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Interception of Intermediates in Phosphine Oxidation by Mesityl Nitrile-*N*-oxide using Frustrated Lewis Pairs

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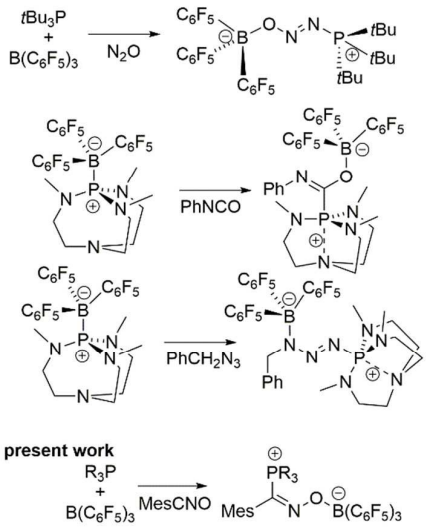
Phosphine oxidation by MesCNO is rapid, however, an FLP strategy intercepts the 1,3 addition products including [MesC(R$_3$P)NOB(C$_6$F$_5$)$_3$] (R = Ph **1**, *p*-tol **2**), [MesC(Mes$_2$PH)NOB(C$_6$F$_5$)$_3$] **3** (MesC(NOB(C$_6$F$_5$)$_3$)Ph$_2$P)$_2$(CH$_2$)$_n$ (n = 2: **4**, 3: **5**) and [MesC(Ph$_3$P)NOB(C$_6$F$_4$H)$_3$] **6**. These species are shown to react with *t*BuOK or [Bu$_4$N]F permitting the oxidation to proceed via a process involving borane dissociation. Similarly, the equilibrium established by **1** with B(C$_6$F$_4$H)$_3$ and **6** with B(C$_6$F$_5$)$_3$ provide experimental support for the "Cummins mechanism" for these phosphine oxidations.

Introduction

The emergency of the concept of "frustrated Lewis pairs" (FLPs) a decade ago, was predicated on the finding that combinations of Lewis acids and bases could activate the dihydrogen molecule in a heterolytic fashion.[1-4] Nonetheless, this field has broadened dramatically in recent years, as the chemistry has been shown to extend to equilibria where free Lewis acids and bases are accessible from the corresponding adducts.[5] In addition, recent work has provided evidence of radical pathways, and thus homolytic cleavages in FLP chemistry.[6-7] These developments notwithstanding, FLP chemistry has also spawned numerous advances in main group hydrogenation catalysis, including elaborations to highly selective asymmetric reductions. FLPs has also been exploited to capture small molecules.[1-4] For example, olefins, dienes, alkynes, cyclopropanes, CO_2,[8] CO,[9-13] SO_2,[14-15] RNSO[16] and NO[17-20] have all been shown to react with FLPs[21] (Scheme 1) to given products derived from the three components. Interestingly, in these cases, pairwise combinations of the Lewis acid, the Lewis base , and the substrate lead to no reactions. On the other hand, FLPs can also be exploited to divert reactions and intervene in cases where pairwise reactions are known. For example, the reaction of N_2O with phosphines results in phosphine oxidation. However, the reaction of FLPs with N_2O prompted its capture as *t*Bu$_3$PN$_2$OB(C$_6$F$_5$)$_3$.[22] In recent work,[23] we have shown that reactions of FLPs can intervene in the azide oxidation of phosphines, or in the Lewis acid mediated cyclization of isocyanates. In both of these cases, the presence of FLPs rather than the individual reagents allows the interception of these substrates.

To this end, we noted the Cummins group has exploited the reagent mesityl nitrile-*N*-oxide (MesCNO, Mes = 2,4,6-trimethylphenyl) to effect the oxidation of triarylphosphines, the complexes (Ar(*t*Bu)N)$_3$V,[24] (Ar(*t*Bu)N)$_3$MoP[24-28] and the diphosphane, (Me$_2$C$_4$H$_6$)$_2$P$_2$.[29] These oxygen atom transfer reactions (Scheme 2) are reported to be facile and proceed rapidly "within minutes" and this ease is attributable to the low N-O bond



Scheme 1 Examples of FLP reactions where FLP intervenes in pairwise reaction.

dissociation enthalpy (BDE) in MesCNO (52 kcal/mol). In probing the mechanism, Cummins *et al.*[29] showed that reaction of carbene and MesCNO afforded the adduct in which the carbene binds to the electrophilic carbon atom of MesCNO. This led these authors to propose that phosphines react in a similar fashion, forming corresponding adducts with MesCNO which rearranges to a 4-membered ring transition state which effects oxygen atom transfer liberating phosphine oxide and MesCN. While this proposed pathway was also supported by computational data, the intermediate phosphine-MesCNO adducts were not isolable nor

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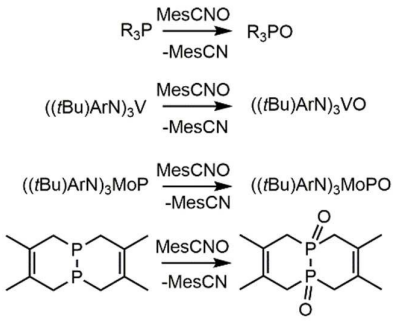
spectroscopically observable. In this communication, we exploit FLPs to intervene in the oxidation of a series of phosphines by MesCNO, providing further experimental data in support of the "Cummins mechanism".



Scheme 2 Examples of oxygen atom transfer reactions using MesCNO.

Results and Discussion

The addition of one equivalent of MesCNO to a suspension of freshly prepared $[Ph_3PB(C_6F_5)_3]$ in CH_2Cl_2 led to the dissolution of the insoluble adduct yielding a clear and colourless solution. After 20 minutes, analysis by multinuclear NMR spectroscopy revealed complete consumption of the starting materials and formation of a new species **1**, which was isolated as a white powder in 88 % yield. In the $^{31}P\{^1H\}$ NMR spectrum, **1** exhibited a sharp new resonance at 5.4 ppm. The $^{19}F\{^1H\}$ NMR spectrum showed a small chemical shift gap between the resonances attributable to the *meta* and *para* fluorine atoms of the perfluorinated arene rings, consistent with the presence of a four-coordinate borate centre. This was further supported by the $^{11}B\{^1H\}$ NMR spectrum of **1**, which displayed a sharp resonance at 0.5 ppm. Together, these data were consistent with **1** being derived from the combination of the Lewis acid-base adduct and MesCNO. 1,3 Addition to the CNO fragment was proposed based on the analogy to reactions with RNSO, prompting the formulation of **1** as the zwitterionic product $[MesC(Ph_3P)NOB(C_6F_5)_3]$ (Scheme 3). Dissolution of **1** in benzene and layering with pentane at ambient temperature yielded diffraction quality single crystals. The subsequent crystallographic study confirmed the above formulation of **1**. In the solid state, the phosphine and borane fragments are disposed in a pseudo-*transoid* orientation with B-O, P-C and C-N distances of 1.522(3) Å, 1.841(3) Å and 1.284(3) Å, respectively. The corresponding P-C-N and N-O-B were determined to be 123.8(2)° and 116.3(2)°, respectively. This geometry results in a through-space P-O distance of 2.874(2) Å. This geometry is reminiscent of that seen in the species $[tBu_3PN_2OB(C_6F_5)_3]$.[22]

In a similar fashion, $(p\text{-tol})_3P$ reacted with $B(C_6F_5)_3$ and MesCNO to give the product formulated as $[MesC(R_3P)NOB(C_6F_5)_3]$ (R = *p*-tol, **2**), isolated in 41 % yield. The corresponding reaction of Mes_2PH, $B(C_6F_5)_3$ and MesCNO in CH_2Cl_2 gave the product **3** in 65 % yield (Scheme 3). The diagnostic P-H resonance was identified at -39.1 ppm as a doublet with a coupling constant of 518 Hz in the $^{31}P\{^1H\}$ NMR spectrum, typical for P(V) $^1J_{PH}$ constants.[31] Other spectroscopic parameters were similar to those seen for **1** and **2**, suggesting the formulation of **3** as $[MesC(Mes_2PH)NOB(C_6F_5)_3]$.

In contrast, Mes_3P reacted very slowly with $B(C_6F_5)_3$ and MesCNO. After 24 h, while resonances attributable to free phosphine and the 1,3-addition product were observed in the $^{31}P\{^1H\}$ NMR spectrum, this product was not isolable. Similarly, reactions of $Ph_2P(C_6F_5)/B(C_6F_5)_3$/MesCNO and $P(C_6F_4CF_3)_3/B(C_6F_5)_3$/MesCNO generated the 1,3-addition products *in situ* in low yields but were not amenable to clean isolation. No reaction was observed in the corresponding reactions of $PhP(C_6F_5)_2$ and $P(C_6F_5)_3$. This latter observation is presumably a result of the electron-deficient nature of these phosphines, making them both poor nucleophiles and difficult to oxidize.

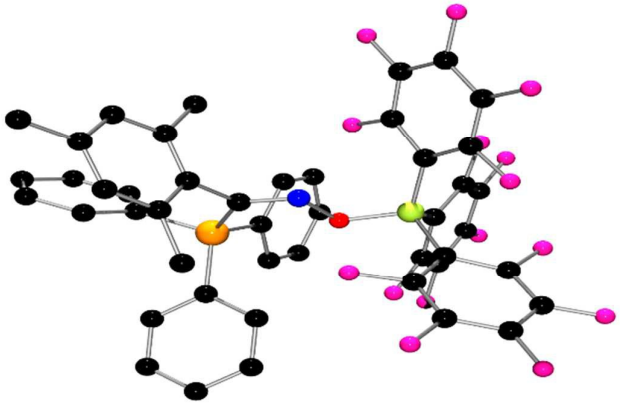
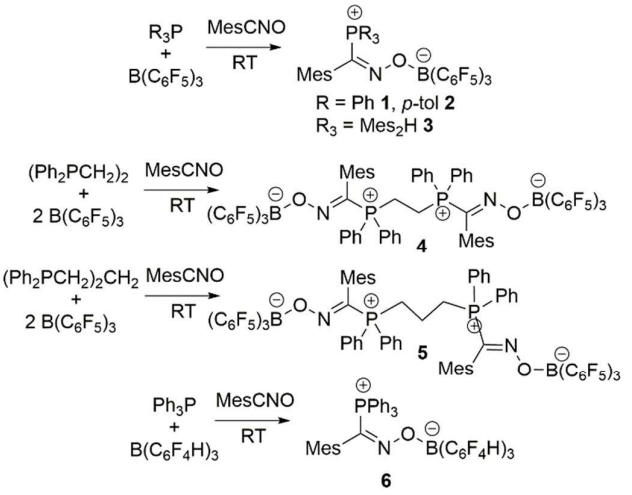


Figure 1 POV-ray depiction of **1**. C: black; F: pink; P: orange; B: yellow-green; N: blue; O: red.



Scheme 3 Synthesis of **1-6**.

The corresponding reactions of bidentate phosphines with two equivalents of both $B(C_6F_5)_3$ and MesCNO were probed. $(Ph_2P)_2(CH_2)_2$ (dppe) was combined with $B(C_6F_5)_3$ and MesCNO, resulting in a $^{31}P\{^1H\}$ NMR spectrum which showed a new resonance at 12.6 ppm attributable to the product **4**. The corresponding $^{19}F\{^1H\}$ NMR spectrum showed resonances at -

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133.8, -160.0, and -165.7 ppm. The $^{11}B\{^1H\}$ NMR spectrum of **4** displayed a sharp resonance at 0.1 ppm. These data supported the assignment of **4** as a di-zwitterionic salt containing two phosphonium and borate centres, $(MesC(NOB(C_6F_5)_3)Ph_2PCH_2)_2$ (Scheme 3). Crystallographic study of **4** was confirmed this formulation (Figure 2). The crystallographic C_2 symmetry places the two PCNOB fragments on opposite sides of the diphosphine unit. The B-O, P-C and C-N distances in **4** were found to be 1.528(3) Å, 1.844(3) Å and 1.283(3) Å. The corresponding P-C-N and N-O-B were determined to be 124.0(2)° and 109.8(2)°, respectively. In a similar fashion, reaction of $(Ph_2P)_2(CH_2)_3$ (dppp) with two equivalents of $B(C_6F_5)_3$ and MesCNO afforded a new species **5** in 88% yield, which exhibited a singlet resonance at 9.8 ppm in the $^{31}P\{^1H\}$ NMR spectrum. This and the related NMR data supported the formulation of **5** as $(MesC(NOB(C_6F_5)_3)Ph_2PCH_2)_2CH_2$ (Scheme 3).

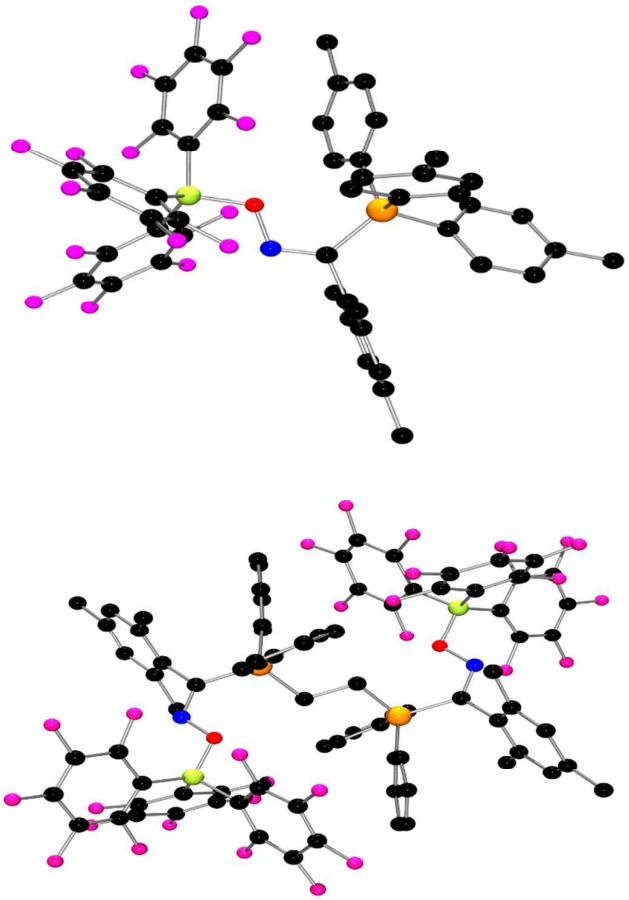


Figure 2 POV-ray depiction of **2** (top) and **4** (bottom) C: black; F: pink; P: orange; B: yellow-green; N: blue; O: red.

This synthetic protocol was amenable to alternative boranes. For example, combination of PPh_3, MesCNO and $B(C_6F_4H)_3$ afforded compound **6**. (Scheme 3). The formulation of **6** as $[MesC(Ph_3P)NOB(C_6F_4H)_3]$ was consistent with the spectroscopic data and confirmed by crystallographic study (Figure 3). The metric parameters of **6** were found to be very similar to those described for **1** with B-O, P-C and C-N distances of 1.514(5) Å, 1.806(5) Å and 1.284(5) Å, respectively and the corresponding P-C-N and N-O-B are 125.9(3)° and 114.8(3)°, respectively.

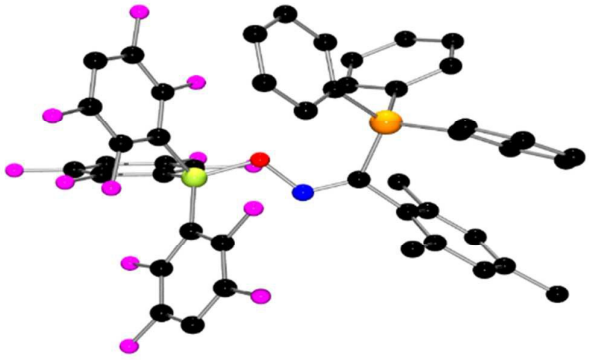
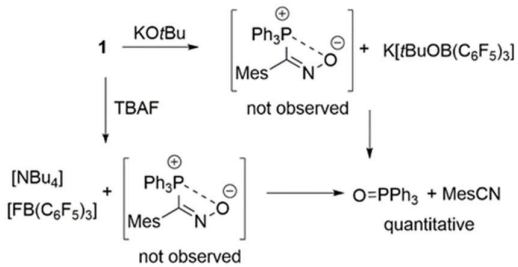


Figure 3 POV-ray depiction of **6**. C: black; F: pink; P: orange; B: yellow-green; N: blue; O: red.

The isolation of compounds **1-6** illustrate that the presence of the Lewis acids precludes the normal course of phosphine oxidation by MesCNO. The B-O bonds in these products presumably provide both steric and electronic deterrents to the molecular reorientation that is required for oxygen atom transfer. This infers that removal of the borane from species **1-6** would prompt phosphine oxidation. To confirm this premise, **1** was treated with excess of potassium tert-butoxide (KO*t*Bu) or excess tetrabutylammonium fluoride ($[Bu_4N]F$) (Scheme 4). The corresponding $^{31}P\{^1H\}$ NMR data after 30 minutes showed complete conversion of **1** to Ph_3PO with the liberation of nitrile. Additionally, upon addition of excess KO*t*Bu or $[Bu_4N]F$ to a mixture of **1** and P(*p*-tol)$_3$, $^{31}P\{^1H\}$ NMR spectroscopy revealed consumption of **1** with the quantitative and exclusive formation of Ph_3PO together without oxidation of P(*p*-tol)$_3$. Collectively, these data are consistent with a dissociative equilibrium in which borane is liberated from **1**. This allows borane capture by *t*-butoxide or fluoride generating [MesC(Ph_3P)NO] which then undergoes oxygen atom transfer effecting phosphine oxidation.



Scheme 4 Reactions of **1** with TBAF and KO*t*Bu.

Seeking further evidence for borane dissociation an EXSY study of **1** with equimolar amount of $B(C_6F_5)_3$ was undertaken. While this showed no exchange of the Lewis acid on the NMR time scale, addition of one equivalent of $B(C_6F_4H)_3$ to **1** led to slow chemical exchange. After 16 hours at ambient temperature, this mixture equilibrated to give a mixture of **1**, $B(C_6F_5)_3$ and **6** (Scheme 4) with a ratio of **1: 6** of a 70:30 (Scheme 5). The prevalence of **1** in this equilibrium is consistent with the slightly lower Lewis acidity of $B(C_6F_4H)_3$. In

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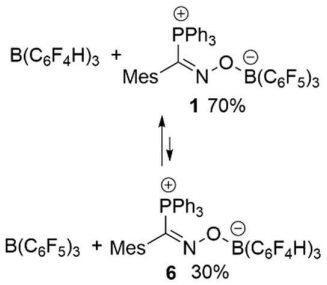
the converse experiment, addition of $B(C_6F_5)_3$ to **6** resulted in the same equilibrium mixture after standing for 16 hours.



Scheme 5 Lewis acid exchange equilibrium.

Despite the rapid oxidation of phosphines by MesCNO, FLPs intervene in the reactions of phosphine with MesCNO intercepting the 1,3-addition products **1-6**. This binding to the oxygen atom precludes oxygen atom transfer from nitrogen to phosphorus. Lewis acid dissociation from these species is documented and this provides an avenue for Lewis acid exchange. In addition, capture of liberated borane by KO*t*Bu or $[Bu_4N]F$ permits the oxygen atom transfer to occur effecting oxidation of the nitrile-bound phosphine.

Conclusions

These data are consistent with the Cummins[29]proposition that the direct oxidation of phosphine by MesCNO proceeds via initial interaction of phosphine with the electron deficient C atom of MesCNO, generating the species that is captured by borane in the presence of an FLP. We are continuing to explore FLP systems to develop applications for reactions of small molecules and catalysis and to garner insight into reaction mechanisms.

Experimental Section

General Remarks All reactions and work-up procedures were performed under an inert atmosphere of dry, oxygen-free N_2 by means of standard Schlenk techniques or glovebox techniques (VAC glovebox equipped with a -25 °C freezer) unless otherwise specified. All glassware was oven-dried and cooled under vacuum before use. Dichloromethane (DCM) were distilled over CaH_2. Pentane and hexane were collected from a Grubbs-type column system manufactured by Innovative Technology and degassed. Solvents were stored over activated 4 Å molecular sieves. Molecular sieves, type 4 Å (pellets, 3.2 mm diameter) purchased from Sigma Aldrich were activated prior to usage by iteratively heating under vacuum for 24 hours. $CDCl_3$ purchased from Cambridge Isotope Laboratories was vacuum distilled, further degassed, and stored over activated 4 Å molecular sieves in the glovebox for at least 8 hours prior to use. Unless otherwise mentioned, chemicals were purchased from Sigma Aldrich or TCI. Mesityl nitrile *N*-oxide (MesCNO) was prepared using literature methods.[32] $B(C_6F_5)_3$ was purchased from Boulder Scientific and sublimed under vacuum at 85 °C prior to use. NMR spectra were recorded at room temperature (298K) unless otherwise mentioned on a Bruker Avance III 400 MHz, an Agilent DD2 500, an Agilent DD2 600, and an Agilent DD2 700 Spectrometers. Spectra were referenced to the residual solvent signals ($CDCl_3$: ^{1}H= 7.26 ppm and ^{13}C = 77.2 ppm). Chemical shifts (δ) are reported in ppm and coupling constants (*J*) are listed as absolute values in Hz. Multiplicities are reported as singlet (s), doublet (d), triplet (t), multiplet (m), overlapping (ov), and broad (br). High-resolution mass spectra (HRMS) were obtained on a JMS-T100LC JOEL DART mass spectrometer. Elemental analyses for C, H, and N were performed by ANALEST (University of Toronto) employing a Perkin Elmer 2400 Series II CHNS Analyser.

X-ray Diffraction Studies: Single crystals were coated with paratone oil, mounted on a cryoloop and frozen under a stream of cold nitrogen. Data were collected on a Bruker Apex2 X-ray diffractometer at 150(2) K for all crystals using graphite monochromated Mo-Kα radiation (0.71073 Å). Data were collected using Bruker APEX-2 software and processed using SHELX and an absorption correction applied using multi-scan within the APEX-2 program. All structures were solved and refined by direct methods within the SHELXTL package. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre.

Mass Spectrometry Studies: All attempts to observe the products by high-resolution mass spectrometry failed due to the instability of these compounds under mass spectrometry conditions, by either ESI or DART methods. In positive mode, the protonated phosphonium cation or protonated phosphine oxide were observed. By negative mode, $[HO\text{-}B(C_6F_5)_3]$ or $[H_2NO\text{-}B(C_6F_5)_3]$ were observed.

Synthesis of $[MesC(Ph_3P)NOB(C_6F_5)_3]$ (1) PPh_3 (65.3 mg, 0.25 mmol, 1 equiv.) and $B(C_6F_5)_3$ (127.9 mg, 0.25 mmol, 1 equiv.) were combined in 2 mL CH_2Cl_2. To the resulting suspension, a solution of MesCNO (40.3 mg, 0.25 mmol, 1 equiv.) in 1 mL of CH_2Cl_2 was added dropwise, yielding a clear and homogenous solution. After 20 minutes, 5 mL of cold pentane was added with vigorous stirring which led to the precipitation of a white precipitate. The solution was then decanted and dried in vacuo, yielding the desired product as a white powder. Yield: 206.5 mg (88% isolated yield). Diffraction quality single crystals were obtained through slow diffusion of pentane into benzene at room temperature. ^{1}H NMR (600 MHz, $CDCl_3$, 253 K): δ 7.80 (m, 4H, Ar), 7.67 (m, 2H, Ar), 7.48 (m, 5H, Ar), 7.18 (m, 2H, Ar), 6.71 (m, 2H, Ar), 6.64 (s, 2H, *m*-H, Mes), 2.16 (s, 3H, *p*-CH_3, Mes), 1.90 (s, 6H, *o*-CH_3, Mes).^{19}F{1H} NMR (377 MHz, $CDCl_3$): δ -132.3 (d, $^3J_{FF}$ = 22.6 Hz, 2F, *o*-C_6F_5), -160.0 (t, $^3J_{FF}$ = 20.8 Hz, 1F, *p*-C_6F_5), -165.5 (m, 2F, *m*-C_6F_5). ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$): δ 5.4 (s). ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ 0.5 (s).^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 148.09 (dm, 239 Hz, C_6F_5), 140.28 (d, 3 Hz), 139.11 (dm, 252 Hz, C_6F_5), 139.08 (d, 4 Hz), 136.84 (dm, 232 Hz, C_6F_5), 134.49 (b), 133.92 (d, 11 Hz), 132.76, 132.48, 129.62 (b), 129.03, 128.74, 128.60, 21.14, 20.75. Elemental analysis: Calc.: C 59.06%, H 2.80%, N 1.51%. Exp.: C 58.76%, H 2.46%, N 1.43%

Synthesis of $[MesC((p\text{-}tol)_3P)NOB(C_6F_5)_3]$ (2) Solutions of P(*p*-tol)$_3$ (43.9 mg, 0.14 mmol, 1 equiv.) and $B(C_6F_5)_3$ (73.8 mg, 0.14 mmol, 1 equiv.) were combined in 4 mL of CH_2Cl_2. The mixture remained homogeneous. To this solution, 2 mL of CH_2Cl_2 were carefully layered and the solution was left undisturbed for 5 minutes. A solution of MesCNO (23.2 mg, 0.14 mmol, 1 equiv.) in 2 mL CH_2Cl_2 was then carefully layered on top of the reaction vial. This final 3-layer mixture was left undisturbed for 48 hours at

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ambient temperature. After this time, clear and colourless diffraction-quality crystals precipitated from the yellow reaction mixture. The solvent was decanted and the crystalline product washed with pentane (3 x 5 mL), then dried in vacuo. Yield: 57.8 mg (41% isolated yield). Note: the yield can be improved by cooling the filtrate to -35 °C over one week, yielding additional product as an amorphous white precipitate. Once precipitated from solution, compound **2** has very low solubility in common organic solvents, preventing full characterization by multinuclear NMR spectroscopy. ^{1}H, ^{11}B{^{1}H}, ^{19}F{^{1}H} and ^{31}P{^{1}H} NMR spectra are reported. Chemical connectivity and bulk purity are unambiguously confirmed by single-crystal X-ray diffraction studies and elemental analysis, respectively. ^{1}H NMR (600 MHz, THF-d_8, 313 K): δ 7.72-7.26 (br, 12 H, Ar), 6.67 (s, 2H, *m*-H, Mes), 2.38 (br, 9H, *p*-CH_3, Ar), 2.15 (s, 3H, *p*-CH_3, Mes), 1.95 (s, 6H, *o*-CH_3, Mes). ^{19}F{^{1}H} NMR (377 MHz, THF-d_8): δ -134.6 (m, 2F, *o*-B(C_6F_5)$_3$), -164.4 (m, 1F, *p*-B(C_6F_5)$_3$), -169.5 (m, 2F, *m*-B(C_6F_5)$_3$); ^{31}P{^{1}H} NMR (162 MHz, THF-d_8): δ 4.0 (s); ^{11}B{^{1}H} NMR (128 MHz, THF-d_8): δ -2.4 (b); Elemental Analysis: Calc.: C 60.20%, H 3.30%, N 1.43%. Exp.: C 59.45%, H 3.29%, N 1.45%

Synthesis of [MesC(Mes$_2$PH)NOB(C_6F_5)$_3$] (3) $PMes_2H$ (31.8 mg, 0.12 mmol, 1 equiv.) and B(C_6F_5)$_3$ (60.2 mg, 0.12 mmol, 1 equiv.) were combined in 2 mL CH_2Cl_2. To the resulting suspension, a solution of MesCNO (18.9 mg, 0.12 mmol, 1 equiv.) in 1 mL of CH_2Cl_2 was added dropwise to the light-yellow solution. After 20 minutes, the solvent was removed in vacuo to yield a faint yellow gel. Yield: 72.1 mg (65% isolated yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.10 (d, $^{1}J_{PH}$ = 510.8 Hz, 1H, PH), 7.46–7.45 (ov, 6H, P(Mes)$_2$), 2.89-2.84 (ov, 18H, Mes), 2.74-2.68 (ov, 9H, Mes). ^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$): δ -133.7 (d, $^{3}J_{FF}$ = 23.4 Hz, 2F, *o*-C_6F_5), -161.5 (t, $^{3}J_{FF}$ = 20.4 Hz, 1F, *p*-C_6F_5), -166.4 (m, 2F, *m*-C_6F_5). ^{31}P NMR (162 MHz, $CDCl_3$): δ -39.1 (d, $^{1}J_{PH}$ = 518.4 Hz,).^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ 0.1 (s).^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 148.02 (dm, 240 Hz, C_6F_5), 144.84 (d, 3 Hz), 143.40 (d, 10 Hz), 140.04, 139.12 (dm, 248 Hz, C_6F_5), 139.01 (d, 3 Hz), 138.19 (d, 13 Hz), 136.82 (dm, 247 Hz, C_6F_5), 131.33 (d,11 Hz), 129.28, 126.19(d, 13 Hz), 121.34 (b) 114.18 (d, 80 Hz), 22.59, 22.52, 21.89, 21.25, 21.24, 21.07. The resonance for the ipso-B(C_6F_4H)$_3$ carbon is likely not observed. Elemental analysis: Calc.: C 58.56%, H 3.63%, N 1.48%. Exp.: C 58.09%, H 3.41% N 1.50%.

Synthesis of (MesC(NOB(C_6F_5)$_3$)Ph$_2$PCH$_2$)$_2$ (4) A 1 mL CH_2Cl_2 solution of dppe (10.0 mg, 0.025 mmol) was combined with a 1 mL CH_2Cl_2 solution of B(C_6F_5)$_3$ (25.0 mg, 0.050 mmol). A white precipitate formed. To this suspension, a solution of MesCNO (8.0 mg, 0.050 mmol) in 1 mL of DCM was added dropwise. After 20 mins, 5 mL of cold pentane was added with vigorous stirring, yielding a white precipitate. The product was washed with 10 mL of pentane and collected by filtration. Yield: 38 mg (87% isolated yield). Diffraction quality single crystals were grown by vapour diffusion of hexane into a CH_2Cl_2 solution. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (m, 4H, Mes), 8.01-7.90 (ov, 20H, P(C_6H_5)$_3$), 4.01 (br, 4H, CH_2), 2.79 (s, 6H, *p*-CH_3, Mes), 2.55 (s, 12H, *o*-CH_3, Mes).^{19}F {^{1}H} NMR (377 MHz, $CDCl_3$): δ -133.8 (d, $^{3}J_{FF}$ = 24.9 Hz, 2F, *o*-C_6F_5), -160.0 (t, $^{3}J_{FF}$ = 20.7 Hz, 1F, *p*-C_6F_5), -165.7 (m, 2F, *m*-C_6F_5). ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$): δ 12.6 (s). ^{11}B {^{1}H} NMR (128 MHz, $CDCl_3$): δ 0.1 (s). ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$): δ 148.07 (dm, 240 Hz, C_6F_5), 140.31, 139.23(dm, 248 Hz, C_6F_5), 137.62 (d, 3 Hz), 137. 03 (dm, 244 Hz, C_6F_5), 134.90 (d, 3 Hz), 133.77 (d, 10Hz), 129.69, 129.44 (d, 13 Hz), 128.94, 127.80 (d, 16 Hz), 121.49 (b), 117.13 (d, 82 Hz), 29.91, 21.07, 20.59. The resonance for the ipso-B(C_6F_4H)$_3$ carbon is likely not observed. Elemental analysis: Calc.: C 56.45%, H 2.66%, N 1.61%. Exp.: C 55.64%, H 2.53%, N 1.60%

Synthesis of (MesC(NOB(C_6F_5)$_3$)Ph$_2$PCH$_2$)$_2$CH$_2$ (5) A 1 mL CH_2Cl_2 solution of dppp (16 mg, 0.039 mmol) was added to a 1 mL CH_2Cl_2 solution of B(C_6F_5)$_3$ (40 mg, 0.078 mmol). To the mixture, a solution of MesCNO (13 mg, 0.078 mmol) in 1 mL of CH_2Cl_2 was added dropwise. After 20 mins, 5 mL of cold pentane was added with vigorous stirring, yielding a white precipitate. The solution was then decanted, yielding the desired product as a white powder. Yield: 51.4 mg (88% isolated yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28-8.24 (m, 4H, Mes), 8.03-7.90 (ov, 15H, P(C_6H_5)$_3$), 4.02 (br, 4H, CH_2), 2.79 (s, 6H, *p*-CH_3, Mes), 2.55 (s, 12H, *o*-CH_3, Mes), 1.95 (br, 2H, CH_2). ^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$): δ -133.7 (d, $^{3}J_{FF}$ = 22.6 Hz, 2F, *o*-C_6F_5), -160.3 (t, $^{3}J_{FF}$ = 18.9 Hz, 1F, *p*-C_6F_5), -165.8 (m, 2F, *m*-C_6F_5). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 9.8 (s). ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ 0.3 (s). ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 147.84 (dm, 241 Hz, C_6F_5), 140.08, 139.00 (dm, 250 Hz, C_6F_5), 137.61 (d, 3 Hz), 136.73 (dm, 236 Hz, C_6F_5), 134.68 (d, 3 Hz), 133.57 (d, 11 Hz), 130.44 (d, 11 Hz), 129.22 (d, 12 Hz), 128.72, 127.57 (d, 16 Hz), 116.90 (d, 80 Hz), 34.14, 31.61, 20.89, 20.41, 14.10 (d, 10 Hz). The resonance for the ipso-B(C_6F_4H)$_3$ carbon is likely not observed. Elemental analysis: Calc.: C 56.68%, H 2.75%, N 1.59%. Exp.: C 56.42%, H 2.65%, N 1.61%

Synthesis of [MesC(Ph$_3$P)NOB(C_6F_4H)$_3$] (6) Solutions of PPh_3 (22.0 mg, 0.084 mmol, 1 equiv.) and B(C_6F_4H)$_3$ (38.5 mg, 0.084 mmol, 1 equiv.) were combined in 3 mL of CH_2Cl_2, yielding a white precipitate. To this heterogenous mixture, a solution of MesCNO (13.6 mg, 0.084 mmol, 1 equiv.) in 1 mL CH_2Cl_2 was added dropwise. After complete addition of MesCNO, the reaction mixture was clear and homogeneous. The solvent removed in vacuo, and the white solid was recrystallized from benzene/pentane at room temperature over 24 hours. Yield: 52.5 mg (71 % isolated yield). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 8.0-7.1 (b, 15H, P(C_6H_5)$_3$), 6.7 (m, 3H, B(C_6F_4H)$_3$), 6.6 (s, 2H, CH, Mes), 2.16 (s, 3H, *p*-CH_3, Mes), 1.93 ppm (s, 6H, *o*-CH_3, Mes). ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$, 298 K): δ -132.9 (m, *o*-B(C_6F_4H)$_3$), -143.4 ppm (m, *m*-B(C_6F_4H)$_3$). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 298 K): δ 5.5 ppm (s); ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$, 298 K): δ 0.1 (br); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 298 K): δ 148.21 (dm, 248 Hz, C_6F_5), 145.34 (dm, 255 Hz, C_6F_5), 139.95, 139.15, 134.50 (d, 164 Hz), 131.83 (d, 35 Hz), 130.29 (b), 129.62, 128.74 (b), 128.08, 119.17 (dt, 84 Hz, 8 Hz), 102.57 (dt, 166 Hz, 22 Hz), 21.40, 20.14. The resonance for the ipso-B(C_6F_4H)$_3$ carbon is likely not observed. Elemental Analysis: Calc.: C 62.75%, H 3.21%, N 1.59%. Exp.: C 62.52%, H 3.40%, N 1.62%.

Conflicts of interest

There are no conflicts to declare.

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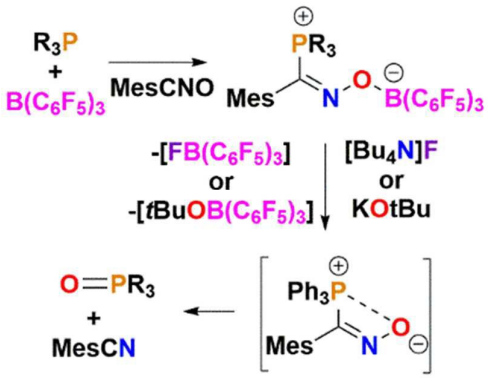

While phosphine oxidation by MesCNO is rapid, FLPs can be used to intercept 1,3-addition intermediates products. These species react with *t*BuOK or $[Bu_4N]F$ permitting the oxidation to proceed via a process involving borane dissociation, providing experimental support for the Cummins mechanism"