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ARTICLE

The Phosphinoboration of Acyl Chlorides

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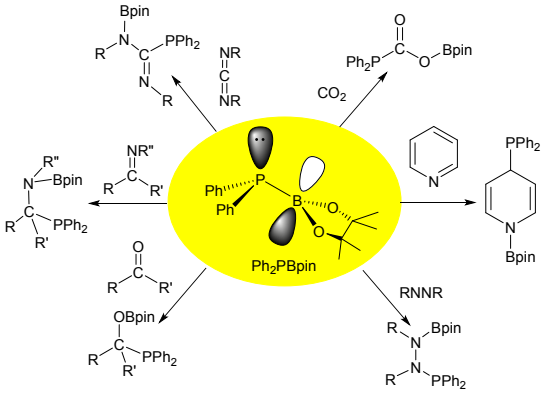
This investigation examines the reactivity of phosphinoboronate esters Ph_2PBpin (pin = 1,2-$O_2C_2Me_4$) and Ph_2PBcat (cat = 1,2-$O_2C_6H_4$), as well as other phosphinoboron species, with various aryl and aliphatic acyl chlorides. These reactions proceed smoothly to give acyl phosphines of the type $RC(O)PR'_2$ along with loss of a boron-chloride compound. In some cases, a second equivalent of the phosphinoboron species can add to the C=O double bond at elevated temperatures to give the corresponding diphosphines $RC(OBR''_2)(PR'_2)_2$. These ambiphilic diphosphines behave like substituted 1,1-bis(diphenylphosphino)methane) derivatives in a reaction of $PhC(OBpin)(PPh_2)_2$ (**2a**) with $(\eta^5\text{-}C_9H_7)Rh(\eta^2\text{-coe})_2$ (coe = *cis*-cyclooctene) afforded the indenyl rhodium complex $(\eta^5\text{-}C_9H_7)Rh(PhC(OBpin)(PPh_2)_2)$ (**3a**) where the phosphines are bound to the metal centre in a κ^2-P,P bidentate manner.

Introduction

Over the past few decades there has been considerable interest in the chemistry of B-E-containing compounds (E = H, B, Si, O, N, etc), especially in addition reactions with unsaturated small molecules such as alkenes, alkynes, carbonyl groups and imines.[1] Although hydroborations (E = H),[2] diborations (E = B),[3] and silylborations (E = Si)[4] are well-known reactions, the analogous chemistry with boron-main group compounds where E contains a lone pair of electrons is much less studied. Indeed, only recently have oxyboration[5] and aminoboration[6] reactions drawn much attention. Significant π-dative bonding from the heteroatoms directly bound to boron can increase the stability of these species and therefore reduce their reactivities in the corresponding addition reactions.[7] Our groups have designed a series of phosphinoboronate esters (E = P) containing primarily single B-P bonds that have shown remarkable activity in uncatalysed or base-mediated addition of aldehydes, ketones, imines, N-heterocyclic aromatics, carbodiimide derivatives, and even with carbon dioxide (Scheme 1).[8] A concurrent study by Su and co-workers reported cycloaddition reactions of simple B=P compounds to dienes and nitriles where the corresponding products maintained a single B-P bond.[9] In that study, they also reported the reduction of benzophenone. Interestingly, Grubba and co-workers have elegantly designed a family of diaminophosphinoboranes for the capture and reduction of carbon dioxide.[10] The ability to introduce both a Lewis basic phosphide (PR_2) and a Lewis acidic boryl (BR_2) group into a variety of compounds has tremendous potential in frustrated Lewis pair (FLP) chemistry.[11] Indeed, we have recently reported on the application of the BNNP FLPs derived from phosphinoborane addition to diazobenzene chemistry.[12]



Scheme 1 The phosphinoboration of carbonyl groups, imines, carbodiimides, carbon dioxide, pyridine, and diazobenzene using Ph_2Bpin.

Acyl phosphines are used in industry as photoinitiators for radical-induced polymerization reactions[13] for automotive coatings, adhesives, latex composition kits, and various dental and orthodontic materials.[14] Known methodologies to such photoinitiators exploit pyrophoric, toxic, expensive reagents that are often difficult to handle.[15] For example, the groups of Liotta, Becker, Grützmacher and Mézailles have developed methods to acylphosphines based on the chemistry of PH_3 and MPH_2 (M = Li, Na, K) as nucleophiles.[16] More recently, P-carbonyl derivatives have been prepared from reactions of salts of $[PCO]^-$ anion,[17] while Cummins *et. al.* have described a synthetic route based on a masked phosphinidene reagent.[18] In the present manuscript, we

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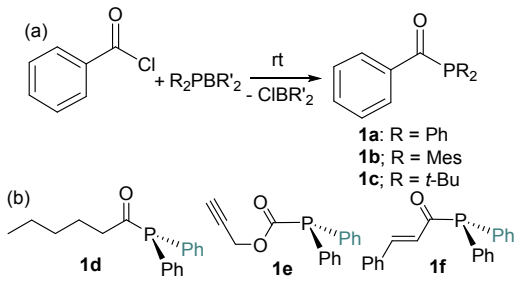
document the utility of phosphinoboranes in reactions with acyl-chlorides as a route to acyl phosphines. Further reactions with phosphinoboranes to give addition across the carbonyl fragment are also probed as an avenue to uniquely derived diphosphino-methanes.

Results and Discussion

Our initial attempts focussed on reactions involving benzoyl chloride, PhC(O)Cl, and Ph_2PBpin (pin = 1,2-$O_2C_2Me_4$). The reaction proceeded smoothly at room temperature to give known compounds $PhC(O)PPh_2$ (**1a**)[19] and ClBpin[20] without the need for a catalyst precursor or additional base to activate the P-B bond (Scheme 2a). The formation of these products presumably arises either from a sigma-bond type metathesis reaction involving a four-centred transition state or *via* initial addition of the phosphinoboronate ester to the C=O double bond followed by elimination of the ClBpin species. Monitoring the reaction by multinuclear NMR spectroscopy, however, showed no evidence for this latter pathway.



Scheme 2 The phosphinoboration of acyl chlorides.

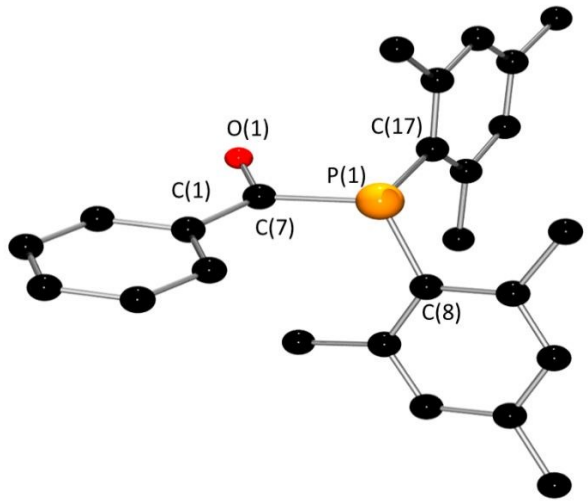
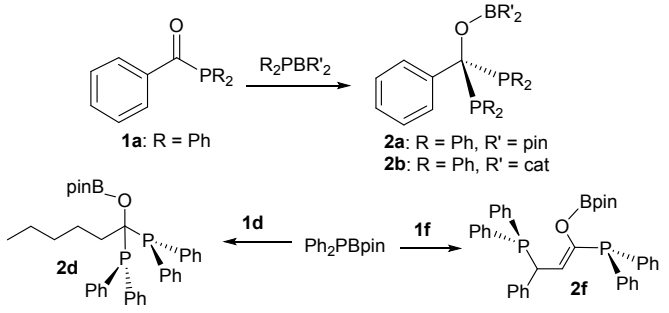


Fig. 1 The molecular structure of **1b** drawn at the 50% probability level with hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (°): P(1)-C(8) 1.8306(19), P(1)-C(17) 1.8356(18), P(1)-C(7) 1.860(2), O(1)-C(7) 1.219(2), C(1)-C(7) 1.500(2); C(8)-P(1)-C(17) 110.68(8), C(8)-P(1)-C(7) 113.72(8), C(17)-P(1)-C(7) 102.35(9), O(1)-C(7)-P(1) 118.94(14), C(1)-C(7)-P(1) 118.63(13).

The generality of this reaction was subsequently probed with the investigation of the addition of other phosphinoboron species to benzoyl chloride. As expected, reactions between Ph_2PBcat (cat = 1,2-$O_2C_6H_4$) or Ph_2BMes_2 (Mes = mesityl) and PhC(O)Cl also gave **1a** with complete conversion, along with the concomitant formation of ClBcat and $ClBMes_2$, respectively. Altering the substituents on the phosphorus group allowed the generation of the acyl phosphines $PhC(O)PMes_2$ (**1b**) and $PhC(O)Pt\text{-}Bu_2$ (**1c**) using Mes_2PBcat, $t\text{-}Bu_2PBcat$, or $t\text{-}Bu_2PBMes_2$. Compounds **1b** and **1c** were characterized fully using multinuclear NMR spectroscopy and elemental analysis. The $^{31}P\{^1H\}$ NMR spectra showed a sharp singlet for these compounds with quite different chemical shifts, the sterically encumbered electron-withdrawing mesityl derivative **1b** is found at -2.9 ppm while the bulky electron-donating *t*-butyl derivative **1c** is observed at 39.5 ppm. A single-crystal X-ray diffraction study on **1b** confirmed the connectivity (Figure 1). The molecular metrics are well within the range for related structures.[18-21]

The corresponding reactions of aliphatic hexanoyl chloride and the ester derivative propargyl chloroformate with Ph_2PBpin proceeded smoothly at room temperature to give **1d** and **1e**, respectively. These reactions were quantitative affording the new phosphorous-containing species with complete conversion of the starting acyl chloride (Scheme 2). Reaction of *trans*-cinnamoyl chloride with Ph_2PBpin gave a complicated mixture of products including the expected acyl phosphine **1f**, along with ClBpin. Unfortunately, reactions of Ph_2PBpin with 9-fluorenone-4-carbonyl chloride also gave a mixture of products arising from competing addition to the ketone group along with decomposition of the starting phosphinoboronate ester.



Scheme 3 The phosphinoboration of acyl phosphines.

Further addition of Ph_2PBpin to **1a** proceeded slowly at elevated temperatures to give the corresponding diphosphine **2a** (Scheme 3). These same conditions could be used on aliphatic acyl phosphine **1d** to selectively give **2d**. Attempts to facilitate the similar addition of a second equivalent of Ph_2PBpin to the alkyne group **1e** proved unsuccessful, even at elevated temperatures and with the use of a Rh catalyst. This lack of reactivity is in stark contrast to our previous study using terminal aromatic alkynes where the 1,1-addition products were prepared by employing rhodium precatalysts.[8d] The diphosphine derived by addition to *in-situ* generated **1f** could eventually be generated under these harsher conditions but resulted in a mixture of 1,2- and 1,4-addition products; the latter species **2f** being the major species in solution.

The addition of the more Lewis acidic phosphinoboronate ester Ph_2PBcat to acylphosphine **1a** also proceeded at room temperature to give the corresponding addition product **2b** as the only new boron-containing product in solution.

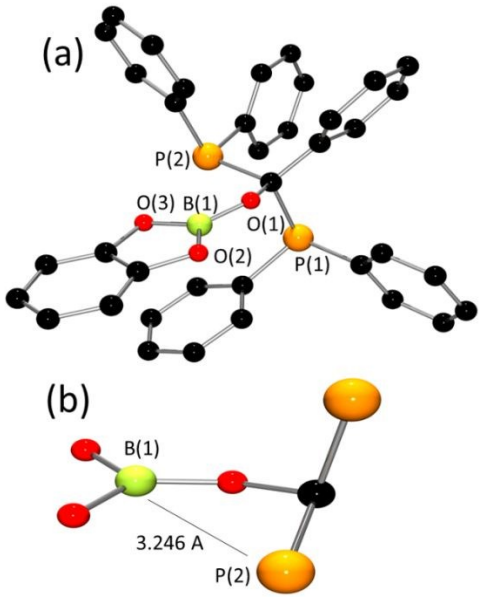


Fig. 2 The molecular structure of **2b** drawn at the 50% probability level with hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (°): P(1)-C(25) 1.917(2), P(2)-C(25) 1.940(2), B(1)-O(1) 1.353(3), B(1)-O(2) 1.392(3), B(1)-O(3) 1.396(3); O(1)-B(1)-O(2) 117.6(2), O(1)-B(1)-O(3) 129.6(2), O(2)-B(1)-O(3) 112.51(18), P(1)-C(25)-P(2) 102.83(10), B(1)-O(1)-C(25) 132.31(17).

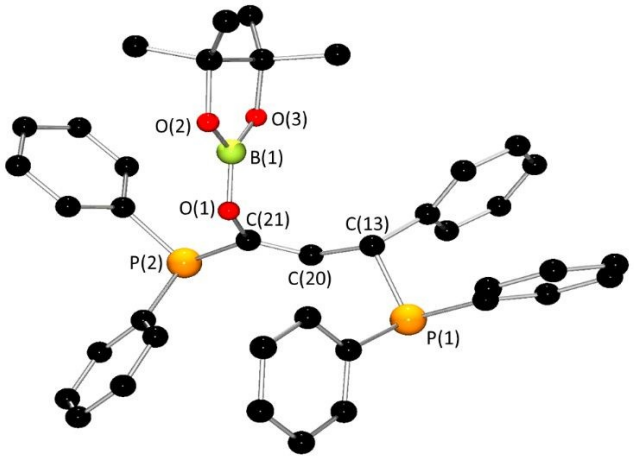
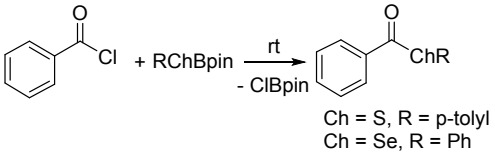


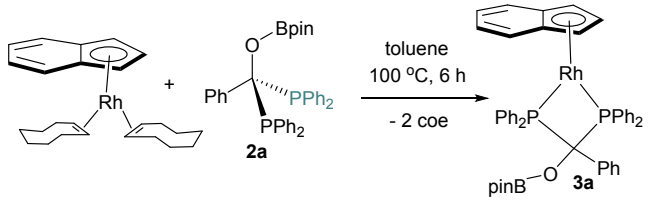
Fig. 3 The molecular structure of **2f** drawn at the 50% probability level with hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (°): P(1)-C(13) 1.883(2), P(2)-C(21) 1.821(2), O(1)-B(1) 1.363(3), O(2)-B(1) 1.367(3), O(3)-B(1) 1.359(3), C(20)-C(21) 1.328(3), C(13)-C(20) 1.505(3); O(3)-B(1)-O(1) 126.3(2), O(3)-B(1)-O(2) 115.0(2), O(1)-B(1)-O(2) 118.6(2), C(21)-C(20)-C(13) 127.0(2), C(20)-C(21)-O(1) 121.5(2), C(20)-C(21)-P(2) 120.90(18).

In support of the formulation of these products, X-ray diffraction studies of **2b** and the 1,4-addition product **2f** were performed (Figures 2, 3). In the case of **2b**, it is interesting to note that there are two distinct P-C bond distances with the P(1)-C(25) bond length of 1.917(2) Å while the P(2)—C(25) bond is slightly elongated at 1.940(2) Å. This disparity is thought to arise from a weak interaction of the P(2) atom with the Lewis acid boron atom which are somewhat close between the two at 3.246(2) Å. This suggests that this compound could have potential applications in FLP chemistry. [11,22] In the case of **2f,** the bond distances and angles are typical for related species and the short C(20)-C(21) distance of 1.328(3) Å and the large C(21)-C(20)-C(13) angle of 127(2)° are consistent with a C=C double bond.

Efforts to extend such additions to sterically-encumbered diphosphines via additions of Ph_2PBMes_2, *t*-Bu_2PBMes_2, and *t*-Bu_2PBcat to **1a** or **1c** proved unsuccessful. However, related additions of TolSBpin and PhSeBpin[23] to acyl chlorides were effective. For example, reaction of PhC(O)Cl with these reagents afforded ClBpin and the known derivatives PhC(O)STol and PhC(O)SePh respectively,[24] although higher temperatures and extended times were required in comparison to the analogous reactions of Ph_2PBpin (Scheme 4).



Scheme 4 Synthesis of acyl chalcogenides.



Scheme 5 Synthesis of indenyl rhodium complex **3a**.

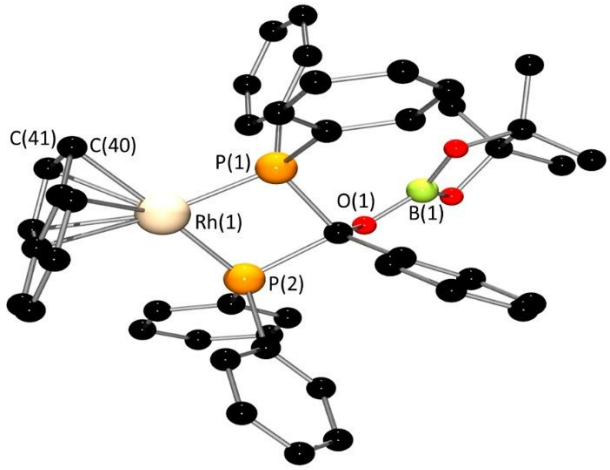


Fig. 4 The molecular structure of **3a** drawn at the 50% probability level with hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (°): Rh(1)-P(1) 2.1847(7), Rh(1)-P(2) 2.1991(7), Rh(1)-C(48) 2.277(3), Rh(1)-C(40) 2.253(3), Rh(1)-C(41) 2.221(3), Rh(1)-C(42) 2.388(3), Rh(1)-C(47) 2.406(3); P(1)-Rh(1)-P(2) 75.08(2).

Access to elementally pure samples of **2a** prompted interest in its coordination chemistry. This together with our long-standing

interest in indenyl rhodium complexes as pre-catalysts for numerous chemical transformations[25] led to the reaction of (η^5-C_9H_7)Rh(η^2-coe)$_2$ (coe = *cis*-cyclooctene) with **2a**. The resulting complex (η^5-C_9H_7)Rh(PhC(OBpin)(PPh_2)$_2$) **3a** was formed as the only new phosphorous-containing species in solution along with the concomitant liberation of cyclooctene (Scheme 5). Complex **3a** was easily isolated *via* precipitation and characterized fully using multinuclear NMR spectroscopy and elemental analysis. The $^{31}P\{^1H\}$ NMR spectrum for **3a** displays a doublet at 44.0 ppm with a coupling constant of J_{PRh} = 198 Hz, typical for indenyl Rh(I) complexes. [25] The ^{11}B NMR spectrum shows a broad peak at 20 ppm consistent with a three coordinate boron atom. ^1H and $^{13}C\{^1H\}$ NMR data for the indenyl ring suggest there is the expected slight slip-fold distortion away from the η^5-isomer towards the η^3-allylic form.[25,26]

The structure of **3a** was confirmed in the solid state *via* a single crystal X-ray diffraction study (Figure 4). These data confirm the bidentate chelation of **2a** to Rh with no significant interaction of the boron atom with the metal centre. In the solid state it appears the indenyl ligand displays a pronounced slippage away from the planar η^5-indenyl ring as the Rh-C distances to the quaternary carbons C(42) and C(47) are longer than the 'allylic' CH carbons C(41), C(40) and C(48) where the slip parameter difference is ΔM-C = 0.147(3) Å. The acute bite angle of the two phosphorous atoms of 75.08(2) is similar to other related κ^2-P,P-(dppm)Rh(I) complexes.[27]

Experimental

Materials and methods

All manipulations were performed in a MB Unilab glove box produced by MBraun or using standard Schlenk techniques under an inert atmosphere of anhydrous N_2. Reagents and solvents were obtained from Sigma-Aldrich, Strem Chemicals, TCI Chemicals or Alfa Aesar. Dry, oxygen-free solvents (dichloromethane, toluene, and *n*-pentane) were prepared using an Innovative Technologies solvent purification system or deoxygenated and distilled over sodium benzophenone. $CDCl_3$ (Aldrich) was deoxygenated, distilled over CaH_2, then stored over 3 Å molecular sieves before use. C_6D_6 (Aldrich) was deoxygenated, distilled over sodium benzophenone, then stored over 3 Å molecular sieves before use. Ph_2PBpin, Ph_2PBcat,[8d] Ph_2PBMes_2,[7b, 7c] *t*-Bu_2PBcat,[8c] Mes_2PBcat,[28] and (η^5-C_9H_7)Rh(η^2-coe)$_2$[25d] were prepared as previously reported. NMR spectra were obtained on an Agilent DD2-500 MHz, a Bruker AvanceIII-400 MHz, or a Varian Mercury-300 MHz spectrometer where ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, and $^{11}B\{^1H\}$ NMR chemical shifts (δ/ppm) are referenced to Me_4Si, Me_4Si, H_3PO_4, and $BF_3{\cdot}OEt_2$, respectively. NMR spectra were also 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 $F_3B{\cdot}OEt_2$ (^{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 and hydrogen were performed at the University of Toronto using a PerkinElmer 2400 Series II CHNS analyser.

Synthesis of $PhC(O)PPh_2$ (1a).[12] In a 20 mL vial, a solution of the given phosphinoborane (Ph_2PBpin, Ph_2PBcat or Ph_2PBMes_2) (0.1 mmol) was prepared in CH_2Cl_2 (3 mL). A solution of benzoyl chloride (14 mg, 0.1 mmol) in CH_2Cl_2 (3 mL) was added at ambient temperature and the reaction mixture was left to stir for 24 h. The solution was then dried *in vacuo*, recrystallized by layering with pentane and CH_2Cl_2, decanted and washed with cold pentane (3 x 2 mL) to afford a yellow solid (Ph_2PBpin: 28 mg, 95% isolated yield, Ph_2PBcat: 28 mg, 96% isolated yield, Ph_2PBMes_2: 27 mg, 94% isolated yield). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.97 (m, 2H, Ar), 7.48-7.32 (ov m, 13H, Ar); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 213.0 (d, J_{CP} = 37 Hz), 139.3 (d, J_{CP} = 35 Hz), 135.0 (d, J_{CP} = 19 Hz), 133.3, 132.8 (d, J_{CP} = 6 Hz), 129.6, 128.8 (d, J_{CP} = 9 Hz), 128.6, 128.4 (d, J_{CP} = 9 Hz); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ: 14.1.

Synthesis of $PhC(O)PMes_2$ (1b). In a 20 mL vial, a solution of Mes_2PBcat (38.8 mg, 0.1 mmol) was prepared in CH_2Cl_2 (3 mL). A solution of benzoyl chloride (14 mg, 0.1 mmol) in CH_2Cl_2 (3 mL) was added at ambient temperature and the reaction mixture was left to stir for 24 h. The solution was then dried *in vacuo* and washed with cold pentane (3 x 2 mL) to afford a yellow oil. Yield: 35 mg (94%). ^1H NMR (500 MHz, C_6D_6) δ: 8.11 (m, 2H, Ar), 6.98-6.89 (ov m, 3H, Ar), 6.68 (m, 4H, Ar), 2.35 (s, 12H, CH_3), 2.00 (s, 6H, CH_3); $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6) δ: 211.0 (d, J_{CP} = 37 Hz), 143.9 (d, J_{CP} = 15 Hz), 141.3 (d, J_{CP} = 43 Hz), 139.4 (d, J_{CP} = 1 Hz), 132.6 (d, J_{CP} = 2 Hz), 130.3 (d, J_{CP} = 5 Hz), 128.6 (d, J_{CP} = 1 Hz), 128.4, 128.0 (d, J_{CP} = 2 Hz), 23.5 (d, J_{CP} = 14 Hz), 21.0. $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6) δ: -2.9. Anal. calcd. for $C_{25}H_{27}OP$ (374.46 g·mol^{-1}): C, 80.19; H, 7.27. Found: C, 80.07; H, 7.34.

Synthesis of $PhC(O)PtBu_2$ (1c). In a 20 mL vial, a solution of the given phosphinoborane (*t*-Bu_2PBcat or *t*-Bu_2PBMes_2) (0.1 mmol) was prepared in CH_2Cl_2 (3 mL). A solution of benzoyl chloride (14 mg, 0.1 mmol) in CH_2Cl_2 (3 mL) was added at ambient temperature and the reaction mixture was left to stir for 24 h. The solution was then dried *in vacuo* and washed with cold pentane (3 x 2 mL) to afford a yellow oil (*t*-Bu_2PBcat: 23 mg, 92% isolated yield, *t*-Bu_2PBMes_2: 24 mg, 94% isolated yield). ^1H NMR (500 MHz, C_6D_6) δ: 8.25 (m, 2H, Ar), 7.13-7.05 (ov m, 3H, Ar), 1.24 (d, J_{HP} = 5.0 Hz, 9H, *t*-Bu), 1.22 (d, J_{HP} = 5.0 Hz, 9H, *t*-Bu); $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6) δ: 218.2 (d, J_{CP} = 40 Hz), 144.2 (d, J_{CP} = 35 Hz), 133.1 (d, J_{CP} = 2 Hz), 129.1 (d, J_{CP} = 13 Hz), 128.6 (d, J_{CP} = 2 Hz), 33.4 (d, J_{CP} = 22 Hz), 30.5 (d, J_{CP} = 13 Hz); $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6) δ: 39.5. Anal. calcd. for $C_{15}H_{23}OP$ (250.32 g·mol^{-1}): C, 71.97; H, 9.26. Found: C, 71.98; H, 9.26.

Synthesis of *n*-pentylC(O)PPh_2 (1d). A mixture of hexanoyl chloride (100 mg, 0.74 mmol) and Ph_2PBpin (232 mg, 0.74 mmol) in toluene (5 mL) was stirred for 4 hours at RT.

Removal of solvent and ClBpin *in vacuo* afforded **1d** as a colourless oil. Yield: 198 mg (94%). ^{1}H NMR (400 MHz, C_6D_6) δ: 7.45 (m, 4H, Ar), 7.04-6.99 (ov m, 6H, Ar), 2.33 (td, J_{HH} = 7.3 Hz, J_{HP} = 3.2 Hz, 2H, C(O)CH_2), 1.46 (quint, J_{HH} = 7.3 Hz, 2H, C(O)CH$_2$CH_2), 1.05-0.88 (ov m, 4H, 2 × CH_2), 0.67 (t, J_{HH} = 7.3 Hz, 3H, CH_3); ^{13}C{^{1}H} NMR (100 MHz, C_6D_6) δ: 221.4 (d, J_{CP} = 41 Hz), 134.8 (d, J_{CP} = 18 Hz), 133.3 (d, J_{CP} = 8 Hz), 129.3, 128.6 (d, J_{CP} = 8 Hz), 45.3 (d, J_{CP} = 45 Hz), 31.2, 24.0 (d, J_{CP} = 4 Hz), 22.4, 13.8; ^{31}P{^{1}H} NMR (162 MHz, C_6D_6) δ: 16.0. Anal. calcd. for $C_{18}H_{21}OP$ (284.33 g·mol^{-1}): C, 76.04; H, 7.44. Found: C, 75.55; H, 7.40.

Synthesis of HCCCH$_2$OC(O)PPh$_2$ (1e). To a stirred toluene (1 mL) solution of propargyl chloroformate (25 mg, 0.21 mmol) was added a toluene (1 mL) solution of Ph_2PBpin (66 mg, 0.21 mmol). The reaction was allowed to proceed for 18 h at RT at which point the solvent and ClBpin were removed *in vacuo* to afford **1e** as a colourless oil. Yield: 54 mg (95%). ^{1}H NMR (400 MHz, C_6D_6) δ: 7.46 (m, 4H, Ar), 7.01-6.97(ov m, 6H, Ar), 4.27 (d, J_{HH} = 2.3 Hz, 2H, CH_2), 1.83 (t, J_{HH} = 2.3 Hz, 1H, C≡CH); ^{13}C{^{1}H} NMR (100 MHz, C_6D_6) δ: 178.0 (d, J_{CP} = 18 Hz), 134.6, (d, J_{CP} = 19 Hz), 132.6 (d, J_{CP} = 7 Hz), 129.5, 128.6 (d, J_{CP} = 8 Hz), 77.6, 74.9, 51.8; ^{31}P{^{1}H} NMR (162 MHz, C_6D_6) δ: -2.1. Anal. calcd. for $C_{16}H_{13}O_2P$ (268.25 g·mol^{-1}): C, 71.64; H, 4.88. Found: C, 71.18; H, 4.96.

Synthesis of PhC(OBpin)(PPh$_2$)$_2$ (2a). A mixture of benzoyl chloride (100 mg, 0.71 mmol) and Ph_2PBpin (466 mg, 1.49 mmol) in toluene (3 mL) was heated at 110˚C for 5 days. Removal of solvent and ClBpin *in vacuo* afforded an oily yellow solid which was triturated with 5 mL of hexane. The resulting solid was collected by suction filtration to afford **2a** as a white solid. Yield: 328 mg (77%); mp 126-128˚C. ^{1}H NMR (400 MHz, C_6D_6) δ: 7.92 (m, 4H, Ar), 7.65 (m, 4H, Ar), 7.31 (d, J_{HH} = 7.8 Hz, 2H, Ar), 7.04-6.94 (ov m, 7H, Ar), 6.89-6.85 (ov m, 6H, Ar), 6.81 (t, J_{HH} = 7.3 Hz, 1H, Ar), 6.70 (t, J_{HH} = 7.3 Hz, 1H, Ar), 0.70 (s, 12H, pin); ^{11}B NMR (128 MHz, C_6D_6) δ: 20 (br); ^{13}C{^{1}H} NMR (100 MHz, C_6D_6) δ: 141.2 (t, J_{CP} = 3 Hz), 136.9, (ov dd, J_{CP} = 13, 12 Hz), 136.4 (ov dd, J_{CP} = 7, 6 Hz), 135.7 (ov dd, J_{CP} = 13, 12 Hz), 135.5 (ov dd, J_{CP} = 5, 4 Hz), 128.9, 128.4, 127.9 (ov dd, J_{CP} = 4, 3 Hz), 127.7 (ov dd, J_{CP} = 5, 4 Hz), 127.5 (ov dd, J_{CP} = 7, 6 Hz), 126.5, 125.6, 87.0 (t, J_{CP} = 43 Hz), 82.3, 24.3; ^{31}P{^{1}H} NMR (162 MHz, C_6D_6) δ: 15.0. Anal. calcd. for $C_{37}H_{37}BO_3P_2$ (602.45 g·mol^{-1}): C, 73.77; H, 6.19. Found: C, 73.53; H, 6.24.

Synthesis of PhC(OBcat)(PPh$_2$)$_2$ (2b). In a 20 mL vial, a solution of Ph_2PBcat (61 mg, 0.2 mmol) was prepared in CH_2Cl_2 (3 mL). A solution of benzoyl chloride (14 mg, 0.1 mmol) in CH_2Cl_2 (3 mL) was added at ambient temperature and the reaction mixture was left to stir for 24 h. The solution was then dried *in vacuo*, recrystallized by layering with pentane and CH_2Cl_2, decanted and washed with cold pentane (3 x 2 mL) to afford a colourless crystalline solid. Yield: 54 mg (90%); mp 143-145˚C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.63 (m, 4H, Ar), 7.55 (m, 4H, Ar), 7.24-7.07 (ov m, 14H, Ar), 7.01-6.95 (ov m, 3H, Ar), 6.90-6.78 (ov m, 4H, cat); ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ: 21 (br); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 147.7, 139.8 (t, J_{CP} = 3 Hz), 136.2 (dt, J_{CP} = 34 Hz, 12 Hz), 134.2 (t, J_{CP} = 5 Hz), 133.4 (t, J_{CP} = 6 Hz), 129.6, 129.1, 127.9 (dt, J_{CP} = 6 Hz, 4 Hz), 127.0 (t, J_{CP} = 7 Hz), 126.8, 126.0 (d, J_{CP} = 1 Hz), 121.8, 111.6, 88.5 (t, J_{CP} = 43 Hz); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ: 12.3. Anal. calcd. for $C_{37}H_{29}BO_3P_2$ (594.38 g·mol^{-1}): C, 74.77; H, 4.92. Found: C, 74.93; H, 4.88.

Synthesis of *n*-pentylC(OBpin)(PPh$_2$)$_2$ (2d). A mixture of hexanoyl chloride (100 mg, 0.74 mmol) and Ph_2PBpin (487 mg, 1.56 mmol) in toluene (3 mL) was heated at 110ºC for 5 days. Removal of solvent and ClBpin *in vacuo* afforded a pale yellow oil which was dissolved in 5 mL of hexane and stored at -30˚C. The resulting precipitate was collected by suction filtration to afford **2d** as a white solid. Yield: 308 mg (69%); mp 106-109˚C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.71 (m, 4H, Ar), 7.59 (m, 4H, Ar), 7.30-7.24 (ov m, 6H, Ar), 7.12 (t, J_{HH} = 7.8 Hz, 2H, Ar), 7.04 (t, J_{HH} = 7.3 Hz, 4H, Ar), 2.04 (td, J_{HH} = 7.3 Hz, J_{HP} = 3.7 Hz, 2H, C(OBpin)CH_2), 1.57 (quint, J_{HH} = 7.6 Hz, 2H, C(O)CH$_2$CH_2), 1.11-1.04 (ov m, 14H, CH_2 & pin), 0.89 (quint, J_{HH} = 7.6 Hz, 2H, CH_2), 0.71 (t, J_{HH} = 7.6 Hz, 3H, CH_3); ^{11}B NMR (128 MHz, $CDCl_3$) δ: 20 (br); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 136.0 (t, J_{CP} = 13 Hz), 135.9 (t, J_{CP} = 13 Hz), 135.5 (t, J_{CP} = 3 Hz), 134.7 (t, J_{CP} = 6 Hz), 129.0, 128.7, 128.0 (t, J_{CP} = 4 Hz), 127.6 (t, J_{CP} = 4 Hz), 86.3 (t, J_{CP} = 36 Hz), 82.1, 38.1 (t, J_{CP} = 8 Hz), 32.3, 25.8 (t, J_{CP} = 13 Hz), 24.5, 22.4, 14.0; ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ: 11.2. Anal. calcd. for $C_{36}H_{43}BO_3P_2$ (596.48 g·mol^{-1}): C, 72.49; H, 7.27. Found: C, 72.76; H, 7.31.

Synthesis of Ph$_2$PCH(Ph)CH=C(OBpin)PPh$_2$ (2f). To a stirred CH_2Cl_2 (2 mL) solution of *trans*-cinnamoyl chloride (40 mg, 0.24 mmol) was added a CH_2Cl_2 (2 mL) solution of Ph_2PBpin (150 mg, 0.48 mmol). The reaction was allowed to proceed for 18 h at 25°C at which point solvent was removed under vacuum to afford a waxy colourless solid. The mixture was dissolved in hexane (20 mL) and stored at -30˚C. Pale yellow crystals formed and were collected by suction filtration to afford **2f** as a pale yellow solid. Yield: 62 mg (41%); mp 107-112˚C. ^{1}H NMR (400 MHz, C_6D_6) δ: 7.63 (m, 2H, Ar), 7.39 (m, 2H, Ar), 7.29 (m, 4H, Ar), 7.12-7.10 (ov m, 2H, Ar), 7.06-7.04 (ov m, 3H, Ar), 6.97-6.89 (ov m, 12H, Ar), 5.99 (d ov dd, J_{HH} = 10.5 Hz, J_{HP} = 6.9, 6.9 Hz, 1H, *H*C=), 4.96 (dd, J_{HH} = 10.5 Hz, J_{HP} = 2.8 Hz, 1H, *H*CPPh$_2$), 0.80 (s, 6H, pin), 0.74 (s, 6H, pin); ^{11}B NMR (128 MHz, C_6D_6) δ: 21 (br); ^{13}C{^{1}H} NMR (100 MHz, C_6D_6) δ: 150.6 (dd, J_{CP} = 20, 9 Hz), 140.6 (d, J_{CP} = 10 Hz), 137.6 (d, J_{CP} = 18 Hz), 136.4 (d, J_{CP} = 11 Hz), 135.8 (d, J_{CP} = 11 Hz), 135.5 (d, J_{CP} = 18 Hz), 134.9 (d, J_{CP} = 20 Hz), 134.6 (d, J_{CP} = 20 Hz), 133.7 (d, J_{CP} = 19 Hz), 133.3 (d, J_{CP} = 17 Hz), 129.2, 129.1, 129.0, 128.6, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.7 (dd, J_{CP} = 34, 13 Hz), 126.0 (d, J_{CP} = 2 Hz), 82.9, 43.0 (dd, J_{CP} = 17, 8 Hz), 24.4, 24.0; ^{31}P{^{1}H} NMR (162 MHz, C_6D_6) δ: 7.2, -1.1. Anal. calcd. for $C_{39}H_{39}BO_3P_2$ (628.48 g·mol^{-1}): C, 74.53; H, 6.25. Found: C, 74.76; H, 6.34.

Synthesis of (η^5-C$_9$H$_7$)Rh(PhC(OBpin)(PPh$_2$)$_2$) (3a). To a stirred toluene (3 mL) solution of (η^5-C$_9$H$_7$)Rh(η^2-coe)$_2$ (100 mg, 0.23 mmol) was added a toluene (2 mL) solution of PhC(OBpin)(PPh$_2$)$_2$ (136 mg, 0.23 mmol). The reaction was heated at 100ºC for 6 h at which point the volume of solvent

was halved *in vacuo* and the solution stored at -30°C. A precipitate was collected by suction filtration and washed with cold toluene (2 × 1 mL) to afford (η^5-C_9H_7)Rh(PhC(OBpin)(PPh_2)$_2$) as an orange solid. Yield: 90 mg (48%); mp 171-173°C. ^{1}H NMR (400 MHz, C_6D_6) δ: 7.92 (m, 4H, Ar), 7.66 (m, 4H, Ar), 7.39 (m, 2H, Ar), 7.24 (2nd order m, 2H, IND), 7.03 (2nd order m, 2H, IND), 6.99 (ov dd, J_{HH} = 7.3 Hz, 4H, Ar), 6.93-6.86 (ov m, 7H, Ar), 6.55 (br m, 4H, Ar), 6.24 (ov td, J_{HH} = J_{HRh} = 2.8 Hz, 1H, IND), 5.86 (d, J_{HH} = 2.8 Hz, 2H, IND), 0.72 (s, 12H, pin); ^{11}B NMR (128 MHz, C_6D_6) δ: 20 (br); ^{13}C{^{1}H} NMR (100 MHz, C_6D_6) δ: 137.7 (t, J_{CP} = 4 Hz), 135.9 (t, J_{CP} = 16 Hz), 135.4 (t, J_{CP} = 7 Hz), 135.3, (t, J_{CP} = 8 Hz), 134.6 (t, J_{CP} = 15 Hz), 129.0, 128.8, 128.0, 127.0 (t, J_{CP} = 5 Hz), 126.9 (t, J_{CP} = 5 Hz), 126.1 (br s, 2C), 120.7, 118.6, 114.4, 105.7 (t, J_{CP} = 17 Hz), 93.2 (d, J_{CRh} = 5 Hz), 82.8, 71.6 (td, J_{CP} = 8 Hz, J_{CRh} = 3 Hz), 24.2; ^{31}P{^{1}H} NMR (162 MHz, C_6D_6) δ: 44.0 (d, J_{PRh} = 198.1 Hz). Anal. calcd. for $C_{46}H_{44}BO_3P_2Rh$ (820.50 g·mol^{-1}): C, 67.34; H, 5.41. Found: C, 67.96; H, 5.36.

X-Ray Diffraction Studies Single crystals of **1b** and **2b** were grown from CH_2Cl_2 solutions layered with pentane while crystals of **2f** and **3a** were grown from saturated hexane or toluene solutions, respectively. The crystals were coated with paratone oil, mounted on a cryoloop and frozen under a stream of cold nitrogen. Data were collected on a Bruker Apex2 X-ray diffractometer (**1b**, **2b**, and **2f**) or a Bruker Photon 100 CMOS diffractometer (**3a**) using graphite monochromated Mo-Kα radiation (0.71073 Å). Data were collected using Bruker APEX-2 or APEX-3 software and processed using SHELX[29] and an absorption correction applied using multi-scan within the APEX-2 or APEX-3 program.[30] All structures were solved and refined by direct methods within the SHELXTL package. Crystallographic information for **1b**, **2b**, **2f**, and **3a** has also been deposited with the Cambridge Crystallographic Data Centre (CCDC 1984246-1984249). 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).

Conclusions

Herein we have described the reactivity of phosphinoboronate esters Ph_2PBpin and Ph_2PBcat, as well as other phosphinoboron species, with various acyl chlorides to give acyl phosphines with the by-product boron-chloride. In addition, in several cases, reactions with a second equivalent of phosphinoboron results in addition to the C=O double bond affording the corresponding diphosphines RC(OBR"$_2$)(PR'$_2$)$_2$. Such derivatives are shown to chelate to Rh affording a substituted *bis*-phosphino-methane complex with a pendant borane fragment. While we continue to explore the reactivity of systems containing B-P bonds, we are also pursuing the potential of such addition products in FLP chemistry. The results of these studies will be reported in due course.

Conflicts of interest

There are no conflicts to declare.

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