Lewis acid mediated P–P bond hydrogenation and hydrosilylation†

Stephen J. Geier and Douglas W. Stephan*

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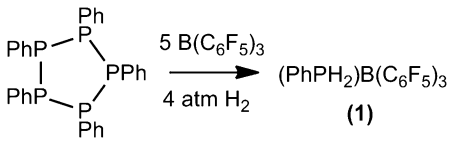
The reaction of H_2, R_3SiH or R_2SiH_2 with P_5Ph_5 in the presence of stoichiometric $B(C_6F_5)_3$ results in excellent yields of the phosphine–borane adducts $(PhPH_2)B(C_6F_5)_3$, $((R_3Si)PhPH)B(C_6F_5)_3$ and $((R_2SiH)PhPH)B(C_6F_5)_3$, respectively.

The recent renaissance in the chemistry of the main group elements has nowhere been shown more clearly than in the chemistry of phosphorus.[1] For example, the interception of unprecedented new P-based chains[2] and clusters[3] stabilized by carbene ligands has been described by the groups of Robinson[4] and Bertrand.[5] Shaffer *et al.*[6] have reported the characterization of nanostructures derived from elemental P. In addition, Cummins *et al.*[7–9] have developed a highly innovative and elegant, metal-mediated synthesis of P_3As. Collectively, these findings illustrate remarkable and artful methods to assemble new elemental allotropes and binary materials. In a related vein, the functionalization of polyalkyl- or polyaryl-phosphines has been extensively explored by Burford and co-workers.[10–23] Very recently Weigand *et al.*[24] have integrated elemental P with phosphenium cations affording the discovery of unprecedented cationic P-clusters $[Ph_2P_5]^+$, $[Ph_4P_6]^{2+}$, and $[Ph_6P_7]^{3+}$.

Targeting applications of the reactivity of P–P bonds, we have reported a Rh-catalyst for the hydrogenation and silylation of P–P bonds providing secondary phosphines and silylphosphines.[25] Concurrent with these studies, we have also demonstrated that bulky polyphosphines do not form classical Lewis acid–base adducts with $B(C_6F_5)_3$ and thus these combinations of reagents behave as "frustrated Lewis pairs" (FLPs).[26,27] Exploiting the reactivity of such systems, we have recently shown that such FLPs react with alkynes to effect the addition of P and B to the alkyne affording zwitterionic polyphosphino-phosphonium-alkenyl-borates.[28] This finding of FLP reactivity prompted us to probe the possibility of reduction of P–P bonds *via* FLP-hydrogenation.[29–31] Thus, in this communication, we report the high yielding, stoichiometric hydrogenation and hydrosilylation of the P–P bonds of P_5Ph_5 mediated by the Lewis acid $B(C_6F_5)_3$.

A 1 : 1 mixture of P_5Ph_5–$B(C_6F_5)_3$ was exposed to 4 atm of H_2. This resulted in the formation of a new species (**1**) which was shown spectroscopically to be the phenylphosphine–borane adduct, $(PhPH_2)B(C_6F_5)_3$.[32,33] In addition, the corresponding reaction with D_2 gave rise to a ^{31}P NMR signal at −43.6 ppm and a ^2D signal at 5.09 ppm with J_{P-D} of 64 Hz. The mother liquors of these reactions were observed to contain residual P_5Ph_5. Altering the stoichiometry to employ 5 equivalents of $B(C_6F_5)_3$ per equivalent of P_5Ph_5 resulted in the quantitative conversion to (**1**) which was subsequently isolated in 91% yield as a crystalline solid [eqn (1)].



(1)

In a similar procedure, a mixture of P_5Ph_5 and five equivalents of $B(C_6F_5)_3$ was treated with excess Et_3SiH. Over the course of 12 hours, this resulted in the quantitative conversion to the silylphosphine–borane adduct $((Et_3Si)PhPH)B(C_6F_5)_3$ (**2**)[33] as evidenced by the observation of the single ^{31}P NMR signal at −46.6 ppm. Quaternization of B is consistent with the ^{19}F NMR signals at −129.8, −156.5 and −163.7 ppm and the ^{11}B NMR resonance at −12.3 ppm. Formation of the secondary phosphine is confirmed by the ^1H NMR resonance attributable to the P–H proton at 4.72 ppm, with $^1J_{P-H}$ = 345 Hz. This product (**2**) was easily isolated in nearly quantitative yield and subsequently characterized by X-ray crystallography (Fig. 1).‡ The structural data confirm the formation of the secondary silylphenylphosphine adduct of $B(C_6F_5)_3$ with P–B and P–Si bond distances of 2.093(6) Å and 2.333(2) Å, respectively. The former is similar to the B–P bond lengths in the adducts $(R_2PH)B(C_6F_5)_3$ (R = Ph 2.098(3) Å, *t*Bu 2.094(7) Å)[34,35] while the P–Si distance is typical.[36–40]

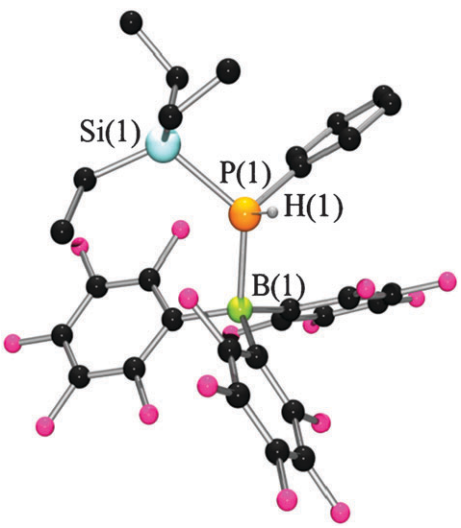


Fig. 1 POV-ray drawing of (**2**).

Department of Chemistry, University of Toronto, 80 St George St, Toronto, Ontario, Canada M5S3H6.
E-mail: dstephan@chem.utoronto.ca

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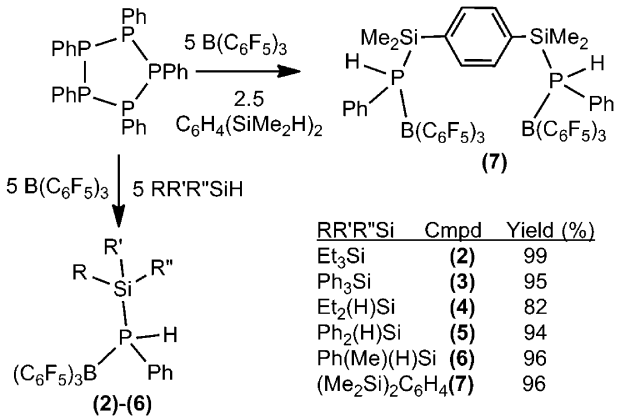

RR'R"Si	Cmpd	Yield (%)
Et_3Si	**(2)**	99
Ph_3Si	**(3)**	95
$Et_2(H)Si$	**(4)**	82
$Ph_2(H)Si$	**(5)**	94
Ph(Me)(H)Si	**(6)**	96
$(Me_2Si)_2C_6H_4$	**(7)**	96

Scheme 1 Synthesis of (**2**)–(**7**).

In a similar fashion a series of silanes was employed to reduce P_5Ph_5 to the analogous adducts, $((RR'R''Si)Ph{\cdot}PH)B(C_6F_5)_3$ (**3**)–(**7**)[33] (Scheme 1). Isolated yields ranged between 82–96%. The $^{31}P\{^1H\}$ NMR signals for these products were broad presumably due to P coupling to B, however P–H coupling was evident in ^1H NMR spectrum of each product. Of particular interest is the diastereomeric product derived from the P_5Ph_5 reduction with $Ph(Me)SiH_2$, *i.e.* $((PhMeSiH)PhPH)B(C_6F_5)_3$ (**6**). The $^{31}P\{^1H\}$ NMR spectrum of this product shows two resonances at −40.9 and −41.6 ppm in a 4 : 5 ratio indicating a slight preference for the formation of one of the diastereomers under these conditions. In addition, use of 2.5 equivalents of the disilane $C_6H_4(SiHMe_2)_2$ affords the bis-phosphine–borane adduct (**7**) in high yield.

Mechanistically, the hydrogenation reaction is thought to proceed *via* initial heterolytic cleavage of H_2 by P_5Ph_5–$B(C_6F_5)_3$ to give $[P_5Ph_5H][HB(C_6F_5)_3]$. The proposition of such an intermediate is supported by our recent report of the formation of $[tBu_2P(PHtBu_2)][HB(C_6F_5)_3]$ *via* treatment of tBu_4P_2 and $B(C_6F_5)_3$ with H_2. Moreover, Burford and co-workers have isolated a series of alkylated cationic species of the general formula $[P_5Ph_5R]^+$, the alkylated analogs to the proposed intermediate. Subsequent attack on the transient phosphino-phosphonium salt by the borohydride counterion prompts extrusion of (**1**) with formal liberation of "P_4Ph_4". This proposition is consistent with the previously observed reaction of Me_3P with $[P_4Cy_4Me]^+$, which results in nucleophilic attack on the cationic P, forming the new cation $[Me_3PPCyMe]^+$ and P_3Cy_3.[12] As P_4Ph_4 is not observed spectroscopically, the nature of the P-containing intermediates remains unclear; nonetheless, the complete conversion of P_5Ph_5 to primary or secondary phosphine–borane adducts, in this case (**1**), results from subsequent reaction.

The hydrosilylations of P_5Ph_5 to give **2–7** are thought to proceed *via* a mechanism similar to $B(C_6F_5)_3$ catalyzed hydrosilations of imines and carbonyl-compounds studied by Piers and co-workers.[41–43] In those cases, interaction of borane with the Si–H bond is followed by attack of the Lewis base at silicon. In the present case, attack of the polyphosphine at silicon would generate transient intermediate salts of the form $[P_5Ph_5SiR_3][HB(C_6F_5)_3]$, which are subsequently attacked by the borohydride anion $[HB(C_6F_5)_3]$, at the phosphonium center to yield the secondary silylphosphine adduct of $B(C_6F_5)_3$.

In conclusion, combination of P_5Ph_5 and $B(C_6F_5)_3$ produces a frustrated Lewis pair, that can activate H_2 or secondary or tertiary silanes to yield the phosphine adducts $(PhPH_2)B(C_6F_5)_3$, $((R_3Si)PhPH)B(C_6F_5)_3$ and $((R_2SiH)PhPH)B(C_6F_5)_3$, respectively. While the present reductions proceed stoichiometrically, these observations represent rare examples of metal-free reductions of P–P bonds. Moreover, these findings point to the possibility of metal-free catalysts for the synthesis of primary and secondary phosphines from P–P bonded species. Such developments could also provide avenues to asymmetric catalysis offering unique routes to phosphines that are chiral at P. Efforts to develop such metal-free catalysts are on-going.

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Notes and references

‡ X-Ray data: **2**: $C_{30}H_{21}BF_{15}PSi$, a = 9.5286(7) Å, b = 9.8618(7) Å, c = 17.2444(13) Å, α = 95.866(3)°, β = 99.447(3)°, γ = 105.895(2)°, V = 1518.74(19) Å^3, space group: $P\bar{1}$, total data: 7604, data ($>2\sigma$): 5223, R_{int}: 0.0541, variables: 438, R ($>2\sigma$) = 0.0675, R_w ($>2\sigma$) = 0.1697, GOF = 1.077.

1 C. A. Russell, *Angew. Chem., Int. Ed.*, 2009, **48**, 4895–4897.
2 J. D. Masuda, W. W. Schoeller, B. Donnadieu and G. Bertrand, *Angew. Chem., Int. Ed.*, 2007, **46**, 7052–7055.
3 J. D. Masuda, W. W. Schoeller, B. Donnadieu and G. Bertrand, *J. Am. Chem. Soc.*, 2007, **129**, 14180–14181.
4 Y. Wang, Y. Xie, P. Wei, R. B. King, H. F. Schaefer-III, P. v. R. Schleyer and G. H. Robinson, *J. Am. Chem. Soc.*, 2008, **130**, 14970–14971.
5 O. Back, G. Kuchenbeiser, B. Donnadieu and G. Bertrand, *Angew. Chem., Int. Ed.*, 2009, **48**, 5530–5533.
6 R. A. L. Winchester, M. Whitby and M. S. P. Shaffer, *Angew. Chem., Int. Ed.*, 2009, **48**, 3616–3621.
7 C. C. Cummins, *Angew. Chem., Int. Ed.*, 2006, **45**, 862–870.
8 J. S. Figueroa and C. C. Cummins, *J. Am. Chem. Soc.*, 2004, **126**, 13916–13917.
9 N. A. Piro, J. S. Figueroa, J. T. McKellar and C. C. Cummins, *Science*, 2006, **313**, 1276–1279.
10 N. Burford, T. S. Cameron, P. J. Ragogna, E. Ocando-Mavarez, M. Gee, R. McDonald and R. E. Wasylishen, *J. Am. Chem. Soc.*, 2001, **123**, 7947–7948.
11 N. Burford, C. A. Dyker and A. Decken, *Angew. Chem., Int. Ed.*, 2005, **44**, 2364–2367.
12 N. Burford, C. A. Dyker, M. Lumsden and A. Decken, *Angew. Chem., Int. Ed.*, 2005, **44**, 6196–6199.
13 N. Burford, A. D. Phillips, H. A. Spinney, M. Lumsden, U. Werner-Zwanziger, M. J. Ferguson and R. McDonald, *J. Am. Chem. Soc.*, 2005, **127**, 3921–3927.
14 N. Burford, A. D. Phillips, H. A. Spinney, K. N. Robertson, T. S. Cameron and R. McDonald, *Inorg. Chem.*, 2003, **42**, 4949–4954.
15 N. Burford, P. J. Ragogna, R. McDonald and M. J. Ferguson, *J. Am. Chem. Soc.*, 2003, **125**, 14404–14410.
16 N. Burford, P. J. Ragogna, R. McDonald and M. J. Ferguson, *Chem. Commun.*, 2003, 2066–2067.
17 N. Burford, P. J. Ragogna, K. Sharp, R. McDonald and M. J. Ferguson, *Inorg. Chem.*, 2005, **44**, 9453–9460.
18 C. A. Dyker and N. Burford, *Chem. Asian J.*, 2008, **3**, 28–36.
19 C. A. Dyker, N. Burford, G. Menard, M. D. Lumsden and A. Decken, *Inorg. Chem.*, 2007, **46**, 4277–4285.
20 C. A. Dyker, N. Burford, M. D. Lumsden and A. Decken, *J. Am. Chem. Soc.*, 2006, **128**, 9632–9633.

21 C. A. Dyker, S. D. Riegel, N. Burford, M. D. Lumsden and A. Decken, *J. Am. Chem. Soc.*, 2007, **129**, 7464–7474.
22 J. J. Weigand, N. Burford, A. Decken and A. Schulz, *Eur. J. Inorg. Chem.*, 2007, 4868–4872.
23 J. J. Weigand, S. D. Riegel, N. Burford and A. Decken, *J. Am. Chem. Soc.*, 2007, **129**, 7969–7976.
24 J. J. Weigand, M. Holthausen and R. Fröhlich, *Angew. Chem., Int. Ed.*, 2009, **48**, 295–298.
25 S. J. Geier and D. W. Stephan, *Chem. Commun.*, 2008, 99–101.
26 D. W. Stephan, *Org. Biomol. Chem.*, 2008, **6**, 1535–1539.
27 D. W. Stephan, *Dalton Trans.*, 2009, 3129–3136.
28 S. J. Geier, M. A. Dureen, E. Y. Ouyang and D. Stephan, *Chem.–Eur. J.*, 2009, DOI: 10.1002/chem.200902369.
29 P. A. Chase, T. Jurca and D. W. Stephan, *Chem. Commun.*, 2008, 1701–1703.
30 P. A. Chase, G. C. Welch, T. Jurca and D. W. Stephan, *Angew. Chem., Int. Ed.*, 2007, **46**, 8050–8053.
31 V. Sumerin, F. Schulz, M. Nieger, M. Leskela, T. Repo and B. Rieger, *Angew. Chem., Int. Ed.*, 2008, **47**, 6001–6003.
32 J.-M. Denis, H. Forintos, H. Szelke, L. Toupet, T.-N. Pham, P.-J. Madec and A.-C. Gaumont, *Chem. Commun.*, 2003, 54–55.
33 (**1**): yield: 110 mg (91%). Spectral data were identical to published data.[32] $^{31}P\{^{1}H\}$ NMR −43.6 (br); ^{2}D 5.09 (d, J_{P-D} = 64 Hz). All silylphosphine adducts were prepared in a similar fashion, thus only one preparation is described: to a solution of P_5Ph_5 (22 mg, 0.041 mmol) in 4 mL of dichloromethane was added $B(C_6F_5)_3$ (100 mg, 0.20 mmol). To this solution was added Et_3SiH (50 mg, 0.43 mmol). The mixture was allowed to stir overnight whereupon the solvent was removed. X-Ray quality crystals of (**2**) were grown from hexanes at −35 °C. (**2**): yield: 142 mg (99%). Anal. calcd for $C_{30}H_{21}BF_{15}PSi$: C, 48.93; H, 2.87%; found: C, 49.07; H, 3.02%. ^{1}H NMR (C_6D_6): 0.54 (m, 15 H, CH_2CH_3), 4.72 (d, $^{1}J_{P-H}$ = 345 Hz, 1H, P*H*), 6.66 (td, $^{3}J_{H-H}$ = 7 Hz, $^{4}J_{H-P}$ = 2 Hz, 2H, *o*-C*H*), 6.77 (td, $^{3}J_{H-H}$ = 7 Hz, *J* = 2 Hz, 1H, *p*-C*H*), 6.85 (ddd, $^{3}J_{H-H}$ = 10 Hz, $^{3}J_{H-H}$ = 7 Hz, $^{4}J_{P-H}$ = 2 Hz, 2H, *m*-C*H*). ^{19}F NMR (C_6D_6): −129.8 (br s, *o*-C_6F_5), −156.5 (br s, *p*-C_6F_5), −163.7 (br s, *m*-C_6F_5). $^{31}P\{^{1}H\}$ NMR (C_6D_6): −46.6 (br s, $\nu_{1/2}$ ~400 Hz); ^{11}B NMR (C_6D_6): −12.3 (br s); $^{13}C\{^{1}H\}$ NMR (C_6D_6) partial: 4.4 (d, *J* = 8 Hz), 6.8 (d, *J* = 3 Hz), 128.9 (d, *J* = 9 Hz), 130.7 (d, *J* = 3 Hz), 133.6 (d, *J* = 7 Hz). (**3**): yield: 164 mg (95%). Anal. calcd for $C_{42}H_{21}BF_{15}PSi$: C, 57.29; H, 2.40%; found: C, 57.34; H, 2.57%. ^{1}H NMR (C_6D_6): 5.59 (d, $^{1}J_{P-H}$ = 347 Hz, P–*H*), 6.49 (td, *J* = 8 Hz, *J* = 2 Hz, 2H, *o*-C*H*), 6.66 (td, *J* = 7 Hz, *J* = 2 Hz, 1H, *p*-C*H*), 6.78 (ddd, $^{3}J_{H-H}$ = 10 Hz, $^{3}J_{H-H}$ = 8 Hz, $^{4}J_{P-H}$ = 2 Hz, 2H, *m*-C*H*), 6.94 (t, *J* = 7 Hz, 6H), 7.05 (t, *J* = 7 Hz, 3H, *p*-C*H*), 7.40 (dd, *J* = 8 Hz, *J* = 1 Hz, 6H); ^{19}F NMR (C_6D_6): −129.2 (br s, *o*-C_6F_5), −155.1 (br s, *p*-C_6F_5), −163.0 (br s, *m*-C_6F_5). $^{31}P\{^{1}H\}$ NMR (C_6D_6): −45.3 (br s); ^{11}B NMR (C_6D_6): −11.7 (br s); $^{13}C\{^{1}H\}$ NMR (C_6D_6) partial: 122.2 (d, *J* = 40 Hz), 128.4, 130.6 (d, *J* = 3 Hz), 131.3, 134.6 (d, *J* = 6 Hz), 136.4 (d, *J* = 1 Hz). (**4**): yield: 57 mg (82%). Anal. calcd for $C_{28}H_{17}BF_{15}PSi$: C, 47.48; H, 2.42%; found: C, 47.22; H, 2.90%. ^{1}H NMR (C_6D_6): 0.30 (m, 4H, CH_2CH_3), 0.51 (t, $^{3}J_{H-H}$ = 8 Hz, 6H, CH_2CH_3), 3.83 (d, $^{2}J_{P-H}$ = 29 Hz, 1H, Si–*H*), 4.73 (d, $^{1}J_{P-H}$ = 357 Hz, 1H, P–*H*), 6.55 (td, $^{3}J_{H-H}$ = 8 Hz, $^{4}J_{P-H}$ = 2 Hz, 2H, *m*-C_6H_5), 6.69 (m, 3H, *o*-C_6H_5, *p*-C_6H_5). ^{19}F NMR (C_6D_6) *δ*: −129.8 (br s, *o*-C_6F_5), −156.2 (t, $^{3}J_{F-F}$ = 21 Hz, *p*-C_6F_5), −163.5 (td, $^{3}J_{F-F}$ = 21 Hz, $^{4}J_{F-F}$ = 5 Hz, *m*-C_6F_5). $^{31}P\{^{1}H\}$ NMR (C_6D_6): −53.7 (br s); ^{11}B NMR (C_6D_6): −12.8 (br s); $^{13}C\{^{1}H\}$ NMR (C_6D_6) partial: 2.5 (d, *J* = 4 Hz), 3.3 (d, *J* = 6 Hz), 7.3 (d, *J* = 3 Hz), 7.7 (d, *J* = 3 Hz), 129.7 (d, *J* = 10 Hz), 131.1 (d, *J* = 3 Hz), 133.4 (d, *J* = 7 Hz). (**5**): yield: 147 mg (94%). Anal. calcd for $C_{36}H_{17}BF_{15}PSi$: C, 53.75; H, 2.31%; found: C, 54.20; H, 2.81%. ^{1}H NMR (C_6D_6): 5.46 (dd, $^{2}J_{P-H}$ = 27 Hz, $^{3}J_{H-H}$ = 5 Hz, 1H, Si*H*), 5.63 (1H, dd, $^{1}J_{P-H}$ = 363 Hz, $^{3}J_{H-H}$ = 5 Hz, 1H, P*H*), 6.81 (td, *J* = 8 Hz, *J* = 2 Hz, 2H), 6.95 (m, 2H), 7.09 (t, *J* = 7 Hz, 2H),7.29 (m, 8H), 7.70 (dd, *J* = 8 Hz, *J* = 2 Hz, 2H), 7.75 (1H, dd, *J* = 8 Hz, *J* = 2 Hz, 1H), 7.82 (dd, *J* = 8 Hz, *J* = 2 Hz, 1H). ^{19}F NMR (C_6D_6): −129.4 (d, $^{3}J_{F-F}$ = 21 Hz, *o*-C_6F_5), −156.4 (br s, *p*-C_6F_5), −163.3 (br s, *m*-C_6F_5). $^{31}P\{^{1}H\}$ NMR (C_6D_6): −47.1 (br s); ^{11}B NMR (C_6D_6): −12.8 (br s); $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2) partial: 128.9 (d, *J* = 10 Hz), 131.1 (d, *J* = 3 Hz), 133.8 (d, *J* = 7 Hz), 135.5 (d, *J* = 17 Hz), 135.5 (d, *J* = 17 Hz). (**6**): yield: 64 mg (96%). Anal. calcd for $C_{31}H_{15}BF_{15}PSi$: C, 50.16; H, 2.04%; found: C, 50.18; H, 2.26%. ^{1}H NMR ($CDCl_3$): 0.50 (dd, $^{3}J_{P-H}$ = 7 Hz, $^{2}J_{H-H}$ = 4 Hz, 3H, $CH_{3\,major}$), 0.67 (dd, $^{3}J_{P-H}$ = 6 Hz, $^{2}J_{H-H}$ = 4 Hz, 3H, $CH_{3\,minor}$), 4.86 (d, $^{2}J_{P-H}$ = 29 Hz, 1H, Si–*H*), 5.03 (d, $^{1}J_{P-H}$ = 357 Hz, 1H, P–H_{minor}), 5.13 (d, $^{1}J_{P-H}$ = 363 Hz, P–H_{major}), 6.92 (dd, $^{3}J_{P-H}$ = 11 Hz, *J* = 8 Hz, 1H, *o*-PC_6H_5), 7.07 (dd, $^{3}J_{P-H}$ = 11 Hz, *J* = 8 Hz, 1H), 7.12–7.48 (m, 8 H). ^{19}F NMR ($CDCl_3$): −130.0 (br s), −156.6 (t, *J* = 27 Hz, *p*-$C_6F_{5\,minor}$), −156.7 (t, *J* = 27 Hz, *p*-$C_6F_{5\,minor}$), −163.5 (m, *m*-C_6F_5). $^{31}P\{^{1}H\}$ NMR (C_6D_6): -40.9_{minor}, -41.6_{major}; ^{11}B NMR ($CDCl_3$): −13.1 (br s); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) partial: 128.9 (d, *J* = 21 Hz), 129.1 (d, *J* = 10 Hz), 129.5 (d, *J* = 10 Hz), 131.3 (d, *J* = 3 Hz), 131.6 (d, *J* = 3 Hz), 131.7 (d, *J* = 1 Hz), 131.9 (d, *J* = 1 Hz), 135.0 (d, *J* = 10 Hz). (**7**): yield: 134 mg (96%). Anal. calcd for $C_{58}H_{28}BF_{15}P_2Si_2$: C, 48.56; H, 1.97%; found: C, 48.46; H, 2.18%. ^{1}H NMR ($CDCl_3$): 0.44 (d, *J* = 6 Hz, 6H), 0.50 (d, *J* = 6 Hz, 6H), 4.88 (2H, d, $^{1}J_{P-H}$ = 354 Hz, 2H, P–*H*), 6.87 (m, 4H), 7.12 (t, *J* = 7 Hz, 4H), 7.18 (d, *J* = 2 Hz, 4H), 7.30 (t, *J* = 7 Hz, 2H). ^{19}F NMR ($CDCl_3$): −130.0 (br s, *o*-C_6F_5), −156.7 (t, $^{3}J_{F-F}$ = 22 Hz, *p*-C_6F_5), −163.5 (t, $^{3}J_{F-F}$ = 21 Hz, *m*-C_6F_5). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): −37.0 (br s); ^{11}B NMR ($CDCl_3$): −15.3 (br s); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) partial: 0.1 (d, *J* = 11 Hz), 0.7 (d, *J* = 10 Hz), 0.8 (d, *J* = 10 Hz), 125.1 (d, *J* = 5 Hz), 124.6 (d, *J* = 5 Hz), 132.4 (d, *J* = 10 Hz), 134.5 (d, *J* = 3 Hz), 136.9, 137.1 (d, *J* = 6 Hz), 140.3 (dm, *J* = 247 Hz, C*F*), 151.3 (dm, *J* = 244 Hz, C*F*).
34 G. C. Welch, L. Cabrera, P. A. Chase, E. Hollink, J. D. Masuda, P. Wei and D. W. Stephan, *Dalton Trans.*, 2007, 3407–3414.
35 G. C. Welch, R. Prieto, M. A. Dureen, A. J. Lough, O. A. Labeodan, T. Holtrichter-Rossmann and D. W. Stephan, *Dalton Trans.*, 2009, 1559–1570.
36 R. T. Boere and J. D. Masuda, *Can. J. Chem.*, 2002, **80**, 1607–1617.
37 M. Okazaki, K. A. Jung and H. Tobita, *Organometallics*, 2005, **24**, 659–664.
38 M. A. Petrie and P. P. Power, *J. Chem. Soc., Dalton Trans.*, 1993, 1737–1745.
39 O. Tardif, Z. M. Hou, M. Nishiura, T. Koizumi and Y. Wakatsuki, *Organometallics*, 2001, **20**, 4565–4573.
40 O. Tardif, M. Nishiura and Z. M. Hou, *Tetrahedron*, 2003, **59**, 10525–10539.
41 J. M. Blackwell, D. J. Morrison and W. E. Piers, *Tetrahedron*, 2002, **58**, 8247–8254.
42 J. M. Blackwell, E. R. Sonmor, T. Scoccitti and W. E. Piers, *Org. Lett.*, 2000, **2**, 3921–3923.
43 D. J. Parks and W. E. Piers, *J. Am. Chem. Soc.*, 1996, **118**, 9440–9441.

