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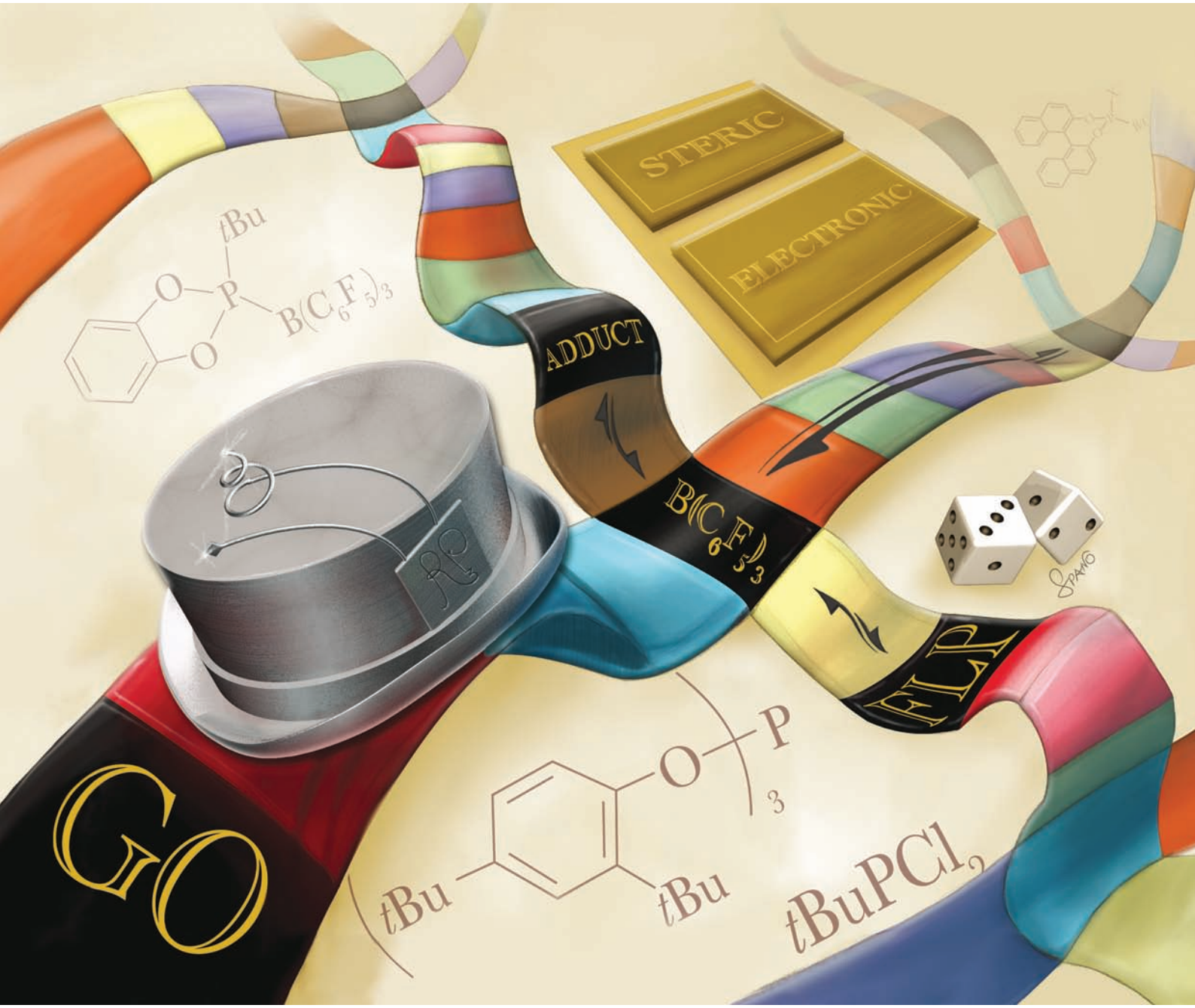

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PAPER

Chloro- and phenoxy-phosphines in frustrated Lewis pair additions to alkynes†

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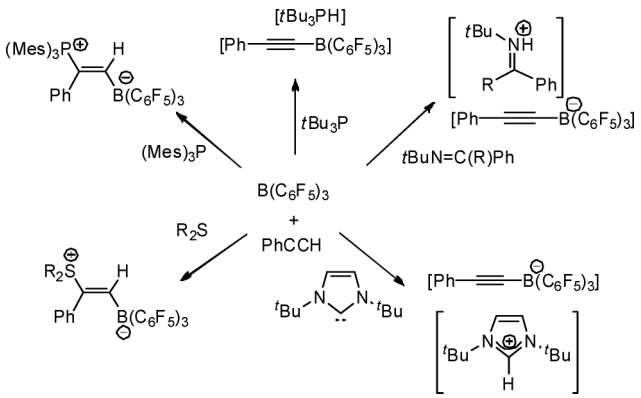
The reaction of tBu($C_6H_4O_2$)P, with the borane $B(C_6F_5)_3$ gives rise to NMR data consistent with the formation of the classical Lewis acid–base adduct tBu($C_6H_4O_2$)P($B(C_6F_5)_3$) (**1**). In contrast, the NMR data for the corresponding reactions of tBu($C_{20}H_{12}O_2$)P and Cl($C_{20}H_{12}O_2$)P with $B(C_6F_5)_3$ were consistent with the presence of equilibria between free phosphine and borane and the corresponding adducts. Nonetheless, in each case, the adducts tBu($C_{20}H_{12}O_2$)P($B(C_6F_5)_3$) (**2**) and Cl($C_{20}H_{12}O_2$)P-($B(C_6F_5)_3$) (**3**) were isolable. The species **1** reacts with PhCCH to give the new species tBu($C_6H_4O_2$)-P(Ph)C═CHB($C_6F_5)_3$ (**4**) in near quantitative yield. In an analogous fashion, the addition of PhCCH to solutions of the phosphines tBu($C_{20}H_{12}O_2$)P, tBuPCl$_2$ and (C_6H_3(2,4-tBu$_2$)O)$_3$P each with an equivalent of $B(C_6F_5)_3$ gave rise to L(Ph)C═CHB($C_6F_5)_3$ (L = tBu($C_{20}H_{12}O_2$)P **5**, tBuPCl$_2$ **6** and (C_6H_3(2,4-tBu$_2$)O)$_3$P 7). X-Ray data for **1**, **2**, **6** and **7** are presented. The implications of these findings are considered.

Introduction

"Frustrated Lewis pairs" (FLPs) were first derived from the combination of a sterically hindered Lewis base and a sterically bulky Lewis acid.[1–4] These combinations of molecules have been shown to have remarkable reactivity as a result of the availability of unquenched Lewis acidity and basicity. In what is considered the most dramatic demonstration of this chemistry, FLPs have been shown to effect the heterolytic cleavage of H_2.[5–13] However these systems also effect a wide range of other new reactivity including the activation of alkynes,[14–17] dienes,[18] olefins,[19] boranes,[20] disulfides,[21] N_2O,[22–24] CO_2 [25–30] as well as effecting the ring opening of THF and ethers and lactones.[31–34]

The variability of the Lewis acid and bases has been explored to some extent. While much of the initial demonstration of this chemistry was done employing bulky phosphines and $B(C_6F_5)_3$, the analogous chemistry using bulky amines quickly followed. Subsequent worked showed that sterically demanding carbenes,[35,36] pyridines[32,37] and N-heterocycles[38] were effective in H_2 splitting by FLPs, while N-donors, sulfides and C-donors derived from pyrroles effected FLP reactions with terminal alkynes (Scheme 1).[14–16] Variation in the Lewis acid has received has received lesser attention although the electrophilic alane $Al(C_6F_5)_3$,[15,16] boranes of the form $RB(C_6F_5)_2$ and $B(C_6F_4H)_3$[39] have been utilized. More recently FLP chemistry of CO_2 has been demonstrated with the Al-halides AlX_3 (X = Cl, Br, I),[25,26]



Scheme 1 Examples of FLP alkyne addition reactions.

although this proved accessible only with the bulky phosphines.

In the known FLP chemistry in which phosphines have been employed, the reactive systems have largely been limited to combinations of trialkyl- or triarylphosphines and $B(C_6F_5)_3$. We have also reported hydrogen activation with bulky phosphinites tBu$_2$POR (R = Ph, tBu) and tBu$_2$PCl in combination with $B(C_6F_5)_3$.[40] Recently we have reported that the sterically demanding secondary phosphine $(C_6H_2Me_3)_2PH$ and the primary phosphine $(C_6H_2tBu_3)PH_2$ are also capable of effecting FLP addition to alkynes (Scheme 1).[15] In the present work, we explore the utility of phosphines that incorporate halides and phenoxide substituents, demonstrating that electron deficient and electron-rich donors are capable of FLP additions to alkynes. The implications of these findings are considered.

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Experimental

General procedures

All preparations were done under an atmosphere of dry, O_2-free N_2 by usage of an Innovative Technology glovebox and a Schlenk vacuum line. Solvents were purified with a Grubbs-type column system manufactured by Innovative Technology and dispensed into thick-walled Schlenk glass bombs equipped with Young-type Teflon valve stopcocks (pentanes, hexanes, toluene, CH_2Cl_2) or were dried over the appropriate agents and distilled into the same kind of Young bombs ($CHCl_3$). All solvents were thoroughly degassed after purification (repeated freeze-pump-thaw cycles). Deuterated solvents were dried over the appropriate agents (CaH_2 for CD_2Cl_2, $CDCl_3$), vacuum-transferred into Young bombs, and degassed accordingly. All NMR spectra were recorded on Bruker Avance-300 or 400 spectrometers. All chemical shifts of ^1H and ^{13}C spectra are given relative to $SiMe_4$ and referenced to the residual solvent signal. Those of ^{11}B, ^{19}F and ^{31}P NMR spectra are given relative to an external standard (^{11}B, $(Et_2O)BF_3$; ^{19}F, $CFCl_3$; ^{31}P, 85% H_3PO_4). In some instances, signal and/or coupling assignment was derived from two-dimensional NMR experiments. Chemical shifts are reported in ppm and coupling constants as scalar values in Hz. Combustion analyses were performed in house by employing a Perkin-Elmer CHN analyzer.[41] Chemicals were obtained from Strem Chemicals, Inc. (USA) and from Sigma Aldrich. $tBu(C_6H_4O_2)P$ and $tBu(C_{20}H_{12}O_2)P$ were prepared following literature preparations.[42]

Preparation of $tBu(C_6H_4O_2)P(B(C_6F_5)_3)$ (1), $tBu(C_{20}H_{12}O_2)P(B(C_6F_5)_3)$ (2) and $Cl(C_{20}H_{12}O_2)P(B(C_6F_5)_3)$ (3)

These compounds were synthesized in a similar fashion, thus only one preparation will be detailed. To a solution of $tBu(C_{20}H_{12}O_2)P$ (72 mg, 0.195 mmol) in CH_2Cl_2 (5 mL) was added $B(C_6F_5)_3$ (100 mg, 0.195 mmol). The solution was allowed to stir for 4 h. All volatiles were removed *in vacuo* and the residue was washed with hexanes (2 × 2 mL) and again dried in vacuo.

(1) Yield: 135 mg (98%).^1H NMR ($CDCl_3$) δ: 7.07(dd, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 4 Hz, 2H), 6.99 (dd, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 4 Hz, 2H), 1.12 (d, $^3J_{PH}$ = 15 Hz, 9H). ^{11}B NMR ($CDCl_3$) δ: –8.7 (br. s). ^{19}F NMR ($CDCl_3$) δ: –128.2 (d, $^3J_{FF}$ = 18 Hz, 6F, *o*-C*F*), –158.9 (t, $^3J_{FF}$ = 20 Hz, 3F, *p*-C*F*), –163.3 (td, $^3J_{FF}$ = 22 Hz, $^4J_{FF}$ = 22 Hz, 6F, *m*-C*F*). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 178.8 (s). ^{13}C NMR (partial, $CDCl_3$) δ: 25.2 (d, J_{PC} = 6 Hz), 88.0 (d, J_{PC} = 4 Hz), 112.6 (d, J_{PC} = 6 Hz), 128.1, 137.2 (dm, J_{FC} = 253 Hz), 141.1 (dm, J_{FC} = 258 Hz), 146.5 (d, J_{FC} = 6 Hz), 148.2 (dm, J_{FC} = 245 Hz). Anal. Calcd. for $C_{28}H_{13}BF_{15}O_2P$ (%) C: 47.49, H: 1.85; found C: 47.57, H: 2.15.

(2) Yield: 165 mg (96%). ^1H NMR (CD_2Cl_2) δ: 8.02 (d, $^3J_{HH}$ = 9 Hz, 1H), 7.94 (d, $^3J_{HH}$ = 8 Hz, 1H), 7.88 (d, $^3J_{HH}$ = 8 Hz, 1H), 7.71 (d, $^3J_{HH}$ = 9 Hz, 1H), 7.59 (d, $^3J_{HH}$ = 9 Hz, 1H), 7.35 (m, 4H), 7.46 (q, $^3J_{HH}$ = 8 Hz, 2H), 7.35 (d, $^3J_{HH}$ = 9 Hz, 1H), 7.22 (t, $^3J_{HH}$ = 7 Hz, 2H), 7.06 (d, $^3J_{HH}$ = 9 Hz, 2H), 1.06 (d, $^3J_{PH}$ = 15 Hz, 9H). ^{11}B NMR (CD_2Cl_2) δ: 12.2 (br. s). ^{19}F NMR (CD_2Cl_2) δ: –126.3 (br. s, 6F, *o*-C*F*), –151.7 (br. s 3F, *p*-C*F*), –162.2 (br. s, 6F, *m*-C*F*). $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ: 167.4 (s). ^{13}C NMR (partial, CD_2Cl_2) δ: 149.0 (d, J_{PC} = 15 Hz), 148.5 (dm, J_{FC} = 241 Hz), 148.4 (d, J_{PC} = 8 Hz), 141.5 (d, J_{FC} = 254 Hz), 137.5 (dm, J_{FC} = 249 Hz), 133.3, 132.8, 131.9 (d, J_{PC} = 16 Hz), 131.3, 129.9, 128.1, 127.5, 127.1, 126.5, 126.1, 121.7 (d, J_{PC} = 3 Hz), 121.0, 120.4 (d, J_{PC} = 3 Hz), 120.2 (d, J_{PC} = 3 Hz), 43.1 (d, J_{PC} = 15 Hz), 26.6 (d, J_{PC} = 5 Hz). Anal. Calcd. for $C_{42}H_{21}BF_{15}O_2P$ (%) C: 57.04, H: 2.39; found C: 53.27, H: 2.75.

(3) Yield: 165 mg (98%). ^1H NMR ($CDCl_3$) δ: 8.08 (d, $^3J_{hH}$ = 9 Hz, 1H), 8.01 (m, 2H), 7.98 (d, $^3J_{HH}$ = 9 Hz, 1H), 7.55 (m, 2H), 7.50 (d, $^3J_{HH}$ = 9 Hz, 1H), 7.35 (m, 4H), 7.15 (d, $^3J_{HH}$ = 9 Hz, 1H). ^{11}B NMR ($CDCl_3$) δ: 29.5 (br. s). ^{19}F NMR ($CDCl_3$) δ: –128.0 (d, $^3J_{FF}$ = 19 Hz, 6F, *o*-C*F*), –147.9 (br. s 3F, *p*-C*F*), –161.2 (t, $^3J_{FF}$ = 20 Hz, 6F, *m*-C*F*). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 162.5 (s). ^{13}C NMR (partial, $CDCl_3$) δ: 112.7, 120.0 (d, J_{PC} = 3 Hz), 121.0 (d, J_{PC} = 2 Hz), 122.5 (d, J_{PC} = 4 Hz), 122.7 (d, J_{PC} = 3 Hz), 126.1 (d, J_{PC} = 5 Hz), 127.0 (d, J_{PC} = 13 Hz), 127.1, 128.6 (d, J_{PC} = 10 Hz), 130.8, 131.2, 132.0, 132.6, 137.6 (dm, J_{FC} = 252 Hz), 143.4 (d, J_{FC} = 252 Hz), 147.2 (d, J_{PC} = 9 Hz), 148.3, 148.4, 148,5 (dm, J_{FC} = 248 Hz). Anal. Calcd. for $C_{38}H_{12}BF_{15}O_2PCl$ (%) C: 52.90, H: 1.40; found C: 52.69, H: 1.68.

Synthesis of $L(Ph)C{=}CHB(C_6F_5)_3$ (L = $tBu(C_6H_4O_2)P$ 4, $tBu(C_{20}H_{12}O_2)P$ 5, $tBuPCl_2$ 6, $(C_6H_3(2,4\text{-}tBu_2)O)_3P$ 7)

These compounds were synthesized in a similar fashion, thus only one preparation will be detailed. To a solution of *tert*-butyl(catechol)phosphine (38 mg, 0.195 mmol) and $B(C_6F_5)_3$ (100 mg, 0.195 mmol) in dichloromethane (5 mL) was added phenyl acetylene (30 mg, 0.29 mmol). The solution was allowed to stir for 4 h. All volatiles were removed *in vacuo* and the residue was washed with hexanes (2 × 2 mL) and again dried in vacuo.

(4) Yield: 157 mg (99%). ^1H NMR ($CDCl_3$) δ: 9.10 (d, $^3J_{PH}$ = 37 Hz, 1H, PC = C*H*), 7.27 (m, 2H), 7.20 (dd, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 4 Hz, 2H), 7.10 (t, $^3J_{HH}$ = 7 Hz, 2H, m-CH), 6.96 (d, $^3J_{HH}$ = 7 Hz, 2H, o-CH), 1.38 (d, $^3J_{PH}$ = 19 Hz, 9H, C(CH_3)$_3$). ^{11}B NMR ($CDCl_3$) δ: –16.2 (d, $^3J_{PB}$ = 17 Hz). ^{19}F NMR ($CDCl_3$) δ: –132.1 (d, $^3J_{FF}$ = 22 Hz, 6F, *o*-C*F*), –161.4 (t, $^3J_{FF}$ = 20 Hz, 3F, *p*-C*F*), –166.1 (td, $^3J_{FF}$ = 21 Hz, $^4J_{FF}$ = 8 Hz, 6F, *m*-C*F*). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 107.7 (q, $^3J_{PB}$ = 17 Hz). ^{13}C NMR (partial, $CDCl_3$) δ: 144.5 (d, J_{PC} = 3 Hz), 132.3, 129.4 (d, J_{PC} = 6 Hz), 129.2 (d, J_{PC} = 3 Hz), 129.0, 128.6 (d, J_{PC} = 2 Hz), 128.5, 114.0 (d, J = 9 Hz), 37.6 (d, $^1J_{PC}$ = 57 Hz), 23.9. Anal. Calcd. for $C_{36}H_{19}BF_{15}O_2P$ (%) C: 53.36, H: 2.36; found C: 54.02, H: 2.82.

(5) Yield: 186 mg (97%). ^1H NMR ($CDCl_3$) δ: 8.96 (d, $^3J_{PH}$ = 35 Hz, 1H, PC = C*H*), 8.03 (m, 3H), 7.96 (d, $^3J_{HH}$ = 8 Hz, 1H), 7.57 (q, $^3J_{HH}$ = 8 Hz, 1H), 7.35 (ov m, 4H), 7.20 (d, J = 9 Hz, 1H), 7.07 (d, $^3J_{HH}$ = 9 Hz, 1H), 7.02 (td, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 1 Hz, 1H, *p*-C*H*), 6.85 (t, $^3J_{HH}$ = 8 Hz, 2H, *m*-C*H*), 6.42 (br s, 2H, *o*-C*H*), 1.43 (d, $^3J_{PH}$ = 18 Hz, 9H, C(CH_3)$_3$). ^{11}B NMR ($CDCl_3$) δ: –16.3 (d, $^3J_{PB}$ = 16 Hz). ^{19}F NMR ($CDCl_3$) δ: –131.1 (d, $^3J_{FF}$ = 22 Hz, 6F, *o*-C*F*), –161.8 (t, $^3J_{FF}$ = 22 Hz, 3F, *p*-C*F*), –166.3 (td, $^3J_{FF}$ = 22 Hz, $^4J_{FF}$ = 7 Hz, 6F, *m*-C*F*). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 91.1 (q, $^3J_{PB}$ = 16 Hz). ^{13}C NMR (partial, $CDCl_3$) δ: 147.1 (d, J_{PC} = 10 Hz), 145.3 (d, J_{PC} = 10 Hz), 132.9, 132.7, 132.5, 132.4, 132.1, 132.0 (d, J_{PC} = 1 Hz), 129.3 (d, J_{PC} = 5 Hz), 129.0 (d, J_{PC} = 21 Hz), 129.0, 128.5, 128.0 (ov m), 127.7 (d, J_{PC} = 20 Hz), 127.1 (d, J_{PC} = 3 Hz), 126.9, 38.0 (d, $^1J_{PC}$ = 67 Hz), 25.1. Anal. Calcd. for $C_{50}H_{27}BF_{15}O_2P$ (%) C: 60.87, H: 2.76; found C: 60.44, H: 2.48.

(6) Yield: 146 mg (97%). ^1H NMR ($CDCl_3$) δ: 9.16 (d, $^3J_{PB}$ = 49 Hz, 1H, PC = C*H*), 7.29 (t, $^3J_{HH}$ = 7 Hz 2H), 7.17 (t, $^3J_{HH}$ = 7 Hz, 2H), 6.95 (dd, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 2 Hz, 2H), 1.54 (d, $^3J_{PH}$ = 25 Hz, 9H, C(CH_3)$_3$) ^{11}B NMR ($CDCl_3$) δ: –15.9 (d, $^3J_{BP}$ = 21 Hz). ^{19}F NMR ($CDCl_3$) δ: –130.7 (d, $^3J_{FF}$ = 23 Hz, 6F, *o*-C*F*), –159.7

Table 1 Crystallographic data

	1	**2**	**6**	**7**·C_6H_{14}
Formula	$C_{28}H_{13}BF_{15}O_2P$	$C_{42}H_{21}BF_{15}O_2P$	$C_{30}H_{15}BCl_2F_{15}P$	$C_{68}H_{69}BF_{15}O_3P$
wt	708.16	884.37	773.10	1261.01
Cryst. syst.	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space grp	$P2_1/n$	$P2_1$	$P2_1/c$	$P2_1/n$
a/Å	10.8146(14)	15.6025(6)	13.4163(4)	15.2876(6)
b/Å	12.6680(15)	11.5308(4)	18.3323(5)	17.8123(7)
c/Å	19.986(2)	21.2356(7)	14.0090(5)	26.9165(12)
α (°)	90	90	90	90
β (°)	93.540(4)	103.904(2)	118.077(1)	104.511(2)
γ (°)	90	90	90	90
V/Å^3	2732.9(6)	3708.5(2)	3040.05	7095.7(5)
Z	4	4	4	4
d(calc)/g cm^{-3}	1.721	1.584	1.689	1.180
R(int)	0.0622	0.0467	0.0342	0.0870
μ/mm^{-1}	0.232	0.189	0.382	0.119
Total data	6288	33228	6934	16272
$>2\sigma(F_o^2)$	3819	13881	4546	8842
Variables	424	1099	442	787
R ($>2\sigma$)	0.0495	0.0437	0.0394	0.0708
R_w	0.1196	0.0949	0.0915	0.2030
GOF	0.996	0.988	1.001	1.051
Flack Param.		0.05(8)		

(t, $^3J_{FF}$ = 21 Hz, 3F, *p*-C*F*), –164.5 (br.t, $^3J_{FF}$ = 22 Hz, 6F, *m*-C*F*). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 119.5 (q, $^3J_{PB}$ = 21 Hz). ^{13}C NMR (partial, $CDCl_3$) δ: 148.0 (dm, J_{FC} = 240 Hz), 138.8 (dm, J_{FC} = 221 Hz), 136.6 (dm, J_{FC} = 246 Hz), 131.4 (d, J_{PC} = 19 Hz), 130.0 (d, J_{PC} = 7 Hz), 129.4 (d, J_{PC} = 8 Hz), 128.5 (d, J_{PC} = 3 Hz), 46.8 (d, J_{PC} = 29 Hz), 24.5 (d, J_{PC} = 2 Hz). Anal. Calcd. for $C_{30}H_{15}BCl_2F_{15}P$ (%) C: 46.61, H: 1.96; found C: 47.37, H: 2.38.

(7) Yield: 130 mg (53%). ^1H NMR ($CDCl_3$) δ: 9.45 (d, $^3J_{PH}$ = 44 Hz, 1H, PC = C*H*), 7.44 (t, J = 2 Hz, 3H), 7.34 (d, $^3J_{HH}$ = 9 Hz, 3H), 7.22 (dd, $^3J_{HH}$ = 9 Hz, J = 2 Hz, 3H), 7.10 (td, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz, 1H, *p*-C*H*), 6.90 (t, $^3J_{HH}$ = 8 Hz, 2 H, *m*-C*H*), 6.51 (d, $^3J_{HH}$ = 7 Hz, 2H, *o*-C*H*). ^{11}B NMR ($CDCl_3$) δ: –16.4 (d, $^3J_{PB}$ = 20 Hz). ^{19}F NMR ($CDCl_3$) δ: –130.9 (d, $^3J_{FF}$ = 23 Hz, 6F, *o*-C*F*), –161.9 (t, $^3J_{FF}$ = 20 Hz, 3F, *p*-C*F*), –166.4 (t, $^3J_{FF}$ = 22 Hz, 6F, *m*-C*F*). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 15.0 (q, $^3J_{PB}$ = 20 Hz). ^{13}C NMR (partial, $CDCl_3$) δ: 150.1, 147.2 (d, J_{PC} = 9 Hz), 138.4 (d, J_{PC} = 9 Hz), 129.5 (d, J_{PC} = 6 Hz), 129.0 (d, J_{PC} = 4 Hz), 128.4 (d, J_{PC} = 3 Hz), 125.2, 118.3 (d, J_{PC} = 3 Hz), 35.1, 35.0, 31.4, 30.2. Anal. Calcd. for $C_{68}H_{69}BF_{15}O_3P$ • 1 eq. hexane (as per crystal structure) (%) C: 65.97, H: 6.21; found C: 66.19, H: 6.57.

X-Ray data collection and reduction

Crystals were coated in Paratone-N oil in the glovebox, mounted on a MiTegen Micromount and placed under an N_2 stream, thus maintaining a dry, O_2-free environment for each crystal. The data were collected on a Bruker Apex II diffractometer. The data were collected at 150(±2) K for all crystals. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. Data were corrected for absorption effects using the empirical multiscan method (SADABS).

Structure solution and refinement

Non-hydrogen atomic scattering factors were taken from the literature tabulations.[43] The heavy atom positions were determined using direct methods employing the SHELXTL direct methods routine.[44–46] The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on F, minimizing the function $\omega (F_o - F_c)^2$ where the weight ω is defined as $4F_o^2/2\sigma (F_o^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes, respectively. In the final cycles of each refinement, all non-hydrogen atoms were assigned anisotropic temperature factors in the absence of disorder or insufficient data. In the latter cases atoms were treated isotropically. C–H atom positions were calculated and allowed to ride on the carbon to which they are bonded assuming a C–H bond length of 0.95 Å. H-atom temperature factors were fixed at 1.10 times the isotropic temperature factor of the C-atom to which they are bonded. The H-atom contributions were calculated, but not refined. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of residual electron densities in each case were of no chemical significance (Table 1). In the case of **7**, the severe disorder of the included solvent precluded a chemically reasonable model and thus the data were squeezed using PLATON to obtain the final solution.

Results and discussion

Lewis acid–base adducts

The reaction of *t*Bu($C_6H_4O_2$)P, with the borane $B(C_6F_5)_3$ gives rise to NMR data consistent with the formation of a classical Lewis acid–base adduct. For example, a single broad resonance in the ^{11}B NMR spectrum at –8.7 ppm is attributable to *t*Bu($C_6H_4O_2$)P($B(C_6F_5)_3$) **(1)**. This species also gives rise to a gap between the ^{19}F NMR signals attributable to the *meta*- and *para*-fluorines of 4.4 ppm as well as a $^{31}P\{^1H\}$ NMR resonance at 178.8 ppm, consistent with adduct formation. This assignment was subsequently confirmed crystallographically (Fig. 1). In this case, the P–B bond distance was found to be 2.069(3) Å, while the remaining metric parameters were unexceptional.

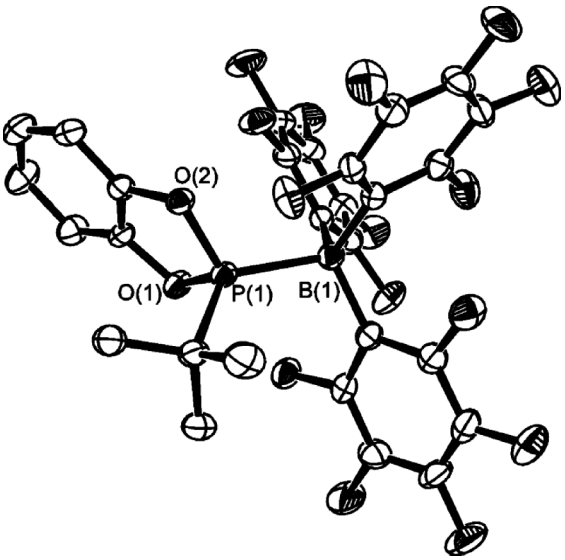


Fig. 1 ORTEP drawing of **1**, 50% thermal ellipsoids are shown, hydrogen atoms are omitted for clarity.

In contrast, the NMR data for the corresponding reactions of tBu($C_{20}H_{12}O_2$)P and Cl($C_{20}H_{12}O_2$)P with B(C_6F_5)$_3$ gave rise to ^{11}B NMR signals at 12.2 and 29.5 ppm and gaps between the *meta*- and *para*-fluorines in the ^{19}F NMR spectra 10.5 and 13.3 ppm, respectively. The corresponding ^{31}P{^{1}H} NMR resonances are seen at 167.4 and 162.5 ppm. These data are consistent with the presence of equilibria between free phosphine and borane and the corresponding adducts (Scheme 2). Nonetheless, in each of these cases, removal of the solvent afforded isolation of the adducts formulated as tBu($C_6H_4O_2$)P(B(C_6F_5)$_3$) **(1)**, tBu($C_{20}H_{12}O_2$)P(B(C_6F_5)$_3$) **(2)** and Cl($C_{20}H_{12}O_2$)P(B(C_6F_5)$_3$) **(3)** in high yields. The presence of the equilibria in the latter cases suggests that steric demands of the phosphine substituents plays a critical role. X-ray crystallography was used to characterize **2** (Fig. 2). This species is as expected with quaternized B centers and B–P bond length of 2.072(4) Å, respectively.

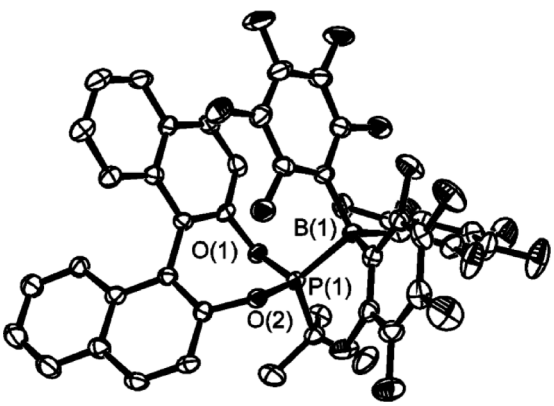
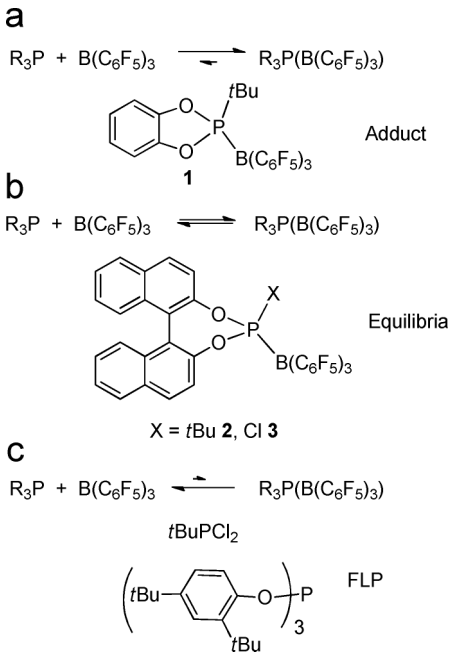


Fig. 2 ORTEP drawing of one of the molecules of **2** in the asymmetric unit, 50% thermal ellipsoids are shown, hydrogen atoms are omitted for clarity.

The exclusive formation of **1** in solution (Scheme 2(a)), while **2** exists in equilibrium at room temperature clearly points to the impact of steric demand on the stability of the adduct (Scheme 2(b)). A similar situation may be ascribed to the observation of the equilibrium for **3**, although this could also be attributed in part to the diminished basicity of Cl($C_{20}H_{12}O_2$)P as a result of the presence of the electron withdrawing chloride substituent. In exploring this ambiguity, we noted that the combination of (C_6H_3(2,4-tBu$_2$)O)$_3$P or tBuPCl$_2$ with B(C_6F_5)$_3$ resulted in NMR data identical with the constituents of the mixtures, unperturbed by the presence of the other reagent. Thus these mixtures appear to be exclusively FLPs (Scheme 2(c)). In the case of (C_6H_3(2,4-tBu$_2$)O)$_3$P, the inability to form a Lewis acid–base adduct is clearly attributable to steric demands of the bulky phenoxide substituents. This view is consistent with our initial notions of FLPs. However the latter case of tBuPCl$_2$ is different as the inability to form an adduct in this case can be attributed to the electron withdrawing substituents on the P atom. In this case, one could argue that the "frustration" is derived from an electronic effect rather than steric factors.

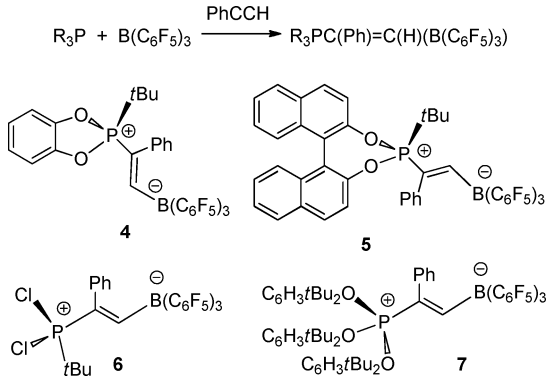


Scheme 2 Examples of Lewis Acid–base equilibria from adduct to FLP.

FLP Reactivity with PhCCH

Despite the fact that **1** is an isolable adduct of tBu($C_6H_4O_2$)P and B(C_6F_5)$_3$, subsequent addition of PhCCH results in the formation of a new species **4** in near quantitative yield. The ^{1}H NMR spectrum of **4** exhibits a distinctive signal at 9.10 ppm with a $^3J_{PH}$ coupling of 37 Hz. The ^{11}B NMR signal at –16.2 ppm is characteristic of an anionic B center. Consistent with this is the small gap of 4.7 ppm between the ^{19}F NMR resonances arising from the *meta*- and *para*-fluorines. The ^{31}P{^{1}H} NMR spectrum of **4** shows a quartet at 107.7 ppm with a P–B coupling of 18 Hz. This small coupling, also observed in the B spectrum, is consistent with a *trans* substitution of B and P on an olefinic fragment, prompting the formulation of **4** as tBu($C_6H_4O_2$)P(Ph)C=CHB(C_6F_5)$_3$ (Scheme 3).

In an analogous fashion, the addition of PhCCH to solutions of the phosphines tBu($C_{20}H_{12}O_2$)P, tBuPCl$_2$ and (C_6H_3(2,4-tBu$_2$)O)$_3$



Scheme 3 Synthesis of the FLP addition products **4–7**.

P each with an equivalent of $B(C_6F_5)_3$ gave rise to new products **5–7**, respectively (Scheme 3). These products were isolated in yields ranging from 53–97%. The lower yield of **7** is attributed to the hexane solubility resulting from the *t*Bu substituted aryl rings on the phosphine. Similar to **4**, each of these products showed a distinctive resonance in the ^{1}H NMR spectra at 8.96, 9.16 and 9.45 ppm, attributable to an olefinic proton. The ^{11}B NMR spectra of **5–7** were consistent with the presence of the anionic borate fragment with ^{11}B signals at –16.3, –15.8 and –16.4, respectively. Similarly, the ^{19}F spectral data supported this aspect of the formulation. $^{31}P\{^{1}H\}$ NMR spectra were consistent with the quaternization of P with resonances at 91.1, 119.5 and 15.0 ppm respectively. Each of these signals shows P–B coupling on the order of 17–20 Hz, similar to that seen for **4**. Collectively these data support the formulation of **5–7** as $L(Ph)C{=}CHB(C_6F_5)_3$ (L = *t*Bu($C_{20}H_{12}O_2$)P **5**, *t*BuPCl$_2$ **6** and (C_6H_3(2,4-*t*Bu$_2$)O)$_3$P **7**).

The nature of **4–7** was further confirmed *via* crystallographic characterization of **6** and **7** (Fig. 3, 4). These data confirm the *trans*-addition of phosphine and borane to PhCCH. The resulting newly formed P–C and B–C bonds were found to 1.794(2) Å and 1.642(3) Å and 1.755(4) Å and 1.642(6) Å, respectively in **6** and **7**. The C=C double bonds were typical being 1.345(3) Å in both **6** and **7**.

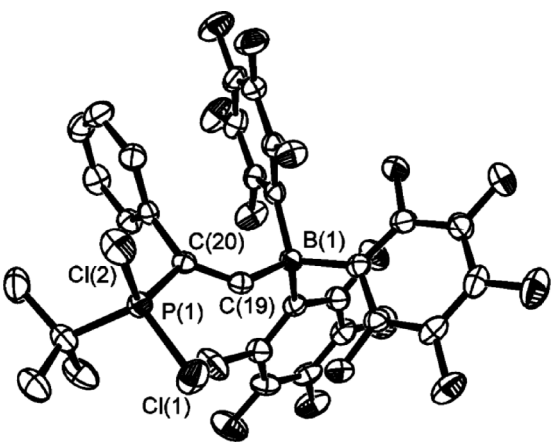


Fig. 3 ORTEP drawing of **6**, 50% thermal ellipsoids are shown, hydrogen atoms are omitted for clarity.

The nature of the species **4**–7 is similar to those previously reported for the trimolecular reaction of FLPs and alkynes. Nonetheless, these examples illustrate several important aspects of

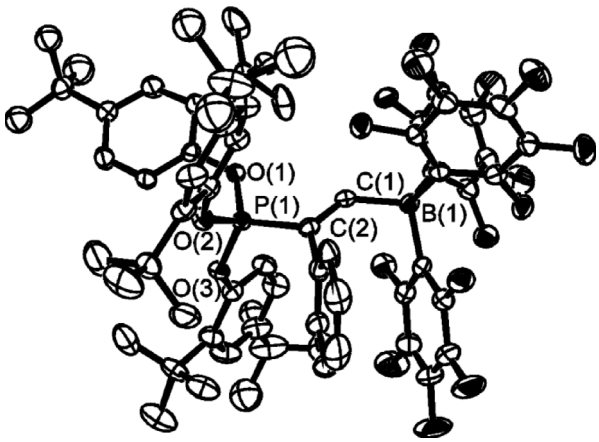


Fig. 4 ORTEP drawing of **7**, 50% thermal ellipsoids are shown, hydrogen atoms are omitted for clarity. Only one conformation of the disordered *t*Bu groups are shown.

FLP chemistry. Firstly, the formation of **4**, despite the formation of an apparent "tight" adduct (compound **1**) demonstrates that even if not evident by spectroscopy, an indiscernible equilibrium may allow the reactions of seemingly classical Lewis acid–base adduct. This notion is further confirmed by a previously report of the reactivity of the seemingly robust adduct $Ph_3P(B(C_6F_5)_3)$ with alkyne.[15] A second teaching from the present observations relates to the formation of **5**–7. While the steric demands of *t*Bu($C_{20}H_{12}O_2$)P and (C_6H_3(2,4-*t*Bu$_2$)O)$_3$P allow for the generation of an FLP with $B(C_6F_5)_3$ and subsequent reactivity to give **5** and 7, the formation of **6** is a rare example where electronic factors "frustrates" adduct formation, permitting the FLP addition to alkyne to occur.

Conclusion

In this work we broadened the range of phosphines that effect FLP addition reactions to alkynes. While FLPs derived from phosphines with phenoxide substituents and $B(C_6F_5)_3$ are shown to span the range from strong adduct to non-interacting FLPs, all of these systems react with alkynes. Similarly, phosphines with electron withdrawing chloride substituents do not form classical adducts with borane, yet subsequent addition of the FLP to alkyne proceeds. The factors relating FLP formation and subsequent reactivity continue be the subject of study in our laboratories.

Notes and references

1 D. W. Stephan, *Org. Biomol. Chem.*, 2008, **6**, 1535–1539.
2 D. W. Stephan, *Dalton Trans.*, 2009, 3129–3136.
3 D. W. Stephan, *Chem. Commun.*, 2010, **46**, 8526–8533.
4 D. W. Stephan and G. Erker, *Angew. Chem. Int. Ed.*, 2010, **49**, 46–76.
5 P. A. Chase, T. Jurca and D. W. Stephan, *Chem. Commun.*, 2008, 1701–1703.
6 P. A. Chase, G. C. Welch, T. Jurca and D. W. Stephan, *Angew. Chem., Int. Ed.*, 2007, **46**, 8050–8053.
7 D. W. Stephan, S. Greenberg, T. W. Graham, P. Chase, J. J. Hastie, S. J. Geier, J. M. Farrell, C. C. Brown, Z. M. Heiden, G. C. Welch and M. Ullrich, *Inorg. Chem.*, 2011, DOI: 10.1021/ic200663v.
8 G. C. Welch, R. R. S. Juan, J. D. Masuda and D. W. Stephan, *Science*, 2006, **314**, 1124–1126.
9 G. C. Welch and D. W. Stephan, *J. Am. Chem. Soc.*, 2007, **129**, 1880–1881.

10 D. P. Huber, G. Kehr, K. Bergander, R. Fröhlich, G. Erker, S. Tanino, Y. Ohki and K. Tatsumi, *Organometallics*, 2008, **27**, 5279–5284.
11 P. Spies, G. Erker, G. Kehr, K. Bergander, R. Fröhlich, S. Grimme and D. W. Stephan, *Chem. Commun.*, 2007, 5072–5074.
12 P. Spies, S. Schwendemann, S. Lange, G. Kehr, R. Fröhlich and G. Erker, *Angew. Chem., Int. Ed.*, 2008, **47**, 7543–7546.
13 H. D. Wang, R. Fröhlich, G. Kehr and G. Erker, *Chem. Commun.*, 2008, 5966–5968.
14 M. A. Dureen, C. C. Brown and D. W. Stephan, *Organometallics*, 2010, **29**, 6422–6432.
15 M. A. Dureen, C. C. Brown and D. W. Stephan, *Organometallics*, 2010, **29**, 6594–6607.
16 M. A. Dureen and D. W. Stephan, *J. Am. Chem. Soc.*, 2009, **131**, 8396–8397.
17 M. A. Dureen and D. W. Stephan, *J. Am. Chem. Soc.*, 2010, **132**, 13559–13568.
18 M. Ullrich, K. S. H. Seto, A. J. Lough and D. W. Stephan, *Chem. Commun.*, 2009, 2335–2337.
19 J. S. J. McCahill, G. C. Welch and D. W. Stephan, *Angew. Chem., Int. Ed.*, 2007, **46**, 4968–4971.
20 M. A. Dureen, A. Lough, T. M. Gilbert and D. W. Stephan, *Chem. Commun.*, 2008, 4303–4305.
21 M. A. Dureen, G. C. Welch, T. M. Gilbert and D. W. Stephan, *Inorg. Chem.*, 2009, **48**, 9910–9917.
22 R. C. Neu, E. Otten, A. Lough and D. W. Stephan, *Chem. Sci.*, 2011, **2**, 170–176.
23 R. C. Neu, E. Otten and D. W. Stephan, *Angew. Chem. Int. Ed.*, 2009, **48**, 9709–9712.
24 E. Otten, R. C. Neu and D. W. Stephan, *J. Am. Chem. Soc.*, 2009, **131**, 9918–9919.
25 G. Ménard and D. W. Stephan, *J. Am. Chem. Soc.*, 2010, **132**, 1796–1797.
26 G. Ménard and D. W. Stephan, *Angew. Chem., Int. Ed.*, 2011, DOI: 10.1002/anie.201103600.
27 C. M. Mömming, E. Otten, G. Kehr, R. Fröhlich, S. Grimme, D. W. Stephan and G. Erker, *Angew. Chem., Int. Ed.*, 2009, **48**, 6643–6646.
28 X. X. Zhao and D. W. Stephan, *Chem. Commun.*, 2011, **47**, 1833–1835.
29 A. E. Ashley, A. L. Thompson and D. O'Hare, *Angew. Chem., Int. Ed.*, 2009, **48**, 9839–9843.
30 A. Berkefeld, W. E. Piers and M. Parvez, *J. Am. Chem. Soc.*, 2010, **132**, 10660–10661.
31 B. Birkmann, T. Voss, S. J. Geier, M. Ullrich, G. Kehr, G. Erker and D. W. Stephan, *Organometallics*, 2010, **29**, 5310–5319.
32 S. J. Geier and D. W. Stephan, *J. Am. Chem. Soc.*, 2009, **131**, 3476.
33 C. Kreitner, S. J. Geier, L. J. E. Stanlake, C. Caputo and D. W. Stephan, *Dalton Trans.*, 2011, **40**, 6771–6777.
34 G. C. Welch, J. D. Masuda and D. W. Stephan, *Inorg. Chem.*, 2006, **45**, 478–480.
35 P. A. Chase and D. W. Stephan, *Angew. Chem., Int. Ed.*, 2008, **47**, 7433–7437.
36 D. Holschumacher, T. Bannenberg, C. G. Hrib, P. G. Jones and M. Tamm, *Angew. Chem., Int. Ed.*, 2008, **47**, 7433–7437.
37 S. J. Geier, A. L. Gille, T. M. Gilbert and D. W. Stephan, *Inorg. Chem.*, 2009, **48**, 10466–10474.
38 S. J. Geier, P. A. Chase and D. W. Stephan, *Chem. Commun.*, 2010, **46**, 4884–4886.
39 M. Ullrich, A. J. Lough and D. W. Stephan, *Organometallics*, 2010, **29**, 3647–3654.
40 R. C. Neu, E. Y. Ouyang, S. J. Geier, X. X. Zhao, A. Ramos and D. W. Stephan, *Dalton Trans.*, 2010, **39**, 4285–4294.
41 Repeated attempts to obtain elemental analysis on crystallize samples results in analyses where the C determined was low while the H was expected. This situation has been seen before for fluorinated borane derivatives and is attributed to the formation of B-Carbides during combustion.
42 M. Wieber and W. R. tIoos, *Monatsh. Chem.*, 1970, **101**, 776–781.
43 D. T. Cromer and J. T. Waber, *Int. Tables X-Ray Crystallogr.*, 1974, **4**, 71–147.
44 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 1990, **46**, 467–473.
45 G. M. Sheldrick, Bruker AXS Inc Madison, WI, 2000.
46 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2007, **64**, 112–122.

