteroatom-substituted styrenes\textsuperscript{a}

| L | Ar | T | Time\textsuperscript{b} | Conv.\textsuperscript{c} | ee\textsuperscript{d} |
|---|---|---|---|---|---|
| 1 | (S)-H-MOP | 4-ClC\textsubscript{6}H\textsubscript{4} | rt | 1 h | >99\% | 78 (R) |
| 2 | (S)-H-MOP | 4-ClC\textsubscript{6}H\textsubscript{4} | 0 °C | 24 h | >99\% | 94 (R) |
| 3 | (S)-5a | 4-ClC\textsubscript{6}H\textsubscript{4} | rt | 18 h | >99\% | 86 (R) |
| 4 | (S)-5a | 4-ClC\textsubscript{6}H\textsubscript{4} | 0 °C | 336 h | <5\% | — |
| 5 | (S)-H-MOP | 4-MeOC\textsubscript{6}H\textsubscript{4} | rt | 10 min | >99\% | 35 (R) |
| 6 | (S)-H-MOP | 4-MeOC\textsubscript{6}H\textsubscript{4} | 0 °C | 12 h | >99\% | 58 (R) |
| 7 | (S)-5a | 4-MeOC\textsubscript{6}H\textsubscript{4} | rt | 70 min | >99\% | 78 (S) |
| 8 | (S)-5a | 4-MeOC\textsubscript{6}H\textsubscript{4} | 0 °C | 240 h | >99\% | 85 (R) |

\textsuperscript{a}The catalyst was generated in situ from the ligand (0.50 mol\%) and [Pd(η\textsubscript{3}-C\textsubscript{3}H\textsubscript{5})Cl\textsubscript{2} (0.125 mol\%) and reacted with styrene (10 mmol) and trichlorosilane (12 mmol). \textsuperscript{b}Time taken for reaction to reach completion. \textsuperscript{c}Determined by \textsuperscript{1}H NMR spectroscopy. \textsuperscript{d}ee determined by chiral GC; absolute configuration assigned by comparison of the sign of optical rotation to literature (ESI). \textsuperscript{e}Reaction stopped.
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