Air-Stable Chiral Primary Phosphines: A Gateway to MOP Ligands with Previously Inaccessible Stereoelectronic Profiles

Arne Ficks, William Clegg, Ross W. Harrington, and Lee J. Higham*

School of Chemistry, Bedson Building, Newcastle University, Newcastle upon Tyne, NE1 7RU, U.K.

Supporting Information

ABSTRACT: The air-stable chiral primary phosphines 1a,b facilitate the synthesis of previously inaccessible or hard-to-access chiral MOP-type ligands 2a,b−5a,b, which can be prepared in one-pot reactions. These derivatives have been prepared to allow for a unique comparison of their differing structural and electronic profiles, determined here by a number of experimental and theoretical studies. Phosphiranes 2a,b and phosphonites 5a,b are electron-poor compounds, with the former possessing exceptional thermal stability. Conversely, the dimethylarylphosphines 3a,b and bis(dimethylamino)arylphosphines 4a,b are good electron donors, and, in contrast to earlier reports, the dialkylarylphosphines were found to be remarkably air-stable. The ligands were coordinated to platinum(II), and the weak trans-influence of the highly strained phosphiranes 2a,b was revealed both in solution and in the solid state. The steric parameters of the ligands were investigated by the allyl rotation of their methallylpalladium(II) complexes, which showed subtle differences in exchange rates. Aryl side-on coordination of the MOP-backbone to palladium(II) was observed for complexes with a non-coordinating counterion and structurally analyzed in the case of ligand 4b. The asymmetric induction and catalytic activity of 2a,b−5a,b were tested in the hydroysilylation of styrene as well as the allylic alkylation of (rac)-(E)-1,3-diphenylallyl acetate. Major differences in reactivity were related back to the electronic parameters of the ligands.

INTRODUCTION

In transition-metal-catalyzed asymmetric synthesis, the design of the chiral ligand is crucial for transferring the stereochemical information effectively onto the substrate.1 A fine balance of steric and electronic properties is often necessary to achieve high asymmetric induction while ensuring good catalytic activity. It is therefore desirable to obtain characteristic values for each ligand that describe their steric and electronic effects. The separation of electronic and steric parameters for phosphorus(III) ligands was profoundly influenced by Tolman,2 and his seminal study was used as the foundation for numerous experimental and theoretical works thereafter, which have been thought-provoking for those involved in ligand design.3 One impediment to the actual synthesis, comparison, and classification of related but different functionalities on a given “RP” backbone is the lack of a convenient precursor that allows for the synthesis of phosphines with electron-donating/accepting, aryl/alkyl, sterically encumbered/small, strained/open, or carbon/heteroatom functionality. Herein we show that primary phosphines 1a/b provide such a route.

Furthermore, these precursors are the first air-stable primary phosphines that can be made in both the (R) and (S) enantiomers, in multigram quantities.4 They are significant because they constitute what can be considered the parent of an important class of chiral monophosphines, Hayashi’s MOP ligands (Chart 1, left),5,6 which are based on an atropisomeric binaphthyl skeleton and are capable of catalyzing a number of asymmetric transformations.7 Importantly, because primary phosphines are readily functionalized, it ought to be possible to synthesize MOPs with stereoelectronic profiles very different from those reported to date. Prior modification of MOPs has been somewhat limited but demonstrates the significance of ligand design: different substitution in the 2′-position (most commonly H or OMe) caused major changes in the catalytic behavior,5 and the aryl substituents on the phosphorus have also been modified in order to increase the catalytic performance.8 Significant deviations from diaryl P-substitution (e.g., alkyl instead of aryl substituents) have seldom been introduced, as a result of synthetic difficulties in accessing these...
derivatives via the standard methodologies used to construct these ligands.9

Primary phosphines are readily functionalized by substitution of their P-bound hydrogen atoms, but their reputation as highly air-sensitive, toxic, and pyrophoric compounds has inhibited their use in synthetic methodology.10 In stark contrast to this, the chiral primary phosphines 1a,b are both air-stable (Chart 1) by virtue of their extended π-conjugation, in accordance with our DFT-based model.4c Here we show that these primary phosphines facilitate the synthesis of MOP derivatives which have so far proven inaccessible or elusive, in one-pot procedures. In the first instance, we wished to compare the effect on the stereoelectronic profile of ligands that contain a highly strained phosphirane11a moiety to that of the corresponding unstrained dimethyl analogue, and therefore we prepared 2a,b and 3a,b (Scheme 1). Second, we wanted to synthesize the novel bis(dimethylamino)phosphines 4a,b and dimethyl phosphonites 5a,b so as to evaluate the effect different α-heteroatoms have on the ligand properties. The structural and electronic impact of the ligands is shown by a number of experimental and theoretical analyses, most notably in their palladium(II) and platinum(II) complexes, which have been studied in detail in solution and in the solid state. The ramifications of these differences in the asymmetric hydroxylation of styrene and the asymmetric allylic alkylation of rami5a studied in detail in solution and in the solid state. The and electronic impact of the ligands is shown by a number of

The dimethylphosphine analogues 3a,b were first reported by Stryker and co-workers, but their copper hydride complexes were found to be ineffective for the reduction of ketones;9f further studies by Shi et al. were carried out on their application as catalysts in the aza-Baylis–Hillman reaction.13 Synthetic pathways to obtain 3a,b are known from earlier reports, via coupling of dimethylphosphine oxide with the appropriate binaphthyl trilolate, followed by a reduction of the oxide.9d However, rather than employing a somewhat circuitous route, whereby one must first prepare the dialkylphosphine oxide, we were keen to develop an efficient one-pot synthesis, starting from our primary phosphines 1a,b, which we have prepared efficiently on a large scale.4b After investigating a number of unsuccessful halogenation methods, we prepared the corresponding dichlorophosphines by adapting Weller’s procedure.4c Thus, 1a,b were reacted with phosphorus pentachloride in toluene to generate the respective dichlorophosphines in situ (Scheme 1, path (ii)), and after removal of the volatiles in vacuo, further reactions were performed in the same reaction vessel. Initially, we attempted the methylation by adding a solution of methylthiium in diethyl ether, but this resulted in the formation of a mixture of compounds. Instead, we found that a much cleaner reaction was achieved when methylmagnesium chloride in tetrahydrofuran was used as the methylating agent (Scheme 1, path (iii)). Analysis of the crude reaction mixtures by 31P NMR showed complete conversions to the desired products (−54.0 ppm for 3a,b), which were obtained in good yields (76%/73% respectively) after purification on silica media. The ligands were found to be air-stable after the compounds were left open to the atmosphere for 7 days, neat or in chloroform solution. This observation differs from an earlier report in which the authors stated that these compounds were air-sensitive,9a although our DFT model predicts that 3a,b would be air-stable (SOMO energies of the radical cations are −9.05 eV (3a) and −8.83 eV (3b)).4c

While the ramifications of ring strain will be assessed by comparing the properties of 2a,b and 3a,b, the effect of α-heteroatom substitution on the phosphorus can be established by synthesizing bis(dimethylamino)phosphines 4a,b and the phosphonites 5a,b. Amino substituents are known to lend σ-donor strength to the phosphorus, arising from electron donation of the nitrogen lone pairs.15 Aminophosphines are commonly prepared by condensation reactions of phosphorus(III) halides with secondary amines.16 Hence, we were able to use our primary phosphines 1a,b as starting materials to generate the respective dichlorophosphines in situ (vide supra); these were then treated with dimethylamine under basic conditions to give 4a,b (Scheme 1, path (iv)) in very good yields (93%/89% respectively after purification). The 31P NMR spectra show typical resonances for bis-heteroatom-substituted 3-coordinated phosphines at 99.9 ppm (4a) and 101.0 ppm (4b). Ligands 4a,b are moderately sensitive toward moisture and protic solvents such as alcohols, but purification on alumina media with reagent-grade solvents was possible, and no evidence for oxidation of these ligands in air was found. Generally, 4a,b can be handled in air without the need for an inert environment, but they should be stored in closed vials to avoid hydrolysis on prolonged exposure to moisture.

To complete our comparative study, we synthesized the dimethyl phosphonite ligands 5a,b from 1a,b via methanolysis of the respective dichlorophosphine intermediates in the presence of triethylamine (Scheme 1, path (v)). The crude

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Scheme 1. Ligand Synthesisa

![Scheme 1](image)

a Reaction conditions: (i) 2MeLi, Cl(CH2)2Cl, THF, −78 °C to rt; (ii) PCl3, toluene; (iii) 2MeMgCl, THF, −78 °C to rt; (iv) 2Me2NH, NEt3, THF; (v) 2MeOH, NEt3, CH2Cl2.

RESULTS AND DISCUSSION

Ligand Synthesis and Stability. The chiral phosphiranes 2a,b possess a highly strained, three-membered phosphorus heterocycle which confers greater s-character on the donor orbital. This ultimately leads to weaker σ-donor, but better π-acceptor properties compared to their unstrained counterparts.15 Despite the fact that phenylphosphirane is thermally unstable at room temperature,14 2a,b were prepared from 1a,b in a straightforward one-step reaction procedure to give 2a,b in essentially quantitative yield; both ligands demonstrate exceptional thermal stability for an unconstrained phosphirane ring (Scheme 1, path (i)).11a

![dx.doi.org/10.1021/om500582w](image)
products were found to decompose on silica and alumina media. The generated amine-salt impurity was therefore separated by filtration of a toluene suspension of the ligand through a pad of Celite. Ligands 5a,b were usually obtained with >90% purity by $^{31}\text{P}$ NMR. Their resonances in the $^{31}\text{P}$ NMR spectra are located at lower field relative to the other ligands in this study (157.5 ppm for 5a, 155.8 ppm for 5b), caused by the electronegative methoxy substituents on the phosphorus atom. Ligands 5a,b are prone to hydrolysis and should therefore be stored and handled under nitrogen.

**Assessment of Structural and Electronic Properties.** The $J_{\text{PSe}}$ coupling in $\text{R}_3\text{P(Se)}_2$ compounds can be used to determine the effective electronegativity of the substituents on the phosphorus atom. $^{17}$ The $J_{\text{PSe}}$ magnitude is inversely correlated to the σ-donor strength of a $\text{R}_3\text{P}$ ligand; electron-donating substituents cause the coupling constant to decrease. Sterically demanding substituents can indirectly influence the coupling if the bond angles on the phosphorus are widened; the s-character of the phosphorus lone pair is thereby reduced, resulting in increased Lewis basicity. $^{18}$

The respective $\text{ArP(Se)}_2$ derivatives were prepared by the reaction of ligands 3a,b, 4a,b, and 5a,b with potassium selenocyanide. $^{19}$ We were unable to obtain any selenide product formation for the phosphiranes 2a,b, even at elevated temperatures and prolonged reaction times. For the $\text{ArP(Se)}_2$ derivatives of the dimethylphosphines 3a,b we found lower coupling constant values than for the respective derivatives of ligands 4a,b and 5a,b, corresponding to a better σ-donor character (Table 1). This is in accord with expectations, as the electronegative nitrogen atoms in 4a,b and, to a greater extent, the oxygen atoms in 5a,b reduce the σ-donor strength of the phosphorus atom.

In order to include phosphiranes 2a,b in a comparative study of electronic properties, we synthesized trans-$\text{[Rh(}L_3\text{)(CO)]}$ complexes ($L_3$ = phosphorus ligand) and measured the symmetric carbonyl stretching frequencies in their IR spectra. A higher vibrational wavenumber indicates a lower net-donor property of $L_3$, as the reduced electron density on the metal allows for less back-bonding into the antibonding $\pi^*$-orbitals of the carbonyl. $^{20}$ The IR spectra were recorded in dichloromethane solution, since packing effects in the solid state may have a significant influence on the observed values. $^{21}$ We found that 3a,b are the strongest net donors (1965, 1963 cm$^{-1}$), followed by 4a,b (1972, 1969 cm$^{-1}$), 2a,b (1983, 1985 cm$^{-1}$), and 5a,b (1999, 1996 cm$^{-1}$). The weak donating properties of phosphiranes 2a,b compared to their dimethylphosphine counterparts 3a,b can be attributed to their pyramidalized structures, which result in increased s-character of the donor orbitals. As such, phosphiranes 2a,b show weaker net donation than $\text{PPh}_3$ (1979 cm$^{-1}$) but are better donors than the BABAR-Phos$^{22}$ phosphirane ligand (1991 cm$^{-1}$), in which the three-membered ring is encapsulated into a rigid backbone.

Electronic descriptors measuring the donor abilities of our ligands were calculated from their HOMO orbital energy levels and proton affinity (PA) in a series of DFT calculations (calculated at the B3LYP/6-31G* level of theory). For tertiary phosphines, the energy of the HOMO typically corresponds to the lone pair of the phosphorus, and PA is a measure of its σ-basicty; the two values have been found to correlate fairly well for a range of phosphorus ligands. $^{23}$ The HOMO energies were calculated from the optimized structures of the free ligands and are given in Table 1. We observed lower $E_{\text{HOMO}}$ values in the direct comparison of H-MOP derivatives (a ligand series) to their respective OMe-MOP counterparts (b ligand series). The spatial representations of the HOMO orbitals (Figure 1) reveal their distribution on the binaphthyl backbone and also on the methoxy group in the OMe-MOP derivatives (b). It is interesting how the 2’ substituent significantly affects the calculated HOMO energies: The presence of the methoxy group causes a general increase in the HOMO energy for the “b” series of ligands, which implies improved σ-donor properties relative to its analogue in the “a” series. Inspection of the HOMO energies in Table 1 shows, somewhat surprisingly, that the dimethyl-substituted phosphine 3a has a calculated HOMO energy sandwiched between those of the phosphiranes 2a and 2b.

In contrast to this, the PA values allow for ranking according to ligand type, rather than backbone substitution (Table 1). The energy was calculated from the differential in molecular energies of the DFT-optimized structure of the free ligand and the optimized structure of the protonated ligand (protonated on the phosphorus). $^{23,24}$ Their magnitude increases (indicating an increasing σ-basicty) in the order 2a,b $<$ 5a,b $<$ 3a,b $<$ 4a,b. In comparison to the relative trend of the net donor properties from the experimentally determined values for $\nu(\text{CO})$, it appears that the calculated σ-basicty suggested by both the
HOMO and PA values may be somewhat overestimated for the heteroatom-substituted derivatives. This is further evidence that caution ought to be used when rationalizing experimental behavior from the calculation of relatively simple parameters in isolation.

To gain insight into the structural properties of the ligands, we next calculated the symmetric deformation coordinate. The $S'_i$ parameter, introduced by Orpen et al.,\textsuperscript{28} is an alternative to Tolman’s cone angle ($\theta_p$).\textsuperscript{2,26} Its use is appropriate for MOP-type compounds in particular, since the $\theta_p$ parameter would be dominated by the bulky binaphthyl group.\textsuperscript{27} As a measure of flattening or pyramidalization around the phosphorus, $S'_i$ is defined as the sum of $Z$--$P$--$R$ angles ($\alpha_i$) minus the sum of $R$--$P$--$R$ angles ($\beta_i$), with $Z$ describing the coordinated atom of the ligand (Figure 2). A modified descriptor, $S_a$, is used for free ligands, where $Z$ is a vector perpendicular to the plane containing the three substituents of the phosphorus.\textsuperscript{28} The $S_i$ values were determined from the optimized minimal energy geometries of each ligand at the B3LYP/6-31G* level (Table 1). The pyramidalization of the phosphiranes $2a,b$ is recognized by unusually large $S_i$ values (130.1° and 127.5°, respectively). In contrast, $3a,b$ and $4a,b$ exhibit much smaller $S_i$ values of similar magnitudes (51.7°--53.7°), which is unsurprising in the absence of ring strain. The values are increased for $5a,b$ (59.5° and 62.2°, respectively) in comparison to the other unstrained derivatives.

**Platinum(II) Coordination Properties.** To investigate the structural and electronic behavior of our ligands upon coordination to a metal center, we prepared a series of square planar platinum(II) complexes. Solution studies of these compounds can give an insight into the nature of the phosphorus–platinum bonds by virtue of the $J_{PP}$ coupling constants in their NMR spectra.\textsuperscript{29} It has been suggested that the main contributor to the one-bond coupling is the Fermi interaction of the two nuclei involved.\textsuperscript{30} This means that the $s$-component of the $P$--Pt bond has a direct influence on the coupling constant, yielding larger values with increasing $s$-orbital overlap. However, $p$- and $d$-effects will indirectly affect the $s$-orbital interaction; previous reports have shown that there is a good correlation between the $J_{PP}$ magnitude and the Pt--P bond length.\textsuperscript{31} This relationship allows for the determination of cis and trans influences in platinum complexes, i.e., the ability of a ligand to weaken the bond to a substituent in the cis/trans position,\textsuperscript{2} which then helps in rationalizing the $\sigma$-donor and $\pi$-acceptor properties of the ligands.\textsuperscript{33,34} Complementary studies, using X-ray crystallographic analysis to determine the bond lengths, are available to supplement the data acquired in solution.

Platinum(II) dichloride complexes with the general formula [Pt$(L_p)$Cl$_2$] ($L_p$ = phosphorus ligand) were synthesized from the reaction of cis-[Pt$(\eta^2\text{-}\text{cod})$Cl$_2$] with the appropriate ligand (Figure 3). In solution and in the solid state, the selective formation of cis-6a,b or cis-7b (Figure 4) was observed when phosphiranes $2a,b$ or dimethylphosphine $3b$, respectively, were used as ligands. Under the same reaction conditions $4b$ gave trans-8b (Figure 5) with complete selectivity. The $^{31}P$ NMR spectra show the expected singlet resonance together with satellites for the doublet produced by coupling to $^{195}$Pt; for the cis complexes the $J_{PP}$ coupling is larger in cis-6a,b (4170, 4160 Hz) compared to cis-7b (3647 Hz) as a result of the higher $s$-character of the phosphirane donor orbitals.\textsuperscript{33} The $J_{PP}$ coupling in trans-8b (2955 Hz) is significantly smaller compared to the cis complexes, because of the stronger reciprocal trans influence of the phosphine ligands compared to the trans influence of a chloride ligand. Selected bond lengths and angles for the solid-state structures of cis-6a,b, cis-7b, and trans-8b are given in Table 2.

Phosphirane complexes cis-6a,b form shorter Pt--P bonds (2.204(3)–2.212(2) Å) than the dimethylphosphine derivative.
cis-7b (2.241(4) Å, 2.241(3) Å), which is attributed to their more pyramidalized structure.

The Pt–P bond lengths are further elongated in trans-8b (2.307(3) Å, 2.313(3) Å) due to the relatively strong reciprocal trans influence, in agreement with the NMR data. The strong pyramidalization of the phosphirane group is retained upon complexation and manifests itself in large S′ values for cis-6a,b (98.0−105.4°; calculated from X-ray data). For cis-7b and trans-8b, the adjacent groups around the phosphorus are only slightly tilted out of the plane, resulting in much smaller S′ values (17.9−21.5°).

For further evaluation of the relative cis and trans influences, we synthesized unsymmetrical platinum(II) complexes with the formula [Pt(P1)Cl2] (selected NMR data are given in Table 3).4 The reaction of two equivalents of phosphinate ligand (P1) with [Pt(P(t-Bu)2)Cl2] proceeded quantitatively in all instances (Figure 3). In the case of phosphiranes 2a,b and dimethyl phosphonites 3a,b, we observed the formation of both cis and trans isomers of the corresponding platinum complexes depending on the ligand. NOESY experiments showed no exchange of the two isomers on the NMR time scale, and additional NMR spectra that were recorded after leaving the complexes in solution for 24 h yielded unchanged cis/trans ratios. In previous reports about related platinum(II) complexes the trans products have been found to convert to their cis isomers over time.39 When the bis(dimethylamino)phosphines 4a,b or the dimethyl phosphinates 5a,b were used as ligands, the trans-11a,b or trans-12a,b isomers were formed exclusively, displaying typical JPP coupling constants of 543−604 Hz in their 31P NMR spectra (Figure 6 shows 11b).

The fast relaxation time of the platinum nucleus in the compounds enabled the collection of 109Pt NMR spectra (Figure 7). For the [Pt(P1)Cl2] series, resonances for the trans complexes are observed downfield (−3839 to −3941 ppm) to the corresponding cis isomers (−4401 to −4501 ppm, Table 3). The phosphiranes in cis-9a,b induce strong shielding of the platinum nucleus and show an upfield shift of ~100 ppm compared to cis-10a,b. The strongest deshielding effects were found for complexes of the heteroatom-substituted ligands in trans-11a,b and trans-12a,b (−3839 to −3881 ppm).

### Table 2. Selected Bond Distances (Å), Angles (°), and S′ Data from X-ray Crystallographic Analysis

| complex | Pt−P1 | Pt−P2 | Pt−Cl1 | Pt−Cl2 | P1−Pt−P2 | P1−Pt−Cl1 | P1−Pt−Cl2 | C11−Pt−Cl2 | S′ (P1) | S′ (P2) |
|---------|-------|-------|--------|--------|----------|-----------|-----------|------------|---------|---------|
| cis-6a  | 2.212(2) | 2.209(2) | 2.337(2) | 2.334(2) | 97.02(8) | 175.90(10) | 177.57(10) | 90.52(8) | 98.0 | 103.6 |
| cis-6b  | 2.204(3) | 2.338(3) | 2.339(3) | 96.92(14) | 169.05(10) | 87.06(10) | 89.36(11) | 90.42(15) | 105.4 | 17.9 |
| cis-7b  | 2.241(4) | 2.343(4) | 2.292(3) | 2.307(2) | 170.37(10) | 90.52(8) | 90.42(15) | 90.42(15) | 24.3 | 21.3 |
| trans-8b| 2.307(3) | 2.313(3) | 2.293(3) | 2.307(2) | 178.76(12) | 90.52(8) | 90.42(15) | 90.42(15) | 105.7 | 24.0 |
| trans-9b| 2.304(3) | 2.284(3) | 2.293(3) | 2.308(0) | 176.90(5) | 90.52(8) | 90.42(15) | 90.42(15) | 18.7 | 27.8 |
| trans-11a| 2.339(5) | 2.305(0) | 2.301(13) | 2.3080(14) | 91.41(11) | 91.25(5) | 91.41(5) | 91.25(5) | 92.34(5) | 92.15(5) |

*Two-fold rotational symmetry.

### Table 3. Selected NMR Spectroscopic Data of the Platinum Complexes Prepared in This Study

| complex | δ(Pt) (ppm) | JPP (Hz) | δ(P1) (ppm) | JPP(P1) (Hz) | δ(P2) (ppm) | JPP(P2) (Hz) |
|---------|------------|---------|------------|-----------|------------|-----------|
| cis-6a  | −149.2     | 4170    | −149.2     | 4170       | −149.2     | 4170       |
| cis-6b  | −149.3     | 4160    | −149.3     | 4160       | −149.3     | 4160       |
| cis-7b  | −4362      | 3647    | −4362      | 3647       | −4362      | 3647       |
| cis-9a  | −4901      | 3428    | −4901      | 3428       | −4901      | 3428       |
| cis-9b  | −4501      | 3282    | −4501      | 3282       | −4501      | 3282       |
| cis-10a | −4401      | 3412    | −4401      | 3412       | −4401      | 3412       |
| cis-10b | −4412      | 3404    | −4412      | 3404       | −4412      | 3404       |
| trans-8b| −3747      | 2955    | −3747      | 2955       | −3747      | 2955       |
| trans-9a| −3941      | 2871    | −3941      | 2871       | −3941      | 2871       |
| trans-9b| −3921      | 2886    | −3921      | 2886       | −3921      | 2886       |
| trans-10a| −3914     | 2479    | −3914      | 2479       | −3914      | 2479       |
| trans-10b| −3917     | 2464    | −3917      | 2464       | −3917      | 2464       |
| trans-11a| −3869    | 2365    | −3869      | 2365       | −3869      | 2365       |
| trans-11b| −3839    | 2332    | −3839      | 2332       | −3839      | 2332       |
| trans-12a| −3881    | 2402    | −3881      | 2402       | −3881      | 2402       |
| trans-12b| −3859    | 2407    | −3859      | 2407       | −3859      | 2407       |

*Chemical shift in ppm. **Resonance of the ArPR2 ligand in ppm. °Coupling of the ArPR2 ligand in Hz. †Resonance of the P(t-Bu)2 ligand in ppm. ‡Coupling of the P(t-Bu)2 ligand in Hz. §Not determined due to solubility issues.
The interaction of the donor orbital with a symmetric metal-centered s-orbital results in weakened bonds to both cis and trans ligands in 9a,b. In contrast, the trans influence is stronger in 10a,b with a smaller cis influence, because the increased p-character of the ligand donor orbital mainly weakens the bond to the ligand in the trans position, while there is only a small overlap to the orbitals of the ligands in the cis position. The further increased trans effect in 11a,b and 12a,b is an indication of the predominantly p-character of the respective phosphorus donor orbitals in 4a,b and 5a,b.

Slow evaporation from dichloromethane solutions of trans-9b (Figure 9) and trans-11a (Figure 10) yielded crystals suitable for X-ray analysis (selected structural parameters are given in Table 2). The large S<sup>′</sup> value of the phosphirane ligand in trans-9b (105.7°) indicates the strain caused by the heterocycle; the S<sup>′</sup> value of the unstrained bis(dimethylamino)phosphine ligand in trans-11a is only 18.7°. The Pt–P bond length in the PEt<sub>3</sub> ligand is shorter in trans-9b (2.284(3) Å) compared to trans-11a (2.3050(15) Å), which is in agreement with the solution NMR data and confirms the weak trans influence of the phosphirane ligand.

The phosphirane–platinum bond length in trans-9b is shorter compared to that in the bis(dimethylamino)phosphine complex trans-11a (2.304(3) versus 2.3395(15) Å), a result of the more pyramidalized structure of the phosphirane.

**Palladium(II) Coordination.** We next studied the coordination chemistry of 2b–5b on palladium(II), which is often the metal of choice for catalytic reactions of MOP-type ligands,<sup>5b</sup> the reaction of chloro(2-methallyl)palladium dimer with the appropriate phosphine gave the respective palladium chloride complexes 13b–16b (Scheme 2). For all these complexes, the formation of two different isomers was evident by the appearance of two independent resonances in the <sup>31</sup>P NMR spectra, as a consequence of the selective orientation of the methallyl group. In the NOESY spectra, we identified a rapid exchange process caused by the selective orientation of the methallyl fragment that resulted in broadened peaks at room temperature. During that process the protons in the cis position exchange in a syn/anti fashion, while a syn/syn and anti/anti exchange is observed for the protons in the trans position.<sup>36</sup>

The selective opening of the allyl ligand in the trans position is due to the stronger trans effect of the P-donor ligand compared to the chloride ligand.

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**Figure 7.** <sup>195</sup>Pt(1H) NMR (108 MHz) spectra of 9b (cis and trans isomers present) and trans-11b.

**Figure 8.** Models of P-ligand and metal-centered orbitals. Ligands with higher s-character donor orbitals interact with metal-centered s orbitals, weakening cis and trans substituents, whereas those with more p-character interact with p and d orbitals on the metal and show predominantly trans influence.

**Figure 9.** Molecular structure of trans-[Pt(2b)(PEt<sub>3</sub>)Cl<sub>2</sub>] (trans-9b) with 50% probability displacement ellipsoids. Hydrogen atoms omitted.

**Figure 10.** Molecular structure of trans-[Pt(4a)(PEt<sub>3</sub>)Cl<sub>2</sub>] (trans-11a) with 50% probability displacement ellipsoids. Hydrogen atoms omitted for clarity.
Cooling to −25 °C gave rise to sharpened resonances, which allowed for the assignment of the two isomers appearing in ~2:1 (13b, 14b), ~3:2 (15b), and ~9:1 (16b) ratios. Quantitative analysis of the peak integrals in the NOESY spectra at −25 °C yielded exchange rate constants of \( k_{AB} \approx 0.8 \text{ s}^{-1} \) and \( k_{BA} \approx 1.3 \text{ s}^{-1} \) for 13b, \( k_{AB} \approx 0.4 \text{ s}^{-1} \) and \( k_{BA} \approx 0.7 \text{ s}^{-1} \) for 14b, \( k_{AB} \approx 0.1 \text{ s}^{-1} \) and \( k_{BA} \approx 0.2 \text{ s}^{-1} \) for 15b, and \( k_{AB} \approx 0.3 \text{ s}^{-1} \) and \( k_{BA} \approx 3.1 \text{ s}^{-1} \) for 16b. The same experiment at −50 °C showed no evidence of exchange.

In the case of 14b, slow diffusion of diethyl ether into a dichloromethane solution yielded crystals suitable for X-ray crystallographic analysis (Figure 11).

The structure contains two independent isomers which have the (2-methylallyl)palladium unit in different orientations. Pd–P bond lengths are 2.2967(11) and 2.2686(13) Å, shorter than for the two MOP-phosphine allylpalladium complexes previously reported (2.3098(9) and 2.3279(9) Å). The reaction of 14b and 15b with NaBArF was carried out to exchange the chloride for a non-coordinating BArF-anion, giving complexes 17b and 18b (Scheme 2). This frees up a binding site and allows for coordination of the naphthyl group. We were able to obtain the crystal structure of the bis(dimethylamine) derivative 18b which clearly illustrates the P,C coordination mode in the solid state. The distance between the palladium atom and the bonded carbon C11 on the naphthyl ring is 2.302(4) Å (Figure 12). The position of the palladium above the naphthyl ring is moved slightly toward C20, to which the distance is 2.554 Å. The Pd–P distance was found to be 2.2553(11) Å and relates well to other MOP-type complexes as described above.

Interestingly, we detected N bond lengths and angles are inequivalent and show a peculiar pattern. The phosphorus atom carries a shorter bonded planar N atom (N1–P distance 1.653(4) Å, sum of angles around N1 357.7°) and a longer bonded N atom that shows a more pyramidal geometry (N2–P distance 1.683(4) Å, sum of angles at N2 342.7°). The pattern is much less pronounced in the platinum structures trans-8b (Figure 5) and trans-11a (Figure 10), which show only minor distortions around the N atom (sum of angles 355.9°–360.0°). It is assumed that the planarity of the nitrogen arises from electron donation of its lone pair toward the phosphorus. In solution, we observed the formation of two isomers in a 1:1 ratio for both 17b and 18b (caused by rotation of the methallyl group). As the coordination sphere of the palladium atom is filled by side-on bonding to the C1′-carbon (labeled as C11 in the X-ray structure of 18b), we consequently found an upfield shift of C1′ by about 20 ppm in the \(^{13}C\) NMR spectra compared to the free ligands 3b and 4b and the palladium chloride complexes 14b and 15b. The NOESY spectrum of 17b showed exchange of the two isomers at room temperature. Interestingly, we detected syn/anti exchange as well as an apparent allyl rotation, in a relative ratio of 2:3. Quantitative analysis of the methoxy resonances in the NOESY spectrum yielded a combined total exchange rate of \( k_{AB} \approx 0.2 \text{ s}^{-1} \). The exchange rate is therefore smaller than for the related allylpalladium chloride complexes 14b, which gave exchange...
rates of that magnitude at much lower temperature (−25 °C, vide supra). The NOESY spectrum of 18b showed no exchange at room temperature.

We were also interested in coordinating two phosphorus ligands to the palladium center, since these species may form as intermediates in catalytic reaction cycles. The addition of one equivalent of dimethylphosphine ligand 3b to complex 17b resulted in the quantitative formation of 19b (Scheme 2). The product was analyzed by NMR and HRMS; unfortunately, we were unable to obtain crystals for X-ray diffraction. The 13C NMR spectrum gave no further evidence of aryl coordination. The vacated coordination site from the dissociated C1 isomer was observed in the 31P NMR spectrum in the form of intermediates in catalytic reaction cycles.41,42 The addition of ligands to the palladium center, since these species may form as at room temperature.

vide supra (Table 4).8,42 Johannsen and co-workers have proposed two one equivalent of dimethylphosphine ligand to complex 3b (Table 4).42 The reaction of styrene was carried out without additional solvent. Subsequent oxidation of the silane afforded 1-phenylethanol, the absolute configuration of which was determined. Notably, ligands 2a, 4a,b, and 5a,b (entries 1, 2, 9–16) all showed complete consumption of the starting material in less than 24 h reaction time, whereas the OMe-substituted phosphirane 2b (entries 3, 4) and dimethylphosphine derivatives 3a,b (entries 5–8) are significantly less reactive in this transformation. Calculations on the reaction mechanism of the hydrosilylation suggest that the rate-determining step in the catalytic cycle is the reductive elimination.43 Therefore, one might expect that the good donor ligands 3a,b would be less active catalysts, as they favor the higher oxidation state on the metal. More surprising, then, were the high activity of the bis-(dimethylamino)phosphine ligands 4a,b, which are also electron-rich, and the discrepancy in the performance of the phosphiranes 2a,b (Table 4).

The best results were obtained with phosphirane 2a and phosphonite 5a (entries 1, 2 and 13, 14). Both show good activity and enantioselectivity of 70–84%. Their respective OMe-substituted derivatives 2b and 5b (entries 3, 4 and 15, 16) gave inferior selectivities in agreement with the reported values for OMe- and other 2-substituted MOP ligands.44 The bis(dimethylamino) derivatives 4a,b (entries 9–12) gave lower ee values (20–43%), despite being among the most catalytically active catalysts tested. The effect of the L:Pd ratio on the reaction was found to be limited, and only in the case of 3a,b (entries 5–8) did we find more pronounced deviations. The inconsistencies may be caused by the overall low activity for 3a,b as no complete substrate conversions were achieved, but notably in our coordination studies, the dimethylphosphine ligand 3b was the only derivative that gave the palladium complex 19b with a L:Pd ratio of 2:1 (vide supra). Ligands 2a,b, 4a,b, and 5a,b appear to favor the formation of complexes in a 1:1 ratio of L:Pd, even when an excess of ligand is used.

Asymmetric Allylic Alkylation. As another common benchmark reaction, we investigated the asymmetric allylic alkylation of (rac)-(E)-1,3-diphenylallyl acetate (Table 5).45 The nucelophile was generated from dimethyl malonate and bis(trimethylsilyl)acetamide (BSA). This reaction follows a different mechanism than the hydrosilylation one and hence is expected to show an alternative outcome for the investigated ligands. The oxidative addition is regarded as possibly rate-determining, and thus a good donor ligand would be necessary. The subsequent nucelophic substitution furnishes an energetic barrier that favors electron-withdrawing ligands, but in contrast to the oxidative addition the reaction step is irreversible.46

The activity of the catalysts correlates with the net donor strength of the ligands (Table 1 and 5). Consequently, the fastest catalysts were found in 3a,b ligated complexes, giving conversions within less than 4 h (Table 5, entries 3, 4). Good catalytic activities were also found for 4a,b (entries 5–8) but to a lesser extent for 2a,b (entries 1, 2). Reactions with the phosphinite ligands 5a,b were incomplete, even after prolonged reaction times (entries 9, 10), most likely as a result

### Table 4. Pd-Catalyzed Hydrosilylation of Styrene

| entry | ligand  | L-Pd | time (h) | conv (%) | ee (%) |
|-------|---------|------|---------|----------|--------|
| 1     | 2a      | 1:1  | 6       | >99      | 70%    |
| 2     | 2a      | 2:1  | 6       | >99      | 80%    |
| 3     | 2b      | 1:1  | 48      | 65       | 17%    |
| 4     | 2b      | 2:1  | 96      | 50       | 49%    |
| 5     | 3a      | 1:1  | 48      | 11       | 17%    |
| 6     | 3a      | 2:1  | 48      | 88       | 86%    |
| 7     | 3b      | 1:1  | 48      | 15       | 73%    |
| 8     | 3b      | 2:1  | 48      | 15       | 5%     |
| 9     | 4a      | 1:1  | 6       | 86       | 28%    |
| 10    | 4a      | 2:1  | 6       | >99      | 40%    |
| 11    | 4b      | 1:1  | 6       | 84       | 37%    |
| 12    | 4b      | 2:1  | 6       | >99      | 43%    |
| 13    | 5a      | 1:1  | 16      | >99      | 82%    |
| 14    | 5a      | 2:1  | 16      | >99      | 84%    |
| 15    | 5b      | 1:1  | 16      | >99      | 7%     |
| 16    | 5b      | 2:1  | 16      | >99      | 2%     |

*4Catalyst was generated in situ from ligand (0.25 mol%) and [Pd(allyl)]2 (0.125 mol%) and reacted with styrene (10.0 mmol) and chlorotrisilane (12.0 mmol). *5Determined by 1H NMR spectroscopy. *6Determined by chiral HPLC (Lux 5u Cellulose-1 column).
of their poor σ-donor character. The best enantioselectivities were achieved with ligands 3a (41% ee (R)) and 4a (66–67% ee (S)), interestingly yielding their major enantiomers in opposite absolute configurations. In the case of 4a,b we checked for the influence of the L:Pd ratio (2:1 versus 1:1, entries 5–8), but the reaction gave virtually the same outcome.

### CONCLUSIONS

Primary phosphines are versatile ligand precursors that can give rise to a variety of phosphorus compounds. Here, we report preparations of ligands 2a,b, 4a,b, and 5a,b as well as a simplified synthesis of 3a,b, which were achieved in straightforward two-step, one-pot reaction approaches.

We have discussed the unique electronic and steric properties of these different P-ligand functionalities, how they compare with each other, and how this is manifested in their platinum(II) and palladium(II) metal complexes. The highly strained phosphinanes 2a,b have exceptional thermal stability and show remarkably low trans influence, but equally enhanced cis influence, in their platinum(II) complexes as a result of the high s-character of their donor orbital. Their poor donor but good acceptor characteristics compare best to the phosphonites 5a,b. These ligands are best employed in catalytic reactions such as hydrosilylations, where the reductive elimination step has been proposed to be rate-determining.43 Interestingly, the small size of the P-substituents in 2a,b adding to the MOP backbone seems to have little detrimental effect on the enantioselectivities; the steric burden of the phosphinane unit is minimal, yet ee’s of up to 80% were obtained using 2a. Similarly, good results were obtained with the phosphonite 5a,b, yielding up to 84% ee.

Different electronic characteristics are evident in the electron-rich σ-donor ligands, the dimethylphosphines 3a,b and the bis(dimethylamino)phosphines 4a,b. The donor properties of 4a,b seem adaptable to some extent by transferring electron density from either one or two of their nitrogen lone pairs onto the phosphorus (indicated by the degree of distortion around the nitrogen atom). It may be for this reason that, although usually being good donor ligands, 4a,b still show high activity in the hydrosilylation reaction. They are also effective in the allylic alkylation reaction, for which we observed enantioselectivities of up to 67%. Notably, the absolute configuration of the major product was reversed when 4a,b were used compared to the dimethylphosphines 3a,b. That MOP-type phosphines can act as hemilabile ligands via coordination of their aryl backbone has been unambiguously shown by crystallographic analysis of 18b. However, hemilabile binding to saturate the coordination sphere of the metal center may be disfavored when a second P-donor ligand is available. The prominent active species in both catalytic transformations is still somewhat speculative, and further investigations are underway.

### ASSOCIATED CONTENT

#### Supporting Information

Full experimental procedures and crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

#### AUTHOR INFORMATION

**Corresponding Author**

E-mail: lee.higham@ncl.ac.uk. Fax: (+44) 191 222 6929. Tel: (+44) 191 222 5542.

**Notes**

The authors declare no competing financial interest.

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