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Synthesis of unprotected and borane-protected cyclic phosphines using Ru– and Mo– based olefin metathesis catalysts †

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Ru- and Mo-based catalysts can be used in ring closing metathesis (RCM) reactions to synthesise cyclic phosphines protected as their borane complexes. The compatibility of the Schrock Mo-catalyst and the N-heterocyclic carbene Ru-catalysts with this class of substrates is particularly noteworthy as asymmetric RCM (ARCM) is now emerging as a new tool for the preparation of homochiral phosphines. One of the key results is that the Mo-catalyst allows the ring closure of the unprotected diallylphenylphosphine with 95% conversion.

Introduction

As part of our ongoing research program studying the possibility of using ring closing metathesis (RCM) for the preparation of new chiral phosphine ligands,[1] we had reason to study in detail the reactivity of phosphine-borane dienes, trienes and tetraenes in the presence of a series of ruthenium- and molybdenum-based catalysts. We have shown previously that the well-explored Ru catalyst **1**[2] was efficient for the preparation of five-, six- and seven-membered borane complexes of alicyclic phosphines, as well as for the preparation of a bisphosphine but ineffective for the ring closure of diallylphenylphosphine. Unfortunately, we found that **1** was sensitive to steric effects and did not react with a borane complex of a β,β′-disubstituted or β-monosubstituted diene.[1]

Here we present recent investigations with regard to the use of representative ruthenium- and molybdenum-based catalysts (Fig. 1) in the formation of phosphorus heterocycles.

For this study, we selected the newer imidazol-2-ylidene-substituted ruthenium catalysts **2**[3] and **3**[4] for their remarkable thermal stabilities and enhanced RCM activities compared to the original ruthenium-based catalyst **1**. These Ru-based catalysts are particularly attractive not only because of their inertness toward oxygen and moisture but also because of the recent synthesis of efficient homochiral Ru-catalysts. Indeed, Grubbs has reported the synthesis of the first homochiral ruthenium olefin metathesis catalysts and has demonstrated that enantiomeric excesses up to 90% are observed in the desymmetrisation of achiral trienes.[5] More recently, Hoveyda has also demonstrated the feasibility of asymmetric olefin metathesis in ring-opening and cross metathesis examples mediated by a ruthenium-centred system.[6] We also selected the molybdenum catalyst **4** not only for its good tolerance to functional groups but also for its higher reactivity towards sterically congested olefins.[7] In addition, the alkoxide moieties of Mo-based catalysts such as **4** offer an excellent opportunity for incorporation of chirality within the catalyst structure through instalment of homochiral bis-hydroxy ligands. Hence, this class of catalysts also offers the possibility of asymmetric ring closing metathesis (ARCM) by kinetic resolution of racemic compounds or by enantioselective desymmetrisation of prochiral substrates.[8] If catalysts **3** and **4** are compatible with free or borane-protected phosphine derivatives, ARCM could emerge as a powerful tool for the construction of chiral phosphine ligands.[9] The present study sheds new light on the reactivity of catalysts **2**, **3** and **4** towards borane-complexes of a series of bis-, tris- and tetra(alkenyl)-phosphine boranes and of the unprotected commercially available diallylphenylphosphine.

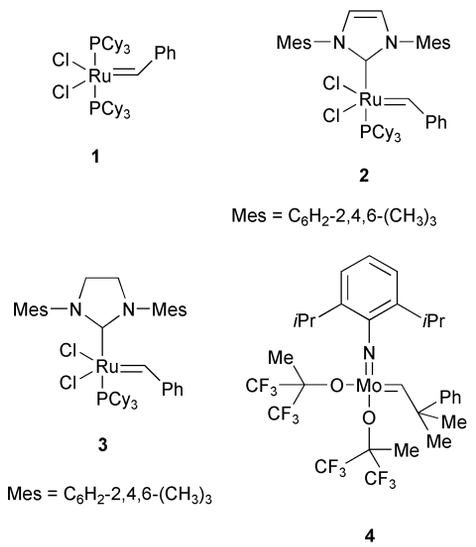

Fig. 1 RCM catalysts.

Results and discussion

A series of substrates **5a**–**f** was prepared for this study. The symmetrical dienes **5a** and **5c** and the tetraene **5f** were prepared in two steps from dichloro(phenyl)phosphine and 1,2-bis(dichlorophosphino)ethane as previously described.[1] The trienes **5d** and **5e** were easily obtained in two steps from trichlorophosphine. The protection of trichlorophosphine was accomplished using $BH_3{\cdot}Me_2S$ in Et_2O followed by triple substitution with the appropriate Grignard reagent to afford the desired trienes **5d** and **5e** in chemical yields of 63% and 85% respectively. The non-symmetrical phosphino-borane diene **5b**

† This is one of a number of contributions from the current members of the Dyson Perrins Laboratory to mark the end of almost 90 years of organic chemistry research in that building, as all its current academic staff move across South Parks Road to a new purpose-built laboratory.

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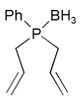
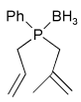
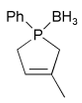
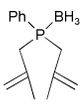
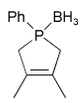
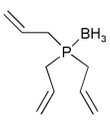
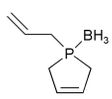
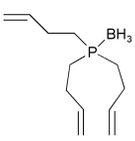
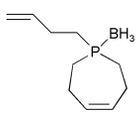
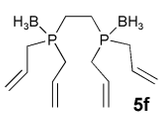
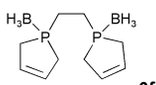
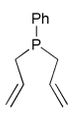
Table 1 RCM of phosphane-boranes **5a**–**f** and the unprotected diallylphenylphosphane **5g**

Entry	Substrate	Product	Cat. **1** (mol%) DCM reflux Reaction time Yield[a]	Cat. **2** (mol%) Toluene 80 °C Reaction time Yield[a]	Cat. **3** (mol%) DCM reflux Reaction time Yield[a]	Cat. **4** (mol%) Toluene 60 °C Reaction time Conversion[b]
1	 **5a**	 **6a**	4% 18 h 90%	6% 36 h 100%	4% 18 h 100%	11% 48 h 100%[a]
2	 **5b**	 **6b**	4% 6 h 0%	8% 30 h 57%[b]	6% 26 h 90%[b]	10% 60 h 0%
3	 **5c**	 **6c**	4% 120 h 0%	14% 192 h 0%	4% 96 h 0%	10% 96 h 0%
4	 **5d**	 **6d**	6% 23 h 62%	8% 24 h 100%	4% 5 h 95%	9% 72 h 95%
5	 **5e**	 **6e**	8% 24 h 64%	8% 22 h 73%[b]	2% 22 h 100%	25% 84 h >95%
6	 **5f**	 **6f**	14% 40 h 57%	10% 28 h 70%	14% 21 h 100%	12% 60 h 70%
7	 **5g**	 **6g**	4% 20 h 0%	8% 72 h 0%	8% 72 h 0%	12.5% 84 h 95%

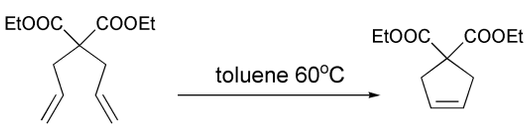
[a] Isolated yield of product. [b] Conversion as determined by ^{1}H NMR or ^{13}C NMR on the crude mixture.

was prepared from the known oxazaphospholidine-borane as previously reported but optimisation of the procedure allowed us to prepare this diene with an improved chemical yield of 97%.[1,10]

A preliminary study revealed that the ring-closing metathesis reactions were best performed in dichloromethane at reflux for catalysts **1** and **3**. For catalysts **2** and **4**, the best results were obtained in toluene at 80 °C and 60 °C, respectively. Our optimised results are summarised in Table 1.[11] All the catalysts **1**–**4** were found to mediate the conversion of diene **5a** into the corresponding cyclic phosphino-borane **6a** although significant differences were observed (entry 1). A maximum yield of 90% was obtained with 4 mol% of the Grubbs catalyst **1** but the Ru-catalysts **2** and **3** led quantitatively to compound **6a**. Higher temperature, catalyst loading and reaction time are necessary for catalyst **2**. Gratifyingly, we found that the Schrock catalyst **4** is compatible with the borane–phosphine functionality of **5a** and afforded the desired product **6a** in 100% yield after 48 hours in toluene at 60 °C. A useful feature of the Ru-catalysts **2** and **3** was their ability to form the trisubstituted alkene **6b** in 57% and 90% conversion, respectively (entry 2). This compound cannot be formed with catalysts **1** or **4**. With the more sterically demanding phosphino-borane diene **5c**, all catalysts **1**–**4** proved ineffective in generating the tetrasubstituted double bond of compound **6c**. No trace of product could be detected in the crude mixture with the unmodified starting material present (entry 3). Both trienes **5d** and **5e** reacted with all four catalysts **1**–**4** to afford the desired products **6d** and **6e** in varying yields (entries 4 and 5). For these substrates, the Ru-based catalyst **3** once more outperformed all other catalysts with only 4 mol% or 2 mol% being necessary to afford the desired cyclised products **6d** and **6e** with isolated yields of 95% and 100%, respectively. Up to 8 mol% of catalyst **2** was necessary to achieve similar yields and catalyst **1** was much less efficient as compounds **6d** and **6e** were obtained with chemical yields of 62% and 64%, respectively. Triene **5d** was almost quantitatively converted to **6d** with 9 mol% of the Schrock catalyst **4**. Interestingly, the reaction of triene **5e** required up to 25 mol% of the Schrock catalyst **4** to reach completion. The tetraene **5f** could be quantitatively converted into the corresponding bisphosphine **6f** in the presence of 14 mol% of catalyst **3**. Catalysts **2** and **4** were both more effective than catalyst **1** for this reaction (entry 6). We also investigated which catalyst might be active for the RCM of the unprotected diallylphenylphosphine (entry 7). As expected, none of the Ru catalysts were suitable. This observation confirms the hypothesis by Grubbs that the presence of the free phosphine disfavours the equilibrium for olefin binding to the catalyst in the first step of a dissociative mechanism for the RCM.[12] In other words, the competition between the better donating phosphine functionality and the olefin leads to complete inhibition of the catalyst. This hypothesis was further supported by control experiments conducted in the group of Nolan *et al*. It was found that the addition of 0.06 equiv. of PCy_3 per equiv of catalyst **2** results in a loss of activity greater than 75% for the ring closing metathesis of diethyl diallylmalonate.[3a] In contrast to these results, there are indications in the literature that molybdenum can tolerate phosphorus or sulfur functionalities because of the relatively crowded pseudo-tetrahedral coordination sphere and a possible mismatch between the relatively hard metal center and a softer donor such as a thioether or a phosphine.[13] It has already been reported in the literature that the cyclometalated aryloxycarbene complex

of tungsten has been successfully employed for the ring closure metathesis of diallylphenylphosphine.[14] However, to our knowledge, there has been no report on the compatibility of free phosphine with the Schrock's Mo-based catalyst **4**. We have found that catalyst **4** afforded the desired cyclised unprotected phosphine **6g** with a 95% conversion suggesting that diene **5g** is compatible with this catalyst.

Further control experiments suggested that the compatibility of free phosphine with catalyst **4** might not be a general feature but is likely to be substrate dependent. Indeed, the addition of 0.1 equivalent of PEt_3 was sufficient to result in a complete loss of activity for the ring closing metathesis of diethyl diallylmalonate (Scheme 1). In contrast, the Schrock catalyst could tolerate the presence of 0.1 equivalent of PCy_3, a more crowded electron donating ligand, as under these conditions 100% of the desired ring closed product was formed. However, the addition of one equivalent of PCy_3 was sufficient to result in a complete loss of activity of the catalyst. Finally, we found that the addition of a weakly donating phosphine such as triphenylphosphine did not result in any loss of activity. Indeed, 100% yield of the desired product was obtained for the RCM of diethyl diallylmalonate in the presence of one equivalent of triphenylphosphine. These results suggest that only relatively hindered weakly donating phosphines will be compatible with the Schrock catalyst **4**.



Conditions	Conversion
1 eq. malonate, 0.1 eq PEt_3, 19 % mol cat. **4**, 60h	0%
1 eq. malonate, 0.1 eq PCy_3, 19 % mol cat. **4**, 89h	100%
1 eq. malonate, 1 eq PCy_3, 19 % mol cat. **4**, 89h	0%
1 eq. malonate, 1 eq PPh_3, 10 % mol cat. **4**, 24h	100%

Scheme 1

Studies aimed at exploring the catalytic kinetic resolution of racemic phosphines as well as the enantioselective desymmetrisation of prochiral phosphines in the presence of homochiral RCM-catalysts are currently under way in our laboratory.

Experimental

Reactions involving the Schrock catalyst **4**, diallylphenylphosphine or triethylphosphine were carried out in a glove box under an atmosphere of argon. All other reactions were conducted in flame-dried apparatus under an atmosphere of argon. Et_2O, THF and toluene were distilled from sodium–benzophenone ketyl radical; dichloromethane was distilled from CaH_2. All other commercial reagents were used without further purification. Reactions were monitored by thin layer chromatography (TLC) using Merck aluminium foil backed sheets precoated with Kieselgel $60F_{254}$. Visualisation of reaction components was achieved with UV lamp (254 nm) and $KMnO_4$ stains. Column chromatography was carried out on Merck Silica gel C60 (40–60 μM). Melting points were recorded on a Philip Harris apparatus and are uncorrected. IR spectra were recorded using a Perkin-Elmer Paragon 1000 FT-IR spectrometer. Peak intensities are reported as strong (s), medium (m), or weak (w). ^{1}H, ^{13}C, ^{11}B and ^{31}P NMR spectra were recorded in $CDCl_3$ on Bruker spectrometers at the frequency indicated and calibrated using the solvent as an internal reference. Chemical shifts are reported in parts per million (ppm) and coupling constants (J) are reported to the nearest 0.1 Hz. The following abbreviations are used to explain multiplicities: s = singlet, d = double, t = triplet, q = quartet, m = multiplet, br = broad. Mass spectra and HRMS were recorded on Micromass GCT using Atmospheric Pressure Chemical Ionisation (NH_3, APCI), Electrospray Ionisation (EI) or Field Ionisation (FI). Microanalyses were performed by "Elemental Microanalysis Limited", Okehampton, Devon.

Diallylphenylphosphino-borane 5a

Borane dimethyl sulfide complex (16.0 ml, 2 M in Et_2O, 32.0 mmol) in Et_2O (30 ml) was added dropwise with stirring to a solution of dichlorophenylphosphine (4.0 ml, 29.5 mmol) in Et_2O (80 ml) at 0 °C. After stirring at this temperature for 45 min, the mixture was added dropwise at 0 °C to freshly prepared allylmagnesium bromide (from reaction of allyl bromide (7.8 ml, 90.1 mmol) with magnesium (6.45 g, 270.0 mmol) in Et_2O (140 ml)). The mixture was warmed to room temperature and stirred for 1.5 h. Water (100 ml) was added and the mixture extracted with Et_2O (3 × 150 ml). The combined organic layers were washed with water (500 ml), NaCl (aq., sat., 500 ml), dried ($MgSO_4$) and the solvents evaporated under vacuum to give an opaque oil. Purification by flash column chromatography (40–60 pet. ether : toluene, 1 : 1) gave **5a** as a colourless oil (4.96 g, 83%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.79 (3H, br q, $J_{H,B}$ = 95.7 Hz), 2.78 (4H, dddd, $J_{H,H}$ = 1.0 Hz, 0.8 Hz, 7.5 Hz, $J_{H,P}$ = 12.0 Hz), 5.15 (2H, ddq, $^2J_{H,H}$ = 1.0 Hz, $^3J_{H,H}$ = 17.5 Hz, $^4J_{H,H}$ = 1.0 Hz, $J_{H,P}$ = 3.4 Hz), 5.21 (2H, ddq, $^2J_{H,H}$ = 1.0 Hz, $^3J_{H,H}$ = 10.5 Hz, $^4J_{H,H}$ = 0.8 Hz, $J_{H,P}$ = 3.0 Hz), 5.78 (2H, dddt, $J_{H,H}$ = 7.5 Hz, 10.5 Hz, 17.5 Hz, $J_{H,P}$ = 4.5 Hz), 7.50–7.58 (3H, m), 7.74–7.76 (2H, m); ^{13}C NMR (100.61 MHz, $CDCl_3$): δ 30.3 (d, $J_{C,P}$ = 34.2 Hz), 120.2 (d, $J_{C,P}$ = 10.1 Hz), 127.2 (d, $J_{C,P}$ = 50.9 Hz), 128.2 (d, $J_{C,P}$ = 6.7 Hz), 128.7 (d, $J_{C,P}$ = 9.7 Hz), 131.5 (d, $J_{C,P}$ = 2.3 Hz), 132.2 (d, $J_{C,P}$ = 8.8 Hz); ^{11}B NMR (80.25 MHz, $CDCl_3$): δ −37.7 (dq, $J_{B,H}$ = 95.7 Hz, $J_{B,P}$ = 58.0 Hz); ^{31}P NMR (125.72 MHz, $CDCl_3$): δ 14.26 (br m); IR (film): 2371 (B–H, s), 1637 (C=C, m) cm^{-1}; HRMS (FI): calculated for $C_{12}H_{18}BP$ ($M^{\bullet}$) 204.1239. Found: 204.1237.

Allyl(2-methylallyl)phenylphosphino-borane 5b

Hydrogen chloride gas was bubbled through a solution of (R_p)-(+)-*N*-[(1*S*,2*R*)-2-hydroxy-1-methylphenylethyl]-*N*-methyl-*P*-allylphosphinamine-*P*-borane (347 mg, 1.1 mmol) in Et_2O (12 ml) at 0 °C, until precipitation of ephedrine chloride was complete (monitored by TLC, toluene : EtOAc, 95 : 5), and the mixture then stirred for a further 15 min at room temperature. The precipitate was removed *via* filtration under argon and the solvent removed *in vacuo* to give a colourless oil. This was taken up in Et_2O (8 ml) and freshly prepared 2-methylallylmagnesium chloride (from reaction of 3-chloro-2-methylpropene (1.0 ml, 10.1 mmol) and magnesium (347 mg, 15.5 mmol) in Et_2O (18 ml)) added dropwise at −78 °C. The mixture was warmed to room temperature and stirred for 1.5 h, then cooled to −10 °C and the reaction quenched with NH_4Cl (aq., sat., 10 ml). The organic phase was washed with water (3 × 50 ml), NH_4Cl (aq., sat., 2 × 50 ml), dried ($MgSO_4$) and the solvents evaporated under vacuum to give a yellow oil. Purification by flash column chromatography (40–60 pet. ether : toluene, 2 : 1) gave **5b** as a colourless oil (223 mg, 97%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.84 (3H, br q, $J_{H,B}$ = 95.2 Hz), 1.74 (3H, d, $J_{H,P}$ = 1.0 Hz), 2.75 (1H, dddd, $J_{H,H}$ = 13.9 Hz, 1.0 Hz, 0.8 Hz, $J_{H,P}$ = 11.7 Hz), 2.80 (1H, dddd, $J_{H,H}$ = 13.9 Hz, 1.0 Hz, 0.8 Hz, $J_{H,P}$ = 12.2 Hz), 2.82 (2H, dddd, $J_{H,H}$ = 7.5 Hz, 1.0 Hz, 0.8 Hz, $J_{H,P}$ = 12.0 Hz), 4.70 (1H, dq, $^2J_{H,H}$ = 1.0 Hz, $^4J_{H,H}$ = 1.0 Hz, $J_{H,P}$ = 3.0 Hz), 4.91 (1H, ddt, $J_{H,H}$ = 1.0 Hz, 0.8 Hz, $J_{H,P}$ = 3.4 Hz), 5.15 (1H, ddq, $^2J_{H,H}$ = 1.0 Hz, $^3J_{H,H}$ = 17.5 Hz, $^4J_{H,H}$ = 1.0 Hz, $J_{H,P}$ = 3.4 Hz), 5.20 (1H, dddt, $J_{H,H}$ = 1.0 Hz, 0.8 Hz, 10.5 Hz, $J_{H,P}$ = 3.0 Hz), 5.78 (1H, dddt, $J_{H,H}$ = 7.5 Hz, 10.5 Hz, 17.5 Hz, $J_{H,P}$ = 4.5 Hz), 7.44–7.52 (3H, m), 7.72–7.77 (2H, m); ^{13}C NMR (100.61 MHz, $CDCl_3$): δ 24.3 (s), 31.2 (d, $J_{C,P}$ = 34.2 Hz), 34.4 (d, $J_{C,P}$ = 31.2 Hz), 115.8 (d, $J_{C,P}$ = 8.1 Hz), 120.1 (d, $J_{C,P}$ = 10.1 Hz), 127.6 (d, $J_{C,P}$ = 50.0 Hz), 128.5 (d, $J_{C,P}$ = 5.0 Hz), 128.6 (d, $J_{C,P}$ = 9.7 Hz), 131.4 (d,

$J_{C,P}$ = 1.6 Hz), 132.3 (d, $J_{C,P}$ = 9.5 Hz), 137.3 (d, $J_{C,P}$ = 6.0 Hz); ^{11}B NMR (80.25 MHz, $CDCl_3$): δ −37.1 (dq, $J_{B,H}$ = 95.6 Hz, $J_{B,P}$ = 57.8 Hz); ^{31}P NMR (101.25 MHz, $CDCl_3$): δ 13.42 (br m); IR (film): 3080 (=CH_2, w), 2916 (w), 2378 (B–H, s), 1638 (C=C, w), 1437 (CH_2–C=C, m) cm^{-1}; HRMS (FI): calculated for $C_{13}H_{20}BP$ ($M^{\bullet}$) 218.1396. Found: 218.1396.

Bis(2-methylallyl)phenylphosphino-borane 5c

Borane dimethyl sulfide complex (7.4 ml, 2 M in diethyl ether, 14.8 mmol), was added dropwise with stirring to dichlorophenylphosphine (2.0 ml, 14.7 mmol) in Et_2O (40 ml) at 0 °C. After stirring at this temperature for 30 min, the mixture was added dropwise at 0 °C to freshly prepared 2-methylallylmagnesium chloride (from reaction of 3-chloro-2-methylpropene (4.4 ml, 44.1 mmol) and magnesium (5.62 g, 231 mmol) in Et_2O (80 ml)). The mixture was warmed to room temperature and stirred for 1 h. Water (50 ml) was added and the mixture extracted with Et_2O (2 × 150 ml). The combined organic layers were washed with NaCl (aq., sat., 200 ml), dried ($MgSO_4$) and the solvents evaporated under vacuum to give an opaque oil. Purification by flash column chromatography (40–60 pet. ether : toluene, 1 : 1) gave **5c** as a white crystalline solid (1.33 g, 39%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.63 (3H, br q, $J_{H,B}$ = 95.2 Hz), 1.75 (6H, d, $J_{H,P}$ = 1.4 Hz), 2.78 (2H, dd, $J_{H,H}$ = 14.3 Hz, $J_{H,P}$ = 10.8 Hz), 2.82 (2H, dd, $J_{H,H}$ = 14.3 Hz, $J_{H,P}$ = 10.8 Hz), 4.70 (2H, br dd, $J_{H,H}$ = 0.8 Hz, $J_{H,P}$ = 3.6 Hz), 4.82 (2H, br dd, $J_{H,H}$ = 0.8 Hz, $J_{H,P}$ = 5.6 Hz), 7.49–7.56 (3H, m), 7.82–7.84 (2H, m); ^{13}C NMR (100.61 MHz, $CDCl_3$): δ 24.4 (d, $J_{C,P}$ = 1.0 Hz), 35.4 (d, $J_{C,P}$ = 31.2 Hz), 115.8 (d, $J_{C,P}$ = 9.1 Hz), 128.1 (d, $J_{C,P}$ = 50.7 Hz), 128.5 (d, $J_{C,P}$ = 10.0 Hz), 131.4 (d, $J_{C,P}$ = 2.5 Hz), 132.5 (d, $J_{C,P}$ = 7.6 Hz), 137.4 (d, $J_{C,P}$ = 6.0 Hz); ^{11}B NMR (80.25 MHz, $CDCl_3$): δ −36.6 (dq, $J_{B,H}$ = 95.8 Hz, $J_{B,P}$ = 56.7 Hz); ^{31}P NMR (125.72 MHz, $CDCl_3$) δ 18.10 (br m); IR (film): 2922 (s), 2385 (B–H, s), 1644 (C=C, m) cm^{-1}; Anal. Calcd for $C_{14}H_{23}PB$: C, 72.30; H, 9.85; found: C, 72.44; H, 9.55%.

Triallylphosphino-borane 5d

Borane dimethyl sulfide complex (12.5 ml, 2 M in Et_2O, 25.0 mmol) in Et_2O (25 ml) was added dropwise with stirring to a solution of phosphorus trichloride (2.0 ml, 22.9 mmol) in Et_2O (60 ml) at 0 °C. After stirring at 0 °C for 1.25 h, the mixture was added dropwise at 0 °C to freshly prepared allylmagnesium bromide (from reaction of allyl bromide (10.0 ml, 116 mmol) and magnesium (5.06 g, 208 mmol) in Et_2O (120 ml)). The reaction mixture was warmed to rt and stirred for 1.5 h. Water (100 ml) was added and the mixture extracted with Et_2O (100 ml). The combined organic layers were washed with hydrochloric acid (2 M, 150 ml) and water (2 × 150 ml), dried ($MgSO_4$) and solvents evaporated under vacuum to give a clear oil. Purification by flash column chromatography (cyclohexane : toluene, 1 : 1) gave **5d** as a clear colourless oil (2.41 g, 63%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.51 (3H, br dq, $J_{H,B}$ = 96.2 Hz, $J_{H,P}$ = 9.5 Hz), 2.51 (6H, dd, $J_{H,H}$ = 7.5 Hz, $J_{H,P}$ = 12.0 Hz), 5.23 (3H, ddd, $J_{H,H}$ = 1.5 Hz, 17.5 Hz, $J_{H,P}$ = 4.5 Hz), 5.29 (3H, ddd, $J_{H,H}$ = 1.5 Hz, 10.5 Hz, $J_{H,P}$ = 3.0 Hz), 5.85 (3H, dddt, $J_{H,H}$ = 7.5 Hz, 10.5 Hz, 17.5 Hz, $J_{H,P}$ = 4.5 Hz); ^{13}C NMR (100.62 MHz, $CDCl_3$): δ 27.9 (d, $J_{C,P}$ = 31.2 Hz) 120.2 (d, $J_{C,P}$ = 10.1 Hz), 128.2 (d, $J_{C,P}$ = 6.0 Hz); ^{11}B NMR (160.41 MHz, $CDCl_3$): δ −37.60 (dq, $J_{B,H}$ = 96.2 Hz, $J_{B,P}$ = 48.1 Hz); ^{31}P NMR (202.40 MHz, $CDCl_3$): δ 14.96 (br m); IR (film): 3085 (=CH_2, m), 2372 (B–H, s), 2340 (B–H, s), 1637 (C=C, m), 1422 (CH_2–C=C, m) cm^{-1}; HRMS (FI): calculated for $C_9H_{15}BP$ ([M–H]$^{\bullet}$) 167.1161. Found: 167.1159.

Tri-but-3-enylphosphino-borane 5e

Borane dimethyl sulfide complex (3.2 ml, 2 M solution in Et_2O, 6.4 mmol) in Et_2O (6 ml) was added dropwise with stirring to a solution of phosphorus trichloride (0.5 ml, 5.7 mmol) in Et_2O (14 ml) at 0 °C. After stirring at this temperature for 1 h, the mixture was added dropwise at 0 °C to freshly prepared 3-butenylmagnesium bromide (from reaction of 4-bromo-1-butene (2.9 ml, 28.6 mmol) and magnesium (2.75 g, 113 mmol) in Et_2O (30 ml)). The mixture was warmed to room temperature and stirred for 2 h. Water (30 ml) was added and the mixture extracted with Et_2O (2 × 30 ml). The combined organic layers were washed with water (2 × 60 ml), dried ($MgSO_4$) and the solvents evaporated under vacuum to give an opaque oil. Purification by flash column chromatography (cyclohexane : toluene, 1 : 1) gave **5e** as a clear colourless oil (905 mg, 85%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.45 (br q, $J_{H,B}$ = 93.8 Hz, 3H), 1.73–1.76 (6H, m), 2.27–2.32 (6H, m), 5.06 (3H, br dq, $^2J_{H,H}$ = 1.5 Hz, $^3J_{H,H}$ = 10.0 Hz, $^4J_{H,H}$ = 1.5 Hz), 5.12 (3H, br dq, $^2J_{H,H}$ = 1.5 Hz, $^3J_{H,H}$ = 17.0 Hz, $^4J_{H,H}$ = 1.5 Hz), 5.87 (3H, dddt, $J_{H,H}$ = 6.5 Hz, 10.0 Hz, 17.0 Hz, $J_{H,P}$ = 3.0 Hz); ^{13}C NMR (125.72 MHz, $CDCl_3$): δ 22.4 (d, $J_{C,P}$ = 37.7 Hz), 26.6 (s), 115.4 (s), 137.3 (d, $J_{C,P}$ = 12.6 Hz); ^{11}B NMR (160.41 MHz, $CDCl_3$): δ −38.14 (dq, $J_{B,H}$ = 93.8 Hz, $J_{B,P}$ = 62.6 Hz); ^{31}P NMR (202.40 MHz, $CDCl_3$): δ 17.90 (br m); IR (film): 3225 (=CH_2, w), 2369 (B–H, s), 1641 (C=C, m), 1415 (CH_2–C=C, m) cm^{-1}; HRMS (FI): calculated for $C_{12}H_{24}BP$ ($M^{\bullet}$) 209.1630. Found: 209.1631.

1,2-Bis(diallylborylphosphino)ethane 5f

Borane dimethyl sulfide complex (4.3 ml, 2 M in diethyl ether, 8.6 mmol) in Et_2O (20 ml) was added dropwise with stirring to a solution of 1,2-bis(dichlorophosphino)ethane (1.0 g, 4.3 mmol) in Et_2O at 0 °C. After stirring at 0 °C for 1 h, the mixture was added dropwise at 0 °C to freshly prepared allylmagnesium bromide (from reaction of allyl bromide (1.85 ml, 21.4 mmol) and magnesium in Et_2O (40 ml)). The mixture was stirred at this temperature for 2.5 h and at rt for 30 min. NH_4Cl (aq., sat., 100 ml) was added and the mixture extracted with Et_2O (2 × 100 ml). The combined organic layers were washed with NaCl (aq., sat., 2 × 100 ml) and water (2 × 100 ml), dried ($MgSO_4$) and the solvents evaporated under vacuum to give an opaque oil. Purification by flash column chromatography (toluene : ethyl acetate, 95 : 5) gave **5f** as a clear oil (236 mg, 27%) which crystallised under high vacuum. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.42 (6H, br q, $J_{H,B}$ = 89.3 Hz), 1.77 (4H, d, $J_{H,P}$ = 3.5 Hz), 2.53 (8H, dd, $J_{H,H}$ = 7.5 Hz, $J_{H,P}$ = 11.0 Hz), 5.24 (4H, br dd, $J_{H,H}$ = 1.0 Hz, 17.0 Hz), 5.31 (4H, br dd, $J_{H,H}$ = 1.0 Hz, 9.8 Hz), 5.81 (4H, dddt, $J_{H,H}$ = 7.5 Hz, 9.8 Hz, 17.0 Hz, $J_{H,P}$ = 2.5 Hz); ^{13}C NMR (125.72 MHz, $CDCl_3$): δ 15.4 (d, $J_{C,P}$ = 31.4 Hz), 28.3 (d, $J_{C,P}$ = 32.7 Hz), 120.6 (d, $J_{C,P}$ = 5.0 Hz), 127.6 (d, $J_{C,P}$ = 3.8 Hz); ^{11}B NMR (160.41 MHz, $CDCl_3$): δ −38.33 (dq, $J_{B,H}$ = 89.3 Hz, $J_{B,P}$ = 52.9 Hz); ^{31}P NMR (202.4 MHz, $CDCl_3$): δ 19.08 (br m); IR (film): 2919 (w), 2364 (B–H, s), 1635 (C=C, w), 1422 (CH_2–C=C, m) cm^{-1}; HRMS (FI): calculated for $C_{14}H_{30}P_2B_2$ ($M^{\bullet}$) 281.1931. Found: 281.1927.

Ring closing metathesis—general procedures

All metathesis reactions were undertaken using one of 4 general procedures. **GP1**: catalyst **1** (2 mol% portion) was added to a solution (*ca.* 0.02 M) of anhydrous phosphane in DCM, which was boiling under reflux. **GP2**: catalyst **2** (2 mol% portion) was added to a solution (*ca.* 0.02 M) of anhydrous phosphane in toluene at 80 °C. **GP3**: catalyst **3** (2 mol% portions) was added to a solution (*ca.* 0.02 M) of anhydrous diene, triene or tetraene in DCM, which was boiling under reflux. **GP4**: a solution of catalyst **4** in degassed toluene was added to a solution of the phosphine in toluene, the sample sealed and removed from the glove box, then heated to 60 °C. In procedures **1**–**3**, reaction was followed by TLC, ^{1}H NMR or mass spectroscopy and further catalyst was added in 2 mol% portions until the diene/triene had been consumed or until further addition produced no discernable change. Volatiles were then removed under vacuum and the residue purified by flash column chromatography. Percentage conversions, where indicated, were determined by

spectroscopy of the crude mixture prior to column chromatography. In procedure **4** volatiles were removed under vacuum and the conversion determined by ^{1}H or ^{13}C NMR.

1-Phenyl-2,5-dihydro-1*H*-phosphole-1-borane 6a

GP1: diallylphenylphosphino-borane **5a** (812 mg, 3.98 mmol), dichloromethane (196 ml), catalyst **1** (132 mg, 0.16 mmol, 4%), 18 h; flash column chromatography (cyclohexane : toluene, 1 : 1) gave **6a** (628 mg, 90%) as a clear oil; **GP2**: diallylphenylphosphino-borane **5a** (52 mg, 0.25 mmol), toluene (12 ml), catalyst **2** (8.5 mg, 0.015 mmol, 6%), 36 h, (48 mg, 100%); **GP3**: diallylphenylphosphino-borane **5a** (53 mg, 0.25 mmol), dichloromethane (12 ml), catalyst **3** (8.9 mg, 0.010 mmol, 4%), 18 h, (50 mg, 100%); **GP4**: diallylphenylphosphino-borane **5a** (48 mg, 0.24 mmol), toluene (12 ml), catalyst **4** (20 mg, 0.026 mmol, 11%), 48 h, (40 mg, 100%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.92 (3H, br dq, $J_{B,H}$ = 95.2 Hz, $J_{P,H}$ = 10.4 Hz), 2.66–2.96 (4H, m), 6.02 (2H, d, $J_{H,P}$ = 21.3 Hz), 7.43–7.54 and 7.71–7.79 (5H, 2 × m); ^{13}C NMR (100.61 MHz, $CDCl_3$): δ 33.2 (d, $J_{C,P}$ 62.4 Hz), 128.6 (d, $J_{C,P}$ = 1.6 Hz), 128.9 (d, $J_{C,P}$ = 9.7 Hz), 131.0 (s) 131.2 (d, $J_{C,P}$ = 3.0 Hz), 131.6 (d, $J_{C,P}$ = 2.5 Hz); ^{11}B NMR (80.25 MHz, $CDCl_3$): δ −36.13 (dq, $J_{B,H}$ = 96.6 Hz, $J_{B,P}$ = 52.6 Hz); ^{31}P NMR (101.25 MHz, $CDCl_3$): δ 25.35 (br m); IR (film) 3019 (=CH_2, m), 2318 (B–H, m), 1637 (C=C, w), 1621 (C=C, w), 1423 (CH_2–C=C, w) cm^{-1}; HRMS (FI): calculated for $C_{10}H_{14}PB$ ($M^{\bullet}$) 176.0926. Found: 176.0918.

1-Phenyl-2,5-dihydro-3-methyl-1*H*-phosphole-1-borane 6b

GP1: allyl(2-methylallyl)phenylphosphino-borane **5b** (63 mg, 0.29 mmol), dichloromethane (15 ml), catalyst **1** (9.5 mg, 0.012 mmol, 4%), 6 h, (0% conv.); **GP2**: allyl(2-methylallyl)phenylphosphino-borane **5b** (68 mg, 0.31 mmol), toluene (16 ml), catalyst **2** (16 mg, 18.7 µmol, 8%), 30 h, (57% conv.); **GP3**: allyl(2-methylallyl)phenylphosphino-borane **5b** (135 mg, 0.62 mmol), dichloromethane (31 ml), catalyst **3** (32 mg, 0.038 mmol, 6%), 26 h, (90% conv.); **GP4**: allyl(2-methylallyl)phenylphosphino-borane **5b** (47 mg, 0.22 mmol), toluene (11.0 ml), catalyst **4** (16.7 mg, 0.022 mmol, 10%), 60 h, (0% conv.). As the product was inseparable from the starting material, the spectra were assigned by comparison with spectra of starting material. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.94 (3H, br q, $J_{H,B}$ = 96.3 Hz,), 2.02 (3H, s), 2.64–2.97 (4H, m), 5.64 (1H, d, $J_{H,P}$ = 23.0 Hz), 7.32–7.55 (2H, m), 7.76–7.80 (3H, m); ^{13}C NMR (100.62 MHz, $CDCl_3$): δ 19.0 (d, $J_{C,P}$ = 8.0 Hz), 33.4 (d, $J_{C,P}$ = 36.2 Hz), 37.1 (d, $J_{C,P}$ = 38.2 Hz), 122.3 (s), 128.8 (d, $J_{C,P}$ = 10.1 Hz), 131.0 (d, $J_{C,P}$ = 9.1 Hz), 131.4 (d, $J_{C,P}$ = 2.0 Hz), 131.6 (d, $J_{C,P}$ = 15.1 Hz), 138.4 (d, $J_{C,P}$ = 3.0 Hz); ^{11}B NMR (160.41 MHz, $CDCl_3$): δ −35.78 (dq, $J_{B,H}$ = 96.3 Hz, $J_{B,P}$ = 64.2 Hz); ^{31}P NMR (202.40 MHz, $CDCl_3$): δ 29.52 (br m); IR (film): 3077 (=CH_2, w), 2934, 2915, 2854 (CH_3, w), 2378 (BH_3, s), 1654 (C=C, w), 1437 (CH_2–C=C, s), 1136 (m), 1113 (m), 1062 (s) cm^{-1}; HRMS (FI): calculated for $C_{11}H_{16}BP$ ($M^{\bullet}$) 190.1083. Found: 190.1088.

1-Allyl-2,3-dihydro-1*H*-phosphole-1-borane 6d

GP1: triallylphosphino-borane **5d** (199 mg, 1.18 mmol), dichloromethane (60 ml), catalyst **1** (57 mg, 0.069 mmol, 6%), 23 h; flash column chromatography (cyclohexane : ethyl acetate, 20 : 1) gave **6d** (104 mg, 62%) as a clear colourless oil; **GP2**: triallylphosphino-borane **5d** (108 mg, 0.64 mmol), toluene (32 ml), catalyst **2** (43 mg, 0.051 mmol, 8%), 24 h, (93 mg, 100%); **GP3:** triallylphosphino-borane **5d** (66 mg, 0.39 mmol), dichloromethane (20 ml), catalyst **3** (13 mg, 0.016 mmol, 4%), 5 h, (44 mg, 95%); **GP4:** triallylphosphino-borane **5d** (50 mg, 0.30 mmol), toluene (14 ml), catalyst **4** (20 mg, 0.026 mmol, 9%), 72 h, (95% conv.); ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.69 (3H, br dq, $J_{H,B}$ 96.3 Hz, $J_{H,P}$ 4.5 Hz), 2.48–2.63 (6H, m), 5.17–5.19 (1H, m), 5.21–5.24 (1H, m), 5.80 (1H, dddt, $J_{H,H}$ = 7.5 Hz, 10.0 Hz, 17.0 Hz, $J_{H,P}$ = 5.0 Hz), 5.88 (2H, d, $J_{H,P}$ = 20.0 Hz); ^{13}C NMR (100.62 MHz, $CDCl_3$): δ 29.0 (d, $J_{C,P}$ = 33.2 Hz), 30.9 (d, $J_{C,P}$ = 28.2 Hz), 119.9 (d, $J_{C,P}$ = 9.1 Hz), 128.1 (s) 128.4 (d, $J_{C,P}$ = 7.0 Hz); ^{11}B NMR (160.41 MHz, $CDCl_3$): δ −36.05 (dq, $J_{B,H}$ = 96.2 Hz, $J_{B,P}$ = 48.1 Hz); ^{31}P NMR (202.40 MHz, $CDCl_3$): δ 29.56 (br m); IR (film) 2362 (B–H, s), 2341 (B–H, s), 1622 (C=C, w), 1437 (CH_2–C=C, m) cm^{-1}; HRMS (FI): calculated for $C_7H_{14}BP$ ($M^{\bullet}$) 140.0926. Found: 140.0931.

1-But-3-enyl-2,3,6,7-tetrahydro-1*H*-phosphepine-1-borane 6e

GP1: tri-but-3-enylphosphino-borane **5e** (208 mg, 0.99 mmol), dichloromethane (50 ml), catalyst **1** (65 mg. 0.079 mmol, 8%), 24 h, (116 mg, 64%); **GP2:** tri-but-3-enylphosphino-borane **5e** (48 mg, 0.23 mmol), toluene (12 ml), catalyst **2** (16 mg, 0.018 mmol, 8%), 22 h, (73% conv.); **GP3:** tri-but-3-enylphosphino-borane **5e** (50 mg, 0.24 mmol), dichloromethane (12 ml), catalyst **3** (4 mg, 0.0048 mmol, 2%), 22 h, (100% conv.); **GP4:** tri-but-3-enylphosphino-borane **5e** (33 mg, 0.16 mmol), toluene (8.0 ml), catalyst **4** (30.6 mg, 0.040 mmol, 25%) 84 h, >95% conversion; ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.53 (3H, br dq, $J_{H,B}$ = 94.2 Hz, $J_{H,P}$ = 10.6 Hz), 1.65–1.78 (4H, m), 1.80–1.87 (2H, m), 2.30–2.43 (4H, m), 2.50–2.59 (2H, m), 5.08 (1H, br dd, $J_{H,H}$ = 1.0 Hz, 10.0 Hz), 5.15 (1H, ddd, $J_{H,H}$ = 1.0 Hz, 17.5 Hz, $J_{H,P}$ = 1.5 Hz), 5.78–5.89 (3H, m); ^{13}C NMR (125.73 MHz, $CDCl_3$): δ 20.8 (d, $J_{C,P}$ = 4.0 Hz), 21.8 (d, $J_{C,P}$ = 33.2 Hz), 23.8 (d, $J_{C,P}$ = 34.2 Hz), 26.6 (s), 115.3 (s), 131.42 (s), 137.5 (d, $J_{C,P}$ = 12.1 Hz); ^{11}B NMR (160.41 MHz, $CDCl_3$): δ −37.58 (dq, $J_{B,H}$ = 94.7 Hz, $J_{B,P}$ = 64.1 Hz); ^{31}P NMR (202.40 MHz, $CDCl_3$): δ 20.97 (br m); IR (film) 3022 (=CH_2, w), 2934 (m), 2860 (w), 2364 (B–H, s), 1640 (m, C=C), 1445 (w), 1412 (CH_2–C=C, w) cm^{-1}; HRMS (FI): calculated for $C_{10}H_{20}BP$ ($M^{\bullet}$) 182.1396. Found: 182.1405.

1,2-Bis(1-boryl-2,5-dihydro-1*H*-phosphol-1-yl)ethane 6f

GP1: 1,2-bis(diallylborylphosphino)ethane **5f** (193 mg, 0.68 mmol), dichloromethane (52 ml), catalyst **1** (78 mg, 0.095 mmol, 14%), 40 h, (88 mg of **6e**, 57% yield); **GP2:** 1,2-bis(diallylborylphosphino)ethane **5f** (171 mg, 0.61 mmol), toluene (60 ml), catalyst **2** (52 mg, 0.061 mmol, 10%), 28 h; flash column chromatography (toluene : ethyl acetate, 95 : 1) gave **6f** (96 mg, 70%) as a clear colourless oil; **GP3:** 1,2-bis(diallylborylphosphino)ethane **5f** (104 mg, 0.36 mmol), dichloromethane (18 ml), catalyst **3** (12 mg, 0.014 mmol, 14%), 21 h, (91 mg of **6f**, 100%); **GP4:** 1,2-bis(diallylborylphosphino)ethane **5f** (50 mg, 0.18 mmol), toluene (9.0 ml), catalyst **4** (16.7 mg, 0.022 mmol, 12%), 60 h, (70% conv.); ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.64 (6H, br q, $J_{H,B}$ = 94.4 Hz), 1.77 (4H, d, $J_{H,P}$ = 3.5 Hz), 2.55 (4H, br d, $J_{H,H}$ = 17.0 Hz), 2.69 (4H, br d, $J_{H,H}$ = 17.0 Hz), 5.92 (4H, d, $J_{H,P}$ = 20.5 Hz); ^{13}C NMR (125.72 MHz, $CDCl_3$): δ 18.8 (d, $J_{C,P}$ = 27.7 Hz), 28.6 (d, $J_{C,P}$ = 33.9 Hz), 127.9 (s); ^{11}B NMR (160.4 MHz, $CDCl_3$): δ −36.9 (dq, $J_{B,H}$ = 94.4 Hz, $J_{B,P}$ = 50.3 Hz); ^{31}P NMR (202.4 MHz, $CDCl_3$): δ 34.61 (br m); IR (film) cm^{-1} 2925 (C–H, m), 2854 (C–H, w), 2368 (B–H, s), 2308 (B–H, m), 1618 (C=C, w), 1402 (CH_2–C=C, w) cm^{-1}; HRMS (FI): calculated for $C_{10}H_{22}B_2P_2$ ($M^{\bullet}$) 225.1305. Found: 225.1300.

1-Phenyl-2,3-dihydro-1*H*-phosphole 6g

GP2: diallylphenylphosphine **5g** (50 µl, 0.25 mmol), toluene (12 ml), catalyst **2** (17 mg, 0.002 mmol, 8%), 72 h (0%); **GP3:** diallylphenylphosphine **5g** (50 µl, 0.25 mmol), CH_2Cl_2 (12 ml), catalyst **3** (17 mg, 0.021 mmol, 8%), 72 h (0%); **GP4:** diallylphenylphosphine **5g** (30 µl, 0.12 mmol), toluene (7.6 ml), catalyst **4** (11.5 mg, 0.015 mmol, 12.5%), 84 h (95% conv.). As product was not separated from starting material, the spectra assigned by comparison with spectra of starting material. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.56–2.88 (4H, m), 5.95 (2H, d, $J_{H,P}$ = 7.1 Hz), 7.30–7.75 (5H, m); ^{13}C NMR (100.64 MHz, $CDCl_3$): δ 34.5 (d, J_{C-P} = 10.0 Hz), 128.6 (s), 128.7 (s), 129.7 (d, J_{C-P} = 5.0 Hz), 131.2 (d, J_{C-P} = 20.0 Hz), 141.6 (d, J_{C-P} =

20.2 Hz); ^{31}P NMR (101.26 MHz, $CDCl_3$): δ −24.23 (s); MS (APCI): *m*/*z* 163.68 (10% $(M + H)^+$).

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