The phosphinoboration of acyl chlorides†

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This investigation examines the reactivity of phosphinoboronate esters Ph2PBpin (pin = 1,2-O2C2Me4) and Ph2PBcat (cat = 1,2-O2C6H4), 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)PR2 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)(PPh2)2 (2a) with (η5-C9H7)Rh(η2-coe)2 (coe = cis-cyclooctene) affording the indenyl rhodium complex (η5-C9H7)Rh(PhC(OBpin)(PPh2)2) (3a) where the phosphines are bound to the metal centre in a κ2-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 oxyboration5 and aminoboration6 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 dianimophosphinoboranes for the capture and reduction of carbon dioxide.10 The ability to introduce both a Lewis basic phosphate (PR3) and a Lewis acidic boryl (BR2) 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 BNPN FLPs derived from phosphinoborane addition to diazobenzene chemistry.12

Acyl phosphines are used in industry as photoinitiators for radical-induced polymerization reactions13 for automotive coatings, adhesives, latex composition kits, and various dental and orthodontic materials.14 Known methodologies to such

Scheme 1 The phosphinoboration of carbonyl groups, imines, carbodiimides, carbon dioxide, pyridine, and diazobenzene using Ph2Bpin.
The 31P{1H} NMR spectra showed a sharp singlet for these species to benzoyl chloride. As expected, reactions between 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 Ph2PBpin (pin = 1,2-O2C2Me4). The reaction proceeded smoothly at room temperature to give known compounds PhC(O)OPh2 (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 phosphinoborinate 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.

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 Ph2PBcat (cat = 1,2-O2C6H4) or Ph2BMes2 (Mes = mesityl) and PhC(O)Cl also gave 1a with complete conversion, along with the concomitant formation of ClBcat and ClBMes2, respectively. Altering the substituents on the phosphorus group allowed the generation of the acyl phosphines PhC(O)PMes2 (1b) and PhC(O)Pr-Bu2 (1c) using Mes2PBcat, t-Bu2PBcat, or t-Bu2PBMeS2. 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 (Fig. 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 Ph2PBpin proceeded smoothly at room temperature to give 1d and 1e, respectively. These reactions were quantitative affording the new phosphorus-containing species with complete conversion of the starting acyl chloride (Scheme 2). Reaction of trans-cinnamyl chloride with Ph2PBpin gave a complicated mixture of products including the expected acylphosphine 1f, along with ClBpin. Unfortunately, reactions of Ph2PBpin 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 phosphinoborinate ester.

Further addition of Ph3PBpin to 1a proceeded slowly at elevated temperatures to give the corresponding diphosphine 2a (Scheme 3). These same conditions could be used on aliphatic acyl phosphate 1d to selectively give 2d. Attempts to facilitate the similar addition of a second equivalent of Ph3PBpin 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.\(^{24}\) The diphosphine derived by addition to \textit{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 phosphinoborinate ester Ph2PBcat to acylphosphine 1a also proceeded at room temperature to give the corresponding...
addition product 2b as the only new boron-containing product in solution.

In support of the formulation of these products, X-ray diffraction studies of 2b and the 1,4-addition product 2f were performed (Fig. 2 and 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 Ph2PBMes2, t-Bu2PBMes2, and t-Bu2PBcat to 1a or 1c proved unsuccessful. However, related additions of TolSBpin and PhSeBpin23 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 Ph2PBpin (Scheme 4).

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 transformations25 led to the reaction of (η5-C9H7)Rh(η2-coe)2 (coe = cis-cyclooctene) with 2a. The resulting complex (η5-C9H7)Rh(PhC(OBpin)(PPh2)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 31P{1H} NMR spectrum for 3a displays a doublet at 44.0 ppm with a coupling constant of $J_{PRh} = 198 \text{ Hz}$, typical for indenyl Rh(I) complexes.25 The 11B NMR spectrum shows a broad peak at 20 ppm consistent with a three coordinate boron atom. 1H and 13C{1H} NMR data for the indenyl ring suggest there is the expected slight slip-fold
distortion away from the \(\eta^5\)-isomer towards the \(\eta^3\)-allylic form.\textsuperscript{25,26}

The structure of 3a was confirmed in the solid state via a single crystal X-ray diffraction study (Fig. 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 interaction of the boron atom with the metal centre. In the single crystal X-ray di

tances to the quaternary carbons C(42) and C(47) are longer (3), Rh(1) 2.277(3), Rh(1) 2.253(3), Rh(1) – C(40) 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).

**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 deoxyge-

nated and distilled over sodium benzophenone. CDCl\(_3\) (Aldrich) was deoxygenated, distilled over CaH\(_2\), then stored over 3 Å molecular sieves before use. C\(_6\)D\(_6\) (Aldrich) was deoxygenated, distilled over sodium benzophenone, then stored over 3 Å molecular sieves before use. Ph\(_2\)Pbin, Ph\(_2\)Pbacat,\textsuperscript{8d} Ph\(_2\)PBMe\(_2\),\textsuperscript{7b,c} t-Bu\(_2\)PBcat,\textsuperscript{8e} Mes\(_2\)Pbacat,\textsuperscript{28} and (\(\eta^5\)-C\(_5\)H\(_5\))Rh(\(\eta^5\)-coc)\textsuperscript{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 \(\text{\(^1\)}\text{H}\), \(\text{\(^{13}\)}\text{C}\text{(\(^{1}\)}\text{H})\), \(\text{\(^{31}\)}\text{P}\text{(\(^{1}\)}\text{H})\), and \(\text{\(^{11}\)}\text{B}\text{(\(^{1}\)}\text{H})\) NMR chemical shifts (\(\delta\)/ppm) are referenced to Me\(_4\)Si, Me\(_4\)Si, H\(_3\)PO\(_4\), and BF\(_3\)-OEt\(_2\), respectively. NMR spectra were also recorded on a JEOL JNM-GSX400 FT NMR (\(\text{\(^1\)}\text{H}\): 400 MHz; \(\text{\(^{11}\)}\text{B}\): 128 MHz; \(\text{\(^{13}\)}\text{C}\): 100 MHz; \(\text{\(^{31}\)}\text{P}\): 162 MHz) spectrometer. Chemical shifts (\(\delta\)) are reported in ppm [relative to residual solvent peaks (\(\text{\(^1\)}\text{H}\) and \(\text{\(^{13}\)}\text{C}\)) or external F\(_3\)B·OEt\(_2\) (\(\text{\(^{11}\)}\text{B}\))] 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).\textsuperscript{19}** In a 20 mL vial, a solution of the given phosphinoborane (Ph\(_2\)Pbin, Ph\(_2\)Pbacat or Ph\(_2\)PBMe\(_2\)) (0.1 mmol) was prepared in CH\(_2\)Cl\(_2\) (3 mL). A solution of benzoyl chloride (14 mg, 0.1 mmol) in CH\(_2\)Cl\(_2\) (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\(_2\)Cl\(_2\), decanted and washed with cold pentane (3 \(\times\) 2 mL) to afford a yellow solid (Ph\(_2\)Pbin: 28 mg, 95% isolated yield, Ph\(_2\)Pbacat: 28 mg, 96% isolated yield, Ph\(_2\)PBMe\(_2\): 27 mg, 94% isolated yield). \(\text{\(^1\)}\text{H}\) NMR (400 MHz, CDCl\(_3\)) \(\delta\): 7.97 (m, 2H, Ar), 7.48–7.32 (ov m, 13H, Ar); \(\text{\(^{13}\)}\text{C}\text{(\(^{1}\)}\text{H})\) NMR (100 MHz, CDCl\(_3\)) \(\delta\): 213.0 (d, \(\text{\(J\text{CP} = 37\)}\) Hz), 139.3 (d, \(\text{\(J\text{CP} = 35\)}\) Hz), 135.0 (d, \(\text{\(J\text{CP} = 19\)}\) Hz), 133.3, 132.8 (d, \(\text{\(J\text{CP} = 6\)}\) Hz), 129.6, 128.8 (d, \(\text{\(J\text{CP} = 9\)}\) Hz); \(\text{\(^{31}\)}\text{P}\text{(\(^{1}\)}\text{H})\) NMR (162 MHz, CDCl\(_3\)) \(\delta\): 14.1.

**Synthesis of PhC(O)PBMe\(_2\) (1b).** In a 20 mL vial, a solution of Mes\(_2\)PBcat (38.8 mg, 0.1 mmol) was prepared in CH\(_2\)Cl\(_2\) (3 mL). A solution of benzoyl chloride (14 mg, 0.1 mmol) in CH\(_2\)Cl\(_2\) (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 \(\times\) 2 mL) to afford a yellow oil. Yield: 35 mg (94%). \(\text{\(^1\)}\text{H}\) NMR (500 MHz, CDCl\(_3\)) \(\delta\): 8.11 (m, 2H, Ar), 6.98–6.89 (ov m, 3H, Ar), 6.68 (m, 4H, Ar), 2.35 (s, 12H, CH\(_2\)), 2.00 (s, 6H, CH\(_3\)); \(\text{\(^{13}\)}\text{C}\text{(\(^{1}\)}\text{H})\) NMR (125 MHz, CDCl\(_3\)) \(\delta\): 211.0 (d, \(\text{\(J\text{CP} = 37\)}\) Hz), 143.9 (d, \(\text{\(J\text{CP} = 15\)}\) Hz), 141.3 (d, \(\text{\(J\text{CP} = 43\)}\) Hz), 139.4 (d, \(\text{\(J\text{CP} = 1\)}\) Hz), 132.6 (d, \(\text{\(J\text{CP} = 2\)}\) Hz), 130.3 (d, \(\text{\(J\text{CP} = 5\)}\) Hz), 128.6 (d, \(\text{\(J\text{CP} = 1\)}\) Hz), 128.4, 128.0 (d, \(\text{\(J\text{CP} = 2\)}\) Hz), 23.5 (d, \(\text{\(J\text{CP} = 14\)}\) Hz), 21.0. \(\text{\(^{31}\)}\text{P}\text{(\(^{1}\)}\text{H})\) NMR (162 MHz, CDCl\(_3\)) \(\delta\): –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)t-Bu\(_2\) (1c).** In a 20 mL vial, a solution of the given phosphinoborane (t-Bu\(_2\)PBcat or t-Bu\(_2\)PBMe\(_2\)) (0.1 mmol) was prepared in CH\(_2\)Cl\(_2\) (3 mL). A solution of benzoyl chloride (14 mg, 0.1 mmol) in CH\(_2\)Cl\(_2\) (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 × 2 mL) to afford a yellow oil (t-Bu2PBcat: 23 mg, 92% isolated yield, t-Bu2PBMes2: 24 mg, 94% isolated yield). 1H NMR (500 MHz, CD2Cl2) δ: 8.25 (m, 2H, Ar), 7.13–7.05 (ov m, 3H, Ar), 1.24 (d, JHF = 5.0 Hz, 9H, t-Bu), 1.22 (d, JHF = 5.0 Hz, 9H, t-Bu); 13C[1H] NMR (125 MHz, CD2Cl2) δ: 218.2 (d, JCP = 40 Hz), 142.4 (d, JCP = 35 Hz), 133.1 (d, JCP = 2 Hz), 129.1 (d, JCP = 13 Hz), 128.6 (d, JCP = 32 Hz), 33.4 (d, JCP = 22 Hz), 30.5 (d, JCP = 13 Hz); 31P{1H} NMR (162 MHz, CD2Cl2) δ: 39.5. Anal. calc'd for C15H23OP (250.32 g mol⁻¹): C, 71.97; H, 9.26. Found: C, 71.98; H, 9.26.

**Synthesis of n-pentylC(O)OPPh2 (1d).** A mixture of hexanoyl chloride (100 mg, 0.74 mmol) and Ph2Pbin (232 mg, 0.74 mmol) in toluene (5 mL) was stirred for 4 hours at RT. Removal of solvent and ClPbin in vacuo afforded 1d as a colourless oil. Yield: 198 mg (94%). 1H NMR (400 MHz, CD2Cl2) δ: 7.45 (m, 4H, Ar), 7.04–6.99 (ov m, 6H, Ar), 2.33 (td, JHH = 7.3 Hz, JHF = 3.2 Hz, 2H, C(O)CH2), 1.46 (quint, JHH = 7.3 Hz, 2H, C(O)CH2CH3), 1.05–0.88 (ov m, 4H, 2 × CH2), 0.67 (t, JHH = 7.3 Hz, 3H, CH3); 13C[1H] NMR (100 MHz, CD2Cl2) δ: 221.4 (d, JCP = 41 Hz), 134.8 (d, JCP = 18 Hz), 133.3 (d, JCP = 8 Hz), 129.3, 128.6 (d, JCP = 45 Hz), 31.2, 24.0 (d, JCP = 4 Hz), 22.4, 13.8; 31P{1H} NMR (162 MHz, CD2Cl2) δ: 16.0. Anal. calc'd for C18H24OP (284.33 g mol⁻¹): C, 76.04; H, 7.44. Found: C, 75.55; H, 7.40.

**Synthesis of HCC(CH2)3OC(O)OPPh2 (1e).** A stirred toluene (1 mL) solution of propargylic chlorofominate (25 mg, 0.21 mmol) was added to a toluene (1 mL) solution of Ph2Pbin (66 mg, 0.21 mmol). The reaction was allowed to proceed for 18 h at RT at which point the solvent and ClPbin were removed in vacuo to afford 1e as a colourless oil. Yield: 54 mg (95%). 1H NMR (400 MHz, CD2Cl2) δ: 7.46 (m, 4H, Ar), 7.01–6.97 (ov m, 6H, Ar), 4.27 (d, JHH = 2.3 Hz, 2H, CH2), 1.83 (t, JHH = 2.3 Hz, 1H, C=CH2); 13C[1H] NMR (100 MHz, CD2Cl2) δ: 178.0 (d, JCP = 18 Hz), 134.6, (d, JCP = 19 Hz), 132.6 (d, JCP = 7 Hz), 129.5, 128.6 (d, JCP = 8 Hz), 77.6, 74.9, 51.8; 31P{1H} NMR (162 MHz, CD2Cl2) δ: –2.1. Anal. calc'd for C14H13O2P (268.25 g mol⁻¹): C, 71.64; H, 4.88. Found: C, 71.18; H, 4.96.

**Synthesis of PhC(O)BPbin(PPh3)2 (2a).** A mixture of benzoyl chloride (100 mg, 0.71 mmol) and Ph2Pbin (466 mg, 1.49 mmol) in toluene (3 mL) was heated at 110 °C for 5 days. Removal of solvent and ClPbin 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. 1H NMR (400 MHz, CD2Cl2) δ: 7.92 (m, 4H, Ar), 7.65 (m, 4H, Ar), 7.31 (d, JHH = 7.8 Hz, 2H, Ar), 7.04–6.94 (ov m, 7H, Ar), 6.89–6.85 (ov m, 6H, Ar), 6.81 (t, JHH = 7.3 Hz, 1H, Ar), 6.70 (t, JHH = 7.3 Hz, 1H, Ar), 0.70 (s, 12H, pin); 11B NMR (128 MHz, CD2Cl2) δ: 20 (br); 13C[1H] NMR (100 MHz, CD2Cl2) δ: 141.2 (d, JCP = 3 Hz), 136.9, (ov dd, JCP = 13, 12 Hz), 136.4 (ov dd, JCP = 7, 6 Hz), 135.7 (ov dd, JCP = 13, 12 Hz), 135.5 (ov dd, JCP = 5, 4 Hz), 128.9, 128.4, 127.9 (ov dd, JCP = 4, 3 Hz), 127.7 (ov dd, JCP = 5, 4 Hz), 127.5 (ov dd, JCP = 7, 6 Hz), 126.5, 125.6, 87.0 (t, JCP = 43 Hz), 82.3, 24.3; 31P{1H} NMR (162 MHz, CD2Cl2) δ: 15.0. Anal. calc'd for C37H37BO2P2 (602.45 g mol⁻¹): C, 73.77; H, 6.19. Found: C, 73.53; H, 6.24.

**Synthesis of PhC(O)BPbin(PPh3)2 (2b).** In a 20 mL vial, a solution of Ph2Pbin (61 mg, 0.2 mmol) was prepared in CH2Cl2 (3 mL). A solution of benzoyl chloride (14 mg, 0.1 mmol) in CH2Cl2 (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 CH2Cl2, decanted and washed with cold pentane (3 × 2 mL) to afford a colourless crystalline solid. Yield: 54 mg (90%); mp 143–145 °C. 1H NMR (500 MHz, CDCl3) 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); 11B[1H] NMR (128 MHz, CDCl3) δ: 21 (br); 13C[1H] NMR (125 MHz, CDCl3) δ: 147.7, 139.8 (t, JCP = 3 Hz), 136.2 (dt, JCP = 34 Hz, 12 Hz), 134.2 (t, JCP = 5 Hz), 134.3 (t, JCP = 6 Hz), 129.6, 129.1, 127.9 (dt, JCP = 6 Hz, 4 Hz), 127.0 (t, JCP = 7 Hz), 126.8, 126.0 (d, JCP = 1 Hz), 121.8, 111.6, 88.5 (t, JCP = 43 Hz); 31P{1H} NMR (162 MHz, CDCl3) δ: 12.3. Anal. calc'd for C37H37BO2P2 (594.38 g mol⁻¹): C, 74.77; H, 4.92. Found: C, 74.93; H, 4.88.
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Hz), 137.6 (d, J_CF = 18 Hz), 136.4 (d, J_CF = 11 Hz), 135.8 (d, J_CF = 11 Hz), 135.5 (d, J_CF = 18 Hz), 134.9 (d, J_CF = 20 Hz), 134.6 (d, J_CF = 20 Hz), 133.7 (d, J_CF = 19 Hz), 133.3 (d, J_CF = 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_CF = 34, 13 Hz), 126.0 (d, J_CF = 2 Hz), 82.9, 43.0 (dd, J_CF = 17, 8 Hz), 24.4, 24.0; 31P{1H} NMR (162 MHz, C6D6) 162 MHz, C6D6) δ: 7.2, -1.1. Anal. calcd for C30H39BO3P2 (628.48 g mol⁻¹): C, 74.53; H, 6.25. Found: C, 74.76; H, 6.34.

Synthesis of (η⁵-C₅H₅-Ni)(PhC(OBpin)(PPh₂)₂) (3a). To a stirred toluene (3 mL) solution of (η⁵-C₅H₅-Ni)Rh(η⁵-coe)₂ (100 mg, 0.23 mmol) was added a toluene (2 mL) solution of PhC(OBpin)(PPh₂)₂ (136 mg, 0.23 mmol). The reaction was heated at 100 °C 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 (η⁵-C₅H₅-Ni)Rh(η⁵-coe)₂ (PPh₂)₂ as an orange solid. Yield: 90 mg (48%); mp 171–173 °C. ¹H NMR (400 MHz, C6D6) δ: 7.92 (m, 4H, Ar), 7.66 (m, 4H, Ar), 7.39 (m, 2H, Ar), 7.24 (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_HH = 2.8 Hz, 1H, IND), 5.86 (d, J_HH = 2.8 Hz, 2H, IND), 0.72 (s, 12H, pin); ¹³B NMR (128 MHz, C6D6) δ: 20 (br); ¹³C{¹H} NMR (100 MHz, C6D6) δ: 137.7 (t, J_CF = 4 Hz), 135.9 (t, J_CF = 16 Hz), 135.4 (t, J_CF = 7 Hz), 135.3, (t, J_CF = 8 Hz), 134.6 (t, J_CF = 15 Hz), 129.0, 128.8, 128.0, 127.0 (t, J_CF = 5 Hz), 126.9 (t, J_CF = 5 Hz), 126.1 (br s, 2C), 120.7, 118.6, 114.4, 105.7 (t, J_CF = 17 Hz), 93.2 (d, J_CΦ = 5 Hz), 82.8, 71.6 (td, J_CF = 8 Hz, J_CΦ = 3 Hz), 24.2; ³¹P{¹H} NMR (162 MHz, C6D6) δ: 44.0 (d, J_PPh = 191 Hz). Anal. calcd for C₃₀H₄₀BO₃P₉R₉ (829.50 g mol⁻¹): C, 67.96; H, 5.36. Found: C, 67.96; H, 5.36.

X-Ray diffraction. Single crystals of 1b and 2b were grown from CH₂Cl₂ 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 SHELXL and an absorption correction applied using multi-scan within the APEX-2 or APEX-3 program. All structures were solved and refined by direct methods within the SHELXLT package. Crystallographic information for 1b, 2b, 2f, and 3a has also been deposited with the Cambridge Crystallographic Data Centre (CCDC 1984246–1984249).

Conclusions

Herein we have described the reactivity of phosphinoborinate esters Ph₂PBpin and Ph₂PBcat, 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. 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 declarations to conflict.

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Notes and references


