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Reactivity of the geminal phosphinoborane $tBu_2PCH_2BPh_2$ towards alkynes, nitriles, and nitrilium triflates†

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The reactivity of the geminal phosphinoborane $tBu_2PCH_2BPh_2$ towards terminal alkynes, nitriles and nitrilium salts is investigated. Terminal alkynes react *via* C–H bond splitting (deprotonation) resulting in the formation of phosphonium borates. In contrast, both nitriles and nitrilium salts undergo addition reactions resulting in the formation of five-membered heterocycles. All compounds were characterized by multinuclear NMR spectroscopy, and single-crystal X-ray structure determinations. Insight into the reaction mechanisms was gained by DFT calculations.

Introduction

Due to the seminal work of Stephan, Erker and co-workers,[1] phosphorus/boron-based frustrated Lewis pairs (FLP) are popular main-group systems that can activate a plethora of small molecules.[2] A sub-class of these FLPs are the pre-organised, geminal phosphinoboranes in which the donor and acceptor sites are separated by a C1-linker and therefore ideally oriented for capturing substrates.[3–9] Recently, the geminal frustrated Lewis pair $tBu_2PCH_2B(Fxyl)_2$ (Fxyl = 3,5-$(CF_3)_2C_6H_3$) was reported by Wagner *et al.* that reacts, amongst other substrates, with terminal alkynes *via* deprotonation to yield phosphonium alkynylborates **A**, and adds to the C≡N bond of acetonitrile to form the five-membered heterocycle **B** (Fig. 1).[10] Erker and co-workers synthesised three geminal phosphinoboranes bearing electron-withdrawing C_6F_5 substituents at both phosphorus and boron atoms that upon reaction with terminal alkynes solely afford the addition products **C–E** (Fig. 1).[11] We developed the non-fluorinated phosphinoborane $tBu_2PCH_2BPh_2$ **1** (Scheme 1) that despite the modest Lewis acidity of the boron moiety is still reactive and can heterolytically split H_2, and capture CO_2 and isocyanates.[12–14] Herein we expand on these studies by investigating the reactivity of **1** towards terminal alkynes,[15] nitriles,[16] and nitrilium salts,[17] and analysing the reaction profiles by DFT calculations.

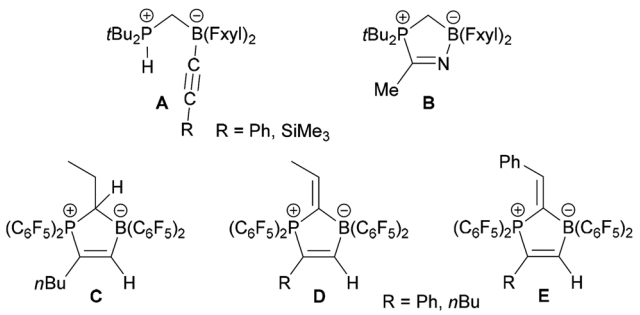

Fig. 1 Products resulting from the reaction of geminal P/B-based FLPs with terminal alkynes and nitriles.

Results and discussion

First, we investigated whether the geminal phosphinoborane $tBu_2PCH_2BPh_2$ **1** reacts with terminal alkynes *via* C–H bond splitting (deprotonation) or *via* P/B addition to the C≡C bond. Treatment of FLP **1** with 5 equiv. of phenyl- and *tert*-butylacetylene for, respectively, 3 and 17 hours at room temperature in toluene afforded **2a,b** as sole products that were isolated as colourless solids in 57% yield after work-up (**2a:** $\delta^{31}P$ = 53.5 ppm, $\delta^{11}B$ = −14.1 ppm, **2b:** $\delta^{31}P$ = 53.5 ppm, $\delta^{11}B$ = −14.5 ppm; Scheme 1). The large ^1J(P,H) coupling constants of **2a,b**

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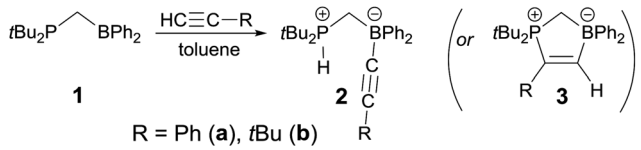
†Electronic supplementary information (ESI) available: Computational details. CCDC 1555966 (**2a**), 1555967 (**2b**), 1555968 (**4**), 1555969 (**5a**), 1557521 (**5b**), 1555970 (**5c**), 1555971 (**7a**), and 1555972 (**7b**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7dt02570j



Scheme 1 Reaction of FLP **1** with phenyl- and *tert*-butylacetylene.

(451.3 and 454.5 Hz, respectively) are characteristic for a P–H bond, indicating that FLP **1** selectively deprotonates terminal alkynes. The molecular structures of **2a**,**b**, obtained by single-crystal X-ray structure determinations (Fig. 2, top), confirm the formation of phosphonium alkynylborates **2a**,**b** that display typical B–C(22) and C≡C bond lengths of 1.5924(17) (**2a**), 1.5971(18) (**2b**) and 1.2091(18) (**2a**), 1.2053(18) Å (**2b**), respectively. To gain more insight into the reaction of **1** with terminal alkynes, we resorted to DFT calculations at the ωB97X-D/6-311G(d,p) level of theory.[18] This revealed in both cases the kinetic product (**2**) to be formed (ΔE = −15.3 (**2a**), −13.4 (**2b**) kcal mol^{-1}) instead of the more stable C≡C addition product **3** (ΔE (**3a**) = −45.2, ΔE (**3b**) = −38.0 kcal mol^{-1}; Scheme 1). Heating **2a** in refluxing *p*-xylene did not result in the formation of **3a**, indicating that the thermodynamically favoured C≡C adducts **3** are not accessible *via* this approach. The strongly Lewis basic phosphine moiety promotes facile deprotonation of the terminal alkyne and consequent addition of the remaining acetylide to boron, which is in agreement with longer reaction times being required when using the less acidic *tert*-butylacetylene (17 h, RT) compared to phenylacetylene (3 h, RT).

The reactions of **1** with internal alkynes, akin to many other P/B-based FLPs,[2,15b] were less productive.[19] For example, treatment of **1** with 20 equiv. of diphenylacetylene in toluene for 16 hours at 60 °C resulted in decomposition of **1** into many unidentifiable products,[20] while in the absence of substrate FLP **1** is stable.[21] Interestingly, the reaction of **1** with 20 equiv. of 3-hexyne in toluene for 16 h at 60 °C gave a similar result, but in this case also some colourless crystals of compound **4** ($\delta^{31}P\{^1H\}$ = 50.3 ppm, $\delta^{11}B$ = −8.8 ppm) precipitated from the reaction mixture. A crystal structure determination established unequivocally the formation of a phosphonium triphenylborate, which is the formal C–H activation product of benzene (Fig. 2, bottom left). The molecular structure of zwitterion **4** displays a cationic P fragment akin to **2a**,**b** and a borate moiety with three almost equal B–C(Ph) bond lengths (1.639(2), 1.643(2), 1.645(2) Å; Fig. 2, bottom). As P/B-based FLP **1** does not react with benzene (nor toluene) directly, the mechanism of formation of **4** is currently unresolved.

Next, we investigated if the moderately Lewis acidic **1** can, just like Wagner's geminal phosphinoborane tBu$_2$PCH$_2$B(Fxyl)$_2$,[10a] react with nitriles. Treatment of FLP **1** with 2 equiv. of benzo-, *tert*-butyl- and acetonitrile for 10 minutes at room temperature in toluene afforded heterocycles **5a–c** as sole products which were isolated as colourless solids in 74, 41, and 70% yield, respectively, after work-up (Scheme 2). The molecular structures of **5a-c** reveal the formation of the desired nitrile P,B addition products displaying typical P–C(22) (1.8835(13), 1.9194(2), 1.8689(14) Å, respectively) and C=N bond lengths (1.2623(17), 1.243(3), 1.2579(19) Å, respectively; Fig. 3).[10] Heating **5c** in refluxing toluene did not result in tautomerisation to the corresponding enamine.[22,23]

The ^{31}P and ^{11}B NMR chemical shifts of phenyl-substituted **5a** ($\delta^{31}P\{^1H\}$ = 85.2 ppm, $\delta^{11}B$ = 5.2 ppm) and methyl-substituted **5c** ($\delta^{31}P\{^1H\}$ = 76.7 ppm, $\delta^{11}B$ = 5.2 ppm) resemble the corresponding values reported for **B** ($\delta^{31}P$ = 81.1 ppm, $\delta^{11}B$ = 4.3 ppm; Fig. 1).[10] In contrast, *tert*-butyl-substituted **5b** displays a distinct, broad signal at $\delta^{31}P\{^1H\}$ = 43.3 ppm at room temperature together with a signal at $\delta^{11}B$ = 64.4 ppm that is characteristic of a tricoordinated diarylalkylborane (*cf.* **1**: $\delta^{31}P$ = 39.4 ppm, $\delta^{11}B$ = 72.3 ppm),[12] which indicates dynamic behaviour. Indeed, VT NMR spectroscopy at 50 °C showed sharp signals at $\delta^{31}P\{^1H\}$: 39.1 and $\delta^{11}B$: 69.8 ppm, confirming the presence of free FLP **1** in solution, while at −60 °C only resonances corresponding to the five-membered ring **5b** were

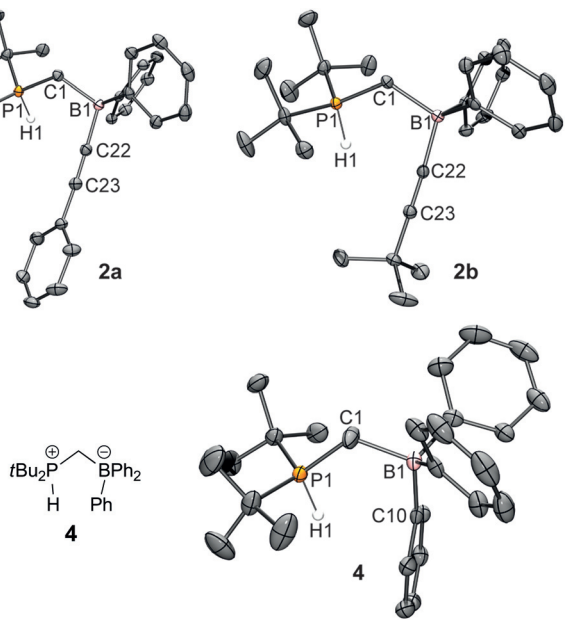
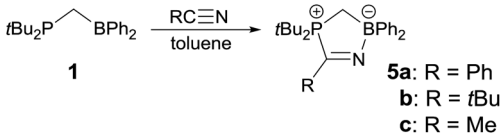


Fig. 2 Molecular structures of **2a**,**b** and **4** in the crystal (displacement ellipsoids are set at 50% probability; hydrogen atoms (except H1) are omitted for clarity). Selected bond lengths [Å], angles, and torsion angles [°] for **2a**: P1–C1 1.7871(12), C1–B1 1.6942(17), B1–C22 1.5924(17), C22–C23 1.2091(18); P1–C1–B1 114.83(8); P1–C1–B1–C22 −46.06(11). **2b**: P1–C1 1.7843(13), C1–B1 1.6948(19), B1–C22 1.5971(18), C22–C23 1.2053(18); P1–C1–B1 117.62(9); P1–C1–B1–C22–33.87(14). **4**: P1–C1 1.7804(16), C1–B1 1.697(2), B1–C10 1.639(2), B1–C16 1.643(2), B1–C22 1.645(2); P1–C1–B1 122.25(11); P1–C1–B1–C10 5.8(2).



Scheme 2 Reaction of FLP **1** with benzonitrile, *tert*-butylnitrile and acetonitrile.

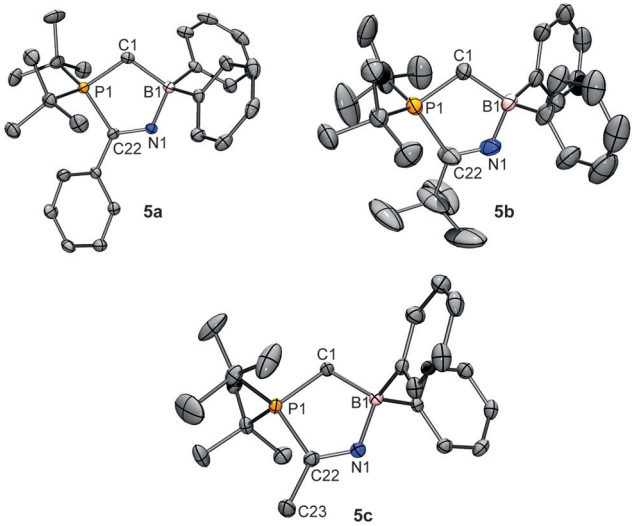


Fig. 3 Molecular structures of **5a–c** in the crystal (displacement ellipsoids are set at 50% probability; hydrogen atoms are omitted for clarity). Selected bond lengths [Å], angles, and torsion angles [°] for **5a**: P1–C1 1.7760(13), C1–B1 1.6856(19), B1–N1 1.5561(17), N1–C22 1.2623(17), C22–P1 1.8835(13); P1–C1–B1 106.31(8); B1–N1–C22–P1 −0.60(15). **5b**: P1–C1 1.7818(16), C1–B1 1.680(2), B1–N1 1.540(2), N1–C22 1.243(3), C22–P1 1.9194(18); P1–C1–B1 106.30(10); B1–N1–C22–P1 3.8(3). **5c**: P1–C1 1.7842(14), C1–B1 1.694(2), B1–N1 1.5586(18), N1–C22 1.2579(19), C22–P1 1.8689(14); P1–C1–B1 104.36(9); B1–N1–C22–P1 2.47(17).

observed ($\delta^{31}P\{^1H\}$ = 89.1 ppm, $\delta^{11}B$ = 4.3 ppm). Line-shape analysis using the Eyring equation (T_c = 0 °C) estimated a free enthalpy of activation of ΔG = 10.6 kcal mol^{-1} for the addition of *tert*-butylnitrile to FLP **1**.

To provide insight into the mode of activation of the three nitriles, we resorted again to DFT calculations at ωB97X-D/6-311G(d,p) level of theory.[18] Benzonitrile is delivered to the FLP cavity through van der Waals complex **vdW-5a** (ΔE = −8.6 kcal mol^{-1}), which converts into Lewis adduct **Int-5a** by N-coordination of PhCN to boron ($\Delta\Delta E_a$ = 8.9 kcal mol^{-1}, $\Delta\Delta E$ = 3.5 kcal mol^{-1}; Fig. 4). In the second step, the phosphine group of **Int-5a** attacks the electrophilic C atom of the coordinated nitrile[24] ($\Delta\Delta E_a$ = 2.4 kcal mol^{-1}, $\Delta\Delta E$ = −13.2 kcal mol^{-1}) affording **5a** with an overall exothermicity of −18.3 kcal mol^{-1}. Acetonitrile showed a similar reaction profile ($\Delta E_{overall}$ = −16.4 kcal mol^{-1}; see Fig. 4), yet *tert*-butylnitrile displays reduced reaction barriers (**vdW-5b**: ΔE = −6.1 kcal mol^{-1}, **Int-5b**: $\Delta\Delta E_a$ = 3.8 kcal mol^{-1}, $\Delta\Delta E$ = −0.5 kcal mol^{-1}; **5b**: $\Delta\Delta E_a$ = 1.8 kcal mol^{-1}, $\Delta\Delta E$ = −7.9 kcal mol^{-1}) and a modest exothermicity of −14.5 kcal mol^{-1}, which concurs with the experimentally observed dynamic behaviour of **5b**.

We were interested to see if blocking the nitrile lone pair would hamper the reaction with the geminal FLP **1**, for which we investigated the use of nitrilium salts as substrates. Treatment of FLP **1** with 0.95 equiv. of phenyl- and *tert*-butyl-substituted nitrilium triflate **6a,b**[17] for 10 minutes at room temperature in DCM afforded the cationic heterocycles **7a,b** that were isolated as pale yellow solids in 95 and 92% yield,

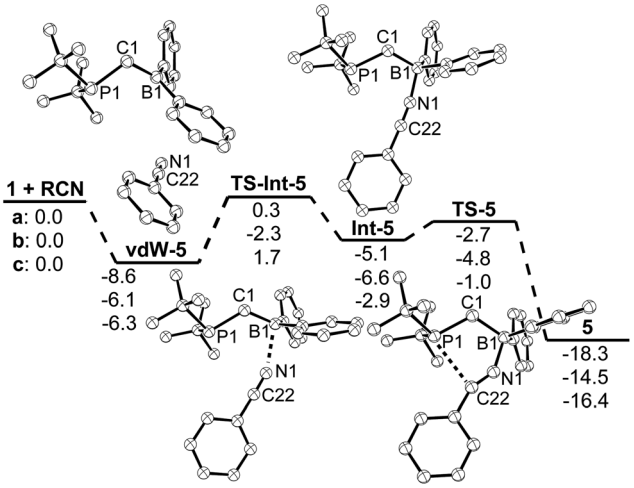
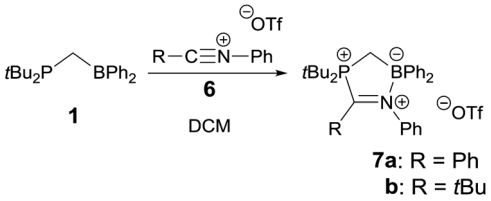


Fig. 4 Relative ωB97X-D/6-311G(d,p) energies (in kcal mol^{-1}) for the conversion of **1** into heterocycles **5a–c** (only the phenyl-substituted species **a** are shown; hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°] for **TS-Int-5a**: B1–N1 2.28753, N1–C22 1.14882; C1–B1–N1 101.729. **Int-5a**: B1–N1 1.59884, N1–C22 1.14378, P1–C22 3.42210; C1–B1–N1 104.935. **TS-5a**: B1–N1 1.59508, N1–C22 1.16268, P1–C22 2.69925; C1–B1–N1 102.594.

respectively (Scheme 3). The molecular structures of **7a,b** represent the formal phenyl cation adducts to the N-lone pair of **5a,b** (Fig. 5), which causes lengthening of the B1–N1 (1.667(5) (**7a**) *vs.* 1.5561(17) (**5a**), 1.663(2) (**7b**) *vs.* 1.540(2) Å (**5b**)) and



Scheme 3 Reaction of FLP **1** with nitrilium triflates **6a,b**.

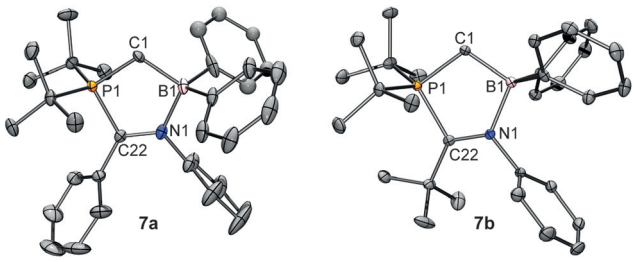


Fig. 5 Molecular structures of **7a** (only one conformation of the disordered phenyl group on boron is shown) and **7b** in the crystal (displacement ellipsoids are set at 50% probability; $[CF_3SO_3]^-$ counter ion, disordered solvent molecules, and hydrogen atoms are omitted for clarity). Selected bond lengths [Å], angles, and torsion angles [°] for **7a**: P1–C1 1.780(3), C1–B1 1.662(5), B1–N1 1.667(5), N1–C22 1.293(4), C22–P1 1.847(3); P1–C1–B1 109.1(2). **7b**: P1–C1 1.781(2), C1–B1 1.642(3), B1–N1 1.663(2), N1–C22 1.295(3), C22–P1 1.898(2); P1–C1–B1 109.78(13).

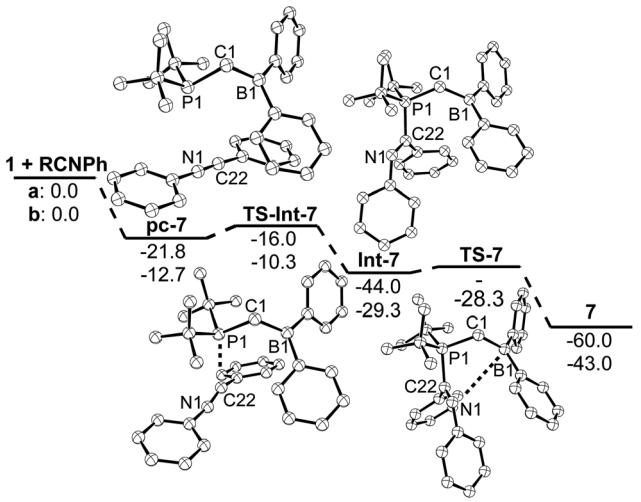


Fig. 6 Relative ωB97X-D/6-311G(d,p) energies (in kcal mol^{-1}) for the conversion of **1** into heterocycles **7a,b** (only the phenyl-substituted species **a** are shown; hydrogen atoms are omitted for clarity; $[CF_3SO_3]^-$ counter ion omitted in the calculations). Selected bond lengths [Å] angles [°] for **TS-Int-7a**: P1–C22 2.79126, N1–C22 1.16887; C1–P1–C22 118.440. **Int-7a**: P1–C22 1.87882, N1–C22 1.26719; C1–P1–C22 113.874, C1–P1–C22–N1 111.510. **TS-7a**: P1–C22 1.87349, N1–C22 1.26411, B1–N1 3.65952; C1–P1–C22 107.823, C1–P1–C22–N1 67.143.

C=N bonds (1.293(4) (**7a**) *vs.* 1.2623(17) (**5a**), 1.295(3) (**7b**) *vs.* 1.243(3) Å (**5b**)) and shortening of the P1–C22 bond (1.847(3) (**7a**) *vs.* 1.8835(13) Å (**5a**)), (1.898(2) (**7b**) *vs.* 1.9194(18) Å (**5b**)). Interestingly, the P1–C22 bond on **7b** (1.898(2) Å) is longer than the one of **7a** (1.847(3) Å), which is likely due to the difference in steric bulk of the substituent, and is also reflected in a different ^{31}P NMR chemical shift (**7a**: $\delta^{31}P\{^1H\}$ = 81.3 ppm, $\delta^{11}B$ = 9.0 ppm, **7b**: $\delta^{31}P\{^1H\}$ = 103.5 ppm, $\delta^{11}B$ = 9.3 ppm). Charge analysis revealed a decrease of electron density on nitrogen from **5a** to **7a** (−0.15 and 0.01 e, respectively), whereas only minor changes were observed for the other atoms in the ring.[25]

We resorted to DFT calculations to unravel the mode of activation (Fig. 6).[18] Again the substrate is delivered to the FLP cavity through a pre-complex (**pc-7a**: ΔE = −21.8 kcal mol^{-1}, **pc-7b**: ΔE = −12.7 kcal mol^{-1}), but in this case the reaction starts with nucleophilic attack of the phosphine at the nitrilium ion[24] forming imine-functionalised phosphonium salt **Int-7** as intermediate (see Fig. 6). Subsequent ring closure by N-coordination of the imine moiety to boron *via* an almost barrier-free transition affords the cationic heterocycles **7** (**7a**: $\Delta\Delta E_a$ = 0.0 kcal mol^{-1}, $\Delta\Delta E$ = −16.0 kcal mol^{-1}, **7b**: $\Delta\Delta E_a$ = 1.0 kcal mol^{-1}, $\Delta\Delta E$ = −13.7 kcal mol^{-1}; Fig. 6) with an overall exothermicity of −60.0 (**7a**) and −43.0 (**7b**) kcal mol^{-1}, respectively.

Conclusions

We have shown that the reaction of terminal alkynes with the geminal P/B-based FLP **1** resulted in the formation of the kinetic phosphonium alkynylborate product *via* C–H bond splitting, and that the thermodynamic C≡C addition product did not form. Addition of both nitriles and nitrilium ions to FLP **1** led instead to the five-membered heterocycles formed *via* a stepwise mechanism, as was supported by DFT calculations. We demonstrated that the geminal P/B-based FLP **1**, despite having a weakly Lewis acidic boron site is suitable for small molecule activation.

Experimental section

General procedures

All manipulations were carried out under an atmosphere of dry nitrogen, using standard Schlenk and drybox techniques. Solvents were purified, dried and degassed according to standard procedures.

^{1}H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker Avance 400 and internally referenced to the residual solvent resonances ($CDCl_3$: ^{1}H δ 7.26 ppm, $^{13}C\{^1H\}$ δ 77.16 ppm; CD_2Cl_2: ^{1}H δ 5.32 ppm, $^{13}C\{^1H\}$ δ 53.84 ppm). $^{31}P\{^1H\}$, ^{31}P, ^{11}B NMR spectra were recorded on a Bruker Avance 400 and externally referenced (85% H_3PO_4, $BF_3{\cdot}OEt_2$). ^{19}F NMR spectra were recorded on a Bruker Avance 250 and externally referenced ($CFCl_3$). Melting points were measured on samples in sealed capillaries and are uncorrected. High resolution mass spectra were recorded on a Bruker MicroTOF with ESI nebulizer. IR spectra were recorded in air on a Shimadzu FTIR-8400S.

FLP **1**,[12] (*N*-phenyl)(phenyl)carbonitrilium triflate and (*N*-phenyl)(*tert*-butyl)carbonitrilium triflate[17] were synthesized according to previous reported literature procedures. All other reagents were purchased from commercial resources and used without further purification.

Synthesis of 2a from 1 and phenylacetylene. Phenylacetylene (81.6 μL, 0.743 mmol, 5 equiv.) was added to a solution of **1** (48 mg, 0.149 mmol, 1 equiv.) in toluene (1 mL) at room temperature. After stirring for 3 hours, *n*-pentane (2 mL) was added, which resulted in the precipitation of white solids from the reaction mixture. Next, the solids were collected by filtration, washed with *n*-pentane (2 mL) and evaporated to dryness to afford **2a** as a white powder in 57% (36 mg, 0.084 mmol). X-ray quality crystals were obtained by cooling a saturated toluene solution of **2a** to −20 °C. Mp. (nitrogen, sealed capillary): 141–147 °C (decomp.). ^{1}H NMR (400.1 MHz, $CDCl_3$, 291 K): δ 7.66 (d, $^3J_{H,H}$ = 7.1 Hz, 4H; *o*-BPh*H*), 7.45 (br. d, $^3J_{H,H}$ = 7.0 Hz, 2H; *o*-CCPh*H*), 7.26 (br. t, $^3J_{H,H}$ = 7.4 Hz, 2H; *m*-CCPh*H*), 7.19 (t, $^3J_{H,H}$ = 7.5 Hz, 5H; *p*-CCPh*H* and *m*-BPh*H*), 7.04 (br. t, $^3J_{H,H}$ = 7.3 Hz, 2H; *p*-BPh*H*), 5.37 (dt, $^1J_{H,P}$ = 451.3 Hz, $^3J_{H,H}$ = 4.8 Hz, 1H; P*H*), 1.34 (dd, $^2J_{H,P}$ = 12.7 Hz, $^3J_{H,H}$ = 4.8 Hz, 2H; CH_2), 1.20 (d, $^3J_{H,P}$ = 15.2 Hz, 18H; C(CH_3)$_3$). ^{11}B NMR (128.4 MHz, $CDCl_3$, 291 K): δ −14.1 (s). $^{13}C\{^1H\}$ NMR (101.6 MHz, $CDCl_3$, 292 K): δ 156.9 (br. s; *ipso*-BPh*C*), 133.6 (s; *o*-BPh*C*), 131.4 (s; *o*-CCPh*C*), 128.1 (s; *m*-CCPh*C*), 127.4 (s; BC*C*Ph), 127.1 (s; *m*-BPh*C*), 126.1 (s; *p*-CCPh*C*), 124.3 (s; *p*-BPh*C*), 100.1 (br. s; *ipso*-CCPh*C*), 31.7 (d, $^1J_{C,P}$ = 37.2 Hz; *C*(CH$_3$)$_3$), 28.0 (s; C(*C*H$_3$)$_3$), 7.4 (br. s; *C*H$_2$), the signal for B*C*CPh was unresolved. ^{31}P NMR (162.0 MHz, $CDCl_3$, 291 K): δ 53.5 (m, $^1J_{P,H}$ = 451.3 Hz,

$^{3}J_{P,H}$ = 15.1 Hz). HR-MS (ESI): 425.2594 [**2a** − H]$^{-}$. Calcd for $C_{29}H_{35}BP^{-}$ 425.2575. IR (cm^{-1}): 3057 (w), 2992 (m), 2967 (m), 2913 (w), 2357 (m), 1813 (w), 1596 (m), 1474 (s), 1429 (m), 1269 (s), 1227 (m), 1182 (m), 1152 (m), 1096 (m), 1069 (m), 1026 (m), 961 (w), 943 (s), 922 (m), 903 (m), 851 (m), 835 (s), 814 (m), 787 (m), 736 (s), 704 (s).

Synthesis of 2b from 1 and *tert*-butylacetylene. *tert*-Butylacetylene (100.6 μL, 0.817 mmol, 5 equiv.) was added to a solution of **1** (53 mg, 0.163 mmol, 1 equiv.) in toluene (1 mL) at room temperature. After stirring for 17 hours, *n*-pentane (2 mL) was added, which resulted in the precipitation of white solids from the reaction mixture. Next, the solids were collected by filtration, washed with *n*-pentane (2 mL) and evaporated to dryness to give **2b** as a white powder in 57% (38 mg, 0.092 mmol). X-ray quality crystals were obtained by cooling a solution of **2b** in toluene and pentane (1 : 1 ratio) to −20 °C. Mp. (nitrogen, sealed capillary): 111–125 °C (decomp.). ^{1}H NMR (400.1 MHz, $CDCl_3$, 293 K): δ 7.66 (d, $^{3}J_{H,H}$ = 7.1 Hz, 4H; *o*-BPh*H*), 7.17 (t, $^{3}J_{H,H}$ = 7.4 Hz, 4H; *m*-BPh*H*), 7.02 (br. t, $^{3}J_{H,H}$ = 7.2 Hz, 2H; *p*-BPh*H*), 5.45 (dt, $^{1}J_{H,P}$ = 454.5 Hz, $^{3}J_{H,H}$ = 4.8 Hz, 1H; P*H*), 1.35 (s, 9H; CCC(CH_3)$_3$), 1.24 (br. d, $^{3}J_{H,P}$ = 15.1 Hz, 20H; PC(CH_3)$_3$ and CH_2). ^{11}B NMR (128.4 MHz, $CDCl_3$, 291 K): δ −14.5 (s). ^{13}C{^{1}H} NMR (101.6 MHz, $CDCl_3$, 293 K): δ 158.1 (br. s; *ipso*-Ph*C*), 133.5 (s; *o*-BPh*C*), 126.9 (s; *m*-BPh*C*), 123.9 (s; *p*-BPh*C*), 109.0 (s; BCC*C*(CH$_3$)$_3$), 32.5 (s; BCCC(*C*H$_3$)$_3$), 31.4 (d, $^{1}J_{C,P}$ = 37.3 Hz; P*C*(CH$_3$)$_3$), 28.4 (s; BC*C*C(CH$_3$)$_3$), 28.0 (d, $^{2}J_{C,P}$ = 1.0 Hz; PC(*C*H$_3$)$_3$), 7.2 (br. s; *C*H$_2$), the signal for B*C*CC(CH$_3$)$_3$ was unresolved. ^{31}P NMR (162.0 MHz, $CDCl_3$, 293 K): δ 53.5 (m, $^{1}J_{P,H}$ = 454.5 Hz, $^{3}J_{P,H}$ = 14.7 Hz). HR-MS (ESI):405.2886 [**2b** − H]$^{-}$. Calcd for $C_{27}H_{39}BP^{-}$ 405.2888. IR (cm^{-1}): 3055 (w), 2965 (m), 2866 (w), 1738 (w), 1464 (m), 1429 (m), 1371 (m), 1356 (m), 1260 (m), 1204 (m), 1186 (m), 1134 (m), 1094 (m), 1065 (m), 1032 (m), 991 (m), 916 (m), 878 (m), 835 (s), 814 (m), 779 (m), 731 (s), 702 (s).

Heating 1 in the presence of diphenylacetylene. Heating **1** (27 mg, 0.08 mmol, 1 equiv.) and diphenylacetylene (100 mg, 1.67 mmol, 20 equiv.) in toluene (0.6 mL) to 60 °C for 16 h resulted in the precipitation of crystals and oil. Analysis of the solution by ^{31}P{^{1}H}, ^{11}B and ^{1}H spectroscopy showed that FLP **1** was still present and many unidentifiable products were observed. Analysis of the oil and crystals, after washing with *n*-pentane and removing all volatiles *in vacuo*, by ^{31}P{^{1}H}, ^{11}B and ^{1}H spectroscopy showed great similarities to the NMR spectra of the reaction of **1** with 3-hexyne.

Heating 1 in the presence of 3-hexyne. *Protocol 1*: Heating **1** (50 mg, 0.154 mmol) in 3-hexyne (1 mL) to 60 °C for 16 h resulted in the precipitation of some crystals and oil. Analysis of the solution by ^{31}P{^{1}H} and ^{11}B spectroscopy showed many unidentifiable products. Analysis of the oil and crystals, after washing with *n*-pentane and removing all volatiles, by ^{31}P{^{1}H}, ^{11}B and ^{1}H spectroscopy in $CDCl_3$ showed fewer signals, yet too many to allow full characterisation. *Protocol 2*: Heating **1** (72 mg, 0.222 mmol) in toluene (1.1 mL) and 3-hexyne (0.5 mL, 20 equiv.) for 16 h resulted in the precipitation of crystals and oil. Analysis of the solution by ^{31}P{^{1}H} and ^{11}B spectroscopy showed that FLP **1** was still present in solution, together with many unidentifiable products. Analysis of the oil and crystals, after washing with *n*-pentane and removing all volatiles, by ^{31}P{^{1}H}, ^{11}B and ^{1}H spectroscopy showed the signals given below. Analysis of the crystals by X-ray crystallography revealed a product containing an extra phenyl group on boron and an additional hydrogen at the phosphorus atom (see Fig. 2, bottom), as if C–H activation of benzene had occurred. ^{1}H NMR (400.1 MHz, $CDCl_3$, 291 K): δ 7.46 (d, $^{3}J_{H,H}$ = 7.1 Hz, 4H; *o*-Ph*H*), 7.14 (t, $^{3}J_{H,H}$ = 7.4 Hz, 4H; *m*-Ph*H*), 7.00 (t, $^{3}J_{H,H}$ = 7.3 Hz, 2H; *p*-Ph*H*), 4.48 (dt, $^{1}J_{H,P}$ = 445.7 Hz, $^{3}J_{H,H}$ = 5.4 Hz, 1H; P*H*), 1.68 (dd, $^{2}J_{H,P}$ = 14.6 Hz, $^{3}J_{H,H}$ = 5.4 Hz, 2H; CH_2), 1.11 (d, $^{3}J_{H,P}$ = 15.2 Hz, 18H; C(CH_3)$_3$). ^{11}B NMR (128.4 MHz, $CDCl_3$, 291 K): δ −8.8 (s). ^{31}P{^{1}H} NMR (162.0 MHz, $CDCl_3$, 291 K): δ 50.3 (s).

Thermal stability of 1. **1** (20 mg) was added to a J Young NMR tube, dissolved in toluene-d_8 (0.5 mL) and heated to 110 °C for 96 h, which resulted in the precipitation of some white solids. The solvent was removed and the residue was dissolved in $CDCl_3$, which indicated that **1** is thermally stable under these conditions. At various times, ^{1}H, ^{11}B{^{1}H} and ^{31}P{^{1}H} NMR were measured, for further details see the ESI.†

Synthesis of 5a from 1 and benzonitrile. Benzonitrile (32 μL, 0.310 mmol, 2 equiv.) was added to a solution of **1** (50.3 mg, 0.155 mmol, 1 equiv.) in toluene (1 mL) at room temperature. After stirring for 10 minutes, *n*-pentane (2 mL) was added, which resulted in the precipitation of white solids from the reaction mixture. The solids were collected by filtration, subsequently washed with *n*-pentane (2 mL) and evaporated to dryness to give **5a** as a white powder in 74% (49 mg, 0.114 mmol). X-ray quality crystals were obtained by cooling a saturated toluene solution of **5a** to −20 °C. Mp. (nitrogen, sealed capillary): 145–177 °C (decomp.). ^{1}H NMR (400.1 MHz, $CDCl_3$, 291 K): δ 7.83 (br. d, $^{3}J_{H,H}$ = 6.2 Hz, 2H; *o*-NCPh*H*), 7.58 (br. d, $^{3}J_{H,H}$ = 7.4 Hz, 4H; *o*-BPh*H*), 7.52–7.44 (m, 3H; *m*-NCPh*H* and *p*-NCPh*H*), 7.20 (t, $^{3}J_{H,H}$ = 7.4 Hz, 4H; *m*-BPh*H*), 7.05 (br. t, $^{3}J_{H,H}$ = 7.2 Hz, 2H; *p*-BPh*H*), 1.50 (d, $^{2}J_{H,P}$ = 9.6 Hz, 2H; CH_2), 1.27 (d, $^{3}J_{H,P}$ = 14.1 Hz, 18H; C(CH_3)$_3$). ^{11}B NMR (128.4 MHz, $CDCl_3$, 291 K): δ 5.2 (s). ^{13}C{^{1}H} NMR (101.6 MHz, $CDCl_3$, 291 K): δ 157.9 (br. s; *ipso*-BPh*C*), 150.4 (d, $^{1}J_{C,P}$ = 5.5 Hz; N*C*Ph), 140.1 (d, $^{2}J_{C,P}$ = 49.4 Hz; *ipso*-NCPh*C*), 132.0 (s; *o*-BPh*C*), 129.6 (s; Ar-NCPh*C*), 128.8 (s; Ar-NCPh*C*), 128.6 (s; *o*-NCPh*C*), 127.1 (s; *m*-BPh*C*), 124.0 (s; *p*-BPh*C*), 34.8 (d, $^{1}J_{C,P}$ = 20.7 Hz; *C*(CH$_3$)$_3$), 28.7 (s; C(*C*H$_3$)$_3$), 12.9 (br. s; *C*H$_2$). ^{31}P{^{1}H} NMR (162.0 MHz, $CDCl_3$, 291 K): δ 85.2 (s). HR-MS (ESI): 325.2237 [**5a** + H − benzonitrile]$^{+}$. Calcd for $C_{21}H_{31}BP^{+}$ 325.2251. Only protonated **1** is observed, not adduct **5a**. IR (cm^{-1}): 3059 (m), 2996 (m), 2974 (m), 2928 (m), 1736 (w), 1593 (m), 1576 (w), 1470 (m), 1443 (m), 1429 (m), 1397 (m), 1370 (m), 1300 (m), 1265 (w), 1215 (m), 1177 (m), 1161 (m), 1140 (m), 1080 (m), 1057 (m), 1001 (m), 930 (s), 903 (m), 870 (s), 810 (m), 768 (s), 741 (s).

Synthesis of 5b from 1 and *tert*-butylnitrile. *tert*-Butylnitrile (69.5 μL, 0.629 mmol, 2 equiv.) was added to a solution of **1** (102 mg, 0.315 mmol, 1 equiv.) in toluene (2 mL) at room temperature. After stirring for 10 minutes, *n*-pentane (4 mL) was added and the mixture was cooled to below −20 °C, which resulted in the precipitation of white solids from the reaction mixture. The solids were collected by filtration, subsequently

washed with *n*-pentane (2 mL) and evaporated to dryness to give **5b** as a white powder in 41% (53 mg, 0.129 mmol). X-ray quality crystals were grown by cooling a solution of toluene and pentane (1 : 1 ratio) to 4 °C. Mp. (nitrogen, sealed capillary): 94–115 °C (decomp.). The NMR spectra were recorded with a concentration of 0.04 g ml^{-1} as the shifts are temperature, concentration and solvent dependent. Analysis of **5b** at room temperature in $CDCl_3$, toluene-d_8 and benzene-d_6 resulted in a shift of the peak in $^{31}P\{^1H\}$ and ^{11}B NMR. ^1H NMR (400.1 MHz, $CDCl_3$, 293 K): δ 7.83–7.75 (m, 4H; *o*-BPh*H*), 7.47–7.37 (m, 6H; *m*-BPh*H* and *p*-BPh*H*), 2.06 (d, $^2J_{H,P}$ = 5.8 Hz; 2H; CH_2), 1.39 (s, 9H; NCC(CH_3)$_3$), 1.15 (d, $^3J_{H,P}$ = 11.1 Hz, 18H; PC(CH_3)$_3$). ^{11}B NMR (128.4 MHz, $CDCl_3$, 293 K): δ 64.4 (s). $^{13}C\{^1H\}$ NMR (101.6 MHz, $CDCl_3$, 294 K): δ 144.8 (br. s; *ipso*-Ph*C*), 136.1 (d, $^1J_{C,P}$ = 2.6 Hz; NC*C*(CH_3)$_3$), 130.4 (s; *o*-BPh*C*), 127.6 (s; *m*-BPh*C*), 125.4 (s; *p*-BPh*C*), 32.5 (d, $^1J_{C,P}$ = 21.6 Hz; P*C*(CH$_3$)$_3$), 29.8 (d, $^2J_{C,P}$ = 12.6 Hz; PC(*C*H$_3$)$_3$), 28.9 (s; NCC(*C*H$_3$)$_3$), 129.2 (s; NC*C*(CH$_3$)$_3$), 19.2 (br. s; *C*H$_2$). $^{31}P\{^1H\}$ NMR (162.0 MHz, $CDCl_3$, 293 K): δ 43.3 (br. s). HR-MS: (ESI): 325.2237 [**5b** + H − *tert*-butylnitrile]$^+$. Calcd for $C_{21}H_{31}BP^+$ 325.2251. Only protonated **1** is observed, not adduct **5b**. IR (cm^{-1}): 3059 (w), 2967 (m), 1618 (w), 1462 (m), 1429 (m), 1371 (m), 1261 (m), 1175 (m), 1142 (m), 1084 (m), 1030 (m), 928 (s), 868 (s), 812 (m), 752 (m), 739 (s).

Synthesis of 5c from 1 and acetonitrile. Acetonitrile (24.2 μL, 0.464 mmol, 2 equiv.) was added to a solution of **1** (75 mg, 0.231 mmol, 1 equiv.) in toluene (1.5 mL) at room temperature. After stirring for 10 minutes, *n*-pentane (3 mL) was added, which resulted in the precipitation of white solids from the reaction mixture. The solids were collected by filtration, subsequently washed with *n*-pentane (2 mL) and evaporated to dryness to give **5c** as a white powder in 70% (59 mg, 0.163 mmol). X-ray quality crystals were obtained by cooling a saturated toluene solution of **5c** to −20 °C. Mp. (nitrogen, sealed capillary): 120–148 °C (decomp.). ^1H NMR (400.1 MHz, $CDCl_3$, 293 K): δ 7.46 (d, $^3J_{H,H}$ = 7.1 Hz, 4H; *o*-Ph*H*), 7.14 (t, $^3J_{H,H}$ = 7.4 Hz, 4H; *m*-Ph*H*), 7.00 (t, $^3J_{H,H}$ = 7.3 Hz, 2H; *p*-Ph*H*), 2.57 (d, $^3J_{H,P}$ = 4.9 Hz, 3H; NCC*H*$_3$), 1.26 (br. d, $^3J_{H,P}$ = 13.8 Hz, 20H; PC(CH_3)$_3$ and CH_2). ^{11}B NMR (128.4 MHz, $CDCl_3$, 293 K): δ 5.2 (s). $^{13}C\{^1H\}$ NMR (101.6 MHz, $CDCl_3$, 293 K): δ 157.8 (br. s; *ipso*-Ph*C*), 147.5 (d, $^1J_{C,P}$ = 10.1 Hz; N*C*CH$_3$), 131.9 (s; *o*-Ph*C*), 127.0 (s; *m*-Ph*C*), 123.9 (s; *p*-Ph*C*), 33.6 (d, $^1J_{C,P}$ = 23.0 Hz; P*C*(CH$_3$)$_3$), 28.4 (s; PC(*C*H$_3$)$_3$), 27.0 (d, $^2J_{C,P}$ = 47.4 Hz; NC*C*H$_3$), 10.8 (br. s; *C*H$_2$). $^{31}P\{^1H\}$ NMR (162.0 MHz, $CDCl_3$, 293 K): δ 76.7 (s). HR-MS (ESI, in DCM/MeCN): 366.2522 [**5c** + H]$^+$. Calcd for $C_{23}H_{33}BNP^+$ 366.2516. IR (cm^{-1}): 3061 (w), 2965 (m), 1634 (m), 1468 (m), 1431 (m), 1375 (m), 1275 (m), 1180 (m), 1144 (m), 1119 (m), 1076 (m), 1051 (m), 1026 (m), 893 (m), 870 (s), 851 (m), 816 (m), 797 (m), 750 (s), 737 (s), 704 (s).

Synthesis of 7a from 1 and (*N*-phenyl)(phenyl)carbonitrilium triflate. DCM (4 mL) was added to a mixture of **1** (148 mg, 0.456 mmol, 1 equiv.) and (*N*-phenyl)(phenyl)carbonitrilium triflate (144.0 mg, 0.437 mmol, 0.95 equiv.) and the reaction mixture was stirred for 10 minutes at room temperature. *n*-Pentane (10 mL) was added, which resulted in the precipitation of white solids that were collected by filtration, washed with *n*-pentane (2 mL) and evaporated to dryness to afford **7a** as a yellow solid in 95% (254 mg, 0.401 mmol). X-ray quality crystals were obtained by layering a DCM solution of **7a** with *n*-pentane at room temperature. Mp. (nitrogen, sealed capillary): 110–130 °C (decomp.). ^1H NMR (400.1 MHz, CD_2Cl_2, 294 K): δ 7.48–7.40 (m, 3H; *p*-CPh*H*, *o*-CPh*H* or *m*-CPh*H*), 7.34–7.26 (m, 2H; *o*-CPh*H* or *m*-CPh*H*), 7.21–7.16 (m, 6H *p*-BPh*H*, *o*-BPh*H* or *m*-BPh*H*), 7.13 (t, *J* = 7.5 Hz, 1H; *p*-NPh*H*), 7.09–7.04 (m, 4H; *o*-CPh*H* or *m*-CPh*H*), 7.04–6.95 (m, 2H; *m*-NPh*H*), 6.54 (d, *J* = 7.8 Hz, 2H; *o*-NPh*H*), 2.18 (d, $^2J_{H,P}$ = 11.1 Hz, 2H; CH_2), 1.49 (d, $^3J_{H,P}$ = 16.8 Hz, 18H; C(CH_3)$_3$). ^{11}B NMR (128.4 MHz, CD_2Cl_2, 293 K): δ 9.0 (s). $^{13}C\{^1H\}$ NMR (101.6 MHz, CD_2Cl_2, 293 K): δ 179.8 (d, $^1J_{C,P}$ = 53.0 Hz; PhN*C*Ph), 148.2 (br. s; *ipso*-BPh*C*), 143.7 (d, $^3J_{C,P}$ = 9.9 Hz; *ipso*-NPh*C*), 133.9 (s; Ar*C*), 133.6 (s; Ar*C*), 132.1 (d, *J* = 12.1 Hz; Ar*C*), 130.9 (s; ArC), 130.6 (s; *p*-NPh*C*), 129.5 (s; *m*-NPh*C*), 128.4–128.2 (m; ArC), 127.6 (s; Ar*C*), 126.3 (s; *o*-NPh*C*), 121.4 (q, $^1J_{C,F}$ = 321.2 Hz; *C*F$_3$), 39.0 (d, $^1J_{C,P}$ = 25.4 Hz; *C*(CH$_3$)$_3$), 28.6 (s; C(*C*H$_3$)$_3$), 7.7 (s; *C*H$_2$). ^{19}F NMR (235.4 MHz, CD_2Cl_2, 292 K): δ −78.8 (s). $^{31}P\{^1H\}$ NMR (162.0 MHz, CD_2Cl_2, 293 K): δ 81.3 (s). HR-MS (ESI): 504.3000 [**7a**]. Calcd for $C_{34}H_{40}BNP^+$ 504.2986. IR (cm^{-1}): 3013 (w), 1738 (w), 1485 (m), 1470 (m), 1429 (w), 1368 (w), 1263 (m), 1227 (m), 1167 (m), 1142 (s), 1080 (m), 1030 (s), 1005 (m), 916 (m), 874 (m), 826 (m), 775 (m), 741 (m), 704 (m).

Synthesis of 7b from 1 and (*N*-phenyl)(*tert*-butyl)carbonitrilium triflate. DCM (4 mL) was added to a mixture of **1** (149 mg, 0.460 mmol, 1 equiv.) and (*N*-phenyl)(*tert*-butyl)carbonitrilium triflate (135.0 mg, 0.436 mmol, 0.95 equiv.) and the reaction mixture was stirred for 10 minutes at room temperature. Upon addition of *n*-pentane (10 mL), white solids precipitated, which were collected by filtration, washed with *n*-pentane (2 mL) and evaporated to dryness to give **7b** as a yellow solid in 92% (254 mg, 0.401 mmol). X-ray quality crystals were obtained by layering a DCM solution of **7b** with *n*-pentane at room temperature. Mp. (nitrogen, sealed capillary): 102–106 °C (decomp.). ^1H NMR (400.1 MHz, CD_2Cl_2, 293 K): δ 7.19 (br. t, $^3J_{H,H}$ = 7.5 Hz, 1H; *p*-NPh*H*), 7.14–7.01 (m, 8H; *m*-BPh*H*, *p*-BPh*H* and *m*-NPh*H*), 6.96–6.86 (m, 4H; *o*-BPh*H*), 6.66 (d, $^3J_{H,H}$ = 7.8 Hz, 2H; *o*-NPh*H*), 1.96 (d, $^2J_{H,P}$ = 11.6 Hz, 2H; CH_2), 1.63 (d, $^3J_{H,P}$ = 17.0 Hz, 18H; PC(CH_3)$_3$), 1.41 (s, 9H; NCC(CH_3)$_3$). ^{11}B NMR (128.4 MHz, CD_2Cl_2, 293 K): δ 9.3 (s). $^{13}C\{^1H\}$ NMR (101.6 MHz, CD_2Cl_2, 293 K): δ 193.3 (d, $^1J_{C,P}$ = 30.0 Hz; PhN*C*C(CH$_3$)$_3$), 147.8 (br. s; *ipso*-BPh*C*), 142.6 (d, $^3J_{C,P}$ = 12.1 Hz; *ipso*-NPh*C*), 134.1 (s; *o*-BPh*C*), 129.9 (s; *p*-NPh*C*), 128.5 (s; *m*-NPh*C*), 127.7 (s; *m*-BPh*C* or *p*-BPh*C*), 127.3 (s; *m*-BPh*C* or *p*-BPh*C*), 125.2 (s; *o*-NPh*C*), 121.4 (q, $^1J_{C,F}$ = 321.2 Hz; *C*F$_3$), 43.2 (d, $^2J_{C,P}$ = 12.2 Hz; *quat*-NC*C*(CH$_3$)$_3$), 42.5 (d, $^1J_{C,P}$ = 19.7 Hz; *quat*-P*C*(CH$_3$)$_3$), 32.4 (d, $^3J_{C,P}$ = 1.9 Hz; NCC(*C*H$_3$)$_3$), 30.0 (d, $^2J_{C,P}$ = 1.1 Hz; PC(*C*H$_3$)$_3$), 8.6 (br. s; *C*H$_2$). ^{19}F NMR (235.4 MHz, CD_2Cl_2, 292 K): δ −78.9 (s). $^{31}P\{^1H\}$ NMR (162.0 MHz, CD_2Cl_2, 293 K): δ 103.5 (s). HR-MS (ESI): 484.3299 [**7b**]. Calcd for $C_{32}H_{44}BNP^+$ 484.3299. IR (cm^{-1}): 2972 (w), 1738 (w), 1485 (m), 1373 (w), 1263 (s), 1223 (m), 1140 (s), 1032 (s), 995 (m), 939 (m), 876 (m), 816 (m), 768 (m), 741 (s), 702 (s).

X-ray crystal structure determination

The single-crystal X-ray diffraction studies were carried out on a Bruker D8 Venture diffractometer with Photon100 detector at 123(2) K using Cu-Kα radiation (**2a**, **4**, **5a**, **5c**, λ = 1.54178 Å) or Mo-Kα radiation (**2b**, **7a**, **7b**, λ = 0.71073 Å). Direct Methods (SHELXS-97)[26] were used for structure solution and refinement was carried out using SHELXL-2014 (full-matrix least-squares on F^2).[27] Hydrogen atoms were localized by difference electron density determination and refined using a riding model (H(P)). Semi-empirical absorption corrections were applied. For **2b**, **5a** and **7b** an extinction correction was applied. The absolute structure of **7a** and **7b** were determined by refinement of Parsons' *x*-parameter.[28] In **7a** the solvent CH_2Cl_2, the triflate anion and one phenyl group were disordered (for details see cif-file). For **5b** 71 268 reflections were measured on a Bruker Kappa ApexII diffractometer with sealed tube and Triumph monochromator (λ = 0.71073 Å) at a temperature of 150(2) K up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.81 Å^{-1}. Intensities were integrated with the EVAL15 software.[29] Multi-scan absorption correction and scaling was performed with SADABS[30] (correction range 0.71–0.75). 10 849 reflections were unique (R_{int} = 0.020), of which 9694 were observed [$I > 2\sigma(I)$]. The structure was solved with Patterson superposition methods using SHELXT.[31] Least-squares refinement was performed with SHELXL-2014[27] against F^2 of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. Hydrogen atoms at C1 were located in difference Fourier maps and refined freely with isotropic displacement parameters. All other hydrogen atoms were introduced in calculated positions and refined with a riding model. Geometry calculations and checking for higher symmetry were performed with the PLATON program.[32]

2a. Colourless crystals, $C_{29}H_{36}BP$, M_r = 426.36, crystal size 0.20 × 0.15 × 0.06 mm, orthorhombic, space group *Pbca* (no. 61), *a* = 16.9924(6) Å, *b* = 16.5973(5) Å, *c* = 17.5163(6) Å, *V* = 4940.1(3) Å^3, *Z* = 8, ρ = 1.147 Mg m^{-3}, μ(Cu-K$_\alpha$) = 1.061 mm^{-1}, *F*(000) = 1840, $2\theta_{max}$ = 144.4°, 39 211 reflections, of which 4859 were independent (R_{int} = 0.032), 284 parameters, R_1 = 0.034 (for 4380 $I > 2\sigma(I)$), wR_2 = 0.095 (all data), *S* = 1.03, largest diff. peak/hole = 0.326/−0.334 e Å^{-3}.

2b. Colourless crystals, $C_{27}H_{40}BP$, M_r = 406.37, crystal size 0.24 × 0.12 × 0.06 mm, triclinic, space group $P\bar{1}$ (no. 2), *a* = 10.0726(4) Å, *b* = 11.0362(4) Å, *c* = 12.2129(4) Å, α = 88.259(1)°, β = 69.614(1)°, γ = 78.174(1)°, *V* = 1244.34(8) Å^3, *Z* = 2, ρ = 1.085 Mg m^{-3}, μ(Mo-K$_\alpha$) = 0.121 mm^{-1}, *F*(000) = 444, $2\theta_{max}$ = 55.0°, 21 399 reflections, of which 5620 were independent (R_{int} = 0.037), 266 parameters, R_1 = 0.041 (for 4651 $I > 2\sigma(I)$), wR_2 = 0.096 (all data), *S* = 1.06, largest diff. peak/hole = 0.324/−0.342 e Å^{-3}.

4. Colourless crystals, $C_{27}H_{36}BP$, M_r = 402.34, crystal size 0.24 × 0.08 × 0.06 mm, orthorhombic, space group *Pbca* (no. 61), *a* = 17.3762(6) Å, *b* = 15.4228(5) Å, *c* = 17.5727(6) Å, *V* = 4709.3(3) Å^3, *Z* = 8, ρ = 1.135 Mg m^{-3}, μ(Cu-K$_\alpha$) = 1.083 mm^{-1}, *F*(000) = 1744, $2\theta_{max}$ = 144.4°, 53 352 reflections, of which 4637 were independent (R_{int} = 0.040), 266 parameters, R_1 = 0.040 (for 4137 $I > 2\sigma(I)$), wR_2 = 0.108 (all data), *S* = 1.02, largest diff. peak/hole = 0.492/−0.291 e Å^{-3}.

5a. Colourless crystals, $C_{28}H_{35}BNP$, M_r = 427.35, crystal size 0.18 × 0.14 × 0.06 mm, monoclinic, space group $P2_1/c$ (no. 14), *a* = 8.1447(2) Å, *b* = 16.6623(4) Å, *c* = 17.5476(4) Å, β = 91.644(1)°, *V* = 2380.4(1) Å^3, *Z* = 4, ρ = 1.192 Mg m^{-3}, μ(Cu-K$_\alpha$) = 1.115 mm^{-1}, *F*(000) = 920, $2\theta_{max}$ = 144.2°, 27 593 reflections, of which 4666 were independent (R_{int} = 0.032), 281 parameters, R_1 = 0.035 (for 4261 $I > 2\sigma(I)$), wR_2 = 0.090 (all data), *S* = 1.04, largest diff. peak/hole = 0.313/−0.319 e Å^{-3}.

5b. Colourless block, $C_{26}H_{39}BNP$, M_r = 407.36, crystal size 0.38 × 0.33 × 0.32 mm^3, monoclinic, *Cc* (no. 9), *a* = 11.4364(4), *b* = 14.5007(5), *c* = 14.8879(6) Å, β = 93.698(2) °, *V* = 2463.80(16) Å^3, *Z* = 4, D_x = 1.098 g cm^{-3}, μ = 0.12 mm^{-1}. 279 parameters were refined with 11 restraints (distances, angles and displacement parameters of the *tert*-butyl groups). $R1/wR_2$ [$I > 2\sigma(I)$]: 0.0440/0.1205. $R1/wR_2$ [all refl.]: 0.0501/0.1258. *S* = 1.032. Flack parameter[28] *x* = 0.015(9). Residual electron density between −0.29 and 0.48 e Å^{-3}.

5c. Colourless crystals, $C_{23}H_{33}BNP$, M_r = 365.28, crystal size 0.16 × 0.08 × 0.04 mm, monoclinic, space group $P2_1/c$ (no. 14), *a* = 8.4981(5) Å, *b* = 18.4460(11) Å, *c* = 13.8292(8) Å, β = 96.972(2)°, *V* = 2151.8(2) Å^3, *Z* = 4, ρ = 1.128 Mg m^{-3}, μ(Cu-K$_\alpha$) = 1.150 mm^{-1}, *F*(000) = 792, $2\theta_{max}$ = 144.2°, 17 000 reflections, of which 4219 were independent (R_{int} = 0.031), 236 parameters, R_1 = 0.041 (for 3682 $I > 2\sigma(I)$), wR_2 = 0.111 (all data), *S* = 1.02, largest diff. peak/hole = 0.343/−0.252 e Å^{-3}.

7a. Colourless crystals, $C_{34}H_{40}BNP^+\cdot CF_3O_3S^-\cdot CH_2Cl_2$, M_r = 738.44, crystal size 0.34 × 0.30 × 0.20 mm, orthorhombic, space group $P2_12_12_1$ (no. 19), *a* = 11.0882(5) Å, *b* = 17.6065(7) Å, *c* = 18.5479(9) Å, *V* = 3621.0(3) Å^3, *Z* = 4, ρ = 1.355 Mg m^{-3}, μ(Mo-K$_\alpha$) = 0.333 mm^{-1}, *F*(000) = 1544, $2\theta_{max}$ = 55.2°, 157 311 reflections, of which 8349 were independent (R_{int} = 0.044), 414 parameters, 151 restraints, R_1 = 0.054 (for 7827 $I > 2\sigma(I)$), wR_2 = 0.135 (all data), *S* = 1.02, largest diff. peak/hole = 0.947/−0.705 e Å^{-3}, *x* = −0.003(9).

7b. Colourless crystals, $C_{32}H_{44}BNP^+\cdot CF_3O_3S^-$, M_r = 633.53, crystal size 0.36 × 0.22 × 0.18 mm, monoclinic, space group *Cc* (no. 9), *a* = 13.6317(8) Å, *b* = 11.9518(8) Å, *c* = 19.7278(13) Å, β = 101.210(2)°, *V* = 3152.8(3) Å^3, *Z* = 4, ρ = 1.335 Mg m^{-3}, μ(Mo-K$_\alpha$) = 0.206 mm^{-1}, *F*(000) = 1344, $2\theta_{max}$ = 55.2°, 63 370 reflections, of which 7264 were independent (R_{int} = 0.028), 389 parameters, 2 restraints, R_1 = 0.027 (for 7090 $I > 2\sigma(I)$), wR_2 = 0.068 (all data), *S* = 1.06, largest diff. peak/hole = 0.313/−0.187 e Å^{-3}, *x* = −0.015(11).

Conflicts of interest

There are no conflicts to declare.

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20 Very few crystals and some oil precipitated in this case too, beside the formation of many soluble, unidentifiable products. The NMR spectra of these crystals and oil showed great similarities to the ones obtained using 3-hexyne, see the Experimental section for further details.

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