Reactivity of the geminal phosphinoborane tBu2PCH2BPh2 towards alkynes, nitriles, and nitrilium triflates


DOI
10.1039/c7dt02570j

Publication date
2017

Document Version
Final published version

Published in
Dalton Transactions

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Citation for published version (APA):
Reactivity of the geminal phosphinoborane \( \text{tBu}_2\text{PCH}_2\text{BPh}_2 \) towards alkynes, nitriles, and nitrilium triflates†

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The reactivity of the geminal phosphinoborane \( \text{tBu}_2\text{PCH}_2\text{BPh}_2 \) 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 \( \text{tBu}_2\text{PCH}_2\text{B(Fxyl)}_2 \) (Fxyl = 3,5-(CF3)2C6H3) was reported by Wagner et al.10 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 C6F5 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 \( \text{tBu}_2\text{PCH}_2\text{BPh}_2 \) (Scheme 1) that despite the modest

Results and discussion

First, we investigated whether the geminal phosphinoborane \( \text{tBu}_2\text{PCH}_2\text{BPh}_2 \) 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: \( \delta^{13}\text{P} = 53.5 \text{ ppm} \), \( \delta^{11}\text{B} = -14.1 \text{ ppm} \), 2b: \( \delta^{13}\text{P} = 53.5 \text{ ppm} \), \( \delta^{11}\text{B} = -14.5 \text{ ppm} \); Scheme 1). The large \( J(P,H) \) coupling constants of 2a,b
Selected bond lengths [Å], angles, and torsion angles are shown for clarity. Selected bond lengths [Å], angles, and torsion angles are set at 50% probability; hydrogen atoms (except H1) are omitted for clarity.

For 2a: P1–C1 1.787(12), B1–C1 1.694(2), B1–C2 1.592(17), C22–C23 1.299(18); P1–C1–B1 1.148(3), P1–C1–C2 1.246(9). P1–C1–B1 1.262(9), P1–C1–C2 1.243(3), P1–C1–C22 1.258(9). P1–C1–B1 1.177(9), B1–C22 1.635(2), B1–C22 1.645(2), P1–C1–B1 1.225(11), P1–C1–B1 1.587(12).
observed (δ\textsuperscript{1}H = 89.1 ppm, δ\textsuperscript{11}B = 4.3 ppm). Line-shape analysis using the Eyring equation (T\textsubscript{c} = 0 °C) estimated a free enthalpy of activation of ΔG = 10.6 kcal mol\textsuperscript{-1} for the addition of tert-butyl-nitrile to FLP 1.

To provide insight into the mode of activation of the three nitriles, we resorted again to DFT calculations at oB97X-D/6-311G(d,p) level of theory.\textsuperscript{18} Benzonitrile is delivered to the FLP cavity through van der Waals complex vdW-5a (ΔE = −8.6 kcal mol\textsuperscript{-1}), which converts into Lewis adduct Int-5a by N-coordination of PhCN to boron (ΔΔE = 8.9 kcal mol\textsuperscript{-1}, ΔΔE = 3.5 kcal mol\textsuperscript{-1}; Fig. 4). In the second step, the phosphine group of Int-5a attacks the electrophilic C atom of the coordinated nitrile\textsuperscript{24} (ΔΔE = 2.4 kcal mol\textsuperscript{-1}, ΔΔE = −13.3 kcal mol\textsuperscript{-1}) affording 5a with an overall exothermicity of −18.3 kcal mol\textsuperscript{-1}. Acetonitrile showed a similar reaction profile (ΔE\textsubscript{overall} = −16.4 kcal mol\textsuperscript{-1}; see Fig. 4), yet tert-butyl-nitrile displays reduced reaction barriers (vdW-5b: ΔE = −6.1 kcal mol\textsuperscript{-1}, Int-5b: ΔΔE = 3.8 kcal mol\textsuperscript{-1}, ΔΔE = −0.5 kcal mol\textsuperscript{-1}; 5b: ΔΔE = 1.8 kcal mol\textsuperscript{-1}, ΔΔE = −7.9 kcal mol\textsuperscript{-1}) and a modest exothermicity of −14.5 kcal mol\textsuperscript{-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 nitrilum salts as substrates. Treatment of FLP 1 with 0.95 equiv. of phenyl- and tert-butyl-substituted nitrilum triflate 6a,b\textsuperscript{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, 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) Å (7a) vs. 1.556(17) Å (5a), 1.663(2) Å (7b) vs. 1.540(2) Å (5b)) and

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**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 1.776(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).

**Fig. 4** Relative oB97X-D/6-311G(d,p) energies (in kcal mol\textsuperscript{-1}) for the conversion of 1 into heterocycles 5a–c (only the phenyl-substituted species 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, C1–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.

**Scheme 3** Reaction of FLP 1 with nitrilum 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\textsubscript{3}SO\textsubscript{3}]\textsuperscript{−} counter ion, disordered solvent molecules, and hydrogen atoms are omitted for clarity). Selected bond lengths [Å], angles, 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), C1–N1 1.295(3), 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).
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.

1H and 31P{1H} NMR spectra were recorded on a Bruker Avance 400 and internally referenced to the residual solvent resonances (CDCl3: 1H δ 7.26 ppm, 31P{1H} δ 16.0 ppm; CD2Cl2: 1H δ 5.32 ppm, 31P{1H} δ 53.84 ppm). 1H, 31P, 1B NMR spectra were recorded on a Bruker Avance 400 and externally referenced (85% H2PO4, BF3·OEt2). 31P NMR spectra were recorded on a Bruker Avance 250 and externally referenced (CFCl3). 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 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 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.). 1H NMR (400.1 MHz, CDCl3, 291 K): δ 7.66 (d, J_{H,H} = 7.1 Hz, 4H; o-BPhH), 7.45 (br. d, J_{H,H} = 7.0 Hz, 2H; o-CPhH), 7.26 (br. t, J_{H,H} = 7.4 Hz, 2H; m-CPhH), 7.19 (t, J_{H,H} = 7.5 Hz, 5H; p-CPhH and m-BPhH), 7.04 (br. t, J_{H,H} = 7.3 Hz, 2H; p-BPhH), 5.37 (dt, J_{H,P} = 451.3 Hz, J_{H,H} = 4.8 Hz, 1H; PhH), 1.34 (dd, J_{H,P} = 12.7 Hz, J_{H,H} = 4.8 Hz, 2H; CH3), 1.20 (d, J_{H,P} = 15.2 Hz, 18H; C(CH3)3). 31B NMR (128.4 MHz, CDCl3, 291 K): δ −14.1 (s). 13C{1H} NMR (101.6 MHz, CDCl3, 292 K): δ 156.9 (br. s; o-BPhC), 133.6 (s; o-BPhC), 131.4 (s; o-CPhC), 128.1 (s; m-CPhC), 127.4 (s; BCPhC), 127.1 (s; m-BPhC), 126.1 (s; p-CPhC), 124.3 (s; p-BPhC), 100.1 (br. s; ipso-CPhC), 31.7 (d, J_{C,P} = 37.2 Hz; C(CH3)3), 28.0 (s; C(CH3)3), 7.4 (br. s; CH3), the signal for BCPhC was unresolved. 31P NMR (162.0 MHz, CDCl3, 291 K): δ 53.5 (m, J_{P,H} = 451.3 Hz, ...
The synthetic procedure was as follows: 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.

Thermal stability of 1. 1 (20 mg) was added to a J Young NMR tube, dissolved in toluene-\textsubscript{d}6 (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\textsubscript{3}, which indicated that 1 is thermally stable under these conditions. At various times, \(^1\text{H}, \(^{11}\text{B}\) and \(^{31}\text{P}\) 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.

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 \(^{31}\text{P}\)\(^{1}\text{H}\), \(^{11}\text{B}\) and \(^{1}\text{H}\) 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 \(^{31}\text{P}\)\(^{1}\text{H}\), \(^{11}\text{B}\) and \(^{1}\text{H}\) 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 \(^{31}\text{P}\)\(^{1}\text{H}\) and \(^{11}\text{B}\) spectroscopy showed many unidentifiable products. Analysis of the oil and crystals, after washing with n-pentane and removing all volatiles, by \(^{31}\text{P}\)\(^{1}\text{H}\), \(^{11}\text{B}\) and \(^{1}\text{H}\) spectroscopy in CDCl\textsubscript{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 \(^{31}\text{P}\)\(^{1}\text{H}\) and \(^{11}\text{B}\) 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 \(^{31}\text{P}\)\(^{1}\text{H}\), \(^{11}\text{B}\) and \(^{1}\text{H}\) 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. \(^{1}\text{H}\) NMR (400.1 MHz, CDCl\textsubscript{3}, 291 K): δ 7.46 (d, \(^{3}\text{J}_{\text{HH}} = 7.4\) Hz, 4H; o-Ph\textsubscript{H}], 7.14 (t, \(^{3}\text{J}_{\text{HH}} = 7.4\) Hz, 4H; m-Ph\textsubscript{H}], 7.00 (t, \(^{3}\text{J}_{\text{HH}} = 7.3\) Hz, 2H; p-Ph\textsubscript{H}], 4.48 (dt, \(^{3}\text{J}_{\text{HP}} = 455.7\) Hz, \(^{3}\text{J}_{\text{HP}} = 5.4\) Hz, 1H; Ph\textsubscript{P}]), 1.68 (dd, (d, \(^{3}\text{J}_{\text{HP}} = 14.6\) Hz, \(^{3}\text{J}_{\text{HP}} = 5.4\) Hz, 2H; CH\textsubscript{3}], 1.11 (d, \(^{3}\text{J}_{\text{HP}} = 15.2\) Hz, 18H; C(CH\textsubscript{3}])\textsubscript{3}]. \(^{11}\text{B}\) NMR (128.4 MHz, CDCl\textsubscript{3}, 291 K): δ −8.8 (s). \(^{31}\text{P}\)\(^{1}\text{H}\) NMR (162.0 MHz, CDCl\textsubscript{3}, 291 K): δ 50.3 (s).
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 0.4 g ml⁻¹ as the shifts are temperature, concentration and solvent dependent. Analysis of 5b at room temperature in CDCl₃, toluene-δ₈ and benzene-δ₆ resulted in a shift of the peak in ¹³C[¹H] NMR. ¹H NMR (400.1 MHz, CDCl₃, 293 K): δ 7.83–7.75 (m, 4H; o-Ph-PHF), 7.47–7.37 (m, 6H; m-Ph-PHF and p-Ph-PHF), 2.06 (d, J_H,P = 5.8 Hz; 2H; CH₅), 1.39 (s, 9H; NCC(CH₃)₃), 1.15 (d, J_H,P = 11.1 Hz, 18H; PC(CH₃)₃). ¹¹B NMR (128.4 MHz, CDCl₃, 293 K): δ 64.4 (s). ¹³C[¹H] NMR (101.6 MHz, CDCl₃, 294 K): δ 144.8 (br. s; ipso-PhC), 136.1 (d, J_C,P = 2.6 Hz; NCC(CH₃)₃), 130.4 (s; o-Ph-PHF), 127.6 (s; m-Ph-PHF), 125.4 (s; p-Ph-PHF), 32.5 (d, J_C,P = 21.6 Hz; PC(CH₃)₃), 29.8 (d, J_C,P = 12.6 Hz; PC(CH₃)₃), 28.9 (s; NCC(CH₃)₃), 129.2 (s; NCC(CH₃)₃), 19.2 (br. s; CH₅). ³¹P[¹H] NMR (162.0 MHz, CDCl₃, 293 K): δ 29.5 (s; C(CH₃)₃), 23.5 (s; C(CH₃)₃), 17.6 (s; C(CH₃)₃), 2.18 (d, J_H,P = 16.8 Hz, 18H; C(CH₃)₃). ¹¹B NMR (128.4 MHz, CDCl₃, 293 K): δ 9.0 (s). ¹³C[¹H] NMR (101.6 MHz, CDCl₃, 293 K): δ 179.8 (d, J_C,P = 53.0 Hz; PhNCP), 148.2 (br. s; ipso-PhC), 143.7 (d, J_C,P = 9.9 Hz; ipso-PhC), 133.9 (s; ArC), 133.6 (s; ArC), 132.1 (d, J = 12.1 Hz; ArC), 130.9 (s; ArC), 130.6 (s; p-Ph-PHF), 129.5 (s; m-Ph-PHF), 128.4–128.2 (m; ArC), 127.6 (s; ArC), 126.3 (s; o-Ph-PHF), 121.4 (q, J_C,P = 321.2 Hz; CF₃), 39.0 (d, J_C,P = 25.4 Hz; C(CH₃)₃), 28.6 (s; C(CH₃)₃), 7.7 (s; CH₅). ¹³P NMR (235.4 MHz, CDCl₃, 292 K): δ −78.8 (s). ³¹P[¹H] NMR (162.0 MHz, CDCl₃, 293 K): δ 81.3 (s). HR-MS (ESI): 504.3000 [7a]. Calcd for C₄₃H₃₂BP⁺: 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 7a from 1 and (N-phenyl)(phenyl)carbonitri- tri triflate. DCM (4 mL) was added to a mixture of 1 (149 mg, 0.460 mmol, 1 equiv.) and (N-phenyl)(phenyl)carbonitril 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 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, CD₂Cl₂, 294 K): δ 7.48–7.40 (m, 3H; p-Ph-PHF, o-Ph-PHF or m-Ph-PHF), 7.34–7.26 (m, 2H; o-Ph-PHF or m-Ph-PHF), 7.21–7.16 (m, 6H p-Ph-PHF, o-Ph-PHF or m-Ph-PHF), 7.13 (t, J = 7.5 Hz, 1H; p-NPh), 7.09–7.04 (m, 4H; o-Ph-PHF or m-Ph-PHF), 7.04–6.95 (m, 2H; n-NPh), 6.54 (d, J = 7.8 Hz, 2H; o-NPh), 2.18 (d, J_H,P = 11.1 Hz, 2H; CH₅), 1.49 (d, J_H,P = 16.8 Hz, 18H; C(CH₃)₃). ¹³B NMR (128.4 MHz, CD₂Cl₂, 293 K): δ 9.0 (s). ¹³C[¹H] NMR (101.6 MHz, CD₂Cl₂, 293 K): δ 179.8 (d, J_C,P = 53.0 Hz; PhNCP), 148.2 (br. s; ipso-PhC), 143.7 (d, J_C,P = 9.9 Hz; ipso-PhC), 133.9 (s; ArC), 133.6 (s; ArC), 132.1 (d, J = 12.1 Hz; ArC), 130.9 (s; ArC), 130.6 (s; p-Ph-PHF), 129.5 (s; m-Ph-PHF), 128.4–128.2 (m; ArC), 127.6 (s; ArC), 126.3 (s; o-Ph-PHF), 121.4 (q, J_C,P = 321.2 Hz; CF₃), 39.0 (d, J_C,P = 25.4 Hz; C(CH₃)₃), 28.6 (s; C(CH₃)₃), 7.7 (s; CH₅). ¹³P NMR (235.4 MHz, CD₂Cl₂, 292 K): δ −78.8 (s). ³¹P[¹H] NMR (162.0 MHz, CD₂Cl₂, 293 K): δ 81.3 (s). HR-MS (ESI): 504.3000 [7a]. Calcd for C₄₃H₃₂BP⁺: 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).

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Dalton Transactions

Paper

Dalton Trans., 2017, 46, 12284–12291 | 12289
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 (2α, 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 R2).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 CH2Cl2, 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 Triumphi monochromator (λ = 0.71073 Å) at a temperature of 150(2) K up to a resolution of (sin θ/λ)max = 0.81 Å⁻¹. Intensities were integrated with the EVAL15 software.29 Multi-scan absorption correction and scaling was performed with SADABS30 (correction range 0.71–0.75). 10 849 reflections were unique (Rint = 0.020), of which 9694 were observed [I > 2σ(I)]. The structure was solved with Patterson superposition methods using SHELXT.31 Least-squares refinement was performed with SHELXL-201427 against F² 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, C26H32BP, Mₚ = 426.36, crystal size 0.20 × 0.15 × 0.06 mm, orthorhombic, space group Pbcn (no. 61), a = 16.9924(6) Å, b = 16.5973(5) Å, c = 17.5163(6) Å, V = 4940.1(3) Å³, Z = 8, ρ = 1.147 Mg m⁻³, μ(Cu-Kα) = 1.061 mm⁻¹, F(000) = 1840, 2θmax = 144.4°, 39 211 reflections, of which 4666 were independent (Rint = 0.035), 281 parameters, R1 = 0.035 (for 4261 I > 2σ(I)), wR2 = 0.090 (all data), S = 1.04, largest diff. peak/hole = 0.313/−0.319 e Å⁻³.

5a. Colourless crystals, C28H33BNP, Mₚ = 473.35, crystal size 0.18 × 0.14 × 0.06 mm, monoclinic, space group P2₁/c (no. 14), a = 8.1447(2) Å, b = 16.6623(4) Å, c = 17.5474(6) Å, β = 91.644(1)°, V = 2380.41(3) Å³, Z = 4, ρ = 1.192 Mg m⁻³, μ(Cu-Kα) = 1.115 mm⁻¹, F(000) = 920, 2θmax = 144.2°, 27 593 reflections, of which 4666 were independent (Rint = 0.032), 281 parameters, R1 = 0.035 (for 4261 I > 2σ(I)), wR2 = 0.090 (all data), S = 1.04, largest diff. peak/hole = 0.313/−0.319 e Å⁻³.

5b. Colourless block, C26H32BP, Mₚ = 407.36, crystal size 0.38 × 0.33 × 0.32 mm³, 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) Å³, Z = 4, Dx = 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/wR2 [I > 2σ(I)]: 0.0440/0.1205. R1/wR2 [all refl.]: 0.0501/0.1258. S = 1.032. Flack parameter28 x = 0.015(9). Residual electron density between −0.29 and 0.48 e Å⁻³.

5c. Colourless crystals, C29H36BP, Mₚ = 365.28, crystal size 0.16 × 0.08 × 0.04 mm, monoclinic, space group P2₁/c (no. 14), a = 8.4981(5) Å, b = 18.4460(11) Å, c = 13.8292(8) Å, β = 96.972(2)°, V = 2151.82(3) Å³, Z = 4, ρ = 1.128 Mg m⁻³, μ(Mo-Kα) = 1.150 mm⁻¹, F(000) = 792, 2θmax = 144.2°, 17 000 reflections, of which 4219 were independent (Rint = 0.031), 236 parameters, R1 = 0.041 (for 3682 I > 2σ(I)), wR2 = 0.111 (all data), S = 1.02, largest diff. peak/hole = 0.343/−0.252 e Å⁻³.

7a. Colourless crystals, C23H33BNP·CF3O2S·CH2Cl2, Mₚ = 738.44, crystal size 0.34 × 0.30 × 0.20 mm, orthorhombic, space group P2₁₂₁₂₁ (no. 19), a = 11.0882(5) Å, b = 17.6065(7) Å, c = 18.5479(9) Å, V = 3621.0(3) Å³, Z = 4, ρ = 1.355 Mg m⁻³, μ(Mo-Kα) = 0.333 mm⁻¹, F(000) = 1544, 2θmax = 55.2°, 157 311 reflections, of which 8349 were independent (Rint = 0.044), 414 parameters, 151 restraints, R1 = 0.054 (for 7827 I > 2σ(I)), wR2 = 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, C23H32BNP·CF3O2S⁻, Mₚ = 633.53, crystal size 0.36 × 0.22 × 0.18 mm, monoclinic, space groupCc (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) Å³, Z = 4, ρ = 1.335 Mg m⁻³, μ(Mo-Kα) = 0.206 mm⁻¹, F(000) = 1344, 2θmax = 55.2°, 63 370 reflections, of which 7264 were independent (Rint = 0.028), 389 parameters, 2 restraints, R1 = 0.027 (for 7090 I > 2σ(I)), wR2 = 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.

Acknowledgements

This work was supported by the Council for Chemical Sciences of The Netherlands Organization for Scientific Research
(NWO/CW) by a VIDI grant (J.C.S.) and benefitted from interactions within the COST Action CM1205 CARISMA (Catalytic Routines for Small Molecule Activation).

Notes and references


18 J.-D. Chai and M. Head-Gordon, *Phys. Chem. Chem. Phys.*, 2008, **10**, 6615–6620. DFT calculations were carried out with Gaussian09 (Revision D.01); see the ESI† for further details.

19 Note that the geminal PhSCH2B(C6F5)2 and [C6F5]2PC (=CHPh)B(C6F5)2 does react with internal alkynes, see: ref. 9 and 11a, respectively.

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.

21 Heating 1 in toluene-δ6 for 96 h to 110 °C indicated good thermal stability. For further details, see the experimental section and ESI†.

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23 Refluxing a mixture of MeCN (9.7 μL, 0.185 mmol) and 1 (60 mg, 0.185 mmol) in toluene (1 mL) led to decomposition of the major species 5c and the formation of many unidentifiable products.  
25 Charge analysis (Voronoi Deformation Density) was performed at BP86/TZ2P using ADF2016.102, for further details see the ESI; † J. A. Rombouts, A. W. Ehlers and K. Lammertsma, J. Comput. Chem., 2017, 38, 1811–1818.  