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Borata–alkene derivatives conveniently made by frustrated Lewis pair chemistry†

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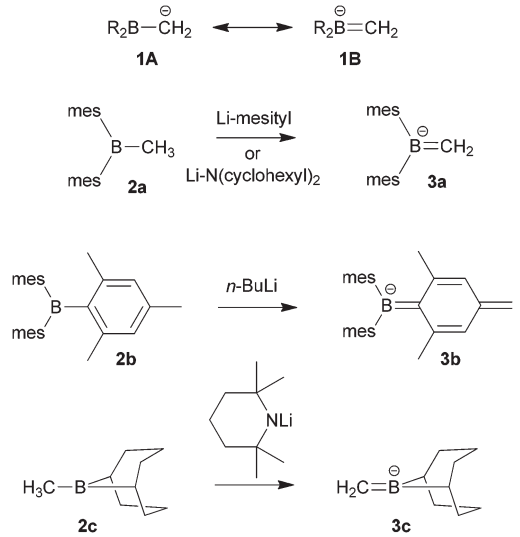
Two (aryl)PXY starting materials (aryl = mesityl or 2,4,6-triisopropylphenyl; X,Y = Cl, Br) were reacted with lithiated conjugated enynes (derived from 2-methylbutenyne or 1-ethynylcyclohexene) to yield the respective (aryl)bis(enynyl)phosphanes. Their reaction with $HB(C_6F_5)_2$ gave the heterocyclic five-membered zwitterionic borata–diene compounds containing the aryl group and one unchanged enynyl substituent at phosphorus. The borata–alkene products were thought to arise from a two step process of regioselective alkyne hydroboration followed by an internal phosphane attack on the boryldiene unit. Three examples of the ring-closed borata–alkene type products were characterized by X-ray diffraction.

Introduction

Borylcarbanions (**1A**) feature a strong structural interaction between the electron-surplus carbon atom and the electron-deficient boron atom. This situation has been described by the borata–alkene resonance form (**1B**). Borata–alkene derivatives[1–9] can in principle be generated by α-deprotonation of suitable neutral borane precursors. However, in many cases a simple Lewis acid/Lewis base adduct formation is favoured and prevents the borata–alkene synthesis. Some notable exceptions are listed in Scheme 1.[7,8] They constitute examples where exceptional steric bulk has apparently made competing adduct formation less favourable.

Berndt *et al.* had described alternative entries to borata–alkenes *via* methyleneborane derivatives. The synthesis of the 1,3-diborata–allene system **4d** is a typical example (see Scheme 2).[9]

We have recently found a unique new synthetic entry to stable borata–alkene derivatives[10] utilizing frustrated Lewis pair (FLP) chemistry.[11] Treatment of *e.g.* the diphenylphosphino substituted conjugated enyne derivative **5** with Piers' borane $[HB(C_6F_5)_2]$[12] (120 °C) gave a product mixture from which the zwitterionic phosphonium/borata–diene compound



Scheme 1

7 was obtained as the main product (see Scheme 3). We assume that compound **7** was formed *via* the intermediate FLP **6** formed by alkyne hydroboration. Ring-closure by internal conjugate addition of the phosphane nucleophile to the boryldiene moiety would then directly lead to the observed product **7**.[10]

We have now found that this new reaction pathway to stable, isolable cyclic phosphonium/borata–diene derivatives is more widely applicable to other types of phosphanyl-substituted enyne systems. We here wish to present some interesting new examples illustrating this recent development.

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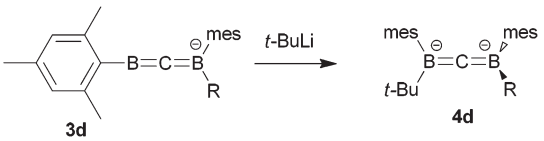
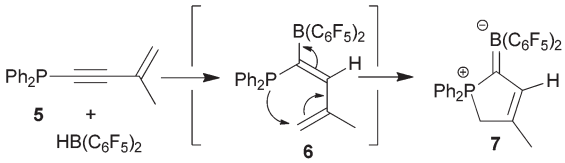
‡X-ray crystal structure analyses.



Scheme 2



Scheme 3

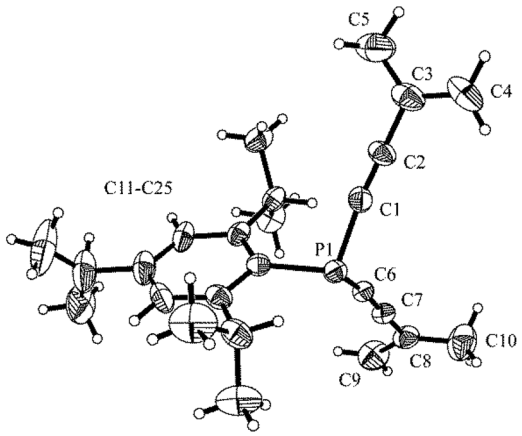


Fig. 1 Molecular structure of compound **10a** (thermal ellipsoids are shown with 30% probability).

Results and discussion

For this study, we prepared a small series of aryl-bis(enynyl)-phosphanes. We used two different bulky aryl groups, namely mesityl (mes) and 2,4,6-triisopropylphenyl (tipp). The reaction of dimesitylmagnesium with PCl_3 gave $mesPCl_2$ that was actually admixed with *ca.* 17% of mesPBrCl and traces of $mesPBr_2$, apparently originating from halide exchange with residual $MgBr_2$. $TippPCl_2$ was similarly prepared and it also contained the bromide derivatives. The pure compound $(tipp)PCl_2$ was characterized by X-ray diffraction (see the ESI† for details).

We then reacted the $mesPCl_2$ substrate with a slight excess (*ca.* 2.5 equiv.) of the lithiated enyne reagent **8a** that was generated *in situ* by the treatment of the corresponding conjugated enyne with *n*-butyl lithium. This gave the phosphane **9a** that was isolated as a colourless microcrystalline solid in 78% yield (see Scheme 4).

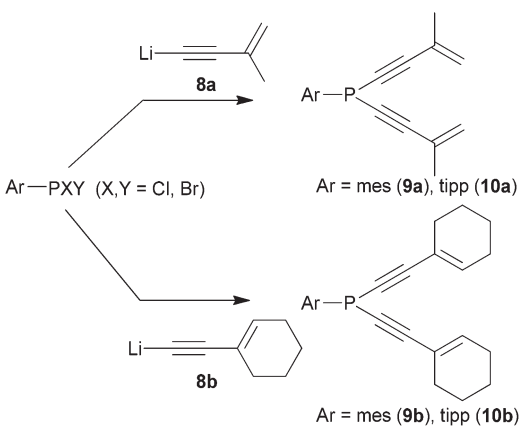
Compound **9a** shows a ^{31}P NMR resonance at δ −83.1. It features the typical ^{1}H NMR signals of the mesityl substituent [*o*-methyl: δ 2.84 (6H), *p*-methyl: δ 2.00 (3H), arene CH: δ 6.71 (2H)]. The pair of symmetry equivalent enynyl substituents at phosphorus shows ^{13}C NMR signals of their acetylenic section at δ 83.2 ($^{1}J_{PC}$ = 2.5 Hz) and 107.2 ($^{2}J_{PC}$ = 10.0 Hz) and of their olefinic part at δ 127.0 ($^{3}J_{PC}$ = 1.8 Hz, C═) and δ 123.1 ($^{4}J_{PC}$ = 2.7 Hz, ═CH_2; corresponding ^{1}H NMR resonances at δ 5.22 and 4.92).

Compound **9b** featuring the cyclohexenyl derived enynyl σ-ligand at phosphorus was prepared analogously by reacting $mesPCl_2$ with the lithiated enyne reagent **8b** (see Scheme 4). Compound **9b** was isolated in *ca.* 90% yield and characterized by C,H elemental analysis and by spectroscopy (for details see the ESI†).

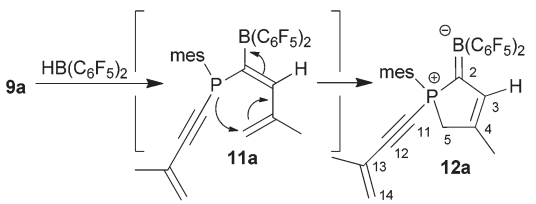
The reaction of **8a** with the more bulky (tipp)PXY cleanly gave the product **10a** (see Scheme 4). It was isolated in 90% yield. The compound shows similar NMR features as its congener (see above and the ESI†). Compound **10a** was characterized by X-ray diffraction (see Fig. 1). It shows the tricoordinate phosphorus atom (sum of bonding angles at P: $\sum P^{CCC}$ = 309.2(2)°) that has the bulky 2,4,6-triisopropylphenyl substituent bonded to it and a pair of enyne substituents [C1–C2: 1.200(6) Å (C6–C7: 1.220(6) Å), C2–C3: 1.440(7) Å (C7–C8: 1.440(6) Å), C3–C4: 1.398(9) Å (C8–C9: 1.393(7) Å), angles P1–C1–C2: 167.6(4)°, C1–C2–C3 179.3(6)°, C2–C3–C4: 117.9(6)°].

We eventually reacted (tipp)PXY with the lithioenyne reagent **8b** and isolated the corresponding phosphane **10b** in 89% yield (see Scheme 4) (see the ESI† for its characterization).

The mesitylbis(enynyl)phosphane **9a** was subjected to the reaction with Piers' borane ($HB(C_6F_5)_2$, one molar equivalent). The reaction mixture in pentane solution was stirred overnight at room temperature. The workup gave the product **12a** in 70% yield (see Scheme 5). Single crystals, suited for the X-ray crystal



Scheme 4



Scheme 5

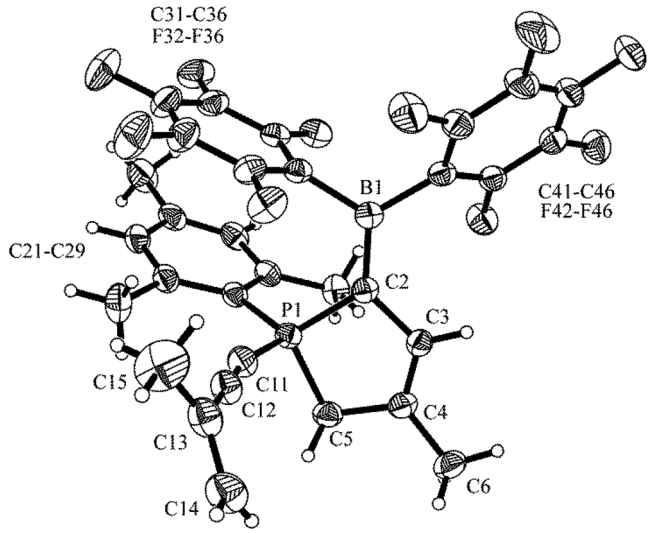


Fig. 2 A view of the molecular structure of compound **12a** (thermal ellipsoids are shown with 30% probability).

Table 1 Selected structural parameters of the borata–alkene derivatives **12a**, **14a** and **14b**[a]

Compound	**12a**	**14a**	**14b**
Ar:	mesityl	mesityl	tipp[b]
B1–C2	1.455(3)	1.446(4)	1.452(5)
C2–C3	1.469(3)	1.468(3)	1.469(5)
C3–C4	1.336(3)	1.330(3)	1.332(5)
C4–C5	1.514(3)	1.520(3)	1.522(4)
P1–C5	1.822(2)	1.836(2)	1.827(3)
P1–C2	1.759(2)	1.767(2)	1.765(3)
P1–C11	1.736(2)	1.735(3)	1.741(3)
C11–C12	1.201(3)	1.191(3)	1.191(4)
$\sum B1^{CCC}$	360.0(2)	360.0(2)	359.6(3)
$\sum C2^{BPC}$	360.0(2)	360.0(2)	358.3(2)

[a] Bond lengths in Å, angles in deg. [b] 2,4,6-Triisopropylphenyl.

structure analysis (see Fig. 2 and Table 1) were obtained from pentane at −35 °C. The structural analysis revealed that one molar equivalent of $HB(C_6F_5)_2$ had been added with the eventual formation of a zwitterionic borata–alkene type compound. It shows a five-membered heterocyclic ring that contains the phosphonium unit. The phosphorus atom bears a mesityl substituent and an intact enynyl group. Adjacent to this we find the borata–alkene unit. The corresponding B1–C2 bond is short (see Table 1); it is in the typical range observed for the few related borata–alkene examples found in the literature (see Scheme 1).[7–9] The B1–C2–C3–C4 unit shows a typical bond length alternation of the newly formed conjugated borata–diene system. We notice that the P1–C2 bond is markedly shorter than the P1–C5 bond as expected for the different carbon hybridization (sp^2 *vs.* sp^3).[13]

In solution compound **12a** shows the $^1H/^{13}C$ NMR signals of the mesityl group at phosphorus and the undisturbed enynyl substituent. We have observed the typical $^1H/^{13}C$ NMR signals of the five-membered zwitterionic core structure (for details see Table 2 and the ESI†). The C_6F_5-groups at the borata–alkene moiety are inequivalent. We monitor two sets of ^{19}F NMR signals originating from the *E*- and *Z*-pentafluorophenyl groups respectively (see the Experimental section; the spectra are depicted in the ESI†).

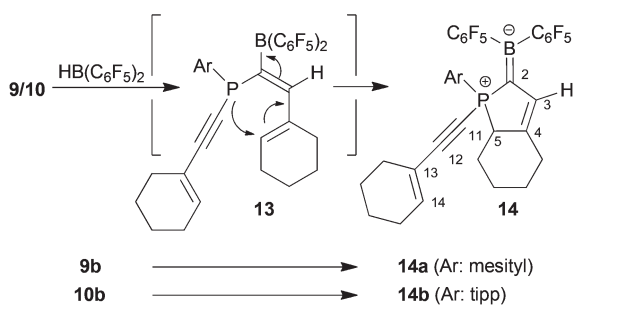
Table 2 Selected NMR data of compounds **12a** and **14a**,**b**[a]

Compound	**12a** mesityl	**14a** mesityl	**14b** tipp[b]
^{11}B	33.5	34.0	33.8
^{31}P	11.4	15.4	16.4
C2	94.7	92.4	95.2
C3	135.9	132.4	133.4
C4	118.5	127.7	125.7
C5	40.6	48.7	48.6
H3	6.36	6.35	6.45
H5	2.59	3.14	3.35
C11	79.3	76.8	77.3
C12	113.3	113.4	111.6
H14	5.34, 4.99	6.22	6.21

[a] In benzene-d_6, chemical shifts δ-scale. [b] 2,4,6-Triisopropylphenyl.

We assume that the formation of the zwitterionic borata–diene product **12a** was initiated by a regioselective hydroboration reaction of the C≡C triple bond of one of the conjugated enynyl substituents at the phosphorus atom of the starting material **9a**. This probably has generated the geminal frustrated Lewis pair **11a**. Under the applied reaction conditions this is apparently not stable. We think that the reactive intermediate **11a** undergoes a rapid internal addition of the phosphane nucleophile to the terminal sp^2-carbon atom of the adjacent boryl-activated conjugated diene unit to directly give the observed product **12a** (Scheme 5).

The phosphanes containing the cyclohexenylacetylide substituents react analogously with $HB(C_6F_5)_2$. Reaction of **9b** with the hydroboration reagent (r.t., overnight) resulted in the formation of the product **14a** (see Scheme 6). It was isolated in 70% yield. Compound **14a** was characterized by X-ray diffraction (see Fig. 3 and Table 1). The X-ray crystal structure analysis revealed that the phosphane had apparently also added internally to an *in situ* generated boryldiene (see Scheme 6). We have found compound **14a** to exhibit a heterobicyclic core structure of annulated five- and six-membered rings. The central zwitterionic five-membered heterocycle contains a close to coplanar *s-trans*-conjugated borata–diene unit [Θ B1–



Scheme 6

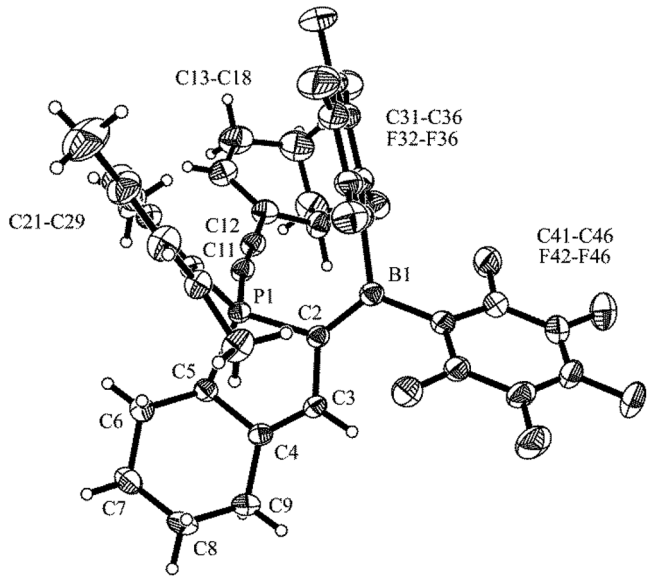


Fig. 3 Molecular structure of compound **14a** (thermal ellipsoids are shown with 30% probability).

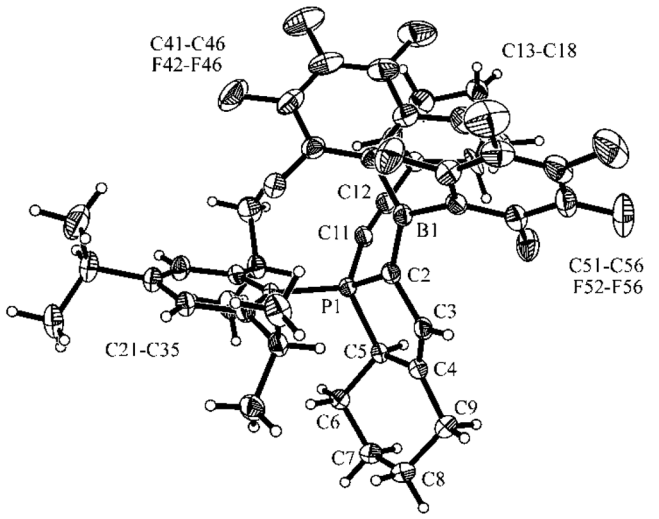


Fig. 4 A projection of the molecular structure of compound **14b** (thermal ellipsoids are shown with 30% probability).

C2–C3–C4: **14a**: −179.0(3)°, **14b**: −157.6(3)°, **12a**: −174.0(2)°]. The adjacent six-membered carbocycle contains one sp^2-hybridized carbon atom at the ring junction (C4). It features a distorted chair-like conformation. We find only one stereoisomer of compound **14a** in the crystal: it exhibits the mesityl substituent at phosphorus in a *cis*-orientation to the adjacent C5–C6 vector [Θ C21–P1–C5–C6 3.9(2)°]. Again, the B1–C2 bond (1.446(4) Å) is markedly shorter than the adjacent B–C(aryl) bonds [B1–C31: 1.610(4) Å, B1–C41: 1.597(4) Å]. One intact enynyl group is still present at the phosphorus atom. It shows bond angles of P1–C11–C12: 171.1(2)°, C11–C12–C13: 176.9(3)°, C12–C13–C14: 116.4(9)°.

In solution compound **14a** features the typical heteronuclear magnetic resonance signals of the borata–alkene boron center[10] and the phosphonium atom (see Table 2).[13] It shows the ^{19}F NMR signals of two inequivalent C_6F_5 substituents at boron, *E*- and *Z*-oriented at the tetrasubstituted formal B═C double bond. For both the $\Delta\delta^{19}F_{m,p}$ NMR chemical shift differences are small. We notice that the C(3)–H hydrogen (δ 6.35) shows a rather large coupling to phosphorus (J_{PH} = 41.4 Hz, ^{13}C: δ 132.4, J_{PC} = 26.0 Hz). The sterically constrained situation around the phosphonium moiety in **14a** has apparently caused a "frozen" rotation around the P–C(mesityl) vector on the NMR time scale. Consequently, we have observed three ^{1}H NMR methyl singlets and a pair of inequivalent arene *m*-CH resonances of the P-mesityl moiety.

The reaction of the (tipp)P(enynyl)$_2$ derivative **10b** with HB(C$_6$F$_5$)$_2$ proceeded analogously. Again, we assume a reaction pathway that involves regioselective alkyne hydroboration followed by internal phosphane addition to the "Michael position" of the boryldiene moiety of the resulting geminal FLP intermediate **13b** to directly give the observed product **14b**. Compound **14b** was isolated in 70% yield. The X-ray crystal structure analysis (see Fig. 4 and Table 1) shows the typical heterobicyclic framework. Again, the B1–C2 bond of the borata–alkene subunit is short. The planes of the C_6F_5 substituents at boron are markedly rotated from the borata–alkene plane. The very bulky tipp substituent is attached to phosphorus, which also bears the single remaining substituted conjugated enyne group. The projection of compound **14b** that is depicted in Fig. 4 shows the chair-shaped conformation of the annulated six-membered carbocycle of the core structure.

Compound **14b** shows similar NMR spectra as the other related zwitterionic phosphonium/borata–alkene examples in this series (see Table 2). The rotation of the bulky *P*-tipp unit is hindered and we, consequently, have observed the ^{1}H NMR signals of inequivalent *m*-CH(arene) moieties (for details see the ESI†).

Conclusions

The unique zwitterionic phosphonium/borata–alkenes (**7**, **12**, **14**) are apparently formed by a very favourable internal addition of the phosphane nucleophile to an adjacent boryl-activated conjugated diene. It seems that the resulting borata–diene systems show considerable thermodynamic stabilization relative to their alleged geminal FLP precursors. The observed very facile formation of the here described products from the easily available functionalized phosphane precursors just by treatment with HB(C$_6$F$_5$)$_2$ constitutes a very attractive synthetic entry to novel borata–alkene derivatives. We are looking forward to investigating their reactivity and to develop novel aspects of the chemistry of the unique borata–alkenes.

Experimental section

Preparation of compound 9a

2-Methylbutenyne (680 mg, 10 mmol, 2.7 eq.) in pentane (80 mL) was cooled to −50 °C and *n*-BuLi (5.9 mL, 1.6 M in

hexane, 9.4 mmol, 2.5 eq.) was added dropwise. The resulting colourless suspension was stirred for 30 min at −50 °C and allowed to warm to rt. Then $mesPCl_2$ (850 mg, 3.7 mmol, 1 eq.) was added in a glovebox and the reaction mixture was stirred for 2 h at rt [completion of the reaction was confirmed by ^{31}P NMR spectroscopy]. Then the insolubles were filtered off over Celite at 40 °C and washed with pentane (20 mL) twice at 40 °C. The clear colourless solution was concentrated to *ca.* 10 mL and the product precipitated at −95 °C. Removal of the supernatant solution by cannula filtration and drying of the residue *in vacuo* yielded compound **9a** as a colourless, microcrystalline solid (830 mg, 3.0 mmol, 78%). Anal. calc. for $C_{19}H_{21}P$: C, 81.40; H, 7.55. Found C, 81.22; H, 7.67. IR (KBr) $\tilde{\nu}$ [cm^{-1}] = 2153 ($\nu_{C\equiv C}$). M.p. 120 °C. Decomp. 209 °C. ^1H NMR (600 MHz, 299 K, benzene-d_6): δ^1H: 6.71 (dm, $^4J_{PH}$ = 3.3 Hz, 2H, *m*-mes), 5.22 (m, 2H, $=CH_2^Z$), 4.92 (m, 2H, $=CH_2^E$), 2.84 (m, 6H, *o*-CH_3^{mes}), 2.00 (s, 3H, *p*-CH_3^{mes}), 1.59 (dd, $^4J_{PH}$ = 1.6 Hz, $^4J_{PH}$ = 1.1 Hz, 6H, CH_3). $^{13}C\{^1H\}$ NMR (151 MHz, 299 K, benzene-d_6): $\delta^{13}C$: 144.8 (d, $^2J_{PC}$ = 19.8 Hz, *o*-mes), 140.8 (d, $^4J_{PC}$ = 1.6 Hz, *p*-mes), 130.0 (d, $^3J_{PC}$ = 5.9 Hz, *m*-mes), 127.0 (d, $^3J_{PC}$ = 1.8 Hz, C=), 126.1 (d, $^1J_{PC}$ = 1.1 Hz, *i*-mes), 123.1 (d, $^4J_{PC}$ = 2.7 Hz, $=CH_2$), 107.2 (d, $^2J_{PC}$ = 10.0 Hz, C≡), 83.2 (d, $^1J_{PC}$ = 2.5 Hz, PC≡), 23.2 (d, $^3J_{PC}$ = 19.1 Hz, *o*-CH_3^{mes}), 22.7 (d, $^5J_{PC}$ = 1.5 Hz, *p*-CH_3^{mes}), 21.0 (CH_3). $^{31}P\{^1H\}$ NMR (243 MHz, 299 K, benzene-d_6): $\delta^{31}P$: −83.1 ($\nu_{1/2} \approx 1$ Hz).

Preparation of compound 9b

Cyclohexenylacetylene (460 mg, 4.3 mmol, 2.2 eq.) in pentane (80 mL) was cooled to −60 °C and *n*-BuLi (2.6 mL, 1.6 M in hexane, 4.1 mmol, 2.1 eq.) was added. The resulting colourless suspension was stirred for 30 min at −60 °C, then allowed to warm to rt and stirred for another 15 min. Then $mesPCl_2$ (480 mg, 2 mmol, 1 eq.) was added and the reaction mixture was stirred for 2 h at rt [completion of the reaction was confirmed by ^{31}P NMR spectroscopy]. Subsequently the insolubles were filtered off over Celite/silica gel (10 : 1) and the obtained residue was washed with pentane (20 mL) twice. The combined clear colourless filtrates were concentrated to *ca.* 15 mL and the colourless product precipitated at −70 °C. Removal of the supernatant solution by cannula filtration and drying *in vacuo* yielded compound **9b** as a colourless wax (680 mg, 1.9 mmol, 90%). Anal. calc. for $C_{25}H_{29}P$: C, 83.30; H, 8.11. Found C, 83.15; H, 8.18. IR (KBr) $\tilde{\nu}$ [cm^{-1}] = 2146 ($\nu_{C\equiv C}$). ^1H NMR (600 MHz, 299 K, benzene-d_6): δ^1H: 6.75 (dm, $^4J_{PH}$ = 3.3 Hz, 2H, *m*-mes), 6.03 (m, 2H, =CH), 2.92 (m, 6H, *o*-CH_3^{mes}), 2.03 (s, 3H, *p*-CH_3^{mes}), 1.98 (m, 4H, β-CH_2), 1.69 (m, 4H, γ′-CH_2), 1.24 (m, 4H, γ-CH_2), 1.19 (m, 4H, δ-CH_2). $^{13}C\{^1H\}$ NMR (151 MHz, 299 K, benzene-d_6): $\delta^{13}C$: 144.7 (d, $^2J_{PC}$ = 19.6 Hz, *o*-mes), 140.4 (d, $^4J_{PC}$ = 1.6 Hz, *p*-mes), 136.5 (d, $^4J_{PC}$ = 2.8 Hz, =CH), 130.0 (d, $^3J_{PC}$ = 5.7 Hz, *m*-mes), 127.1 (d, $^1J_{PC}$ = 1.5 Hz, i-mes), 121.4 (d, $^3J_{PC}$ = 1.7 Hz, C=), 107.8 (d, $^2J_{PC}$ = 10.2 Hz, C≡), 81.4 (d, $^1J_{PC}$ = 0.8 Hz, PC≡), 28.9 (d, $^4J_{PC}$ = 1.7 Hz, β-CH_2), 25.8 (γ′-CH_2), 23.3 (d, $^3J_{PC}$ = 19.3 Hz, *o*-CH_3^{mes}), 22.3 (γ-CH_2), 21.5 (δ-CH_2), 21.0 (*p*-CH_3^{mes}). $^{31}P\{^1H\}$ NMR (243 MHz, 299 K, benzene-d_6): $\delta^{31}P$: −82.8 ($\nu_{1/2} \approx 1$ Hz).

Preparation of compound 10a

2-Methylbutenyne (1.13 g, 17 mmol, 2.5 eq.) in pentane (80 mL) was cooled to 0 °C and *n*-BuLi (10 mL, 1.6 M in hexane, 16 mmol, 2.4 eq.) was added. Subsequently the resulting colourless suspension was stirred for 15 min at 0 °C and for another 15 min at rt. Then tippPXY (2.3 g, 6.8 mmol, 1 eq.) was added in portions in a glovebox. The stirred reaction mixture was then cooled to 0 °C and allowed to warm to rt overnight. The insolubles were filtered off over Celite and washed with pentane (15 mL) twice. Removal of the volatiles *in vacuo* yielded compound **10a** as a colourless solid (2.21 g, 90%). Anal. calc. for $C_{25}H_{33}P$: C, 82.38; H, 9.13. Found C, 82.36; H, 9.28. IR (KBr) $\tilde{\nu}$ [cm^{-1}] = 2150 ($\nu_{C\equiv C}$). M.p. 119 °C. Decomp. 209 °C. ^1H NMR (500 MHz, 298 K, benzene-d_6): δ^1H: 7.16 (d, $^4J_{PH}$ = 3.1 Hz, 2H, *m*-tipp), 5.22 (m, 2H, $=CH_2^Z$), 4.92 (m, 2H, $=CH_2^E$), 4.57 (m, 2H, *o*-CH^{tipp}), 2.73 (sept, $^3J_{HH}$ = 6.9 Hz, 1H, *p*-CH^{tipp}), 1.59 (m, 6H, CH_3), 1.38 (d, $^3J_{HH}$ = 6.7 Hz, 12H, *o*-CH_3^{tipp}), 1.17 (d, $^3J_{HH}$ = 6.9 Hz, 6H, *p*-CH_3^{tipp}). $^{13}C\{^1H\}$ NMR (126 MHz, 298 K, benzene-d_6): $\delta^{13}C$: 155.4 (d, $^2J_{PC}$ = 17.4 Hz, *o*-tipp), 152.3 (d, $^4J_{PC}$ = 1.6 Hz, *p*-tipp), 127.0 (d, $^3J_{PC}$ = 2.0 Hz, C=), 126.4 (*i*-tipp), 123.2 (d, $^4J_{PC}$ = 2.8 Hz, $=CH_2$), 122.8 (d, $^3J_{PC}$ = 5.8 Hz, *m*-tipp), 107.4 (d, $^2J_{PC}$ = 10.0 Hz, C≡), 84.2 (d, $^1J_{PC}$ = 3.0 Hz, PC≡), 34.8 (*p*-CH^{tipp}), 33.2 (d, $^3J_{PC}$ = 19.8 Hz, *o*-CH^{tipp}), 24.9 (*o*-CH_3^{tipp}), 24.0 (*p*-CH_3^{tipp}), 22.8 (d, $^4J_{PC}$ = 1.5 Hz, CH_3). $^{31}P\{^1H\}$ NMR (202 MHz, 298 K, benzene-d_6): $\delta^{31}P$: −88.0 ($\nu_{1/2} \approx 2$ Hz).

Preparation of compound 10b

Cyclohexenylacetylene (640 mg, 6 mmol, 2.4 eq.) in pentane (80 mL) was cooled to −78 °C and *n*-BuLi (3.4 mL, 1.6 M in hexane, 5.5 mmol, 2.2 eq.) was added. Subsequently the resulting colourless suspension was stirred for 1 h at −78 °C and warmed to rt. Then tippPXY (800 mg, 2.5 mmol, 1 eq.) was added in and the reaction mixture was stirred for 3 h at rt [completion of the reaction was confirmed by ^{31}P NMR spectroscopy]. CH_2Cl_2 (5 mL) was added at rt, the insolubles were filtered off over Celite and washed with boiling pentane (20 mL) twice. Removal of the volatiles *in vacuo* yielded compound **10b** as a colourless crystalline solid (985 mg, 89%). Anal. calc. for $C_{31}H_{41}P$: C, 83.74; H, 9.29. Found C, 83.78; H, 9.29. IR (KBr) $\tilde{\nu}$ [cm^{-1}] = 2146 ($\nu_{C\equiv C}$). M.p. 145 °C. Decomp. >250 °C. ^1H NMR (600 MHz, 299 K, benzene-d_6): δ^1H: 7.18 (d, $^4J_{PH}$ = 3.2 Hz, 2H, *m*-tipp), 6.05 (m, 2H, =CH), 4.65 (oct, $^3J_{HH} \approx {}^4J_{PH}$ = 6.8 Hz, 2H, *o*-CH^{tipp}), 2.76 (sept, $^3J_{HH}$ = 6.9 Hz, 1H, *p*-CH^{tipp}), 1.98 (m, 4H, β-CH_2), 1.71 (m, 4H, γ′-CH_2), 1.42 (d, $^3J_{HH}$ = 6.8 Hz, 12H, *o*-CH_3^{tipp}), 1.26 (m, 4H, γ-CH_2), 1.21 (m, 4H, δ-CH_2), 1.20 (d, $^3J_{HH}$ = 6.9 Hz, 6H, *p*-CH_3^{tipp}). $^{13}C\{^1H\}$ NMR (151 MHz, 299 K, benzene-d_6): $\delta^{13}C$: 155.3 (d, $^2J_{PC}$ = 17.2 Hz, *o*-tipp), 151.9 (d, $^4J_{PC}$ = 1.5 Hz, *p*-tipp), 136.6 (dm, $^4J_{PC}$ = 2.7 Hz, =CH), 127.4 (d, $^1J_{PC}$ = 1.5 Hz, *i*-tipp), 122.7 (d, $^3J_{PC}$ = 5.7 Hz, *m*-tipp), 121.4 (d, $^3J_{PC}$ = 1.8 Hz, C=), 108.0 (d, $^2J_{PC}$ = 10.2 Hz, C≡), 82.5 (d, $^1J_{PC}$ = 1.3 Hz, PC≡), 34.8 (*p*-CH^{tipp}), 33.0 (d, $^3J_{PC}$ = 20.0 Hz, *o*-CH^{tipp}), 29.0 (d, $^4J_{PC}$ = 1.6 Hz, β-CH_2), 25.8 (γ′-CH_2), 25.1 (*o*-CH_3^{tipp}), 24.1 (*p*-CH_3^{tipp}), 22.4 (γ-CH_2), 21.6

(δ-CH_2). $^{31}P\{^1H\}$ NMR (243 MHz, 299 K, benzene-d_6): $\delta^{31}P$: −87.6 ($\nu_{1/2} \approx 1$ Hz).

Preparation of compound 12a

Compound **9a** (90 mg, 0.32 mmol, 1 eq.) and $HB(C_6F_5)_2$ (110 mg, 0.32 mmol, 1 eq.) were suspended in pentane (5 mL) at rt and stirred overnight. Then the insolubles were filtered off at rt and washed with pentane (1 mL) three times. The combined organic phases (brown solution) were cooled to −95 °C and the resulting precipitate was allowed to sediment for 1 h at −95 °C. Subsequently the supernatant solution was removed by cannula filtration. Drying of the residue *in vacuo* yielded compound **12a** as a yellow-brown powder (140 mg, 70%). Anal. calc. for $C_{31}H_{22}BF_{10}P$: C, 59.45; H, 3.45. Found C, 58.77; H, 3.48. IR (KBr) $\tilde{\nu}$ [cm^{-1}] = 2168 ($\nu_{C\equiv C}$). M.p. 50 °C. Decomp. >80 °C. ^1H NMR (600 MHz, 299 K, benzene-d_6): δ^1H: 6.50 (dm, $^4J_{PH}$ = 4.6 Hz, 2H, *m*-mes), 6.36 (dm, $^3J_{PH}$ + $^4J_{PH}$ = 44.3 Hz, 1H, H3), 5.34 (sext, $^4J_{HH} \approx {}^2J_{HH} \approx {}^5J_{PH}$ = 1.1 Hz, 1H, $=CH_2^Z$), 4.99 (m, 1H, $=CH_2^E$), 2.59 (dm, $^2J_{PH}$ = 9.4 Hz, 2H, H5), 2.36 (s, 6H, *o*-CH_3^{mes}), 1.94 (s, 3H, *p*-CH_3^{mes}), 1.62 (m, 3H, 4-CH_3), 1.56 (tm, $^4J_{HH} \approx {}^4J_{HH}$ = 1.2 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (151 MHz, 299 K, benzene-d_6): $\delta^{13}C$: 143.8 (d, $^2J_{PC}$ = 11.4 Hz, *o*-mes), 143.5 (d, $^4J_{PC}$ = 3.2 Hz, *p*-mes), 135.9 (d, $^2J_{PC}$ + $^3J_{PC}$ = 24.6 Hz, C3), 131.7 (d, $^3J_{PC}$ = 12.0 Hz, *m*-mes), 127.8 ($=CH_2$)[a], 125.0 (d, $^3J_{PC}$ = 4.4 Hz, C=), 118.5 (d, $^2J_{PC}$ + $^3J_{PC}$ = 13.5 Hz, C4), 116.8 (d, $^1J_{PC}$ = 92.8 Hz, i-mes), 113.3 (d, $^2J_{PC}$ = 24.7 Hz, C≡), 94.7 (br, C2), 79.3 (d, $^1J_{PC}$ = 147.2 Hz, PC≡), 40.6 (d, $^1J_{PC}$ = 64.6 Hz, C5), 22.6 (d, $^3J_{PC}$ = 4.6 Hz, *o*-CH_3^{mes}), 21.1 (CH_3), 20.6 (d, $^5J_{PC}$ = 1.6 Hz, *p*-CH_3^{mes}), 18.2 (d, $^3J_{PC}$ + $^4J_{PC}$ = 11.2 Hz, 4-CH_3), [not listed C_6F_5; [a]from ghsqc]. $^{11}B\{^1H\}$ NMR (192 MHz, 299 K, benzene-d_6): $\delta^{11}B$: 33.5 ($\nu_{1/2} \approx$ 600 Hz). ^{19}F NMR (564 MHz, 299 K, benzene-d_6): $\delta^{19}F$: −129.0 (m, 2F, *o*-$C_6F_5^A$), −131.9 (m, 2F, *o*-$C_6F_5^B$), −156.9 (t, $^3J_{FF}$ = 20.6 Hz, 1F, *p*-$C_6F_5^B$), −158.7 (t, $^3J_{FF}$ = 20.3 Hz, 1F, *p*-$C_6F_5^A$), −163.7 (m, 2F, *m*-$C_6F_5^B$), −164.5 (m, 2F, *m*-$C_6F_5^A$), [$\Delta\delta^{19}F_{mp}$ = 5.8 Hz^A, 6.8 Hz^B]. ^{31}P NMR (243 MHz, 299 K, benzene-d_6): $\delta^{31}P$: 11.4 (dm, $^3J_{PH}$ + $^4J_{PH}$ = 44.3 Hz).

Preparation of compound 14a

$HB(C_6F_5)_2$ (95 mg, 0.28 mmol, 1 eq.) was added to a solution of compound **9b** (105 mg, 0.28 mmol, 1 eq.) in pentane (3 mL) at rt and the reaction mixture was stirred overnight. Then the insolubles were removed by filtration and were washed with pentane (1 mL) twice at rt. The filtrates were combined and all volatiles were removed *in vacuo* to give compound **14a** as a green solid (140 mg, 70%). Anal. calc. for $C_{37}H_{30}BF_{10}P$: C, 62.91; H, 4.28. Found C, 62.38; H, 4.26. IR (KBr) $\tilde{\nu}$ [cm^{-1}] = 2162 ($\nu_{C\equiv C}$). Decomp. >80 °C. ^1H NMR (600 MHz, 299 K, benzene-d_6): δ^1H: 6.70 (m, 1H, *m*-mes), 6.52 (m, 1H, *m*′-mes), 6.35 (dm, $^3J_{PH}$ + $^4J_{PH}$ = 41.4 Hz, 1H, H3), 6.22 (m, 1H, =CH), 3.14 (m, 1H, H5), 2.84 (s, 3H, *o*-CH_3^{mes}), 2.39/1.88 (each m, each 1H, 9-CH_2)[t], 2.38 (s, 3H, *o*′-CH_3^{mes}), 2.00/1.94 (each m, each 1H, β-CH_2)[t], 1.94 (s, 3H, *p*-CH_3^{mes}), 1.72 (m, 2H, γ′-CH_2)[t], 1.48/0.96 (each m, each 1H, 8-CH_2)[t], 1.36/0.95 (each m, each 1H, 7-CH_2)[t], 1.35/0.95 (each m, each 1H, 6-CH_2)[t], 1.29 (m, 2H, γ-CH_2)[t], 1.20 (m, 2H, δ-CH_2)[t], [[t]tentatively assigned]. $^{13}C\{^1H\}$ NMR (151 MHz, 299 K, benzene-d_6): $\delta^{13}C$: 146.5 (d, $^2J_{PC}$ = 15.5 Hz, *o*-mes), 142.9 (d, $^4J_{PC}$ = 3.2 Hz, *p*-mes), 142.4 (d, $^4J_{PC}$ = 3.0 Hz, =CH), 142.0 (d, $^2J_{PC}$ = 6.2 Hz, *o*′-mes), 132.4 (d, $^2J_{PC}$ + $^3J_{PC}$ = 26.0 Hz, C3), 132.1 (d, $^3J_{PC}$ = 13.0 Hz, *m*-mes), 131.3 (d, $^3J_{PC}$ = 10.3 Hz, *m*′-mes), 127.7 (d, $^2J_{PC}$ + $^3J_{PC}$ = 14.9 Hz, C4), 119.3 (d, $^3J_{PC}$ = 4.7 Hz, C=), 117.2 (d, $^1J_{PC}$ = 84.8 Hz, *i*-mes), 113.4 (d, $^2J_{PC}$ = 25.7 Hz, C≡), 92.4 (br m, C2), 76.8 (d, $^1J_{PC}$ = 159.4 Hz, PC≡), 48.7 (d, $^1J_{PC}$ = 61.4 Hz, C5), 30.7 (d, $^3J_{PC}$ = 7.2 Hz, C9)[t], 27.5 (m, C6)[t], 27.5 (m, β-CH_2)[t], 26.6 (C8)[t], 26.2 (d, $^3J_{PC}$ = 13.9 Hz, C7)[t], 26.0 (γ′-CH_2)[t], 25.3 (d, $^3J_{PC}$ = 5.8 Hz, *o*′-CH_3^{mes}), 23.2 (br, *o*-CH_3^{mes}), 21.8 (γ-CH_2)[t], 21.0 (δ-CH_2)[t], 20.7 (d, $^5J_{PC}$ = 1.5 Hz, *p*-CH_3^{mes}), [C_6F_5 not listed; [t] tentatively assigned]. $^{11}B\{^1H\}$ NMR (192 MHz, 299 K, benzene-d_6): $\delta^{11}B$: 34.0 ($\nu_{1/2} \approx$ 850 Hz). ^{19}F NMR (564 MHz, 299 K, benzene-d_6): $\delta^{19}F$: −128.6 (m, 2F, *o*-$C_6F_5^A$), −131.8 (m, 2F, *o*-$C_6F_5^B$), −157.3 (t, $^3J_{FF}$ = 20.6 Hz, 1F, *p*-$C_6F_5^B$), −158.6 (t, $^3J_{FF}$ = 20.5 Hz, 1F, *p*-$C_6F_5^A$), −163.6 (m, 2F, *m*-$C_6F_5^B$), −164.5 (m, 2F, *m*-$C_6F_5^A$), [$\Delta\delta^{19}F_{mp}$ = 5.9 Hz^A, 6.3 Hz^B]. ^{31}P NMR (243 MHz, 299 K, benzene-d_6): $\delta^{31}P$: 15.4 (*ca.* 94%, d, $^3J_{PH}$ + $^4J_{PH}$ = 41.4 Hz), 18.0 (impurity, *ca.* 6%, $\nu_{1/2} \approx$ 65 Hz).

Preparation of compound 14b

Compound **10b** (115 mg, 0.25 mmol, 1 eq.) and $HB(C_6F_5)_2$ (87 mg, 0.25 mmol, 1 eq.) were suspended in pentane (3 mL) at rt and then stirred overnight. Subsequently the reaction mixture was cooled to −35 °C for precipitation. The green supernatant solution was removed by decantation and the residue was washed with pentane (1 mL) at −35 °C twice. Drying of the residue *in vacuo* yielded compound **14b** as a yellow-green solid. Concentration of the filtrate and a second crystallization at −35 °C yields another 20 mg of compound **14b** (overall: 140 mg, 70%). Anal. calc. for $C_{43}H_{42}BF_{10}P$: C, 65.33; H, 5.35. Found C, 65.16; H, 5.35. IR (KBr) $\tilde{\nu}$ [cm^{-1}] = 2163 ($\nu_{C\equiv C}$). M.p. 160 °C. ^1H NMR (600 MHz, 299 K, benzene-d_6): δ^1H: 7.24 (dd, $^4J_{PH}$ = 4.7 Hz, $^4J_{HH}$ = 1.8 Hz, 1H, *m*-tipp), 7.07 (dd, $^4J_{PH}$ = 3.9 Hz, $^4J_{HH}$ = 1.8 Hz, 1H, *m*′-tipp), 6.45 (dm, $^3J_{PH}$ + $^4J_{PH}$ = 40.7 Hz, 1H, H3), 6.21 (m, 1H, =CH), 3.88 (m, 1H, *o*-CH^{tipp}), 3.77 (m, 1H, *o*′-CH^{tipp}), 3.35 (m, 1H, H5), 2.71 (sept, $^3J_{HH}$ = 6.9 Hz, 1H, *p*-CH^{tipp}), 2.43/1.92 (each m, each 1H, 9-CH_2)[t], 1.98/1.88 (each m, each 1H, β-CH_2)[t], 1.74 (m, 2H, γ′-CH_2)[t], 1.65 (d, $^3J_{HH}$ = 6.4 Hz, 3H, *o*-CH_3^{tipp}), 1.63/1.22 (each m, each 1H, 6-CH_2)[t], 1.50/0.99 (each m, each 1H, 8-CH_2)[t], 1.46/1.00 (each m, each 1H, 7-CH_2)[t], 1.30 (m, 2H, γ-CH_2)[t], 1.23 (d, $^3J_{HH}$ = 6.4 Hz, 3H, *o*′-CH_3^{tipp}), 1.21 (m, 2H, δ-CH_2)[t], 1.20/1.19 (each d, each $^3J_{HH}$ = 6.9 Hz, each 3H, *p*-CH_3^{tipp}), 1.09 (d, $^3J_{HH}$ = 6.7 Hz, 3H, *o*-$CH_3'^{tipp}$), 1.01 (d, $^3J_{HH}$ = 6.7 Hz, 3H, *o*′-$CH_3'^{tipp}$), [[t]tentatively assigned]. $^{13}C\{^1H\}$ NMR (151 MHz, 299 K, benzene-d_6): $\delta^{13}C$: 158.1 (d, $^2J_{PC}$ = 16.4 Hz, *o*-tipp), 154.3 (d, $^4J_{PC}$ = 3.1 Hz, *p*-tipp), 154.0 (d, $^2J_{PC}$ = 6.9 Hz, *o*′-tipp), 142.6 (d, $^4J_{PC}$ = 3.1 Hz, =CH), 133.4 (d, $^2J_{PC}$ + $^3J_{PC}$ = 25.5 Hz, C3), 125.7 (d, $^2J_{PC}$ + $^3J_{PC}$ = 14.9 Hz, C4), 124.7 (d, $^3J_{PC}$ = 13.0 Hz, *m*-tipp), 123.4 (d, $^3J_{PC}$ = 10.2 Hz, *m*′-tipp), 119.1 (d, $^3J_{PC}$ = 4.6 Hz, C=), 117.2 (d, $^1J_{PC}$ = 84.4 Hz, *i*-tipp), 111.6 (d, $^2J_{PC}$ = 25.3 Hz, C≡), 95.2 (br dm, $J \approx$ 64 Hz, C2), 77.3 (d, $^1J_{PC}$ = 160.9 Hz, PC≡), 48.6 (d, $^1J_{PC}$ = 60.3 Hz, C5), 34.5 (*p*-CH^{tipp}), 33.0 (d, $^3J_{PC}$ = 6.3 Hz, *o*′-CH^{tipp}), 31.3 (d, $^3J_{PC}$ = 6.0 Hz, *o*-CH^{tipp}), 30.5

(d, $^{3}J_{PC}$ = 7.2 Hz, C9)^{t}, 27.8 (d, $^{4}J_{PC}$ = 1.5 Hz, β-CH_2)^{t}, 27.5 (d, $^{2}J_{PC}$ = 3.3 Hz, C6)^{t}, 27.1 (*o*-CH_3′^{tipp}), 26.5 (C8)^{t}, 26.2 (*o*′-CH_3′^{tipp}), 26.1 (d, $^{3}J_{PC}$ = 14.0 Hz, C7)^{t}, 26.0 (γ′-CH_2)^{t}, 25.1 (*o*′-CH_3^{tipp}), 23.6 (*p*-CH_3^{tipp})^{t}, 23.5 (*o*-CH_3^{tipp})^{t}, 23.4 (*p*-CH_3′^{tipp})^{t}, 21.8 (γ-CH_2)^{t}, 21.0 (δ-CH_2)^{t}, [C_6F_5 not listed; ^{t}tentatively assigned]. $^{11}B\{^{1}H\}$ NMR (192 MHz, 299 K, benzene-d_6): δ^{11}B: 33.8 ($\nu_{1/2} \approx$ 900 Hz). ^{19}F NMR (564 MHz, 299 K, benzene-d_6): δ^{19}F: −128.6 (m, 2F, *o*-$C_6F_5^{A}$), −131.6 (m, 2F, *o*-$C_6F_5^{B}$), −157.4 (t, $^{3}J_{FF}$ = 20.5 Hz, 1F, *p*-$C_6F_5^{B}$), −159.1 (t, $^{3}J_{FF}$ = 20.5 Hz, 1F, *p*-$C_6F_5^{A}$), −163.7 (m, 2F, *m*-$C_6F_5^{B}$), −164.9 (m, 2F, *m*-$C_6F_5^{A}$), [$\Delta\delta^{19}F_{mp}$ = 5.8 Hz^{A}, 6.3 Hz^{B}]. ^{31}P NMR (243 MHz, 299 K, benzene-d_6): δ^{31}P: 16.4 (dm, $^{3}J_{PH}$ + $^{4}J_{PH} \approx$ 41 Hz).

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