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The phosphinoboration of 2-diphenylphosphino benzaldehyde and related aldimines☆

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ABSTRACT

We have investigated the addition of a simple phosphinoboronate ester, Ph_2PBpin (pin = 1,2-$O_2C_2Me_4$), to 2-diphenylphosphinobenzaldehyde (2-$Ph_2PC_6H_4C(O)H$) and related aldimine derivatives (2-$Ph_2PC_6H_4C(NR)H$) as a simple and effective strategy for generating unique diphosphine ligands bearing a pendant Lewis-acid Bpin group. These reactions proceed selectively to give one new product where the phosphide fragment has added to the aldehyde (or imine) carbon atom and the electron-deficient boron group has added to the electron-rich heteroatom. Preliminary studies show these new compounds can ligate to Pd(II) and Pt(II) metal centres. These novel metal complexes, as well as the organic soluble $[MCl_2(coe)]_2$ (M = Pd, Pt, coe = *cis*-cyclooctene) compounds, have been shown to be effective precatalysts in the cyclisation of alkynoic acids to give the corresponding *exo*-dig cyclic lactones. Reactions employing these metal complexes also generated unusual *endo*-dig cyclic lactones not traditionally observed in these cyclisation reactions. For instance, reactions of 4-pentynoic acid also afforded significant amounts of α-angelica lactone, a biologically-important compound traditionally prepared *via* the catalytic dehydration and cyclisation of levulinic acid.

1. Introduction

There has been recent considerable interest in reducing aldehydes, ketones and aldimines using hydridoboranes such as pinacolborane (HBpin: pin = 1,2-$O_2C_2Me_4$) as a gentle, selective and effective method for generating the corresponding alcohols and amines, respectively, upon aqueous workup (Scheme 1a). However, reactions employing HBpin usually require elevated temperatures for prolonged periods of time or a transition metal [1], lanthanide/actinide [2] or a main-group [3] pre-catalyst to affect these reductions. While the analogous reductions using dimetalloid boron sources (R_2B-E; where E = B, SiR_3, OR, etc), such as B_2pin_2, also require either a catalyst or a strong base, these reactions are much less explored [4]. Interestingly, products arising from diborations incorporate a boryl (BR_2) group at the electrophilic carbon and provide a unique methodology for generating substituted alcohol derivatives (Scheme 1b). We have recently reported that the unique phosphinoboronate ester Ph_2PBpin, which contains a predominantly single P–B bond, adds selectively to aldehydes, ketones and aldimines *without the need of any additional catalyst or activating agent*, to give new ambiphilic tertiary phosphines in high yields (Scheme 1c) [5]. Compounds containing phosphine borane appendages have been investigated extensively as frustrated Lewis pairs [6] and as ligands for transition metals [7]. In this study, we have examined the addition of Ph_2PBpin to 2-diphenylphosphinobenzaldehyde [2-$Ph_2PC_6H_4C(O)H$] and the corresponding selected aldimine derivatives [2-$Ph_2PC_6H_4C(NR)H$; R = Ph, 2,6-(iPr)$_2C_6H_3$, $(CH_2)_3Ph$, *c*-C_5H_9, $(CH_2)_3PPh_2$] as a simple route for generating novel ambiphilic diphosphines. These new species have been found to ligate to palladium(II) and platinum(II) metal centres and are active pre-catalysts for the cyclisation of alkynoic acids.

☆ Dedicated to Dr. Richard J. Puddephatt, a brilliant chemist and wonderful person and role model, on the occasion of his 75th birthday.

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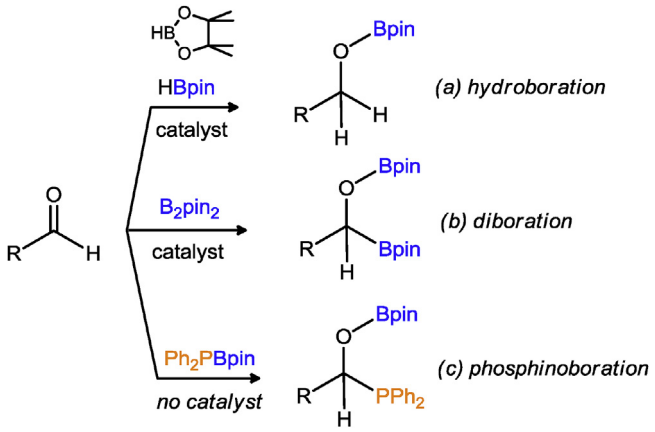
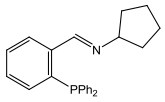


Scheme 1. The (a) hydroboration, (b) diboration, and (c) phosphinoboration of aldehydes.

2. Experimental

2.1. Materials and methods

Reagents and solvents used were obtained from Sigma-Aldrich. $[PdCl_2(\eta^2\text{-coe})]_2$ and $[PtCl_2(\eta^2\text{-coe})]_2$ (coe = *cis*-cyclooctene) [8], **1b** [9], **1c** [10], **1d** [11], **1f** [12] and diphenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phosphine (Ph_2PBpin) [5] were prepared as previously reported. NMR spectra were recorded on a JEOL JNM-GSX400 FT NMR (^1H: 400 MHz; ^{11}B: 128 MHz; ^{13}C: 100 MHz; ^{31}P: 162 MHz) spectrometer. Chemical shifts (δ) are reported in ppm [relative to residual solvent peaks (^1H and ^{13}C) or external $BF_3\cdot OEt_2$ (^{11}B) and H_3PO_4 (^{31}P)]. Multiplicities are reported as singlet (s), doublet (d), triplet (t), quartet (q), quintet (quint), multiplet (m), broad (br) and overlapping (ov) with coupling constants (J) reported in hertz. Melting points were measured uncorrected with a Stuart SMP30 apparatus. Elemental analyses for carbon, hydrogen, and nitrogen were performed at the University of Windsor using a PerkinElmer 2400 combustion CHN analyser. Microwave experiments were performed using an Anton Paar Monowave 400 equipped with a MAS24 autosampler. All reactions were performed under a nitrogen atmosphere in a MBRAUN LABmaster glovebox.

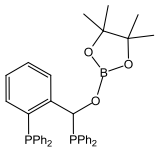


2.2. Synthesis of N-(2-(diphenylphosphino)benzylidene) cyclopentanamine (**1e**)

A mixture of 2-diphenylphosphinebenzaldehyde (200 mg, 0.69 mmol) and cyclopentylamine (59 mg, 0.69 mmol) in toluene (5 mL) in the presence of activated 3 Å molecular sieves was allowed to stand for 3 days at RT. The solution was decanted from the sieves and solvent was removed under vacuum. The resulting oil was used without further purification. Yield: 229 mg (93%). ^1H NMR ($CDCl_3$) δ: 8.80 (d, J_{HP} = 4.6 Hz, 1H, C(*H*) = N), 7.92 (m, 1H, Ar), 7.38–7.25 (ov m, 12H, Ar), 6.83 (m, 1H, Ar), 3.61 (quint, J = 5.7 Hz, 1H, C*H*N), 1.70–1.65 (ov m, 4H, CH_2CHN), 1.60–1.40 (ov m, 4H, CH_2); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 157.3 (d, J_{CP} = 19.1 Hz), 139.9 (d, J_{CP} = 17.2 Hz), 137.1 (d, J_{CP} = 19.1 Hz), 136.8 (d, J_{CP} = 9.5 Hz), 134.1 (d, J_{CP} = 20.0 Hz), 133.3, 129.9, 128.9, 128.8, 128.6 (d, J_{CP} = 7.6 Hz), 127.9 (d, J_{CP} = 4.8 Hz), 71.6, 34.4, 24.8; $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: −12.5 (s).

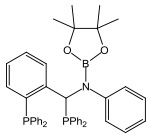
2.3. General synthesis of ligands

A mixture of Ph_2PBpin (200 mg, 0.64 mmol) and the appropriate aldehyde or aldimine in CH_2Cl_2 (10 mL) or toluene (**2c**) was stirred for 3 days. The solvent was removed under vacuum and the residue was washed with hexane (2 × 5 mL) to afford the ligands as white solids.



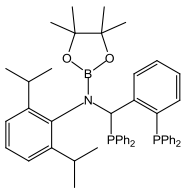
2.3.1. (2-((diphenylphosphino)((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)methyl)phenyl)-diphenylphosphine (**2a**)

Yield: 324 mg (84%); mp 161–163 °C. ^1H NMR ($CDCl_3$) δ: 7.71 (td, J = 7.8 Hz, J = 1.4 Hz, 2H, Ar), 7.45 (m, 1H, Ar), 7.40–7.14 (ov m, 19H, Ar & C*H*P), 7.09 (t, J = 7.8 Hz, 1H, Ar), 7.03 (td, J = 7.3 Hz, J = 1.4 Hz, 1H, Ar), 6.95 (dd, J = 7.3 Hz, J = 4.0 Hz, 1H, Ar), 0.98 (s, 6H, pin), 0.85 (s, 6H, pin); ^{11}B NMR ($CDCl_3$) δ: 22 (br); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 145.9 (d, J_{CP} = 10.5 Hz), 145.6 (d, J_{CP} = 11.5 Hz), 138.1 (d, J_{CP} = 11.5 Hz), 137.4 (d, J_{CP} = 10.5 Hz), 136.3 (d, J_{CP} = 21.1 Hz), 136.0, 134.6, 134.0 (d, J_{CP} = 3.8 Hz), 133.8 (d, J_{CP} = 3.8 Hz), 133.7, 133.5 (d, J_{CP} = 2.9 Hz), 133.4, 133.3, 133.1, 129.6, 129.2, 128.4 (d, J_{CP} = 6.7 Hz), 128.3, 128.2 (d, J_{CP} = 6.7 Hz), 128.1, 128.0 (d, J_{CP} = 3.8 Hz), 127.6, 82.9, 75.3 (dd, J_{CP} = 28.6 Hz, J_{CP} = 13.4 Hz), 24.4, 24.3; $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 6.8 (d, J_{PP} = 24.1 Hz), −20.0 (d, J_{PP} = 24.1 Hz). Anal. calcd. for $C_{37}H_{37}BO_3P_2$ (602.45 g mol^{-1}): C, 73.77; H, 6.19. Found: C, 74.00; H, 6.38.



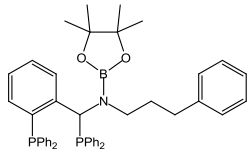
2.3.2. N-((diphenylphosphino)(2-(diphenylphosphino)phenyl) methyl)-4,4,5,5-tetramethyl-N-phenyl-1,3,2-dioxaborolan-2-amine (**2b**)

Yield: 386 mg (89%); mp 187–190 °C. ^1H NMR ($CDCl_3$) δ: 7.90 (td, J = 7.8 Hz, J = 2.2 Hz, 2H, Ar), 7.41–7.34 (ov m, 4H, Ar), 7.28 (ov dd, J = 8.2 Hz, J = 6.9 Hz, 4H, Ar), 7.20 (dd, J = 14.7 Hz, J = 7.3 Hz, 4H, Ar), 7.14 (ov dd, J = 7.3 Hz, J = 6.9 Hz, 4H, Ar), 7.09 (dd, J = 7.3 Hz, J = 2.8 Hz, 1H, Ar), 7.02–6.96 (ov m, 6H, Ar), 6.94–6.87 (ov m, 5H, Ar & C*H*P), 0.86 (s, 6H, pin), 0.83 (s, 6H, pin); ^{11}B NMR ($CDCl_3$) δ: 23 (br); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 145.0 (d, J_{CP} = 19.2 Hz), 144.8 (d, J_{CP} = 20.1 Hz), 142.9, 138.8 (d, J_{CP} = 13.4 Hz), 138.1 (d, J_{CP} = 13.4 Hz), 136.9 (d, J_{CP} = 2.9 Hz), 136.8 (d, J_{CP} = 15.3 Hz), 136.7 (d, J_{CP} = 3.8 Hz), 136.2 (d, J_{CP} = 14.4 Hz), 135.7, 135.4 (d, J_{CP} = 20.1 Hz), 134.4 (d, J_{CP} = 19.2 Hz), 133.7 (d, J_{CP} = 19.2 Hz), 133.2 (d, J_{CP} = 18.2 Hz), 131.8 (d, J_{CP} = 4.8 Hz), 131.6 (d, J_{CP} = 4.8 Hz), 130.9 (d, J_{CP} = 4.8 Hz), 129.0, 128.4 (d, J_{CP} = 4.8 Hz), 128.3 (d, J_{CP} = 2.9 Hz), 128.2 (d, J_{CP} = 5.8 Hz), 128.1 (d, J_{CP} = 4.8 Hz), 128.0 (d, J_{CP} = 9.6 Hz), 127.6, 125.6, 82.5, 59.3 (dd, J_{CP} = 25.9 Hz, J_{CP} = 5.8 Hz), 24.7, 24.2; $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: −7.0 (s), −19.4 (s). Anal. calcd. for $C_{43}H_{42}NBO_2P_2$ (677.56 g mol^{-1}): C, 76.22; H, 6.25; N, 2.07. Found: C, 75.95; H, 6.04; N, 1.87.



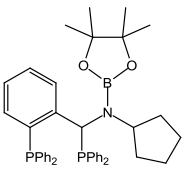
*2.3.3. N-(2,6-diisopropylphenyl)–N-((diphenylphosphino)(2-(diphenylphosphino)phenyl)methyl)-4,4,5,5-tetramethyl-N-phenyl-1,3,2-dioxaborolan-2-amine (**2c**)*

Yield: 351 mg (72%); mp 123–126 °C. ^{1}H NMR ($CDCl_3$) δ: 8.11 (br app t, $J = 6.9$ Hz, 2H, Ar), 7.40–7.34 (ov m, 4H, Ar), 7.29–7.25 (br ov m, 4H, Ar), 7.19–7.11 (ov m, 4H, Ar), 7.06 (td, $J = 7.8$ Hz, $J = 0.9$ Hz, 2H, Ar), 7.01–6.88 (ov m, 8H, Ar & C*H*P), 6.83 (app t, $J = 7.8$ Hz, 2H, Ar), 6.44 (td, $J = 6.9$ Hz, $J = 0.9$ Hz, 2H, Ar), 3.25 (br m, 1H, C*H*(CH_3)$_2$), 2.46 (br m, 1H, C*H*(CH_3)$_2$), 1.30–0.84 (br ov m, 15H, CH(C*H*$_3$) & pin), 0.90 (d, $J = 6.9$ Hz, 3H, CH(C*H*$_3$)), 0.64 (d, $J = 6.9$ Hz, 3H, CH(C*H*$_3$)), 0.26 (br s, 3H, CH(C*H*$_3$)); ^{11}B NMR ($CDCl_3$) δ: 23 (br); ^{13}C{^{1}H} NMR ($CDCl_3$) δ: 149.1 (d, $J_{CP} = 4.8$ Hz), 148.2 (br), 144.9 (br), 138.8 (d, $J_{CP} = 10.5$ Hz), 137.1 (d, $J_{CP} = 12.5$ Hz), 136.6 (d, $J_{CP} = 18.2$ Hz), 135.7 (d, $J_{CP} = 20.1$ Hz), 135.3 (d, $J_{CP} = 15.3$ Hz), 135.2, 134.6 (d, $J_{CP} = 21.1$ Hz), 132.8 (d, $J_{CP} = 17.3$ Hz), 132.5 (d, $J_{CP} = 4.8$ Hz), 132.4 (d, $J_{CP} = 3.8$ Hz), 128.9, 128.7, 128.2 (d, $J_{CP} = 7.7$ Hz), 127.9 (d, $J_{CP} = 7.7$ Hz), 127.8 (d, $J_{CP} = 5.8$ Hz), 127.7, 127.4 (d, $J_{CP} = 6.7$ Hz), 127.3, 127.1 (d, $J_{CP} = 9.6$ Hz), 123.7, 123.1, 82.9, 60.8 (br m), 29.0, 28.9, 25.9, 24.7, 24.6, 23.6, 23.5, 21.3 (br); ^{31}P{^{1}H} NMR ($CDCl_3$) δ: 1.2 (br s), −19.6 (s). Anal. calcd. for $C_{49}H_{54}NBO_2P_2 \cdot 1.5\ C_7H_8$ (900.08 g mol^{-1}): C, 79.39; H, 7.41; N, 1.56. Found: C, 79.58; H, 7.35; N, 1.85.



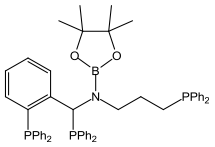
*2.3.4. Synthesis of N-((diphenylphosphino)(2-(diphenylphosphino)phenyl)methyl)-4,4,5,5-tetramethyl-N-(3-phenylpropyl)-1,3,2-dioxaborolan-2-amine (**2d**)*

Yield: 373 mg (81%); mp 182–184 °C. ^{1}H NMR ($CDCl_3$) δ: 8.09 (dt, $J = 8.2$ Hz, $J = 4.1$ Hz, 1H, Ar), 7.55–7.51 (ov m, 2H, Ar), 7.33–7.08 (ov m, 22H, Ar & C*H*P), 7.04 (app t, $J = 7.3$ Hz, 2H, Ar), 6.99–6.96 (ov m, 2H, Ar), 6.35 (t, $J = 7.8$ Hz, 1H, Ar), 3.19 (m, 1H, C*H*H), 3.08 (m, 1H, CH*H*), 2.37–2.21 (ov m, 2H, −C*H*$_2$−), 1.52 (m, 1H, C*H*H), 1.11 (m, 1H, CH*H*), 0.89 (s, 6H, pin), 0.74 (s, 6H, pin); ^{11}B NMR ($CDCl_3$) δ: 23 (br); ^{13}C{^{1}H} NMR ($CDCl_3$) δ: 146.5 (d, $J_{CP} = 19.2$ Hz), 146.2 (d, $J_{CP} = 19.2$ Hz), 143.8 (d, $J_{CP} = 6.7$ Hz), 142.7, 138.5 (d, $J_{CP} = 14.4$ Hz), 137.8 (d, $J_{CP} = 14.4$ Hz), 137.7 (d, $J_{CP} = 4.8$ Hz), 137.6 (d, $J_{CP} = 2.9$ Hz), 137.4 (d, $J_{CP} = 14.4$ Hz), 136.1 (d, $J_{CP} = 12.5$ Hz), 135.8, 135.1 (d, $J_{CP} = 19.2$ Hz), 134.5 (d, $J_{CP} = 19.2$ Hz), 134.0 (d, $J_{CP} = 20.1$ Hz), 133.4 (d, $J_{CP} = 19.2$ Hz), 130.4 (d, $J_{CP} = 4.8$ Hz), 130.2 (d, $J_{CP} = 4.8$ Hz), 129.1, 128.7, 128.4, 128.3 (d, $J_{CP} = 5.8$ Hz), 128.1 (d, $J_{CP} = 12.5$ Hz), 127.9, 127.6, 125.4, 82.0, 58.0 (dd, $J_{CP} = 23.0$ Hz, $J_{CP} = 3.8$ Hz), 44.7 ($J_{CP} = 5.8$ Hz), 33.3, 32.8, 24.6, 24.4; ^{31}P{^{1}H} NMR ($CDCl_3$) δ: −10.5 (br s), −19.7 (s). Anal. calcd. for $C_{46}H_{48}NBO_2P_2$ (719.33 g mol^{-1}): C, 76.77; H, 6.72; N, 1.95. Found: C, 76.85; H, 6.74; N, 1.88.



*2.3.5. N-cyclopentyl-N-((diphenylphosphino)(2-(diphenylphosphino)phenyl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-amine (**2e**)*

Yield: 317 mg (74%); mp 177–180 °C. ^{1}H NMR ($CDCl_3$) δ: 8.04 (ov dt, $J = 8.0$ Hz, $J = 4.1$ Hz, 1H, Ar), 7.55 (td, $J = 7.8$ Hz, $J = 1.8$ Hz, 2H, Ar), 7.38–7.31 (ov m, 3H, Ar), 7.27–7.15 (ov m, 11H, Ar & C*H*P), 7.08 (app t, $J = 6.9$ Hz, $J = 6.9$ Hz, 4H, Ar), 6.97 (ov dt, $J = 14.2$ Hz, $J = 6.4$ Hz, 3H, Ar), 6.24 (ov dd, $J = 7.6$ Hz, $J = 7.1$ Hz, 1H, Ar), 3.75 (quint, $J = 8.2$ Hz, 1H, C*H*N), 1.82 (app q, $J = 8.2$ Hz, 2H, C*H*$_2$CHN), 1.66–1.48 (ov m, 2H, C*H*$_2$CHN), 1.35 (m, 2H, C*H*$_2$), 1.19 (br m, 1H, C*H*H), 0.91 (br m, 1H, CH*H*), 0.87 (s, 6H, pin), 0.79 (s, 6H, pin); ^{11}B NMR ($CDCl_3$) δ: 23 (br); ^{13}C{^{1}H} NMR ($CDCl_3$) δ: 146.5 (d, $J_{CP} = 19.2$ Hz), 146.2 (d, $J_{CP} = 19.2$ Hz), 138.5 (d, $J_{CP} = 14.4$ Hz), 138.2 (d, $J_{CP} = 15.3$ Hz), 138.0 (d, $J_{CP} = 2.9$ Hz), 137.0 (d, $J_{CP} = 12.5$ Hz), 136.7 (d, $J_{CP} = 12.5$ Hz), 135.7 (d, $J_{CP} = 20.1$ Hz), 135.4, 134.4 (d, $J_{CP} = 20.1$ Hz), 134.2 (d, $J_{CP} = 16.3$ Hz), 133.3 (d, $J_{CP} = 18.2$ Hz), 130.5 (d, $J_{CP} = 5.8$ Hz), 130.3 (d, $J_{CP} = 5.8$ Hz), 128.7, 128.5 (d, $J_{CP} = 9.6$ Hz), 128.4, 128.3 (d, $J_{CP} = 4.8$ Hz), 128.0 (d, $J_{CP} = 9.6$ Hz), 127.9 (d, $J_{CP} = 6.7$ Hz), 127.8 (d, $J_{CP} = 7.7$ Hz), 127.5, 81.4, 58.8 (d, $J_{CP} = 22.0$ Hz), 57.0 (d, $J_{CP} = 7.7$ Hz), 32.9 ($J_{CP} = 2.9$ Hz), 24.8, 24.7, 24.5, 24.4; ^{31}P{^{1}H} NMR ($CDCl_3$) δ: −12.6 (br s), −19.7 (s). Anal. calcd. for $C_{42}H_{46}NBO_2P_2$ (669.58 g mol^{-1}): C, 75.34; H, 6.92; N, 2.09. Found: C, 75.48; H, 6.86; N, 2.06.

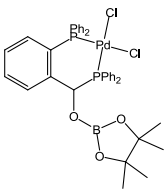


*2.3.6. N-((diphenylphosphino)(2-(diphenylphosphino)phenyl)methyl)–N-(3-diphenylphosphino)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-amine (**2f**)*

Yield: 189 mg (35%); mp 107–110 °C. ^{1}H NMR ($CDCl_3$) δ: 8.04 (ov dt, $J = 7.8$ Hz, $J = 4.1$ Hz, 1H, Ar), 7.52–7.48 (ov m, 2H, Ar), 7.29–7.22 (ov m, 19H, Ar), 7.19–7.01 (ov m, 11H, Ar & C*H*P), 6.90 (dd, $J = 6.9$ Hz, $J = 2.8$ Hz, 1H, Ar), 6.30 (ov dd, $J = 7.8$ Hz, 1H, Ar), 3.18 (m, 1H, C*H*H), 3.08 (m, 1H, CH*H*), 1.66 (m, 2H, C*H*$_2$), 1.29 (m, 2H, C*H*$_2$), 0.84 (s, 6H, pin), 0.67 (s, 6H, pin); ^{11}B NMR ($CDCl_3$) δ: 23 (br); ^{13}C{^{1}H} NMR ($CDCl_3$) (selected data) δ: 81.9, 57.9 (d, $J_{CP} = 24.0$ Hz), 46.3 ($J_{CP} = 5.8$ Hz), 27.6 ($J_{CP} = 5.3$ Hz), 25.1 ($J_{CP} = 11.5$ Hz), 24.6, 24.3; ^{31}P{^{1}H} NMR ($CDCl_3$) δ: −9.8 (br s), −15.0 (s), −19.5 (s). Anal. calcd. for $C_{53}H_{55}NBO_2P_3$ (841.74 g mol^{-1}): C, 75.63; H, 6.59; N, 1.66. Found: C, 75.11; H, 6.66; N, 1.72.

2.4. General synthesis of metal complexes

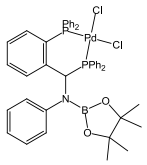
A toluene (5 mL) solution of ligand (0.20 mmol) was added dropwise to a stirred toluene (5 mL) suspension of the appropriate $[MCl_2(coe)]_2$ (0.10 mmol) and the reaction mixture was stirred for 18 h. The resulting precipitate was filtered by suction filtration and washed with hexane (2 × 5 mL) to afford the metal complexes as white solids.



*2.4.1. Palladium complex **3a***

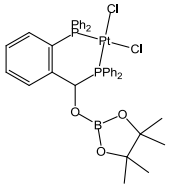
Yield: 131 mg (84%); mp 260–262 °C. ^{1}H NMR ($CDCl_3$) δ: 8.14–8.06 (ov m, 4H, Ar), 7.67–7.33 (ov m, 18H, Ar), 7.12 (br t, $J = 6.9$ Hz, 1H, Ar), 6.63 (br t, $J = 8.2$ Hz, 1H, Ar), 5.84 (br s, 1H, C*H*P), 0.98 (s, 6H, pin), 0.89 (s, 6H, pin); ^{11}B NMR ($CDCl_3$) δ: 21 (br); ^{13}C{^{1}H} NMR ($CDCl_3$) δ: 138.8 (d, $J_{CP} = 6.7$ Hz), 137.0 (d, $J_{CP} = 10.5$ Hz), 135.2 (d, $J_{CP} = 11.5$ Hz), 134.7 (d, $J_{CP} = 8.6$ Hz), 133.0, 132.7 (d, $J_{CP} = 10.5$ Hz), 132.6, 132.0, 131.7, 131.2, 129.7 (d, $J_{CP} = 11.5$ Hz), 129.4, 128.5 (d, $J_{CP} = 12.5$ Hz), 128.0 (d, $J_{CP} = 7.7$ Hz), 127.6, 127.0, 126.2,

125.8 (d, J_{CP} = 9.6 Hz), 125.6, 121.8, 121.2, 83.8, 72.0 (dd, J_{CP} = 30.7 Hz, J_{CP} = 23.0 Hz), 24.6, 24.3; $^{31}P\{^{1}H\}$ NMR ($CDCl_3$) δ: 66.2 (s), 18.1 (s). Anal. calcd. for $C_{37}H_{37}BCl_2O_3P_2Pd$ (779.77 g mol^{-1}): C, 56.99; H, 4.78. Found: C, 56.71; H, 4.78.



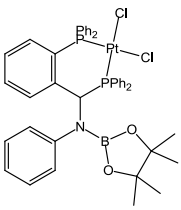
*2.4.2. Palladium complex **3b***

Yield: 149 mg (87%); mp 284–286 °C. ^{1}H NMR ($CDCl_3$) δ: 7.88 (br m, 2H, Ar), 7.66 (t, J = 7.6 Hz, 1H, Ar), 7.51–7.18 (br ov m, 22H, Ar), 6.91 (dd, J = 8.2, 7.8 Hz, 1H, Ar), 6.78 (br m, 2H, Ar), 5.89 (br m, 1H, Ar), 5.54 (br m, 1H, C*H*P), 1.01 (s, 6H, pin), 0.89 (s, 6H, pin); ^{11}B NMR ($CDCl_3$) δ: 23 (br); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ: 140.8 (br m), 135.6, 134.9 (d, J_{CP} = 10.5 Hz), 134.0 (d, J_{CP} = 10.5 Hz), 133.5, 132.0, 131.5 (d, J_{CP} = 1.9 Hz), 131.2, 130.9 (d, J_{CP} = 1.9 Hz), 129.3 (d, J_{CP} = 11.5 Hz), 129.1, 128.6, 128.4 (d, J_{CP} = 13.4 Hz), 128.2 (d, J_{CP} = 11.5 Hz), 127.7 (d, J_{CP} = 10.5 Hz), 125.9 (br m), 125.4 (br m), 124.7 (br m), 123.5 (br m), 83.6, 67.4 (br m), 25.2, 23.6; $^{31}P\{^{1}H\}$ NMR ($CDCl_3$) δ: 66.4 (br s), 14.8 (s). Anal. calcd. for $C_{43}H_{42}NBCl_2O_2P_2Pd$ (854.88 g mol^{-1}): C, 60.41; H, 4.95; N 1.64. Found: C, 60.13; H, 5.12; N, 1.55.



*2.4.3. Platinum complex **4a***

Yield: 151 mg (87%); mp 295 °C (decomposition). ^{1}H NMR ($CDCl_3$) δ: 8.18 (ov dd, J = 8.7 Hz, J = 4.1 Hz, 2H, Ar), 7.98 (br t, J = 8.7 Hz, 2H, Ar), 7.63 (t, J = 6.9 Hz, 1H, Ar), 7.56–7.26 (ov m, 17H, Ar), 7.10 (t, J = 6.9 Hz, 1H, Ar), 6.57 (ov dd, J = 11.5 Hz, J = 8.2 Hz, 1H, Ar), 5.94 (s, J_{HPt} = 13.3 Hz, 1H, C*H*P), 0.97 (s, 6H, pin), 0.88 (s, 6H, pin); ^{11}B NMR ($CDCl_3$) δ: 21 (br); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ: 139.1 (d, J_{CP} = 6.7 Hz), 136.8 (d, J_{CP} = 10.5 Hz), 135.0 (d, J_{CP} = 11.5 Hz), 134.8 (d, J_{CP} = 8.6 Hz), 133.0 (d, J_{CP} = 8.6 Hz), 132.4 (d, J_{CP} = 7.7 Hz), 131.8 (d, J_{CP} = 15.3 Hz), 131.1, 129.4 (d, J_{CP} = 11.5 Hz), 129.1, 128.3 (d, J_{CP} = 11.5 Hz), 127.7 (d, J_{CP} = 7.7 Hz), 127.4, 126.6, 126.2, 125.9, 125.6, 125.1 (d, J_{CP} = 6.7 Hz), 121.8, 121.2, 83.8, 70.3 (dd, J_{CP} = 41.2 Hz, J_{CP} = 16.3 Hz), 24.6, 24.2; $^{31}P\{^{1}H\}$ NMR ($CDCl_3$) δ: 41.5 (d, J_{PP} = 22.2 Hz, J_{PPt} = 3600 Hz), 0.4 (d, J_{PP} = 22.2 Hz, J_{PPt} = 3420 Hz). Anal. calcd. for $C_{37}H_{37}BCl_2O_3P_2Pt$ (868.44 g mol^{-1}): C, 51.17; H, 4.29. Found: C, 51.00; H, 4.24.

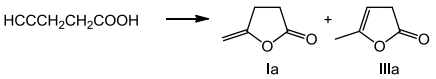


*2.4.4. Platinum complex **4b***

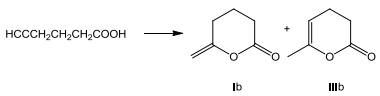
Yield: 157 mg (83%); mp 270 °C (decomposition). ^{1}H NMR ($CDCl_3$) δ: 7.91–7.81 (br ov m, 4H, Ar), 7.77 (t, J = 6.4 Hz, 1H, Ar), 7.64 (t, J = 7.8 Hz, 1H, Ar), 7.49–7.30 (ov m, 16H, Ar), 7.21–7.17 (ov m, 2H, Ar), 6.88 (ov dd, J = 11.9 Hz, J = 7.8 Hz, 1H, Ar), 6.79 (br m, 1H, Ar), 6.70 (br m, 2H, Ar), 5.88–5.72 (br ov m, 2H, Ar), 1.04 (s, 6H, pin), 0.88 (s, 6H, pin); ^{11}B NMR ($CDCl_3$) δ: 23 (br); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ: 147.4 (br), 140.8 (br), 135.4 (br), 135.2 (d, J_{CP} = 10.5 Hz), 134.3 (d, J_{CP} = 10.5 Hz), 133.1 (br), 132.2 (br), 131.9, 131.5, 131.3, 130.6, 129.1 (d, J_{CP} = 9.6 Hz), 128.4, 128.2, 128.0 (d, J_{CP} = 11.5 Hz), 127.6 (d, J_{CP} = 11.5 Hz), 127.3, 126.6, 125.4, 124.3, 123.2, 83.5, 66.3 (br), 25.3, 23.5; $^{31}P\{^{1}H\}$ NMR ($CDCl_3$) δ: 39.1 (s, J_{PPt} = 3460 Hz), −1.8 (s, J_{PPt} = 3520 Hz). Anal. calcd. for $C_{43}H_{42}NBCl_2O_2P_2Pt$ (943.55 g mol^{-1}): C, 54.74; H, 4.49; N, 1.48. Found: C, 55.01; H, 4.56; N, 1.43.

2.5. General procedure for the microwave assisted cyclisation of alkynoic acids with palladium and platinum catalysts

A $CDCl_3$ (0.5 mL) solution of alkynoic acid (25 mg) was added to a $CDCl_3$ (0.5 mL) solution of the desired Pd or Pt catalyst (5 mol%). The reaction mixtures were heated under microwave conditions at 100 °C for 8 h. At regular time intervals, the reaction mixtures were monitored by ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopy to determine the progress of the reaction.



4-pentynoic acid (selected NMR data): ^{1}H NMR ($CDCl_3$) δ: 5.10 (ov qt, J = 2.4, 1.5 Hz) (**IIIa**), 4.73 (ov td, J = 2.4, 2.4 Hz) (**Ia**), 4.30 (ov td, J = 2.8, 2.4 Hz) (**Ia**), 3.15 (ov dq, J = 2.4, 2.4 Hz) (**IIIa**), 2.86 (m) (**Ia**), 2.66 (m) (**Ia**), 1.97 (ov dt, J = 2.4, 1.5 Hz) (**IIIa**); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ: 177.1 (**IIIa**), 175.1 (**Ia**), 155.7 (**Ia**), 153.4 (**IIIa**), 99.2 (**IIIa**), 88.9 (**Ia**), 34.2 (**IIIa**), 28.1 (**IIIa**), 27.8 (**Ia**), 14.2 (**IIIa**).



5-hexynoic acid (selected NMR data): ^{1}H NMR ($CDCl_3$) δ: 4.98 (t, J = 3.8 Hz) (**IIIb**), 4.61 (s) (**Ib**), 4.27 (s) (**Ib**), 2.61 (t, J = 6.1 Hz) (**Ib**), 2.55 (t, J = 7.6 Hz) (**IIIb**), 2.46 (t, J = 6.1 Hz) (**Ib**), 2.26 (m) (**IIIb**), 1.87–1.82 (ov m) (**Ib** & **IIIb**); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ: 169.5 (**IIIb**), 168.0 (**Ib**), 155.5 (**Ib**), 150.2 (**IIIb**), 100.1 (**IIIb**), 93.6 (**Ib**), 30.5 (**Ib**), 28.6 (**IIIb**), 26.4 (**Ib**), 25.2 (**IIIb**), 19.0 (**IIIb**), 18.6 (**Ib**).

NMR spectra of the cyclized products were consistent with reported literature values, 5-methylenedihydrofuran-2(3*H*)-one (**Ia**) and 6-methylenetetrahydro-2*H*-pyran-2-one (**Ib**) [13], 5-methylfuran-2(3*H*)-one (**IIIa**) [14], and 6-methyl-3,4-dihydro-2*H*-pyran-2-one (**IIIc**) [15].

2.6. Catalytic cyclisation using (κ^2-P,P'-2-$Ph_2PC_6H_4CH_2(OH)PPh_2$) $PtCl_2$

Methanol (3 μL, 0.075 mol) was added to a $CHCl_3$ (1 mL) solution of **4a** (65 mg, 0.075 mmol) and the reaction mixture was stirred for 18 h. The resulting precipitate was collected by suction filtration and washed with hexane (2 × 2 mL) to afford a white solid. Yield: 35 mg (63%). ^{1}H NMR (DMSO-d_6) δ: 8.20–8.00 (ov m, 4H, Ar), 7.82–7.21 (ov m, 18H, Ar), 6.81 (m, 1H, Ar), 6.45 (m, 1H, Ar), 5.72 (br s, 1H, O*H*), 5.23 (br s, 1H, C*H*P); $^{31}P\{^{1}H\}$ NMR (DMSO-d_6) δ: 40.8 (d, J_{PP} = 23.2 Hz, J_{PPt} = 3446 Hz), −1.6 (d, J_{PP} = 23.2 Hz, J_{PPt} = 3434 Hz). Poor solubility and stability precluded us obtaining ^{13}C NMR data. However, this compound was tested as a potential catalyst for the cyclisation of 4-pentynoic acid as described previously.

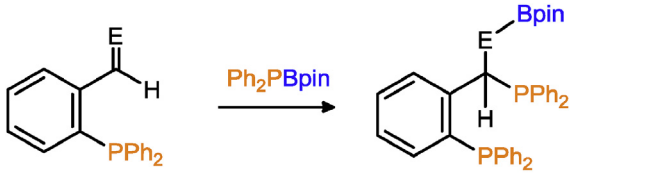
2.7. Crystallographic data and structure refinement summary

Crystals suitable for Xray crystallography were grown from

saturated solutions stored at RT: Et_2O (**2a**,**b**), hexanes (**2c**,**d**), THF (**3a**), CH_2Cl_2:Hex (2:1, **4a**), and CH_2Cl_2 (**4b**). Crystals for investigation were covered in Paratone®, mounted into a goniometer head, and then rapidly cooled under a stream of cold N_2 of the low-temperature apparatus (Oxford Cryostream) attached to the diffractometer. The data were then collected using the APEX3 software suite [16] on a Bruker Photon 100 CMOS diffractometer using a graphite monochromator with MoK_α ($\lambda = 0.71073$ Å) radiation. Data were collected at 170 K (**2a**,**b**,**d**, **3a**, and **4a**,**b**) or 198 K (**2c**). APEX3 software was used for data reductions and SADABS [17] was used for absorption corrections (multi-scan; semi-empirical from equivalents). XPREP was used to determine the space group and the structures were solved and refined using the SHELX [18] software suite as implemented in the OLEX2 [19] program suite. Validation of the structures was conducted using PLATON [20]. Crystallographic information has also been deposited with the Cambridge Crystallographic Data Centre (CCDC 1870262–1870268). Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK fax: + 44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

3. Results and discussion

We have found that addition of Ph_2PBpin to 2-diphenylphosphinobenzaldehyde (**1a**) and the related aldimine derivatives (**1b-f**) proceeded at room temperature without the need for added base or catalyst to give selective formation of the corresponding diphosphines (**2a-f**, Scheme 2) in moderate to high isolated yields (35–89%). All new diphosphines have been characterized by a variety of analytical methods including multinuclear NMR spectroscopy and elemental analysis. By ^1H NMR the C(H) = E resonance at 10.50 ppm (E = O) or ~ 8.8 ppm (E = NR) seen in the starting aldehyde and aldimines disappears upon reduction of the double bond. Additionally, the broad ^{11}B resonance at 34 ppm for Ph_2PBpin shifts to around 22–23 ppm for all ligands indicative of coordination of the Bpin group to the heteroatom [5]. The broad peak for Ph_2PBpin at −63.5 ppm observed by $^{31}P\{^1H\}$ NMR spectroscopy shifts significantly downfield upon reduction of the double bond with the new diphenylpshosphide group appearing anywhere from +1.2 ppm for the bulky 2,6-diisopropylphenyl derivative (**2c**) to −12.6 ppm for the cyclopentyl derivative (**2e**). Coupling between the two inequivalent phosphorus atoms is only observed in **2a** where the $^{31}P\{^1H\}$ NMR spectra shows two doublets at 6.8 and −20.0 ppm with a coupling constant of $^4J_{PP} = 24.1$ Hz.



1a: E = O
1b: E = NPh
1c: E = N-2,6-(iPr)$_2$C$_6$H$_3$
1d: E = N(CH$_2$)$_3$Ph
1e: E = N-c-C$_5$H$_9$
1f: E = N(CH$_2$)$_3$PPh$_2$

2a: E = O
2b: E = NPh
2c: E = N-2,6-(iPr)$_2$C$_6$H$_3$
2d: E = N(CH$_2$)$_3$Ph
2e: E = N-c-C$_5$H$_9$
2f: E = N(CH$_2$)$_3$PPh$_2$

Scheme 2. The phosphinoboration of 2-diphenylphosphinobenzaldehyde and related aldimines to generate novel ambiphilic diphosphines **2a**-**f**.

This value is well within the range for four-bond couplings and even longer range couplings (i.e. nine and ten bonds) have been reported in related diphosphines [21]. Compound **2f** is unique in that it is a triphosphine with three distinct resonances in the $^{31}P\{^1H\}$ NMR spectrum at δ: −9.8, −15.0, and −19.5. No coupling is observed at room temperature (or even −40 °C) presumably due to the flexible nature of the pendant alkyl phosphine chain. Compounds **2a-d** were also characterized by single crystal X-ray diffraction studies, whereupon the molecular structures of **2a** and **2b** are shown in Fig. 1, **2c** and **2d** can be found in the supporting information section, and confirm the selective formation of one product where the Bpin group has added to the heteroatom of the double bond. Bond distances and angles are fully consistent with those reported in related structures [5].

With elementally pure diphosphines in hand, we decided to investigate their ability to ligate late transition metals using the organic-soluble complexes $[MCl_2(coe)]_2$ (M = Pd, Pt; coe = *cis*-cyclooctene) [8]. As expected, reactions with **2a** gave the corresponding complexes **3a** and **4a** in high isolated yields (84 and 87%, respectively), along with loss of the labile cyclooctene ligand (Scheme 3). The $^{31}P\{^1H\}$ NMR data for **3-4a** and **3-4b** show one distinct product with chemically inequivalent phosphine atoms. For instance, two resonances are observed in **4a** at δ 41.5 (d, $J_{PP} = 22.2$ Hz) and 0.4 (d, $J_{PP} = 22.2$ Hz) with ^{195}Pt satellites of $J_{PPt} = 3600$ and 3420 Hz, respectively. As expected, no significant change in the ^{11}B NMR data is observed, suggesting little or no interaction between the Lewis-acidic boron and the metal atom in solution. Complexes **3a**, **4a** and **4b** have also been characterized by single crystal X-ray diffraction studies, the molecular structures of **3a** and **4b** are shown in Fig. 2, while the isoelectronic structure of **4a** is provided in the supporting information section. Once again these solid-state studies confirmed the bidentate nature of the diphosphine ligands and no appreciable interaction of the boron group with the metal centre or these ancillary ligands was observed. All crystal structures are centrosymmetric due to the racemic nature of the diphosphine ligands. Bond distances and angles are consistent with well-known related diphosphine metal complexes [22]. Unfortunately, attempts to generate the corresponding complexes from ligands **2c-f**, derived from the bulkier aldimines, resulted in a complicated mixture of products and isolation of the expected products proved unsuccessful at this time. This result was somewhat disappointing as **2f** should be an interesting and potential tridentate ligand and current studies are focusing on using this compound to coordinate to rhodium and iridium complexes.

We then decided to examine the potential of using these new complexes, **3-4a,b** as precatalysts for the hydroboration of aldehydes using HBpin. Unfortunately, unlike many Lewis-acidic metal centres [1], these complexes failed to facilitate these reductions. We then decided to examine the potential of these complexes to catalyse the cycloaddition of alkynoic acids [23] as this area of research is of considerable recent interest as the resulting cyclic lactones are important in natural products and specialty chemicals with applications in pharmaceutical, agricultural, flavours and fragrances industries [24]. We were encouraged to find that these new complexes, along with the precursor $[MCl_2(coe)]_2$ (M = Pd, Pt) starting materials, were effective in catalysing both 4-pentynoic acid and 5-hexynoic acid to give the corresponding *exo*-dig cyclic lactones (Table 1). Reaction progress was monitored by ^1H NMR spectroscopy and conversion of the starting alkynoic acid was determined by integration of product resonances relative to 1,2-dimethoxybenzene as an internal standard. Reactions were performed under microwave conditions and monitored at regular time intervals to a maximum of 8 h. Formation of the expected product **I** with a negligible amount of the *endo*-dig product **II** in some instances was seen. It is interesting to note, however, that significant

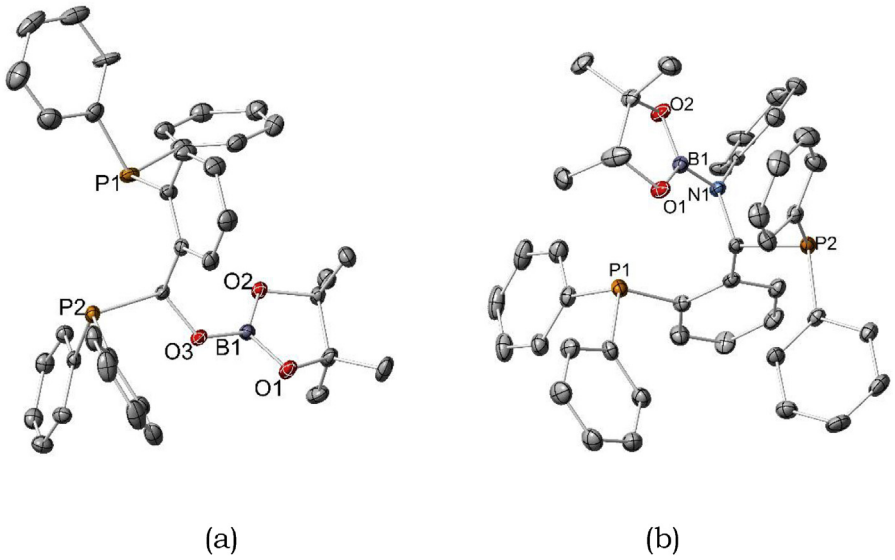


Fig. 1. The molecular structures of **2a** (a) and **2b** (b) with ellipsoids shown at the 30% confidence level. Hydrogen molecules have been omitted for clarity. Selected bond distances (Å) and angles (°) (**2a**): B1–O1 1.3669(16), B1–O2 1.3638(16), B1–O3 1.3536(15), O1–B1–O2 114.94(11), O1–B1–O3 120.43(11), O2–B1–O3 124.62(11); Selected bond distances (Å) and angles (°) (**2b**): B1–O1 1.3725(19), B1–O2 1.3753(19), B1–N1 1.4161(19), O1–B1–O2 113.87(12), O1–B1–N1 124.37(13), O2–B1–N1 121.75(13).

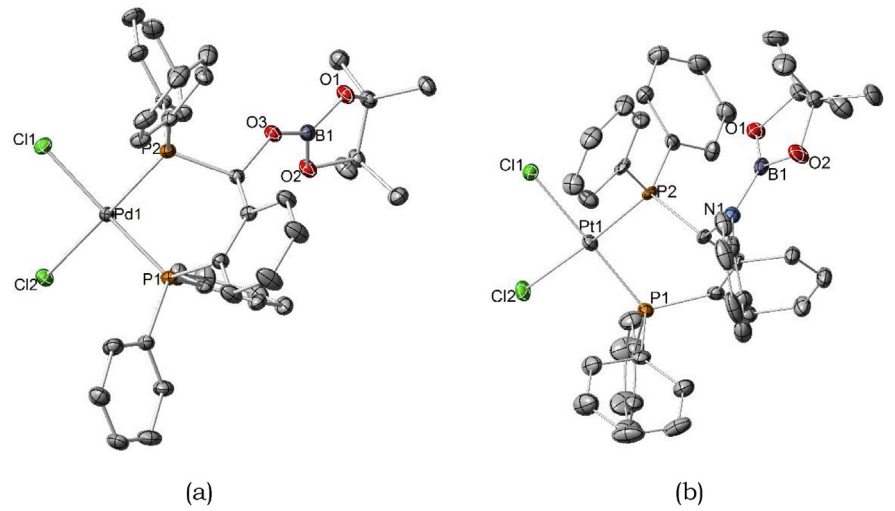
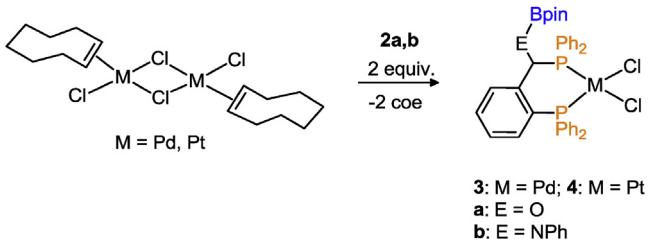


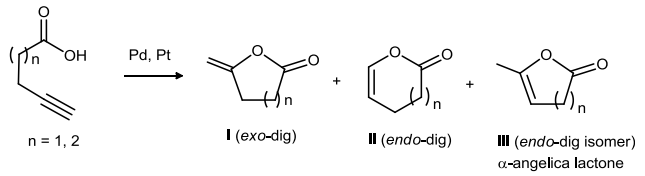
Fig. 2. The molecular structures of **3a** (a) and **4b** (b) with ellipsoids shown at the 30% confidence level. Hydrogen molecules have been omitted for clarity. Selected bond distances (Å) and angles (°) (**3a**): Pd1–P1 2.2452(4), Pd1–P2 2.2390(4), Pd1–Cl1 2.3644(4); Pd1–Cl2 2.3446(4), B1–O1 1.365(2), B1–O2 1.362(2), B1–O3 1.369(2), P1–Pd–P2 91.531(16), Cl1–Pd1–Cl2 93.565(16), O1–B1–O2 115.67(15), O1–B1–O3 120.06(15), O2–B1–O3 124.27(15); Selected bond distances (Å) and angles (°) (**4b**): Pt1–P1 2.2242(18), Pt1–P2 2.2433(12), Pt1–Cl1 2.3429(18); Pt1–Cl2 2.3349(14), B1–O1 1.347(10), B1–O2 1.364(9), B1–N1 1.438(10), P1–Pt1–P2 93.33(8), Cl1–Pt1–Cl2 88.58(8), O1–B1–O2 114.7(7), O1–B1–N1 122.7(6), O2–B1–N1 122.6(7).



Scheme 3. Addition of diphosphines **2a**,**b** to $[MCl_2(coe)]_2$ (M = Pd, Pt).

amounts of the unusual product **III** were also observed in these reactions. Compound **III** was characterized by ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopy and compared to readily available commercial products. Known $[PtCl_2(coe)]_2$ proved to be the most efficient precatalyst showing complete conversion of 4-pentynoic acid at RT after a period of 24 h. Unfortunately, none of the other metal complexes tested showed complete conversion under these conditions thereby necessitating the use of microwave radiation to facilitate the cyclisation. 4-Pentynoic acid was completely converted using $[PtCl_2(coe)]_2$ as the precatalyst after 1 h at 100 °C (entry 7) giving a mixture of the *exo*-dig **I** and *endo*-dig products **II** and **III** in a 41:1:58 ratio while 5-hexynoic acid (entry 10), required 8 h of heating and resulted in a similar product distribution albeit **I** and **III** are the only products seen. Of the platinum complexes tested only the combination of **4a** and 4-pentynoic acid (entry 8) showed complete conversion and in this case the *exo*-dig isomer was the predominant product formed in a ratio of 60:40 (**I**:**III**). Diminished conversions (22–41%) were observed using **4a** and 5-hexynoic acid and **4b** proved to be a poor catalyst with both

Table 1
Catalysed cyclisation of alkynoic acids using Pd(II) and Pt(II) complexes.[a]



Entry	Precatalyst	n	conversion	I	II	III
1	$[PdCl_2(coe)]_2$	1	100	18	0	82
2	**3a**	1	100	63	0	37
3	**3b**	1	69	80	0	20
4	$[PdCl_2(coe)]_2$	2	17	45	0	55
5	**3a**	2	19	100	0	0
6	**3b**	2	12	55	0	45
7	$[PtCl_2(coe)]_2$	1	100[b]	41	1	58
8	**4a**	1	100	59	0	41
9	**4b**	1	41	95	0	5
10	$[PtCl_2(coe)]_2$	2	100	40	0	60
11	**4a**	2	22	97	0	3
12	**4b**	2	25	78	0	22

[a] Reactions carried out in $CDCl_3$ for 8 h at 100 °C using microwave radiation with conversion and product ratios determined by ^1H NMR spectroscopy.
[b] Complete conversion of this reaction occurred after 1 h.

alkynoic acids (entries 9, 11, and 12). The palladium compounds behaved similarly with respect to conversion and product distribution to their platinum anologues where $[PdCl_2(coe)]_2$ (entry 1) and **3a** (entry 2) both showed complete conversion of 4-pentynoic acid to **I** and **III** while **3b** (entry 3) was not able to completely convert the alkynoic acid. Cyclisation of 5-hexynoic acid at 100 °C for 8 h gave low conversions (<20%) for all palladium complexes. The appearance of dark oily solids upon completion of the reaction leads us to believe the compounds were decomposing during these reactions. While numerous metal complexes are known to facilitate the cycloaddition of these substrates [24], the formation of **III** has not yet been reported with these terminal substrates. Indeed, α-angelica lactone **III** is the major product observed in the cyclisation of the internal alkyne but-2-ynoic acid using $[PdCl_2(NCMe)_2]$ [24x]. α-Angelica lactone is a biologically-active molecule used in the food-flavouring industry and is traditionally prepared from the catalysed dehydration and cyclisation of levulinic acid [25]. In this present study, while other pathways are certainly plausible, one possible mechanism for the formation of **III** in these reactions could proceed *via* isomerization of **I** to the more stable isomer **III**. Indeed, we have found that addition of **I** to a catalytic amount of $[PtCl_2(coe)]_2$ and the starting alkynoic acid under these reaction conditions gave significant amounts of isomer **III** after 8 h. Although we were unable to get exclusive formation of these unusual products, future work in our lab will focus on using Pd(II) and Pt(II) complexes to generate these potentially important products.

Finally, we decided to examine the role of the Lewis-acid boryl group in these catalysed reactions and investigated the cyclisation of 4-pentynoic acid using the non-boron containing control complex (κ^2-*P,P'*-2-$Ph_2PC_6H_4CH_2(OH)PPh_2$)$PtCl_2$, which was prepared by the addition of methanol to **4a**. Although conversions were significantly diminished compared to **4a**, owing to the low solubility of (κ^2-*P,P'*-2-$Ph_2PC_6H_4CH_2(OH)PPh_2$)$PtCl_2$ in organic solvents, selectivities were approximately the same, suggesting that the Lewis acidic boron group does not play a significant role in these cyclisations. However, the lipophilic nature of the Bpin increases the solubility of these complexes and makes them more efficient catalyst precursors. We will continue to investigate these novel ligands in catalysis to see if we can utilize the ambiphilic nature of these species, the results of which will be reported in due course.

4. Conclusions

In this preliminary study, we have investigated the addition of a simple phosphinoboronate ester, Ph_2PBpin (pin = 1,2-$O_2C_2Me_4$), to 2-diphenylphosphinobenzaldehyde (2-$Ph_2PC_6H_4C(O)H$) and related aldimine derivatives (2-$Ph_2PC_6H_4C(NR)H$). Reactions proceed smoothly without the need for a catalyst or additive to generate the corresponding diphosphine ligands bearing a pendant Lewis-acid Bpin group where the phosphide fragment has added to the aldehyde (or imine) carbon atom and the electron-deficient boron group has added to the electron-rich heteroatom. All new compounds have been characterized fully including single crystal X-ray diffraction studies on **2a-d** and confirm the regioselective nature of these addition reactions. Preliminary studies show that some of the new diphosphines ligate to Pd(II) and Pt(II) metal centres. Using these new metal complexes, as well as the starting materials $[MCl_2(coe)]_2$ (M = Pd, Pt, coe = *cis*-cyclooctene), as pre-catalysts in the cyclisation of alkynoic acids gave the corresponding *exo*-dig cyclic lactones as well as the unusual *endo*-dig cyclic lactones not traditionally observed in these reactions. For instance, reactions of 4-pentynoic acid also afforded significant amounts of α-angelica lactone, a biologically-important compound traditionally prepared *via* the catalytic dehydration and cyclisation of levulinic acid. Future studies will focus on examining other Pd(II) and Pt(II) complexes as potential precatalysts for the cyclisation of alkynoic acids, the results of which will be reported in due course.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jorganchem.2018.11.001.

References

[1] [a] A. Harinath, J. Bhattacharjee, K.R. Gorantla, B.S. Mallik, T.K. Panda, 2018, Eur. J. Org Chem. (2018) 3180–3192;
[b] J. Wu, H. Zeng, J. Cheng, S. Zheng, J.A. Golen, D.R. Manke, G. Zhang, J. Org. Chem. 83 (2018) 9442–9448;
[c] R.J. Newland, J.M. Lynam, S.M. Mansell, Chem. Commun. 54 (2018) 5482–5485;
[d] L. Li, J. Cheng, G. Zhang, Dalton Trans. 47 (2018) 9579–9584;
[e] N. Zhou, X.-A. Yuan, Y. Zhao, J. Xie, C. Zhu, Angew. Chem. Int. Ed. 57 (2018) 3990–3994;
[f] A. Baishya, S. Baruah, K. Geetharani, Dalton Trans. 47 (2018) 9231–9236;
[g] U.K. Das, C.S. Higman, B. Gabidullin, J.E. Hein, R.T. Baker, ACS Catal. 8 (2018) 1076–1081;
[h] V. Vasilenko, C.K. Blasius, L.H. Gade, J. Am. Chem. Soc. 140 (2018) 9244–9254;
[i] J. Liu, A. Zhang, H. Song, Q. Tong, C.-H. Tung, W. Wang, Chin. Chem. Lett. 29 (2018) 949–953;
[j] Z. Huang, D. Liu, J. Camacho-Bunquin, G. Zhang, D. Yang, L.M. López-Encarnción, Y. Xu, M.S. Ferrandon, J. Niklas, O.G. Poluektov, J. Jellinek, A. Lei, E.E. Bunel, M. Delfarro, Organometallics 36 (2017) 3921–3930;
[k] G.I. Nikonov, ACS Catal. 7 (2017) 7257–7266;
[l] R. Arévalo, C.M. Vogels, G.A. MacNeil, L. Riera, J. Pérez, S.A. Westcott, Dalton Trans. 46 (2017) 7750–7757;
[m] S.R. Tamang, M. Findlater, J. Org. Chem. 82 (2017) 12857–12862;
[n] A.N. Desnoyer, J. Geng, M.W. Drover, B.O. Patrick, J.A. Love, Chem. Eur J. 23 (2017) 11509–11512.
[2] [a] Z. Zhu, P. Dai, Z. Wu, M. Xue, Y. Yao, Q. Shen, X. Bao, Catal. Commun. 112 (2018) 26–30;

[b] D. Yan, P. Dai, S. Chen, M. Xue, Y. Yao, Q. Shen, X. Bao, Org. Biomol. Chem. 16 (2018) 2787–2791;
[c] W. Wang, X. Shen, F. Zhao, H. Jiang, W. Yao, A.S. Pullarkat, L. Xu, M. Ma, J. Org. Chem. 83 (2018) 69–74;
[d] H. Liu, M. Khononov, M.S. Eisen, ACS Catal. 8 (2018) 3673–3677;
[e] S. Chen, D. Yan, M. Xue, Y. Hong, Y. Yao, Q. Shen, Org. Lett. 19 (2017) 3382–3385;
[f] V.L. Weidner, C.J. Barger, M. Delferro, T.L. Lohr, T.J. Marks, ACS Catal. 7 (2017) 1244–1247.
[3] [a] Z. Zhu, X. Wu, X. Xu, Z. Wu, M. Xue, Y. Yao, Q. Shen, X. Bao, J. Org. Chem. 83 (2018) 10677–10683;
[b] A. Harinath, J. Bhattacharjee, N. Jayeeta, P. Hari, T.K. Panda, Dalton Trans. 47 (2018) 12613–12622;
[c] M. Luo, J. Li, Q. Xiao, S. Yang, F. Su, M. Ma, J. Organomet. Chem. 868 (2018) 31–35;
[d] M.K. Bisai, T. Das, K. Vanka, S.S. Sen, Chem. Commun. 54 (2018) 6843–6846;
[e] V.A. Pollard, S.A. Orr, R. McLellan, A.R. Kennedy, E. Hevia, R.E. Mulvey, Chem. Commun. 54 (2018) 1233–1236;
[f] Y. Liu, X. Liu, Y. Liu, W. Li, Y. Ding, M. Zhong, X. Ma, Z. Yang, Inorg. Chim. Acta. 471 (2018) 244–248;
[g] V.A. Pollard, M.Á. Fuentes, A.R. Kennedy, R. McLellan, R.E. Mulvey, Angew. Chem. Int. Ed. 57 (2018) 10651–10655;
[h] H. Stachowiak, J. Kaźmierczak, K. Kuciński, G. Hreczycho, Green Chem. 20 (2018) 1738–1742;
[i] R. McLellan, A.R. Kennedy, R.E. Mulvey, S.A. Orr, S.D. Robertson, Chem. Eur J. 23 (2017) 16853–16861;
[j] H. Osseili, D. Mukherjee, T.P. Spaniol, J. Okuda, Chem. Eur J. 57 (2017) 14292–14298;
[k] D. Wu, R. Wang, Y. Li, R. Ganguly, H. Hirao, R. Kinjo, Inside Chem. 3 (2017) 134–151;
[l] S. Yadav, S. Pahar, S.S. Sen, Chem. Commun. 53 (2017) 4562–4564;
[m] M. Ma, J. Li, X. Shen, Z. Yu, W. Yao, S.A. Pullarkat, RSC Adv. 7 (2017) 45401–45407;
[n] C. Hering-Junghans, I.C. Watson, M.J. Ferguson, R. McDonald, E. Rivard, Dalton Trans. 46 (2017) 7150–7153;
[o] T. Bai, T. Janes, D. Song, Dalton Trans. 46 (2017) 12408–12412;
[p] Y. Wu, C. Shan, J. Ying, J. Su, J. Zhu, L.L. Liu, Y. Zhao, Green Chem. 19 (2017) 4169–4175;
[q] C.-H. Tien, M.R. Adams, M.J. Ferguson, E.R. Johnson, A.W.H. Speed, Org. Lett. 19 (2017) 5565–5568;
[r] M.R. Adams, C.-H. Tien, R. McDonald, A.W.H. Speed, Angew. Chem. Int. Ed. 52 (2017) 16660–16663;
[s] M.K. Bisai, S. Pahar, T. Das, K. Vanka, S.S. Sen, Dalton Trans. 46 (2017) 2420–2424;
[t] J. Schneider, C.P. Sindlinger, S.M. Freitag, H. Schubert, L. Wesemann, Angew. Chem. Int. Ed. 56 (2017) 333–337;
[u] J.R. Lawson, L.C. Wilkins, R.L. Melen, Chem. Eur J. 23 (2017) 10997–11000;
[v] K. Manna, P. Ji, F.X. Greene, W. Lin, J. Am. Chem. Soc. 138 (2016) 7488–7491;
[w] J.K. Jakhar, M.K. Barman, S. Nembenna, Org. Lett. 18 (2016) 4710–4713;
[x] A. Bismuto, S.P. Thomas, M.J. Cowley, Angew. Chem. Int. Ed. 49 (2016) 15356–15359;
[y] Y. Wu, C. Shan, Y. Sun, P. Chen, J. Ying, J. Zhu, L.L. Liu, Y. Zhao, Chem. Commun. 52 (2016) 13799–13802;
[z] A.B. Cuenca, J. Cid, D. García-López, J.J. Carbó, E. Fernández, Org. Biomol. Chem. 13 (2015) 9659–9664.
[4] [a] K.N. Tu, C. Gao, S.A. Blum, J. Org. Chem. 83 (2018), https://doi.org/10.1021/acs.joc.8b01790;
[b] A.B. Cuenca, R. Shishido, H. Ito, E. Fernández, Chem. Soc. Rev. 46 (2017) 415–430;
[c] E.C. Neeve, S.J. Geier, I.A.I. Mkhalid, S.A. Westcott, T.B. Marder, Chem. Rev. 116 (2016) 9091–9161;
[d] M.L. McIntosh, C.M. Moore, T.B. Clark, Org. Lett. 12 (2010) 1996–1999;
[e] H. Zhao, L. Dang, T.B. Marder, Z. Lin, J. Am. Chem. Soc. 130 (2008) 5586–5594;
[f] D.S. Laitar, E.Y. Tsui, J.P. Sadighi, J. Am. Chem. Soc. 128 (2006) 11036–11037;
[g] G. Mann, K. John, R.T. Baker, J. Org. Chem. 2 (2000) 2105–2108;
[h] T.M. Cameron, R.T. Baker, S.A. Westcott, Chem. Commun. (1998) 2395–2396.
[5] [a] S.J. Geier, J.H.W. LaFortune, D. Zhu, S.C. Kosnik, C.L.B. Macdonald, D.W. Stephan, S.A. Westcott, Dalton Trans. 46 (2017) 10876–10885;
[b] S.J. Geier, C.M. Vogels, E.N. Daley, A. Decken, N.R. Mellonie, S. Doherty, S.A. Westcott, Chem. Eur J. 23 (2017) 14485–14499;
[c] E.N. Daley, C.M. Vogels, S.J. Geier, A. Decken, S. Doherty, S.A. Westcott, Angew. Chem. Int. Ed. 54 (2015) 2121–2125.
[6] [a] T.C. Johnstone, G.N.J.H. Wee, D.W. Stephan, Angew. Chem. Int. Ed. 57 (2018) 5881–5884;
[b] D.W. Stephan, Science 354 (2016) aaf7229, https://doi.org/10.1126/science.aaf7229;
[c] D.W. Stephan, Acc. Chem. Res. 48 (2015) 306–316;
[d] M.A. Courtemanche, M.A. Lègarè, L. Maron, F.-G. Fontaine, J. Am. Chem. Soc. 136 (2014) 10708–10717;
[e] M.A. Courtemanche, M.A. Lègarè, L. Maron, F.-G. Fontaine, J. Am. Chem. Soc. 135 (2013) 9326–9329;
[f] D.W. Stephan, G. Erker, Angew. Chem. Int. Ed. 49 (2010) 46–76.
[7] [a] F.-G. Fontaine, E. Rochette, Acc. Chem. Res. 51 (2018) 454–464;
[b] G. Bouhadir, D. Bourissou, Chem. Soc. Rev. 45 (2016) 1065–1079;
[c] J.S. Jones, F. Gabbaï, Acc. Chem. Res. 49 (2016) 857–867;
[d] D.M.P. Mingos, J. Organomet. Chem. 751 (2014) 153–173.
[8] M.P. Shaver, C.M. Vogels, A.I. Wallbank, T.L. Hennigar, K. Biradha, M.J. Zaworotko, S.A. Westcott, Can. J. Chem. 78 (2000) 568–576.
[9] X. Chen, F.J. Femia, J.W. Babich, J. Zubieta, Inorg. Chim. Acta. 315 (2001) 147–152.
[10] B. Crociani, S. Antonaroli, L. Canovese, F. Visentin, P. Uguagliati, Inorg. Chim. Acta. 315 (2001) 172–182.
[11] K. Wajda-Hermanowicz, A. Kochel, R. Wróbel, J. Organomet. Chem. 860 (2018) 30–48.
[12] M.E. Bluhm, O. Walter, M. Döring, J. Organomet. Chem. 713 (2005) 713–720.
[13] N. Conde, R. SanMartin, M.T. Herrero, E. Domínguez, Adv. Synth. Catal. 358 (2016) 3283–3292.
[14] M. Mascal, S. Dutta, I. Gandarias, Angew. Chem. Int. Ed. 53 (2014) 1854–1857.
[15] D. Gasperini, L. Maggi, S. Dupuy, R.M.P. Veenboer, D.B. Cordes, A.M.Z. Slawin, S.P. Nolan, Adv. Synth. Catal. 358 (2016) 3857–3862.
[16] APEX3, Bruker AXS Inc., Madison, WI, USA, 2015.
[17] SADABS, Bruker AXS Inc., Madison, WI, USA, 2008.
[18] G.M. Sheldrick, Acta Crystallogr. A 64 (2008) 112–122.
[19] O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard, H. Puschmann, J. Appl. Crystallogr. 42 (2009) 339–341.
[20] A.L. Spek, J. Appl. Crystallogr. 36 (2003) 7–13.
[21] M. Doskocz, B. Malinowska, P. Młynarz, B. Lejczak, P. Kafarski, Tetrahedron Lett. 51 (2010) 3406–3411.
[22] J.I. van der Vlugt, R. van Duren, J.D. Batema, R. den Heeten, A. Meetsma, J. Fraanje, K. Goubitz, P.C.J. Kamer, P.W.N.M. van Leeuwen, D. Vogt, Organometallics 24 (2005) 5377–5382.
[23] M.J. Geier, C.M. Vogels, A. Decken, S.A. Westcott, Eur. J. Inorg. Chem. (2010) 4602–4610.
[24] [a] U.A. Carrillo-Arcos, S. Porcel, Org. Biomol. Chem. 16 (2018) 1837–1842;
[b] M.J. Rodríguez-Álvarez, N. Ríos-Lombardía, S. Schumacher, D. Pérez-Iglesias, F. Moris, V. Cadierno, J. García-Álvarez, J. González-Sabín, ACS Catal. 7 (2017) 7753–7759;
[c] Y. Ogiwara, K. Sato, N. Sakai, Org. Lett. 19 (2017) 5296–5299;
[d] D. Ke, N.A. Espinosa, S. Mallet-Ladeira, J. Monot, B. Martin-Vaca, D. Bourissou, Adv. Synth. Catal. 358 (2016) 2324–2331;
[e] T.A. Fernandes, A.M. Galvão, A.M. Botelho de Rego, M.F.N.N. Carvalho, J. Polym. Sci., Part A: Polym. Chem. 52 (2014) 3316–3323;
[f] G. Hamasaka, Y. Uozumi, Chem. Commun. 50 (2014) 14516–14518;
[g] R. Nolla-Saltiel, E. Robles-Marín, S. Porcel, Tetrahedron Lett. 55 (2014) 4484–4488;
[h] N.A. Espinosa-Jalapa, D. Ke, N. Nebra, L. Le Goanvic, S. Mallet-Ladeira, J. Monot, B. Martin-Vaca, D. Bourissou, ACS Catal. 4 (2014) 3605–3611;
[i] A. Nagendiran, O. Verho, C. Haller, E.V. Johnston, J.-E. Bäckvall, J. Org. Chem. 79 (2014) 1399–1405;
[j] A. Lumbroso, N. Abermil, B. Breit, Chem. Sci. 3 (2012) 789–793;
[k] K. Ogata, D. Sasano, T. Yokoi, K. Isozaki, H. Seike, H. Takaya, M. Nakamura, Chem. Lett. 41 (2012) 498–500;
[l] E. Tomás-Mendivil, P.Y. Toullec, J. Díez, S. Conejero, V. Michelet, V. Cadierno, Org. Lett. 14 (2012) 2520–2523;
[m] B.Y.-M. Man, M. Bhadbhade, B.A. Messerle, New J. Chem. 35 (2011) 1730–1739;
[n] H. Harkat, A.Y. Dembelé, J.-M. Weibel, A. Blanc, P. Pale, Tetrahedron 65 (2009) 1871–1879;
[o] T.L. Mindt, R. Schlibli, J. Org. Chem. 72 (2007) 10247–10250;
[p] E. Marchal, P. Uriac, B. Legouin, L. Toupet, P. van de Weghe, Tetrahedron 63 (2007) 9979–9990;
[q] J.H.H. Ho, D.S. Black, B.A. Messerle, J.K. Clegg, P. Turner, Organometallics 25 (2006) 5800–5810;
[r] E. Genin, P.Y. Toullec, S. Antoniotti, C. Brancour, J.-P. Genêt, V. Michelet, J. Am. Chem. Soc. 128 (2006) 3112–3113;
[s] I. Takei, Y. Wakebe, K. Suzuki, Y. Enta, T. Suzuki, Y. Mizobe, M. Hidai, Organometallics 22 (2003) 4639–4641;
[t] S. Elgafi, L.D. Field, B.A. Messerle, J. Organomet. Chem. 607 (2000) 97–104;
[u] T. Wakabayashi, Y. Ishii, K. Ishikawa, M. Hidai, Angew. Chem., Int. Ed. Engl. 35 (1996) 2123–2124;
[v] L.B. Wolf, K.C.M.F. Tjen, F.P.J.T. Rutjes, H. Hiemstra, H.E. Schoemaker, Tetrahedron Lett. 39 (1998) 5081–5084;
[w] D.M.T. Chan, T.B. Marder, D. Milstein, N.J. Taylor, J. Am. Chem. Soc. 109 (1987) 6385–6388;
[x] C. Lambert, K. Utimoto, H. Nozaki, Tetrahedron Lett. 25 (1984) 5323–5326.
[25] M.G. Al-Shaal, W. Ciptonugroho, F.J. Holzhäuer, J.B. Mensah, P.J.C. Hausoul, R. Palkovits, Catal. Sci. Technol. 5 (2015) 5168–5173.