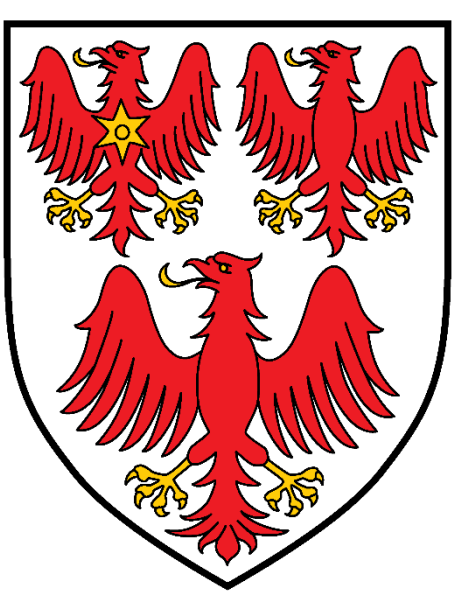
FRUSTRATED LEWIS PAIRS DERIVED FROM XANTHENE AND RELATED BACKBONES



ILI AMIRAH ZULKIFLY

The Queen's College

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ABSTRACT

This thesis examines the synthesis and the reactivity of both novel and previously reported intramolecular dimethylxanthene, dimethylthioxanthene and acridan derived frustrated Lewis pairs (FLPs). Moreover, it also reports on novel acridan-based Lewis bases and acids, and the subsequent reactivity of such species within intermolecular FLPs

Chapter 1 describes the background of FLPs including the history of FLPs, and the literature studies on the reactivity of FLPs in small molecules activation/captures and catalysis. Chapter 2 reports all the experimental methods used in this thesis and the preparation of dimethylthioxanthene and acridan backbone precursors. Chapter 3 introduces an improved method for the preparation of intramolecular dimethylxanthene derived FLPs featuring Lewis acid/base pairs of -$B(C_6F_5)_2$/-PPh_2 and -$B(C_6F_5)_2$/-P*i*Pr_2. This synthesis proceeds through isolated lithium complexes and not only gives higher overall yields than the literature method, but also avoids the use of large excesses of Br_2, pyrophoric *s*BuLi, and column chromatography techniques for purification. In addition, this chapter introduces the synthesis of novel intramolecular derived di*tert*-butyldimethylxanthene and dimethylthioxanthene FLPs with wider P···B separations.

In chapter 4, the preparation of novel species derived from an acridan backbone are discussed. This scaffold was used for the synthesis of a range of disubstituted phosphine (**PNP**) Lewis bases. The large steric bulk of *tert*-butyl, *iso*-propyl and mesityl substituents was shown to prevent clean disubstitution of the phosphine moiety onto the acridan backbone. Phenyl and *para*-tolyl substituents, by contrast, gave the desired disubstituted acridan derivatives, and these species have been characterised spectroscopically and crystallographically. The reactivity of these Lewis bases with the Lewis acid $B(C_6F_5)_3$ has been investigated. Neither donor/acceptor coordination nor frustrated Lewis pair behaviour is observed; unexpected C-H activation of the N-Me group of the acridan backbone is proposed based on spectroscopic data, and the structural authentication of a related derivative. This represents the first example of FLP-mediated sp^3 C-H bond activation. Additionally, the synthesis of a novel intramolecular acridan-derived FLP featuring -PPh_2/-$B(C_6F_5)_2$ as the Lewis base/acid pair has been successfully achieved. This acridan FLP

features a P···B separation (4.451(9) Å), which is slightly wider that the analogous dimethylxanthene FLP. Interestingly, it reacts with H_2 at room temperature in a manner utilizing the proximal N-CH_3 moiety as the Lewis base instead of the PPh_2 group. This result led to related synthesis and reactivity studies of the bis-borane Lewis acid (**BNB**) featuring two pendant $B(C_6F_5)_2$ groups, which also reacts with H_2 at room temperature (1 atm) in similar fashion utilizing B/N cooperativity. Furthermore, this compound also shows unusual C-N bond activation behaviour accompanying the uptake of CO_2 and CO in the presence of *t*Bu_3P.

Chapter 5 reports on further investigations into the reactivity of previously reported dimethylxanthene-based phosphine/borane FLPs towards alkynes. The –PPh_2 and –$PMes_2$ containing systems (featuring $B(C_6F_5)_2$ as Lewis acid component) were found to C-H activate the terminal alkyne PhCCH; the weaker -PPh_2 donor system was found to give rise to an equilibrium mixture of the free FLP and phosphonium acetylide in CD_2Cl_2 solution at room temperature. This system was also found to react with the B-H bonds of HBpin and HBcat via C-B/B-H metathesis reactions that lead to the replacement of the -$B(C_6F_5)_2$ moiety by -Bpin/-Bcat, with accompanying transfer of $HB(C_6F_5)_2$ to the phosphine Lewis base. This transformation underpins the ability of this system to act as a pre-catalyst for the hydroboration of terminal (PhCCH) and internal alkynes (PhCCPh and PhCCMe) with HBpin. The active species is derived from the $HB(C_6F_5)_2$ fragment generated in the borane metathesis reaction.

Chapter 6 presents further reactivity studies of dimethylxanthene FLPs featuring -P*i*Pr_2 and -PPh_2 Lewis bases (with -$B(C_6F_5)_2$ as the Lewis acid) in the activation of Si-H and Sn-H bonds. It was found that the more strongly Lewis basic -P*i*Pr_2 FLP could activate the Si-H bonds in $PhSiH_3$, Ph_2SiH_2 and SiH_4; further reaction leads to Si/B metathesis yielding ‘migrated’ species in a similar fashion to that occurring with HBpin and HBcat. The more weakly Lewis basic -PPh_2 FLP however, was found to be unreactive towards Ph_2SiH_2, Et_3SiH and Ph_3SiH, while the reaction with $PhSiH_3$ leads to the formation of a similar ‘migrated’ species. The -P*i*Pr_2-containing FLP was also found to be reactive towards heavier group 14 hydrides, activating the Sn-H bonds of *n*Bu_3SnH and Ph_3SnH to form zwitterionic phosphonium stannylium hydrides.

ABBREVIATIONS

ε	extinction coefficient
ΔG°	standard reaction free energy
ΔG‡	free energy of activation
ΔH°	standard reaction enthalpy
λ_{max}	wavelength of maximum absorbance
9-BBN	9-borabicyclo[3.3.1]nonane
Ar^F	3,5-bis(trifluoromethyl)phenyl
calc.	calculated
COSY	correlated spectroscopy
Cy	cyclohexyl
d	days, doublet
DFT	Density Functional Theory
Dipp	2,6-di*iso*propylphenyl
equiv.	equivalent(s)
equiv.	equivalent
FLP	frustrated Lewis pair
h	hour(s)
HBcat	catecholborane
HBpIn	pinacolborane
HMBC	heteronuclear multiple bond correlation spectroscopy
HOMO	highest occupied molecular orbital
HSQC	heteronuclear single quantum correlation spectroscopy
*i*Pr	isopropyl
J	coupling constant
K	kelvin
LUMO	lowest occupied molecular orbital
m	meta
m	multiplet
Me	methyl
Mes	mesityl
min	minute(s)
*n*Bu	*normal*-butyl
NMR	nuclear magnetic resonance
NOESY	nuclear overhauser effect spectroscopy
o	ortho
p	para
Ph	phenyl
RT	room temperature
*s*Bu	secondary butyl
SPS	solvent purification system
*t*Bu	*tertiary* butyl
TEMPO	2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl

THF	tetrahydrofuran
TMEDA	tetramethylethylene diamine
TMP	2,2,6,6-tetramethylpiperidine
tol	tolyl
VT	variable temperature

TABLE OF CONTENTS

Chapter 1. Introduction

1.1 Overview

Frustrated Lewis pairs (FLPs) are combinations of a highly sterically encumbered Lewis base (B) and Lewis acid (A) that do not form an adduct in solution.[1] These components (typically a phosphine, PR_3, and a borane, BR'_3) which can be separate molecular entities (i.e. intermolecular FLPs) or combined in one species (intramolecular FLPs). This concept was first developed by Brown in 1942, who found unquenched products from the combination of the bulky base lutidine and $B(CH_3)_3$,[2] but has developed rapidly since 2006 when Stephan reported that the intramolecular FLP *p*-$(Mes_2P)C_6F_4(B(C_6F_5)_2)$ heterolytically cleaves H_2, to form the zwitterionic phosphonium/borate *p*-$(Mes_2PH)C_6F_4(BH(C_6F_5)_2)$.[3]

1.2 Background of Frustrated Lewis Pairs (FLPs)

1.2.1 History of FLPs

The theory of Lewis acids and Lewis bases as species that could accept and donate electron pairs was first described by Gilbert N. Lewis in 1923.[4] Typically, the lowest unoccupied molecular orbital (LUMO) of a Lewis acid is capable of accepting an electron pair from the highest occupied molecular orbital (HOMO) of a Lewis base (**Figure 1.1**) to form a Lewis acid-base adduct held together by a coordinate bond.[5] The chemical combination of Lewis

acids and bases is similar conceptually to that of Bronsted acids and bases, in which the combination of donor and acceptor results in the formation of a neutral compound. The concept of Lewis acidic/basic behaviour has, in recent years, become a cornerstone of the understanding of many reactions in synthetic chemistry.[6]

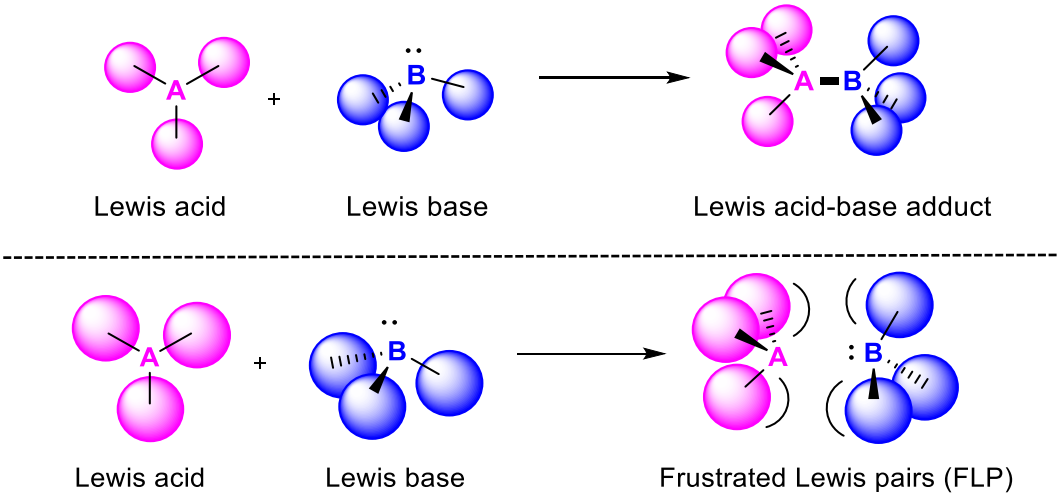
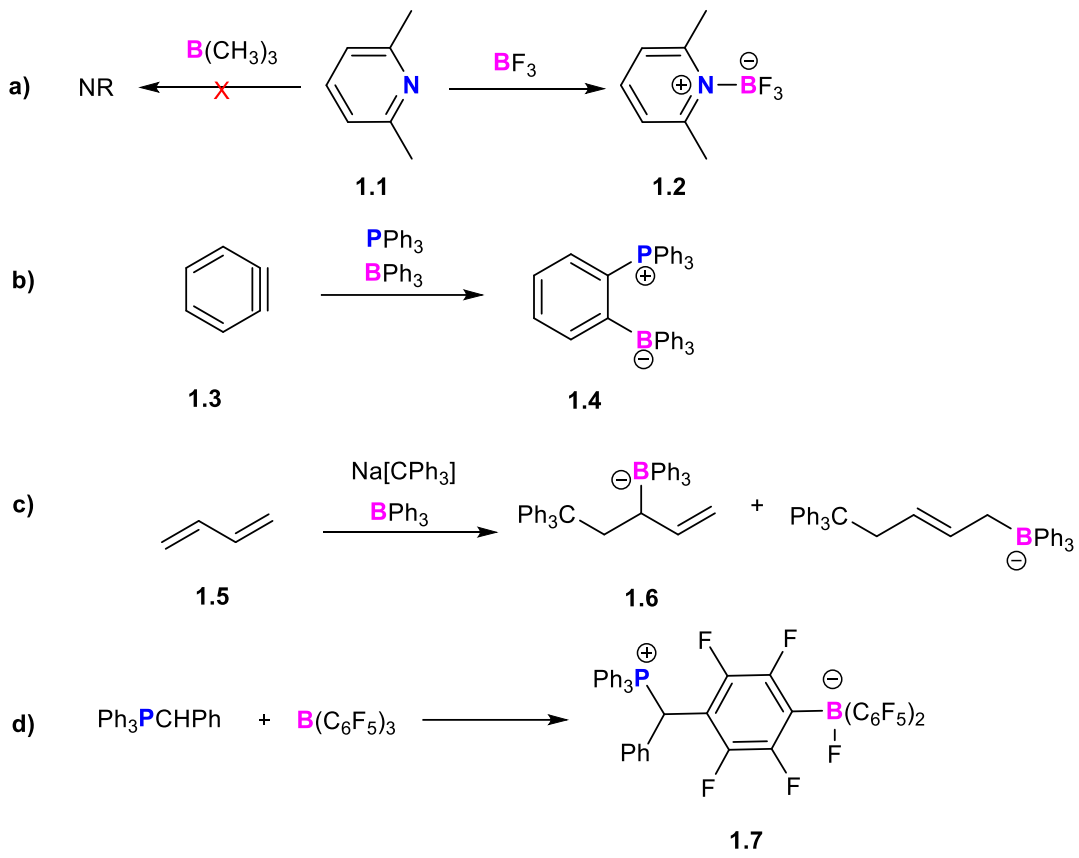


Figure 1.1 (top) Formation of a classical Lewis acid-base adduct; **(bottom**) prevention of adduct formation between highly sterically encumbered Lewis acids and bases: a frustrated Lewis pair (FLP).[7]

The universal nature of Lewis acid-base adduct formation was initially challenged when it was found that there are some exceptions, relating to the interaction between highly sterically hindered acids and bases. In 1942, Brown and coworkers showed that the reaction between a bulky base, lutidine (2,6-dimethylpyridine), and the Lewis acid $B(CH_3)_3$ was unquenched, i.e. it did not lead to N-B bond formation.[2] However, under similar conditions, the reaction of the same base with BF_3 resulted in the formation of a classical adduct following the Lewis acid-base concept (**Scheme 1.1(a)**). Brown attributed this observation to the steric hindrance between the methyl groups on both 2,6-dimethylpyridine and $B(CH_3)_3$.[2]



Scheme 1.1 Early examples of the unusual reactivity of sterically hindered Lewis pairs from **(a)** Brown *et al.*;[2] **(b)** Witting and Benz;[6] **(c)** Tochtermann;[8] and **(d)** Erker *et al.*[9]

Subsequently, several other reactions involving highly sterically encumbered Lewis acids and bases, and giving conceptually similar results were reported. Witting and Benz reported that a zwitterionic o-phenylene linked phosphonium-borate $(C_6H_4)(BPh_3)(PPh_3)$ was formed instead of Lewis acid-base adduct when PPh_3 was reacted with BPh_3 in the presence of benzyne (**Scheme 1.1(b)**).[6] Similar anomalies were reported by Tochtermann, who reported that the addition of BPh_3 and trityl anion to butadiene gives 1,2 and 1,4-addition products (e.g. **1.6**, **Scheme 1.1(c)**) rather than proceeding via the expected polymerization of butadiene or the formation of a Lewis adduct. Tochtermann described this system as an "antagonistisches Paar" [8,10]

Other examples of peculiar results, which with hindsight might be thought of as being due to the formation of frustrated Lewis acid/base pairs have been reported more recently. In the 1990s, Erker *et al.* [9] described the reaction of $B(C_6F_5)_3$ with the ylid $Ph_3P{=}CHPh$ at room temperature, resulting in the formation of the zwitterionic adduct $Ph_3PCH(Ph)B(C_6F_5)_3$. However, at higher temperatures, one of the C_6F_5 groups of the $B(C_6F_5)_3$ unit undergoes nucleophilic aromatic substitution by the ylid to form compound **1.7** (**Scheme 1.1(d)**).

The term 'frustrated Lewis pair' (FLP), however, was first used in 2007 by Stephan *et al.*[3] (see **section 1.3**), and nowadays, the term is widely employed to describe systems in which steric hindrance prevents the formation of an adduct between a Lewis acid and Lewis base, thereby yielding unquenched, and in some cases unprecedented, reactivity.

1.2.2 Types of FLP

1.2.2.1 Intermolecular and intramolecular FLPs

Generally, FLPs can be divided into two broad types: inter- and intramolecular systems. Intermolecular FLPs arise when the Lewis acid and Lewis base are both separate highly bulky entities (**Figure 1.2**).[6] It is thought that this type of FLP engages in interactions via secondary London dispersion forces to bring the acid and base into close proximity an thereby interact with small molecules.[11] Intramolecular FLPs, on the other hand, occur when the acid and base are contained within a single molecule, tethered by a covalent linker that acts as a 'backbone'.[6] In this case, relatively rigid backbone frameworks cause the distance between the acid and base to be more-or-less fixed, allowing for the possibility of a 'pre-organizational effect' in reactions with complementary small molecules (**Figure 1.2**).[12]

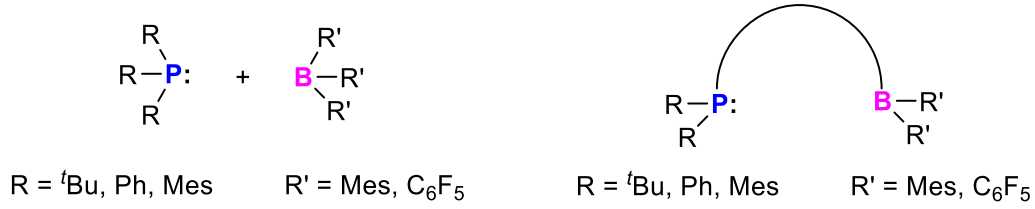


Figure 1.2 Schematic intermolecular **(left)** and intramolecular **(right)** phosphine/borane FLPs.

1.2.3 Factors affecting the reactivity of FLPs

In designing an effective FLP which does not form an adduct in solution and is highly reactive towards small molecule activation, there are two main factors which need to be considered: sterics and electronics.

(i) The first factor relates to the steric bulk of both the Lewis acid and base components.[6] An FLP can be accessed by using suitably bulky functional groups attached to the acidic and basic centres to give a minimum level of steric hindrance to deter the formation of a classical adduct. That said, in some cases, the formation of an adduct does not preclude reactivity as an unquenched FLP, provided that formation of the classical adduct is reversible under reaction conditions. For example, at high temperatures, a classical Lewis acid/base adduct might dissociate in solution to afford the desired FLP (a thermally-induced FLP). In addition, in contrast to intermolecular FLPs (which in most cases rely purely on steric factors to prevent the formation of Lewis acid-base adducts), intramolecular systems can use less bulky substituents provided that the constraints of the backbone linker prevents the formation of a dative interaction.[13]

(ii) Alongside steric bulk, the second variable to consider in designing an FLP which is effective in small molecule capture/activation is the strength of both Lewis acid and base components.[11] The thermodynamic capability of any FLP to activate H_2 is essentially dependent on the magnitude of the proton affinity of the Lewis base (H^+ attachment),[14] and the hydride ion affinity of the Lewis acid (H^- attachment).[15,16,17] For catalytic applications in hydrogenation chemistry, Scott *et al.*[11] reported that optimal activity is achieved if the combined proton and hydride ion affinities are neither too low nor too high. A very low combined proton/hydride ion affinity could lead to a lack of reactivity in initial H_2 cleavage. Conversely, if the proton and hydride ion affinities of the FLP are too high, the H_2-FLP activation product will be excessively stable and unreactive towards the substrate in the subsequent hydrogenation reaction. As such, an intermediate combined proton/hydride ion affinity is needed to effect catalytic reactions.

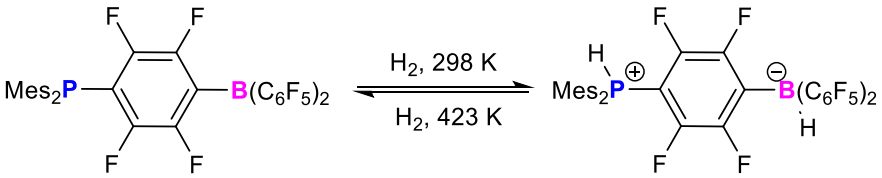
The divergent reactivity of FLP combinations towards H_2 has been probed by Stephan *et al.* by systematically varying the substituents incorporated within a borane Lewis acid and a phosphine Lewis base. From these observations, they found that the FLP combinations tBu$_3$P/B(p-C$_6$F$_5$H)$_3$ and Mes$_3$P/B(C$_6$F$_5$)$_3$ gave rise to irreversible H_2 activation, while reversible H_2 activation was seen for (o-C$_6$H$_4$Me)$_3$P/B(C$_6$F$_5$)$_3$ and no reaction was evident with (C$_6$F$_5$)$_3$P/B(C$_6$F$_5$)$_3$.[18,19] DFT calculations on these FLPs combinations carried out by Zeonjuk *et al.* suggested that the different reactivities possessed by these FLPs towards H_2 are determined by the cumulative strength of the substituents on the phosphorus (Lewis base fragment) and borane (Lewis acid fragment).[20] In this study a thermodynamic partitioning scheme was invoked which divides the overall H_2 activation process into five steps. Each is quantified by a free energy term which sums to the overall free energy (ΔG_{sol}) of the H_2

activation process. The stages are (i) heterolytic splitting of H_2 to a proton and a hydride ion (ΔG_{sol}^{HH}); (ii) dissociation of the FLP into free Lewis acid and base components (ΔG_{sol}^{dis}); (iii) attachment of a proton to the Lewis base (ΔG_{sol}^{PA}); (iv) attachment of a hydride ion to the Lewis acid (ΔG_{sol}^{HA}); and (v) formation of the H_2 activated product, $[PH]^+[HB]^-$ (ΔG_{sol}^{stab}). From these calculations, it was found that the basicity of the Lewis base (assessed by ΔG_{sol}^{PA}) decreases in the order *t*Bu_3P > Mes_3P > (*o*-$C_6H_4Me)_3P$ >>> $(C_6F_5)_3P$, while the calculated Lewis acidities (assessed by ΔG_{sol}^{HA}) are ranked $B(C_6F_5)_3$ > $B(p\text{-}C_6F_4H)_3$. In the case of FLP combinations *t*$Bu_3P/B(p\text{-}C_6F_4H)_3$ (ΔG_{sol} = -32 kJ mol^{-1}) and $Mes_3P/B(C_6F_5)_3$ (ΔG_{sol} = -22 kJ mol^{-1}), each pair contains either a strong base (*t*Bu_3P) or a strong acid ($B(C_6F_5)_3$) that leads to the overall free energy change for H_2 uptake (ΔG_{sol}) being negative. For the FLP combination (*o*-$C_6H_4Me)_3P/B(C_6F_5)_3$, the calculated ΔG_{sol} value (-1 kJ mol^{-1}) is very close to zero, suggesting the possibility for reversible H_2 uptake. Finally, for the $(C_6F_5)_3P/B(C_6F_5)_3$ pairing, ΔG_{sol} is calculated to have a large positive value (+108 kJ mol^{-1}), attributed to the presence of a very weak Lewis base ($(C_6F_5)_3P$), which results in thermodynamically unfavourable H_2 activation.[20,21]

The scope of FLP formation and reactivity has been very widely studied throughout the 15 years since Stephan's landmark paper.[3] FLPs have been constructed using a broad range of Lewis bases (including phosphines, amines, carbenes and ethers) and Lewis acid centres on a range of elements (for example: boron, aluminum, silicon and even phosphorus).[22–29] Since the work reported in this thesis is mainly focused on the reactivity of phosphine-borane FLPs, much of the literature presented in this chapter will focus on phosphine-borane based FLPs. For consideration of the broad scope of FLPs using different Lewis acid/base combinations, the reader is directed to a range of recent reviews on the subject.[1,6,30,31,32]

1.3 H_2 cleavage by FLPs

The first example of dihydrogen activation using an FLP was reported by Stephan *et al.* in 2006.[2] This FLP is an intramolecular system, *p*-(Mes_2P)C_6F_4($B(C_6F_5)_2$), and it heterolytically cleaves H_2 to afford the zwitterionic phosphonium hydroborate *p*-(Mes_2PH)C_6F_4 ($BH(C_6F_5)_2$) (**Scheme 1.2**).



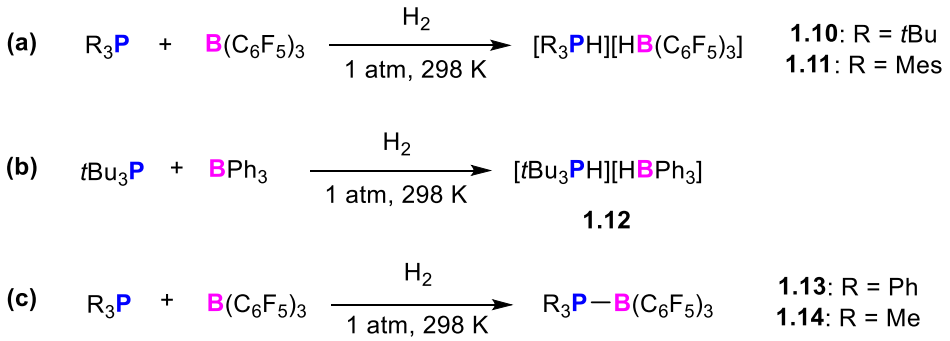
1.8 **1.9**

Scheme 1.2 The first reported example of reversible dihydrogen activation by an FLP.[3]

Despite the presence of both protic and hydridic fragments in the phosphonium hydroborate salt **1.9**, this species was shown to be air stable and required heating to 423 K in toluene to facilitate H_2 release and regenerate FLP **1.8**. Zwitterion **1.9** and the THF adduct of **1.8** were both studied crystallographically, and the liberation of H_2 could conveniently be followed by observing the colour change in solution - from colourless **1.9** to orange-red **1.8** (λ_{max} = 455 nm; ε = 487 L cm^{-1} mol^{-1}). The lack of aggregation of **1.8** was attributed to the steric bulk of the substituents on both phosphorus and boron. In systems analogous to **1.9** where the Mes groups are replaced by more strongly electron donating *t*Bu groups, dihydrogen liberation is not observed due to the stronger P–H bond which prevents proton release.[3]

This type of reactivity was probed further by Stephan and co-workers using simpler, but still bulky, intermolecular phosphine borane systems (**Scheme 1.3**). Reactions of R_3P (R = *t*Bu, Mes) with $B(C_6F_5)_3$ do not result in the formation of adducts, but lead to the formation of

the phosphonium hydroborate salts **1.10** and **1.11** in the presence of H_2 under ambient conditions (**Scheme 1.3 (a)**). Crystallographic studies of compound **1.10** show that the P–H and B–H units are ca. 2.75 Å apart and oriented with the protic and hydridic fragments pointing towards each other. However, despite the favourable pre-organisation for H_2 release, loss of hydrogen was not observed even at elevated temperatures.[18]

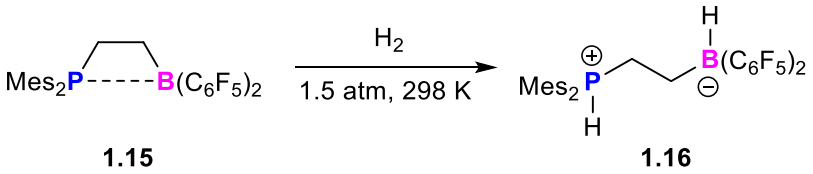


Scheme 1.3 Reactivity of intermolecular FLPs with H_2. [18]

Further experiments showed that the combination of the less Lewis acidic borane BPh_3 with *t*Bu_3P in the presence of H_2 yielded the corresponding phosphonium hydroborate salt **1.12** (**Scheme 1.3(b)**), while the combinations of the less bulky phosphines PPh_3 and PMe_3 with $B(C_6F_5)_3$ under H_2 formed only the classical adducts **1.13** and **1.14** (**Scheme 1.3(c)**). From these studies, Welch and Stephan concluded that the activation of H_2 requires a combination of steric bulk and a minimum combined strength of acidity and basicity (i.e. proton and hydride ion affinities).[18]

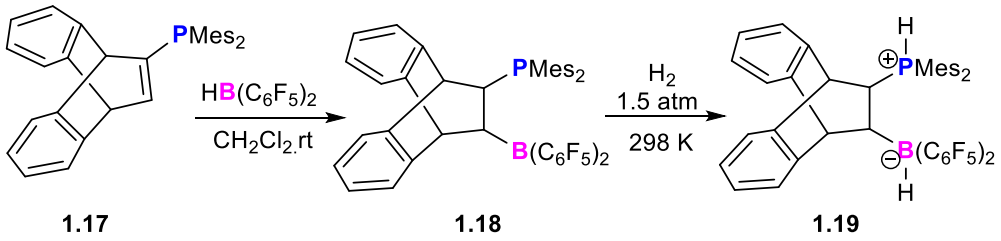
Subsequently, Erker *et al.* reported an intramolecular FLP **1.15** that uses a simple ethylene (CH_2CH_2) group as the backbone linker between $PMes_2$ and $B(C_6F_5)_2$ groups. This system activates H_2 at room temperature to form the zwitterion $Mes_2P(H)CH_2CH_2B(H)(C_6F_5)_2$, **1.16**.[33] The crystal structure of **1.16** revealed that the activated $Mes_2P(H)$- and -$B(H)(C_6F_5)_2$

substituents are in located antiperiplanar to each other at the -CH_2CH_2- backbone, with the protic and hydridic fragment in *trans* position to each other. Although there is no report in this study concerning the reversibility of the H_2 activation process, the borohydride moiety within **1.16** was found to act as a reducing agent towards the carbonyl function of benzaldehyde.[33]



Scheme 1.4 Activation of H_2 by an intramolecular FLP as reported by Erker *et al.*[33]

After the successful activation of the H_2 molecule reported in these three publications on phosphine/borane FLP systems, a vast range of experimental and theoretical studies on FLP reactivity and catalysis has been reported.[1] A very recent example of H_2 activation was reported by Ye *et al.* using the anthracene-derived system **1.18.**[34] FLP **1.18** was synthesized *in situ* from its phosphine precursor **1.17** through a hydroboration reaction using Piers' borane, $HB(C_6F_5)_2$. In similar fashion to other phosphine/borane FLP systems discussed above, the reaction between **1.18** and dihydrogen results in the formation of the phosphonium hydroborate zwitterion **1.19**. In addition to the activation of H_2, FLP **1.18** was found to be highly reactive towards phenyl acetylene, which it activates instantly at room temperature via C-H activation, and could also affect the hydroboration of CO with Piers' borane to form a formyl borane (see **section 1.4.3**).[34] (Further examples of H_2 activation can be found in **section 1.5** onwards).



Scheme 1.5 H_2 activation by FLP **1.18**.[34]

1.3.1 The mechanism of H_2 activation

Since Stephan's landmark paper, the paradigm of using FLP for H_2 activation has been studied in great depth both experimentally and theoretically.[9–11] However, the mechanism of dihydrogen activation by FLPs continues to be a subject of debate. Initial theoretical studies by Papai *et al.* of the mechanism of H_2 activation by the intramolecular FLP P*t*Bu$_3$/B(C$_6$F$_5$)$_3$ suggested that heterolytic H_2 separation occurs through the formation of an initial preorganised, but highly flexible "encounter complex". Subsequently, an early transition state (TS) occurs in which the H_2 molecule interacts with the phosphorus and boron centres simultaneously. This orientation leads to simultaneous electron transfer from the lone pair of the Lewis base to the σ^* orbital of the H−H bond, and also from the σ orbital of H_2 to the empty orbital of the Lewis acid, leading to weakening and ultimately cleavage of the H−H bond (**Figure 1.3**).[36,37]

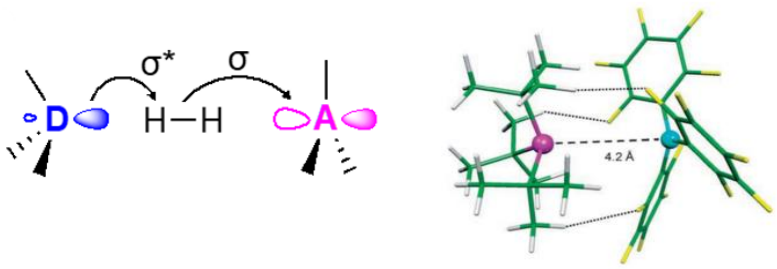


Figure 1.3 (a) synergistic electron-transfer model, and **(b)** "encounter complex" predicting that a P···B separation of 4.2 Å is optimal for the activation of H_2.[38]

The steric hindrance inherent in the FLP system precludes dative bond formation, which destabilises the reactants and lowers the activation barrier for the heterolytic cleavage. Additionally, non-covalent Van der Waals interactions create a weak adduct in which the donor and acceptor sites form a preorganised encounter complex to react in a bimolecular fashion with H_2,[39] with an optimum P···B distance of 4.2 Å for the P*t*Bu$_3$/B(C_6F_5)$_3$ pair.[37] The activation barrier is therefore related to the energetic cost of overlapping the orbitals and distorting the positions of the donor/acceptor sites into the geometry of the encounter complex.[40] Transition state studies suggest the optimum P···B distance for any pair is in the range 4.2-4.8 Å.[37,39]

In contrast to Papai *et al.*, computational studies by Grimme *et al.* in 2010 led to the formulation of alternative mechanism.[41] In this study, the authors suggested that the strong electrostatic force in the internal cavity between the Lewis acid/base pair allows for polarization that causes facile heterolytic H−H bond cleavage.[41] The transition state corresponds to the entrance of H_2 molecule into the strong electric field between the Lewis acid and base. Although this has often been considered the modern view of FLP reactivity,[22,23] detailed studies of the electric field model suggest major flaws.[18] For example,

it has been suggested that a strong electric field would be expected to cause ionization rather than the observed heterolytic cleavage. Therefore, the electron-transfer model is thought to be a more accurate explanation.[42]

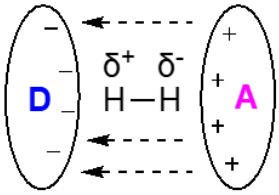


Figure 1.4 Electric field model for H_2 activation by an FLP suggested by Grimme *et. al.*[41]

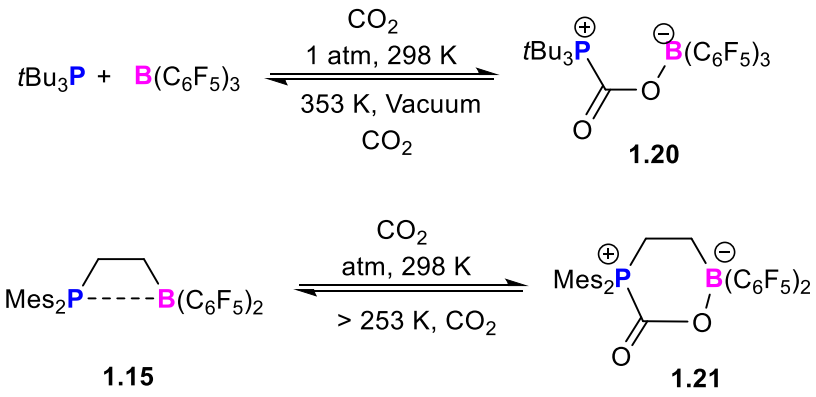
1.4 Small molecules activation and reactivity involving FLPs

1.4.1 CO_2 capture and reduction

The capture of greenhouse gas molecules such as CO_2, N_2O and CO has been extensively studied and has consistently attracted broad interest in the scientific community.[43,44] Other than the activation of H_2, FLPs have also been implicated in a variety of applications involving the capture of these molecules. Carbon dioxide is the primary greenhouse gas and is known to be the major source of global warming.[45–47] This major negative impact of CO_2 has prompted heightened interest in its capture, activation and subsequent utilization. This has involved processes such as the reduction of CO_2 into carbon monoxide, formic acid and methanol.[48–52]

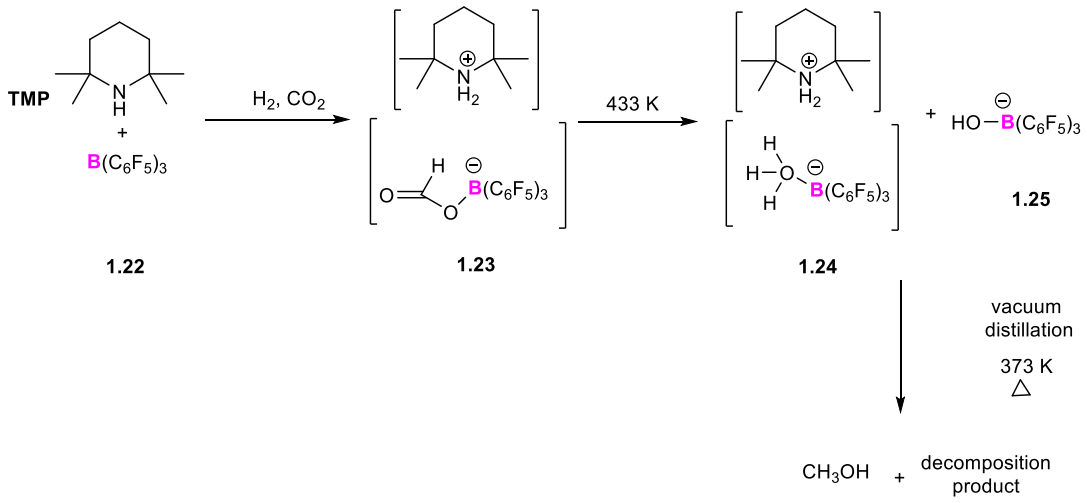
An initial report of the activation of CO_2 by an FLP was published by Stephen and Erker for the inter- and intramolecular FLPs *t*$Bu_3P/B(C_6F_5)_3$ and $Mes_2PCH_2CH_2B(C_6F_5)_2$ (**1.15**)

(**Scheme 1.6**).[53] X-ray crystallographic studies of the respective FLP·CO_2 adducts, **1.20** and **1.21** reveal pseudo-tetrahedral geometries at the phosphorus and boron centres, with the CO_2 molecule linked to the phosphine and borane components through P-C and B-O bonds. Interestingly, both **1.20** and **1.21** release CO_2 at elevated temperatures: at T = 353 K for **1.20** (in BrC_6H_5), and at T = > 253 K for isolated **1.21** (in CH_2Cl_2 or C_6H_7),.[53]



Scheme 1.6 Carbon dioxide capture by FLPs.[53]

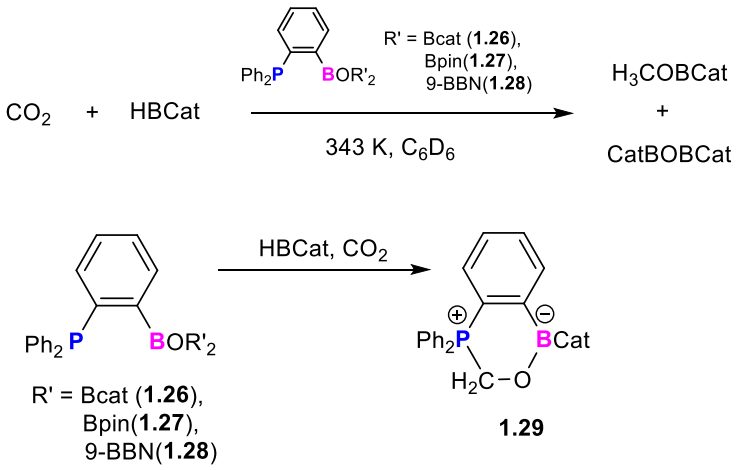
Following this report, further experimental studies of CO_2 capture by FLPs have emerged frequently.[54] Typically, the mode of CO_2 capture involves the Lewis basic component of the FLP bonding with the carbon atom of CO_2, while one of the oxygen atoms forms a B-O bond with the borane Lewis acid site, in a manner similar to the initial systems **1.20** and **1.21** (**Scheme 1.6**).[53,55–58] However, other modes of CO_2 capture can be achieved, including geometries in which both of the CO_2 oxygen atoms bind to two Lewis acid sites. Typically this binding mode necessitates the use of a bifunctional Lewis acid such as $Me_2C{=}C(B(C_6F_5)_2)_2$ or $PhCH_2CH_2C{=}C(B(C_6F_5)_2)_2$. (See also chapter 4, **section 4.1**).[59]



Scheme 1.7 Reduction of CO_2 to methanol shown by Ashley, O'Hare *et al.* [60]

The transformation of CO_2 into reusable and valuable industrial products is an essential part of the 'Circular Economy' to tackle increases in CO_2 emissions.[47] However, this process is very challenging, as CO_2 is thermodynamically stable and a large amount of energy is needed for CO_2 reduction to occur.[45,61,62] A notable study of the reduction of CO_2 by an FLP was carried out by Ashley, O'Hare *et al.* using an intermolecular FLP comprised of TMP (2,2,6,6-tetramethylpiperidine) and $B(C_6F_5)_3$.[60,63] In this study, it was shown that the incorporation of CO_2 and H_2 into the TMP/$B(C_6F_5)_3$, system leads to the formation of the formate system **1.23**, which over 6 days at 433 K, was transformed into methoxide derivative **1.24.** It was suggested that the mechanism of the reaction necessitates high temperatures (433 K) at which free TMP/$B(C_6F_5)_3$, **1.22**, H_2 and the activated CO_2 product **1.23** coexist in equilibrium. Subsequently, free $B(C_6F_5)_3$ is taken up by the second oxygen of the CO_2 fragment of **1.23**, followed by a two-step hydride reduction by **1.22** to form compounds **1.24** and **1.25**. Distillation from these mixtures at 373 K gives methanol in 17-25 % yield.[60]

Derclercq and co-workers have demonstrated the catalytic reduction of CO_2 via a hydroboration reaction using intramolecular FLPs of the type $Ph_2PC_6F_5B(OR)_2$ (where $(OR)_2$ = catecholate (**1.26**), pinacolate (**1.27**) or $-OCH_2C(CH_3)_2CH_2O-$ (**1.28**)).[64] It was found that these FLPs could hydroborate CO_2 catalytically to CH_3OBcat and catBOBcat using catecholborane (HBcat), with high turnover frequencies (TOF > 970 h^{-1}) and high turnover numbers (TON > 2950) at 343 K (**Scheme 1.8(top)**). However, it is believed that the FLPs **1.26-1.28** actually act as pre-catalysts, which readily convert to the true active species **1.29** under these reaction conditions (**Scheme 1.8 (bottom)).**[64]

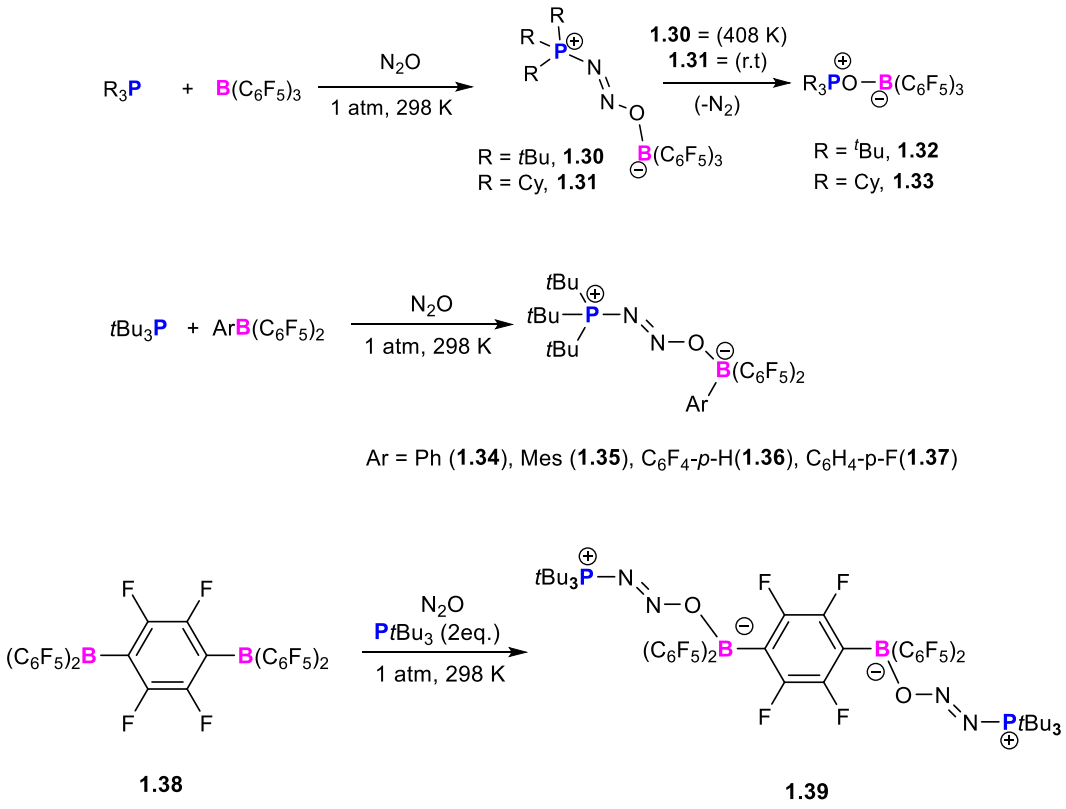


Scheme 1.8 (top) hydroboration of CO_2 by HBcat mediated by an FLP; **(bottom)** formation of the active catalyst **1.29** in the reactions of FLPs **1.26-1.28** with HBcat and CO_2.

1.4.2 N_2O capture by FLPs

Although N_2O is less than one-thousandth as abundant as CO_2, as a greenhouse gas it is almost 300 times more potent compared to CO_2.[65–67] Thus, it was also of interest to find an

FLP that could capture N_2O. The first example of such an FLP was the intermolecular tBu$_3$P/B(C_6F_5)$_3$ system, as demonstrated by Stephan and co-workers.[68] When this system was treated with N_2O (1 atm) at room temperature, the adduct tBu$_3$P·N_2O·B(C_6F_5)$_3$, **1.30**, is formed (**Scheme 1.9**). The crystallographically determined geometry of the P–N=N–O–B fragment in **1.30** features a transoid orientation about the N=N double bond, and a P···B distance of ca. 4.9 Å. However, attempts to reverse the reaction by heating at 408 K for 44 hours resulted instead in the release of N_2 gas forming tBu$_3$PO·B(C_6F_5)$_3$, **1.32** (**Scheme 1.9**). In these studies, Stephan also found that the capture of N_2O by FLPs featuring less basic phosphines is less favourable.[69] Attempts to generate FLP·N_2O complexes by using the (o-tolyl)$_3$P/B(C_6F_5)$_3$ system were not successful, and, while the Cy$_3$P/B(C_6F_4-p-H)$_3$ system gives Cy$_3$P·N_2O·B(C_6F_4-p-H)$_3$ (**1.33**), this adduct rapidly evolves N_2 at room temperature overnight.[70]

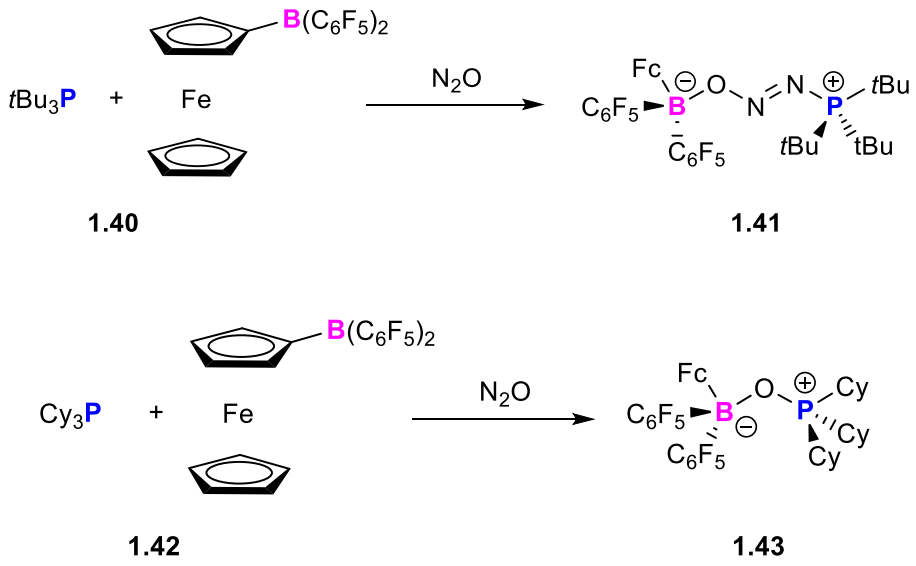


Scheme 1.9 N_2O capture by FLPs.[68–70]

Although the capture of N_2O by an FLP is limited to the use of the strongly basic phosphine tBu$_3$P, there is more scope for variation in the Lewis acid component.[69] FLPs featuring tBu$_3$P and various boranes which are less Lewis acidic than B(C$_6$F$_5$)$_3$ (such as PhB(C$_6$F$_5$)$_2$, MesB(C$_6$F$_5$)$_2$, B(C$_6$F$_5$)$_2$C$_6$F$_4$-*p*-H and B(C$_6$F$_5$)$_2$C$_6$H$_4$-*p*-F) react with N_2O to afford high yields of stable N_2O-FLP adducts, tBu$_3$P·N_2O·ArB(C$_6$F$_5$)$_2$ (Ar = Ph (**1.34**), Mes (**1.35**), C$_6$F$_4$-*p*-H (**1.36**) and C$_6$H$_4$-*p*-F(**1.37**)). Stephan *et al.* also used this concept to capture two molecules of N_2O using the bis-borane (C$_6$F$_5$)$_2$B(C$_6$F$_4$)B(C$_6$F$_5$)$_2$, **1.38**, as the Lewis acid, together with two equivalents of tBu$_3$P (**Scheme 1.9**).[70]

Subsequently, Aldridge *et al.* used the combination of tBu$_3$P and FcB(C$_6$F$_5$)$_2$ (**1.40**) to produce a colorimetric/electrochemical detector for N_2O. When treated with N_2O, **1.40**

yields the ambiphilic adduct tBu$_3$P·N$_2$O·BFc(C$_6$F$_5$)$_2$ (**1.41**).[71] The structure of **1.41** features a similar 'W-shaped' geometry and P···B distance **(Scheme 1.10**) to those reported by Stephan and co-workers.[68] Moreover, the change of colour in solution from maroon to amber (λ_{max} = 434 nm) observed in this reaction offers potential applications in sensing.[71]



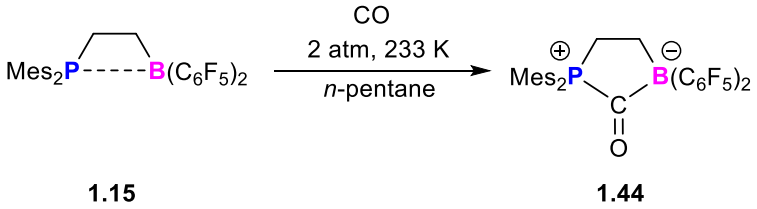
Scheme 1.10 Reaction of the tBu$_3$P or Cy$_3$P/FcB(C$_6$F$_5$)$_2$ systems with FLP with N$_2$O.[71]

The reaction of the less Lewis basic (and less sterically encumbered) Cy$_3$P/B(C$_6$F$_5$)$_3$ system, **1.42** with N$_2$O results in similar colour change in solution from maroon to amber. However, spectroscopic and X-ray data analysis reveals that the product in this case is the phosphine oxide adduct Cy$_3$PO·BFc(C$_6$F$_5$)$_2$, **1.43** (**Scheme 1.10 (bottom)**). The less strongly σ-donating character of Cy$_3$P means that the short-lived intermediate Cy$_3$P·N$_2$O adduct rapidly loses N$_2$ to give Cy$_3$PO.[71] More recently, Aldridge *et al.* have reported another example of N$_2$O capture using a pre-organized intramolecular FLP based on a dimethylxanthene backbone. Interestingly, this system represents the first example of the reversible capture of

N_2O by FLP.[72] The reactivity involved in this reaction is discussed more detail in **section 1.6**.

1.4.3 Reactivity of FLPs with CO and related molecules

In addition to the activation of H_2 and CO_2, the ethylene-bridged phosphine/borane FLP **1.15** synthesized by Erker *et al.*,[33] can also be used for CO capture. Sajid *et al.* exploited this system to take up CO at low temperatures (233 K, 2 atm) giving the carbonyl adduct **1.44** (**Scheme 1.11**).[73] The C=O stretching band for **1.44** was found at 1757 cm^{-1}, consistent with organic carbonyl compounds such as ketones (1740-1720 cm^{-1}), and X-ray crystallographic studies reveal that **1.44** features a five-membered heterocyclic ring in which the phosphine and borane moieties are both attached to the carbon centre of the CO.[73]

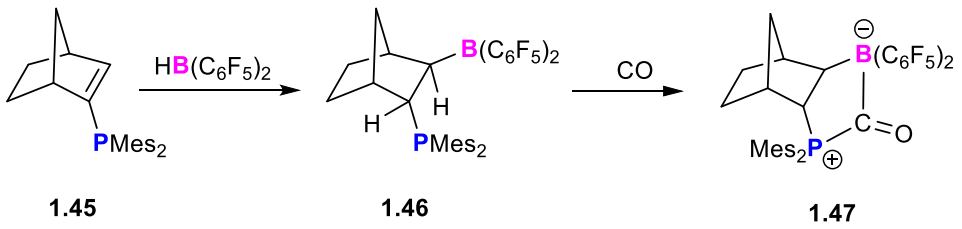


1.15 **1.44**

Scheme 1.11 The first example of CO capture by a phosphine/borane FLP system.[73]

In the same paper, Sajid and co-workers synthesized another novel intramolecular phosphine/borane FLP via the hydroboration of phosphine-norbornene precursor **1.45** with $HB(C_6F_5)_2$. The FLP so generated (**1.46**),[73] reacts with CO give the adduct **1.47**. This adduct was crystallized at low temperatures (< 238 K) as its formation is reversible at temperatures above ca. 243 K. The structure of **1.47** features a 5-membered heterocyclic framework in which the carbon centre is attached to the phosphine and borane moieties in analogous fashion to **1.43**, with a similar C=O stretching vibration at 1791 cm^{-1} being measured by

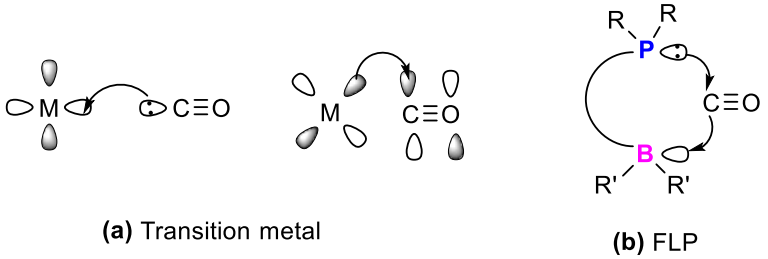
infrared spectroscopy (**Scheme 1.12**). In addition to its reactivity towards CO, FLP **1.46** was also found activate H_2 under ambient conditions.[73]



1.45 **1.46** **1.47**

Scheme 1.12 Formation of FLP **1.46** and its reactivity towards CO.[73]

CO is known to act as a σ-donor and π-acceptor ligand in its bonding to transition metal centres. The interaction between FLP **1.46** and CO is thought to be comparable;[74] However, in contrast to the Dewar–Chatt–Duncanson model, in phosphine/borane systems such as **1.46**, the donor and acceptor site lies on two different atoms, namely the phosphine (Lewis base) and borane (Lewis acid), respectively (**Figure 1.5**).[73]

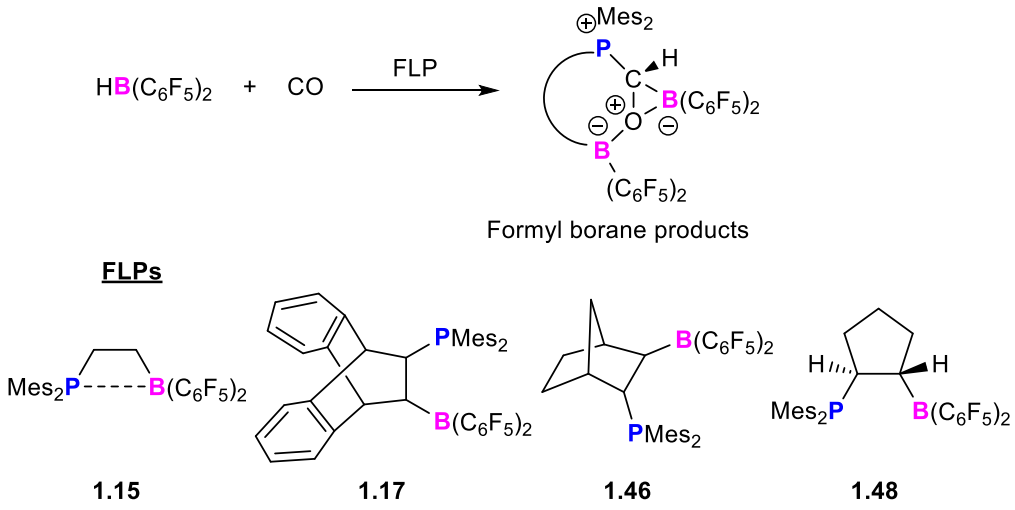


(a) Transition metal **(b)** FLP

Figure 1.5 (a) σ-donation and π-back donation in the bonding of CO to a transition metal centre; **(b)** related donor/acceptor interactions in the binding of CO by a FLP.[1]

The reduction of carbon monoxide into useful industrial organic compounds such as alcohols, ketones and aldehydes has been established using trialkylboranes.[75] However, the reduction of CO with [B]-H containing boranes ([B] = BR_2, R = H, F) could not be achieved. Research by Schlesinger and Burg in late 1930s showed that the reaction of B_2H_6 with CO

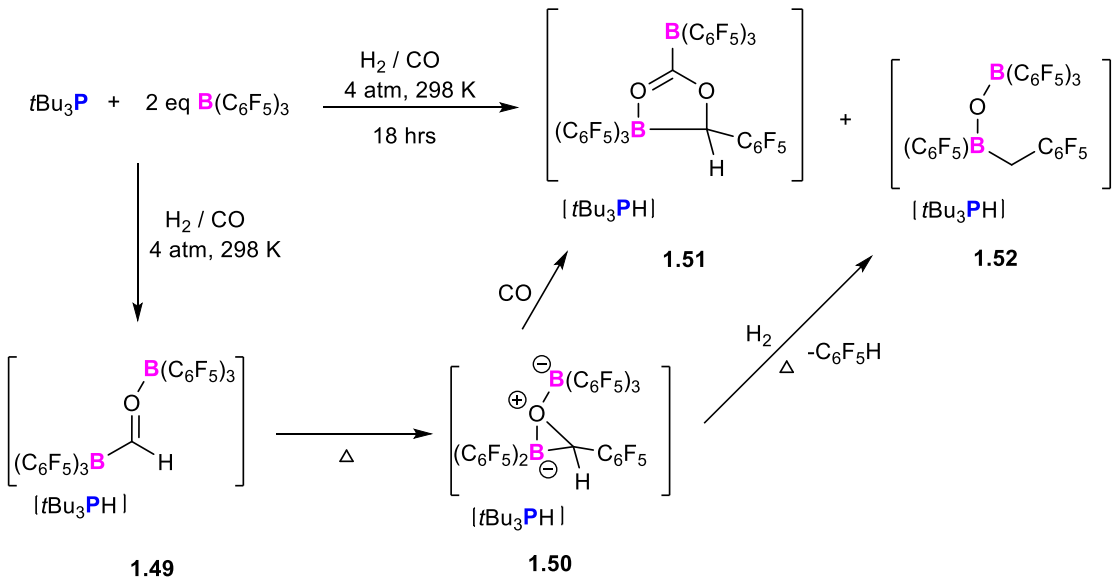
at 373 K (20 atm) leads to the formation of the adduct $H_3B{\cdot}CO$, which does not react further to form formylboranes due to unfavorable thermodynamics; $H_3B{\cdot}CO$ also dissociates at atmospheric pressure.[75] FLPs have been found to change the reactivity of [B]-H containing boranes towards the reduction of CO.[76] For example, Erker *et al.* have reported that the reaction between $HB(C_6F_5)_2$ and CO in the presence of FLPs **1.15**, **1.17, 1.46** or **1.48** leads to the formation of a formyl borane fragment stabilized by interaction with the FLP scaffold.[34,77,78] DFT studies, also performed by Erker and co-workers, revealed that the reduction of CO by Piers' borane to give formyl borane in the absence of an FLP is highly endothermic. However, by involving an appropriate FLP framework this problem could be overcome through the strongly exothermic formation of an η^2-formylborane FLP complex.[77]



Scheme 1.13 Hydroboration of CO with Piers' borane by using FLPs. [34,77,78]

The reactivity of FLPs with CO can be expanded to involve a tandem reaction with a second substrate. Dobrovetsky and Stephan studied the reactivity of FLPs with syn gas (H_2 and CO) taking as an example the simple intermolecular tBu$_3$P/B$(C_6F_5)_3$ system.[79] The reaction of tBu$_3$P and B$(C_6F_5)_3$ (ratio = 1:2) with a $^{13}CO/H_2$ mixture at 4 atm pressure results in the

formation of the formyl borate derivative **1.49** after 2 hours (**Scheme 1.14**). However, when this compound is left for a further 18 hours at room temperature, two new species (**1.51** and **1.52**) were obtained in a ratio of 2:3.

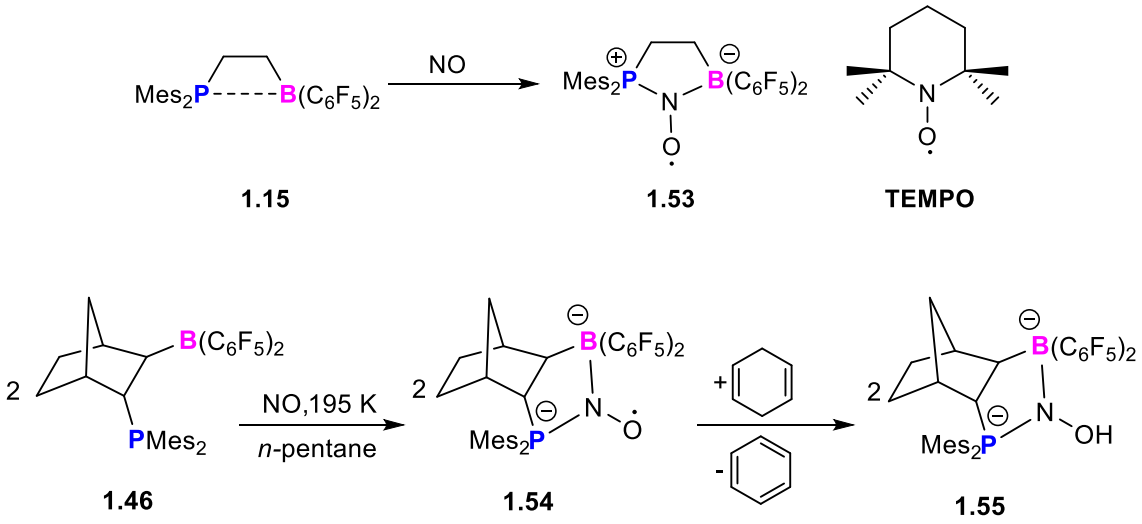


Scheme 1.14 The reaction of tBu$_3$P and B(C$_6$F$_5$)$_3$ with syn gas (H$_2$/CO).[79]

Independent reactivity studies were undertaken to understand the formation of products **1.51** and **1.52** from **1.49**. These revealed that heating an isolated sample of **1.49** in toluene at 363 K (for 2 hours) led to the formation of a new product - epoxy borate anion, **1.50**. Moreover, continuous heating of compound **1.50** with H$_2$ at 343 K resulted in the clean formation of compound **1.52**. Compound **1.51** could be synthesized independently in high yield via the reaction of isolated **1.49** with CO. In this case, the mechanism of the reaction to form **1.51** and **1.52** proceeds through the formation of compound **1.49** as the first step of the reaction, which is itself formed via the activation of dihydrogen by tBu$_3$P/B(C$_6$F$_5$)$_3$, followed by CO insertion into the B-H bond upon addition of a second equivalent of B(C$_6$F$_5$)$_3$. [It is noteworthy that [tBu$_3$PH][HB(C$_6$F$_5$)] does not react with CO, and it forms **1.49** only when

another equivalent of $B(C_6F_5)_3$ is added into the system]. Subsequently, **1.49** undergoes C_6F_5 transfer from $B(C_6F_5)_3$ to the formyl carbon centre to form **1.50**. Compound **1.50** can then react with either CO to afford **1.51** or H_2 affording the phosphonium borane-oxy-borate salt **1.52**.[79]

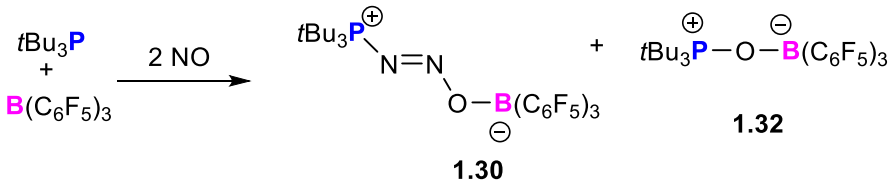
The reaction of FLPs with nitric oxide (NO) has been found to have some features in common with the capture of CO.[80] Erker *et al*. reported the formation of the green coloured *N*-oxyl radical **1.53** from the treatment FLP **1.15** with NO in fluorobenzene.[81] X-ray crystallographic analysis of **1.53** reveals a five-membered heterocyclic compound in which the nitrogen atom forms bonds with both phosphine and borane units, leading to a longer N-O distance (1.2962(17) Å) compared to free NO (1.151 Å). This distance is similar to *N*-oxyl radicals of the type $R_2NO^{\cdot}$ reported in the literature (for example : TEMPO, *d*(N-O) = 1.284(8) Å; **Scheme 1.15**).[82] The EPR signal of **1.53** shows a multi-line pattern centered at g = 2.0089, showing coupling to the ^{14}N nucleus ($A(^{14}N)$ = 18.5 MHz). Due to the radical nature of **1.53**, it is found to be highly reactive in hydrogen atom abstraction reactions from 1,4-cyclohexadiene, cyclohexene and toluene.[81]



Scheme 1.15 Reactions of NO with P/B FLPs. [81,83]

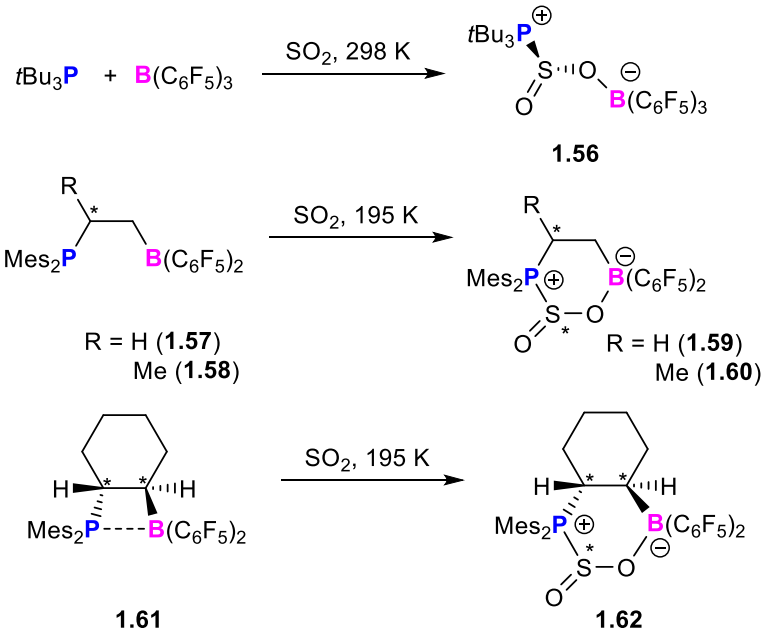
Sajid *et al.* have examined the reactivity of NO with intramolecular phosphine/borane FLPs. Similar to the results found with FLP **1.15** and NO, reaction with **1.46** also leads to the formation of an *N*-oxyl radical **1.54** (**Scheme 1.15** (**bottom**)).[83] The crystal structure of **1.54** features a five-membered heterocycle geometry similar to **1.53**. Moreover, **1.54** is shown to be able to abstract hydride from 1,4-cyclohexadiene at room temperature to form hydroxy compound **1.55** (**Scheme 1.15**).

In a contrast to the formation of *N*-oxyl radical products in the reactions of **1.15** and **1.46** with NO, Erker *et al.* showed that the reaction of *t*Bu$_3$P/B(C$_6$F$_5$)$_3$ affords two species, namely the known FLP·N$_2$O adduct and phosphine oxide adduct **1.32**. This chemistry is related to the disproportionation of NO to N$_2$O and phosphonium oxide (R$_3$P=O) species when NO is exposed to certain phosphines (**Scheme 1.16**). [81]



Scheme 1.16 Reaction of *t*Bu$_3$P/B(C$_6$F$_5$)$_3$ with NO.[81]

Another greenhouse gas that has been found to be reactive towards activation by FLP is sulfur dioxide (SO_2), which is known to react with water molecules in the atmosphere forming sulfuric acid droplets.[84] Sajid *et al*. have reported a series of phosphine/borane FLPs that could capture SO_2.[85] As shown in Scheme **1.17**, the reaction of the FLPs *t*Bu$_3$P/B(C$_6$F$_5$)$_3$, **1.57**, **1.58**, and **1.61** with SO_2 yield the SO_2·FLP adducts **1.56**, **1.59**, **1.60** and **1.62**. X-ray crystallographic studies of these adducts reveal common features of SO_2 connectivity to the phosphine and borane components of the FLP that are superficially very similar to related CO_2-FLP adducts. The sulfur atom is invariably attached to the phosphorus centre, with P–S distances in the range 2.27-2.36 Å, and one of the oxygen atoms of the SO_2 moiety engages in a B-O bond, with B-O distances of around 1.56 Å.[85]

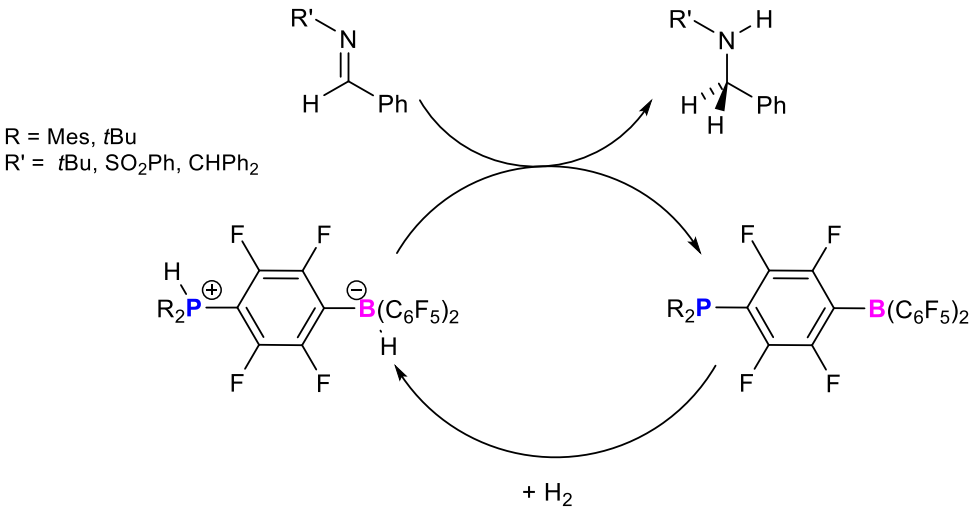


Scheme 1.17 SO_2 activation by phosphine/borane FLPs.[85]

1.5 Catalytic reactivity driven by FLPs

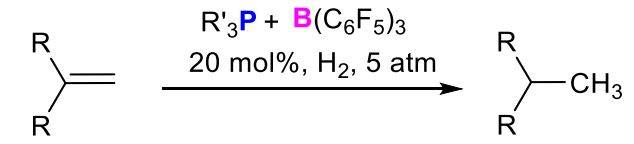
Dihydrogen activation marked the beginning of a period of rapid investigation into the application of FLPs in hydrogenation catalysis. Previously, non-metal hydrogenation catalysts were very rare, with the main examples being KO*t*Bu, which catalyzes the addition of H_2 to benzophenone, albeit under relatively harsh conditions (200 °C, >100 bar H_2).[86,87] Following the report in 2007 that FLP **1.8** could activate H_2 under ambient conditions, Stephan *et al.* also reported that this FLP could catalyze the reduction of sterically bulky imines (**Scheme 1.18**), along with aziridines and protected nitriles.[88] The reduction of bulky imines by H_2 catalyzed by $B(C_6F_5)_3$ alone was reported a year later, in which the imine itself acts as the Lewis base in an FLP system.[89] Mechanistically, H_2 is initially cleaved to form a

hydroborate anion and an iminium cation, which then reacts via hydride transfer to the iminium carbon to yield the amine product.[89]



Scheme 1.18 FLP-catalyzed reduction of imines.[88]

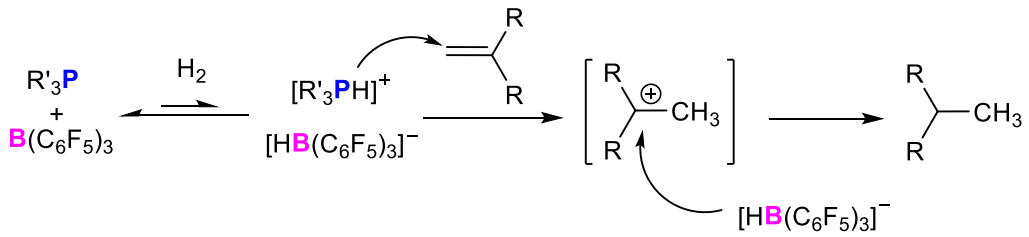
The scope of hydrogenation catalysis using FLPs has been proven to be extremely broad. Paradies and co-workers showed the first example of the catalytic reduction of an olefin, using combinations of $B(C_6F_5)_3$ and a series of relatively weakly Lewis base phosphines, $(C_6F_5)Ph_2P$ (**1.63**), $(C_6F_5)_2PhP$ (**1.64**), $(2,6\text{-}C_6H_3Cl_2)_3P$ (**1.65**) and $(C_{10}H_7)_3P$ (**1.66**) (**Scheme 1.19**).[90] This chemistry, however, is generally only applicable to 1,1-diaryl substituted alkenes.



for R'_3P = $(C_6F_5)Ph_2P$ **(1.63)**, $(C_6F_5)_2PhP$ **(1.64)**,
$(2,6\text{-}C_6H_3Cl_2)_3P$ **(1.65)**, $(C_{10}H_7)_3P$ **(1.66)**

Scheme 1.19 Catalytic hydrogenation of olefins by FLPs.[91]

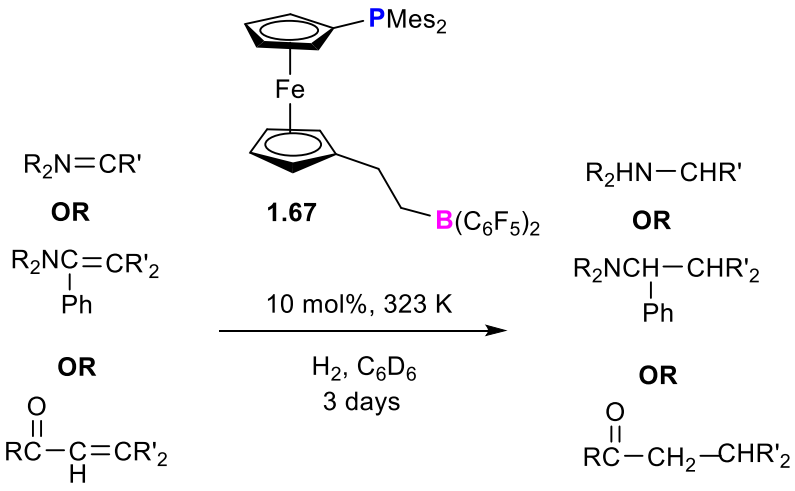
The mechanism of this reaction proceeds through activation of H_2 followed by protonation of the C=C double bond, generating a transient carbocation intermediate, and subsequent hydride transfer from the $[H(BC_6F_5)_3]^-$ anion (**Scheme 1.20**). From this study it was found that the rate of reaction and the yields of the hydrogenation products are highly dependent on the nucleophilicity of the Lewis base used - which relates in turn to the efficacy of the corresponding conjugate acid in the protonation step to generate the carbenium ion intermediate (**Scheme 1.20**). The combination of $B(C_6F_5)_3$/**1.63** only reacts discernibly with hydrogen at very low temperatures (< 223 K), but olefin hydrogenation could occur at room temperature; $B(C_6F_5)_3$/**1.64** on the other hand does not show any H_2 activation due to very weak nucleophilicity, and thus the hydrogenation of the olefin does not proceed at all. $B(C_6F_5)_3$/**1.65** and $B(C_6F_5)_3$/**1.66** could both activate H_2 reversibly at room temperature and give high yields in the catalytic hydrogenation of olefins over a period of 24 hours.[90]



Scheme 1.20 Mechanism for the hydrogenation of 1,1,-diaryl alkenes catalyzed by FLPs.

Subsequently, in 2017, Jian *et al.* reported an intramolecular ferrocene derived FLP **1.67** which could activate H_2 at 1.5 atm (and T <283 K) in C_6D_6. The product of this hydrogen activation was also found to catalyze the selective hydrogenation of imines (C=N) and enamines (NC=C) (to afford tertiary amines) in relatively high yield (99%), together with

some ynones (at the C≡C bond, to obtain the respective saturated ketones), although with lower overall conversion (**Scheme 1.21**) .[91]



Scheme 1.21 Catalytic hydrogenation of imines, enamine and ynones substrates by an intermolecular FLP **1.67** shown by Jian *et al*.[91]

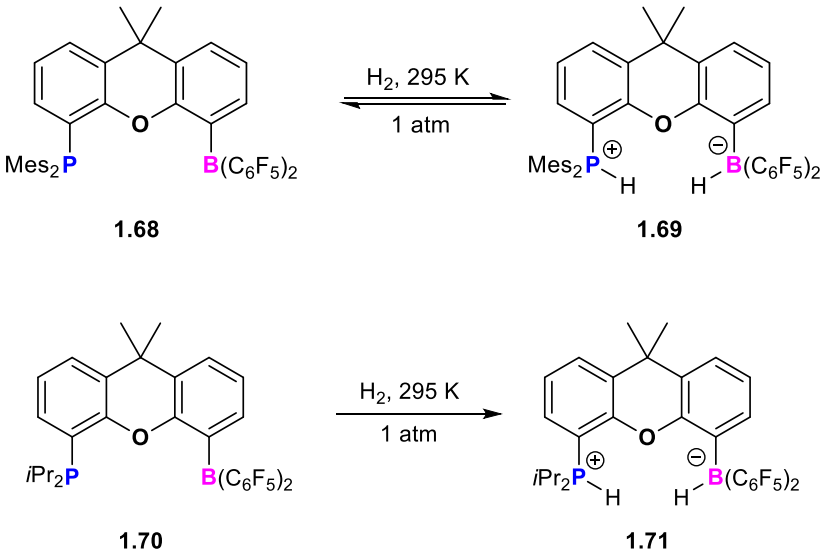
In addition, FLPs featuring bifunctional phosphines as the Lewis base component have been found to cleave H_2 in conjunction with $B(C_6F_5)_3$ as the Lewis acid. These systems have also shown interesting catalytic activity in the hydrogenation of silyl enol ethers and the 'domino' hydrosilylation/hydrogenation of enones (**section 1.7**). [92,93]

1.6 Dimethylxanthene-based FLPs

Although there are many examples of H_2 activation by FLPs, there are only a handful of papers that demonstrate reversible activation of H_2 at room temperature.[19,97] Room temperature reversibility in H_2 activation is challenging; the key to such behaviour is limiting the magnitude of ΔH^o to allow ΔG^o to be driven close zero in the direction of the release of

H_2. Kinetically it also requires $\Delta G^{\ddagger}$ to be small for both activation of H_2 and H^+/H^- recombination.[58,95] This challenge may be overcome through the use of relatively rigid, single-component, xanthene-based FLPs that are preorganized into an appropriate geometry for H_2 activation, thereby reducing the magnitudes of $\Delta S^{\ddagger}$ and $\Delta S°$ for the reaction.[95] Additionally, such xanthene-based systems confine the components of the activated phosphonium hydroborate species into a molecular pocket, making recombination kinetically and thermodynamically more favourable.[72] This means weaker Lewis base/acid pairs can be used because a less exothermic $\Delta H°$ is required to make $\Delta G° < 0$ and drive the reaction.[39]

In 2016, the Aldridge group developed a number of single component FLPs based on a dimethylxanthene backbone that possess P···B separations between 4.2−4.5 Å i.e. similar to the optimum distance for H_2 activation suggested in Papai's model (4.2−4.5 Å).[37,39,72] The P···B separations in FLPs **1.68** ($PMes_2/B(C_6F_5)_2$) and **1.70** ($PiPr_2/B(C_6F_5)_2$) are 4.243(3) Å and 4.487(3) Å, respectively.[38–41] Interestingly, it was found that FLP **1.68** allowed for reversible H_2 activation in solution at room temperature, making it the first system to do so (**Scheme 1.22**).[72]

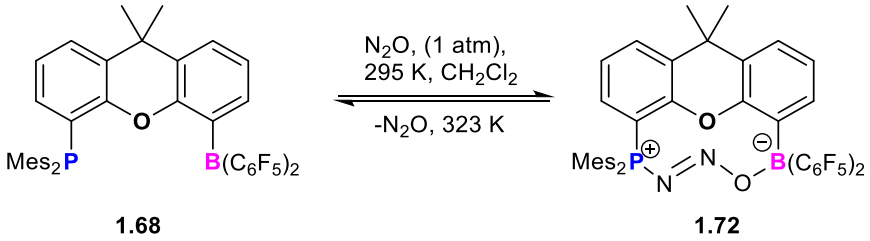


Scheme 1.22 H_2 activation by FLPs **1.68** and **1.70** at room temperature.

Data derived from a Van't Hoff plot provide thermodynamic parameters for the liberation of H_2: $\Delta H° = 38$ kJ mol^{-1} and $\Delta S° = 102$ J mol^{-1} K^{-1}. As predicted by Le Chatelier's principle, the equilibrium can be forced all the way to the activated product by using an overpressure of H_2. Kinetically, the liberation of H_2 is facilitated by the geometry enforced on the activated product. The sterically bulky substituents on both phosphorus and boron are orientated away from each other, so the protic and hydridic fragments are confined in close proximity to one another, allowing for facile recombination.

In contrast to the reversibility exhibited by **1.68**/**1.69**, the related P*i*Pr$_2$/B(C$_6$F$_5$)$_2$ FLP, **1.70**, shows irreversible activation of H_2 at room temperature, despite a similar P···B separation in the free FLP and similar H^+/H^- positions in the activated product. Due to the presence of the more strongly electron donating P*i*Pr$_2$ substituent, the reverse reaction cannot be induced even at elevated temperatures. In this case, the P–H bond is too strong for the reverse reaction to be thermodynamically favourable at any accessible temperature.[72]

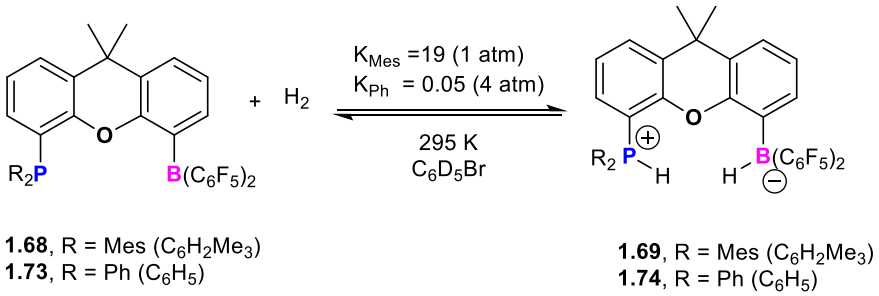
Interestingly, FLP **1.68** was also found trap N_2O (**Scheme 1.23**), consistent with the observation that the P···B distance is similar to previously reported systems used to capture N_2O (**section 1.4**).[67–69,71] In the case of FLP **1.68**, the insertion of N_2O into the scaffold between the phosphine and borane moieties requires slight expansion of the P···B distance, and compression of the P–N–N and N–O–B angles. This aids the release of N_2O at elevated temperatures (323 K) and makes the uptake reversible.[72]



Scheme 1.23 Capture and release of N_2O by FLP **1.68**.

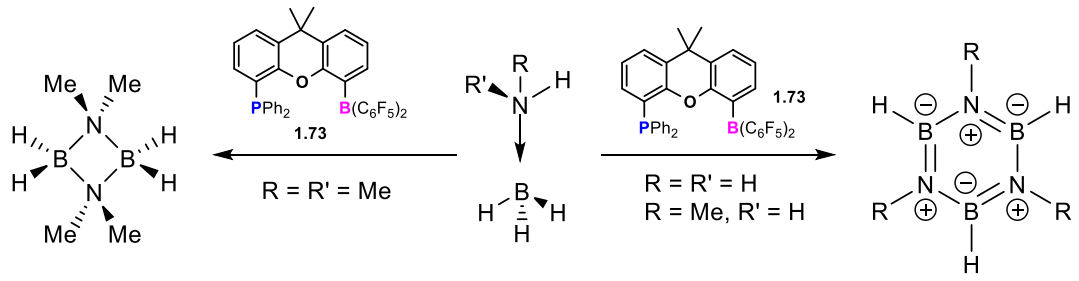
The finding of reversible H_2 activation at room temperature and N_2O capture by FLP **1.68** encouraged Aldridge *et al.* to conduct further studies of the reactivity of dimethylxanthene-based FLPs in catalytic reactions. In 2016, dimethylxanthene FLP **1.73** was synthesized featuring a more weakly Lewis basic PPh_2 substituent, which makes the release of H_2 more thermodynamically favourable from phosphonium hydroborate **1.74** (**Scheme 1.24**).[96] In contrast to the equilibrium mixture of H_2 activation product and free FLP formed in the **1.68**/**1.69** system (which features a **1.69 : 1.68** ratio of ~20 : 1 in bromobenzene at 295 K and 1 atm H_2), it was found that, in the case of FLP **1.73**, only 5% of the activated product, **1.74** was formed at 4 atm pressure and 295 K.[92,96] Moreover, a Van't Hoff plot for the **1.73**/**1.74** system provided thermodynamic parameters for the release of H_2 ($\Delta H°$ = 34 kJ mol^{-1} and $\Delta S°$ = 138 J mol^{-1} K^{-1}), implying a more negative value for $\Delta G°$ for the release of H_2 in the case of **1.74** (ΔG^o = -6.71 kJ mol^{-1}, compared to +7.91 kJ mol^{-1} for **1.69** at 298 K).

As such, **1.73** was expected to be a more active catalyst in dehydrogenation chemistry.[63,72,90,92,96–98]



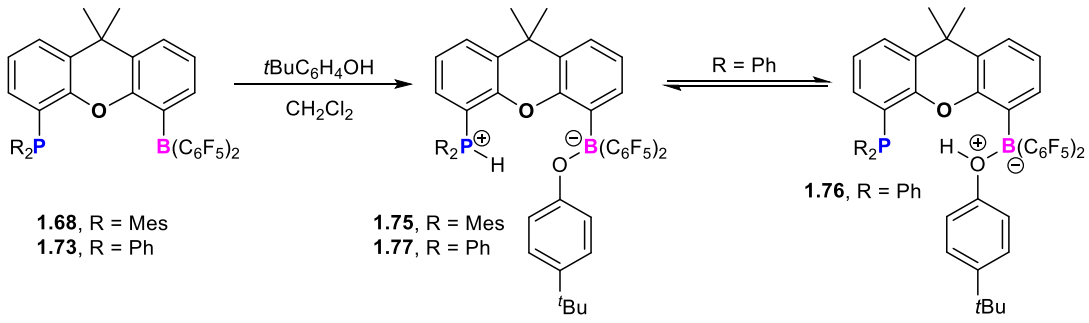
Scheme 1.24 Equilibria between the free FLP and H_2 activation product at 295 K for **1.68** and **1.73**.

Interestingly, the same report by Aldridge *et al.* also reveals that FLP **1.73** could catalyze the dehydrogenation of ammonia- and amine-boranes (**Scheme 1.25**). In this study, it was found that FLP **1.73** acting as a catalyst at 1 mol% loading (at 328 K) could dehydrogenate dimethylamine borane to $H_2B(\mu\text{-}NMe_2)_2BH_2$ (**Scheme 1.25 (left)**), while the corresponding catalytic reactions with ammonia borane and methylamine borane form trimethylborazine and borazine, respectively (**Scheme 1.25 (right))**. The first step of this reaction involves the activation of the B-H bond of the ammonia-/amine-borane in a similar manner to H_2 activation, followed by loss of H_2 by dehydrocoupling of the terminal N-H bond of the BN fragment and the B-H bond of the other borane monomer,[99] resulting in end-growth B-N. Coupling with further equivalents of ammonia-/amine-borane then occurs to form the 4- or 6- membered B-N ring seen in the product. [96,99,100]



Scheme 1.25 Catalytic B-N dehydrocoupling of ammonia and amine boranes by FLP **1.73.**

Recently, further studies by Aldridge *et al.* have focused on the interaction of FLP **1.68** with the O-H bonds in water (H_2O), alcohols (ROH) and phenols (ArOH). It was found that FLP **1.68** formed simple B-bound adducts when reacted with H_2O and alcohols such as methanol and 2-propanol with accompanying changes in colour from yellow to colourless.[101] By contrast, when **1.68** was treated with a more acidic O-H bond, such as that in the phenol, p-*t*BuC_6H_4OH, X-ray crystallographic studies revealed the formation of an O-H activated phosphonium borate zwitterion, **1.75**. In C_6D_6 solution, however, the **1.75** exists in equilibrium with the simple B-bound adduct (**1.76**) analogous to the systems formed with H_2O, methanol and 2-propanol (**Scheme 1.26**).



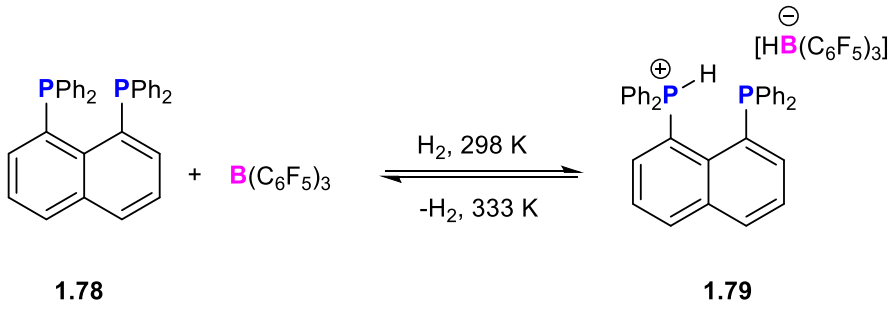
Scheme 1.26 Reaction of FLP **1.68** and **1.73** with p-*t*BuC_6H_4OH.[101]

Consistently, when FLP **1.68**, featuring the more strongly Lewis basic $PMes_2$ substituent was reacted with p-*t*BuC_6H_4OH, the O-H activated product, **1.75**, was found to be stable in solution even at elevated temperature. DFT calculations showed that in dichloromethane the zwitterionic phosphonium borate **1.75** is 34.6 kJ mol^{-1} more stable than the corresponding adduct **1.77**.[99]

The applications of dimethylxanthene-derived FLPs in small molecule activation and catalysis shown are intriguing; the potential of these FLPs in other modes of reactivity (such as hydroboration) are, however, yet to be fully explored. Hence, further experimental and theoretical studies is needed to understand the behaviour of this particular type of intramolecular FLP. The applications of these systems in hydroboration chemistry and in E-H bond activation are reported in this thesis and discussed in chapters 5 and 6.

1.7 Intermolecular FLPs featuring bifunctional phosphines

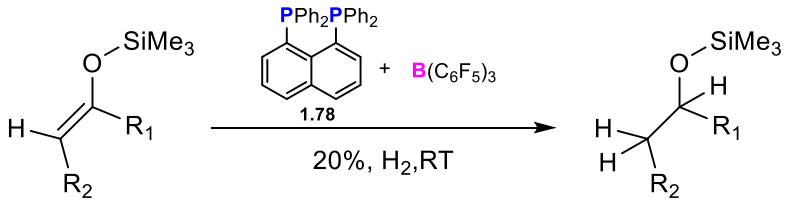
The use of intermolecular phosphine/borane FLPs featuring two phosphorus donor sites to reversibly activate dihydrogen was first reported by Erker *et al.* using 1,8-bis(diphenyl-phosphino)-naphthalene **1.78** and $B(C_6F_5)_3$. This system was found to release H_2 from the zwitterionic phosphonium hydroborate product, **1.79** when heated to 333 K. (**Scheme 1.27**).[92]



1.78 **1.79**

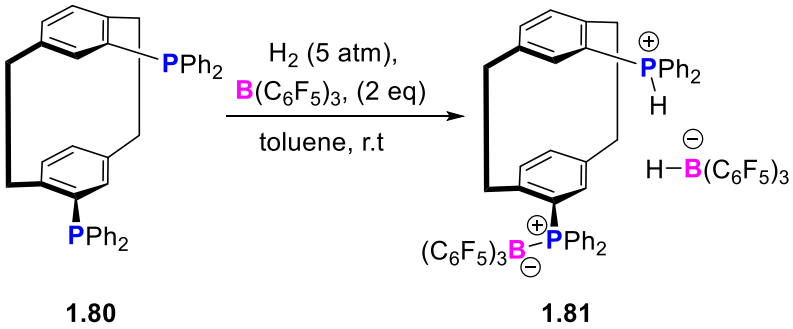
Scheme 1.27 Intermolecular H_2 activation by bisphosphine **1.78** and $B(C_6F_5)_3$.[92]

In this reaction, as with other phosphine/borane FLPs, the bulky phosphorus and borane substituents prevent adduct formation, resulting in heterolytic cleavage of H_2 to yield the phosphonium-hydridoborate salt **1.79**, in which the single proton rapidly exchanges between the two phosphine sites. Moreover, Erker *et al.* found that although there are two phosphine sites (potentially allowing for the activation of more than one H_2 molecule), steric constraints prevent the activation of a second H_2 molecule.[92] In addition, X-ray crystallographic studies of the phosphonium hydroborate salt **1.79** indicate the presence of a weak P-H···H-B bond, with an H···H separation of 2.080(3) Å.[102–104] The facile release of H_2 from **1.79** at 333 K prompted Erker *et al.* to use this FLP system in the catalytic hydrogenation of silyl enol ethers.[92] Hydrogenation of the alkene function was achieved by using 20 mol% of the **1.78**/$B(C_6F_5)_3$ catalyst and 2 atm. pressure of H_2 at room temperature (**Scheme 1.28**).[92]



Scheme 1.28 Catalytic hydrogenation of silyl enol ethers by FLP **1.78**/$B(C_6F_5)_3$.[19]

Grab *et al.* have shown that bisphosphine backbone plays a key role in the activation of dihydrogen. The three isomeric [2.2]paracyclophane-derived bis-phosphines **1.80, 1.82** and **1.83** were found to give different results in H_2 activation when partnered with $B(C_6F_5)_3$.[93] The reaction between cyclophane-bisphosphine **1.80**/$B(C_6F_5)_3$ and dihydrogen resulted in the formation of different products depending on the amount of $B(C_6F_5)_3$ used. Two equivalents of $B(C_6F_5)_3$ are required to allow for clean formation of the phosphonium product **1.81** (**Scheme 1.29**). With only one equivalent of $B(C_6F_5)_3$, a 1:1 mixture of **1.81** and free bisphosphine **1.80**, is generated.

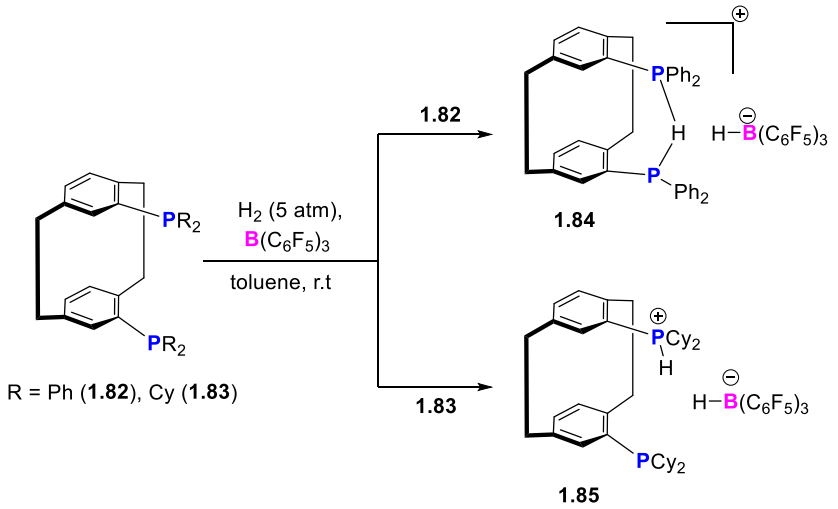


1.80 **1.81**

Scheme 1.29 Activation of H_2 by **1.80**/$B(C_6F_5)_3$ (with a ratio of **1.**80 : $B(C_6F_5)_3$ of 1 : 2).

By changing the positions of the phosphine substituents, the pseudo-geminal bisphosphine **1.82** could be obtained, which requires a different stoichiometry of $B(C_6F_5)_3$ for H_2 activation (to give **1.84**; **Scheme 1.30**). According to Grab *et al.*, the reason for the differences in H_2 activation behaviour between **1.80** and **1.82** is derived from the positions of the two phosphines on the cyclophane backbone. In compound **1.80**, the rigid backbone framework causes the distance between the two phosphine substituents to be in the region of 4.9 Å, while the P···P separation for the pseudo-geminal bis-phosphine **1.82** is smaller at 4.0 Å. In the case of **1.80**, the wider P···P separation allows for the formation of a P-B

donor/acceptor interaction at one of the phosphine functions to form compound **1.81**. Further studies on the catalytic reactivity of these FLPs showed that the **1.80**/$B(C_6F_5)_3$ and **1.82**/$B(C_6F_5)_3$ systems could both catalyze the 'domino' hydrosilylation/hydrogenation reactions of enones.[93]



Scheme 1.30 Activation of H_2 by **1.82**/$B(C_6F_5)_3$ and **1.83**/$B(C_6F_5)_3$.

Recent (unpublished) work in the Aldridge group has centred around the reactions of bifunctional bis-diphenyl phosphine systems **1.86**-**1.87** with $B(C_6F_5)_3$ in order to probe their potential for the activation of H_2 (**Figure 1.6**).[105]

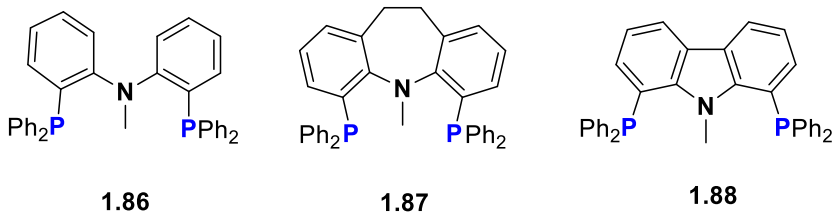
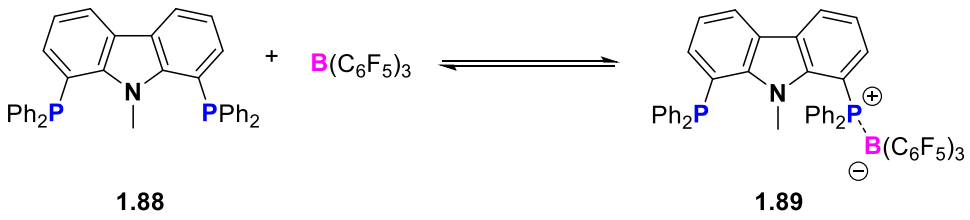


Figure 1.6 Acyclic (**1.86**), azepine-based (**1.87**) and carbazole-based (**1.88**) bis-diphenylphosphine systems.[105]

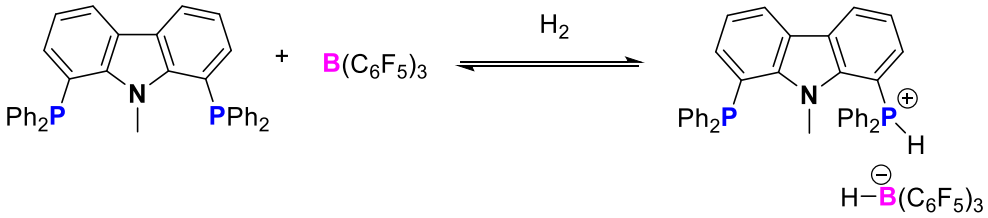
These studies show that phosphines **1.86** and **1.87** irreversibly form 1:1 classical Lewis acid/base adducts with $B(C_6F_5)_3$ because the backbone structures for these compounds are flexible enough to allow access to conformations in which P···B association is sterically accessible. Conversely, the carbazole-based system **1.88** forms an adduct reversibly with $B(C_6F_5)_3$ causing mixture of **1.88**/**1.89** exist in solution phase equilibrium in d_8-toluene (**Scheme 1.31**).



1.88 **1.89**

Scheme 1.31 Equilibrium between **1.88** and **1.89** in d_8-toluene.[105]

The thermodynamic parameters for the association reaction have been determined to be ΔH^o = -77.3 kJ mol^{-1} and ΔS^o = -267.2 J mol^{-1} K^{-1}; consistent with the negative value of ΔS^o, cooling the system shifts the position of equilibrium towards **1.89**, and at temperatures below 258 K, free **1.88** is no longer observed in the $^{31}P\{^1H\}$ NMR spectrum. This system has been shown to activate dihydrogen at low temperatures (**Scheme 1.32**)[105]



1.88 **1.90**

Scheme 1.32 Equilibrium between free FLP **1.88**/$B(C_6F_5)_3$ and **1.90** in d_8-toluene in the presence of dihydrogen.[105]

1.8 Research Outline

As already shown in the literature discussed above, intramolecular dimethylxanthene-based FLPs have shown reactivity towards H_2, in dehydrocoupling reactions and O-H bond activation. However, there are many more interesting patterns of reactivity that might be probed using these FLPs (especially in catalysis) which involve an initial E-H bond activation process. Moreover, a wide range of ligand backbones related to dimethylxanthene are available in the literature - for example by formally changing the O atom with S or NR. As such, new series of intramolecular FLPs based on systematically modified backbones could have the potential for new reactivity and could give further insight into the chemistry of these types of FLP as a function of different P···B separations.

Thus, the work described in this thesis is set out as follows: Chapter 3 covers new improved methods to access existing dimethylxanthene FLPs, together with the synthesis of new FLPs derived from a dimethylthioxanthene backbone. Chapter 4 covers the synthesis and reactivity of novel acridan-based FLPs in small molecular activation. Moreover, this chapter also covers the synthesis and reactivity of acridan-based bis-phosphine systems thereby completing the library of bis-phosphines developed by the Aldridge group (as discussed in **section 1.7** above). Chapter 5 discusses the catalytic activity of existing dimethylxanthene FLPs[72,96] in the hydroboration of internal and terminal alkynes by pinacolborane. Lastly, Chapter 6 reports on the reactivity of existing dimethylxanthene-based FLPs towards E-H bond activation in silanes and stannanes.

1.9 References

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Chapter 2. Experimental Techniques

2.1 Manipulation of air-sensitive compounds

Most of the compounds employed in the research work presented in this thesis are highly sensitive to air and/or moisture. Hence, inert atmosphere techniques were used to manipulate these compounds, rather than traditional bench-top methods.

2.1.1 Inert atmosphere techniques

Inert atmosphere techniques were used for air and/or moisture sensitive compounds, with chemical reactions carried out under an atmosphere of either nitrogen or argon gas. The two methods in this work involved glove box or Schlenk line techniques.

2.1.1.1 Schlenk line techniques

The risk of oxidation or hydrolysis in solution-phase reactions involving air and/or moisture sensitive species can be minimized by conducting the experiment using a Schlenk line. The Schlenk line employs a dual parallel manifold (**Figure 2.1**), with one manifold connected to a purified argon gas supply, and the other to the vacuum pump. Two-way taps act as the connectors to allow the switching of the vessels between inert gas and the vacuum line. The pressure within the vacuum manifold was typically maintained at *ca.* 10^{-2} Torr and monitored using a Pirani gauge. A liquid nitrogen trap is placed between the vacuum manifold and the vacuum pump to prevent vapours of solvents and other volatile

substances from entering the pump. A mercury or oil bubbler was used to provide a pressure release system and a visible means of monitoring the flow of the inert gas.

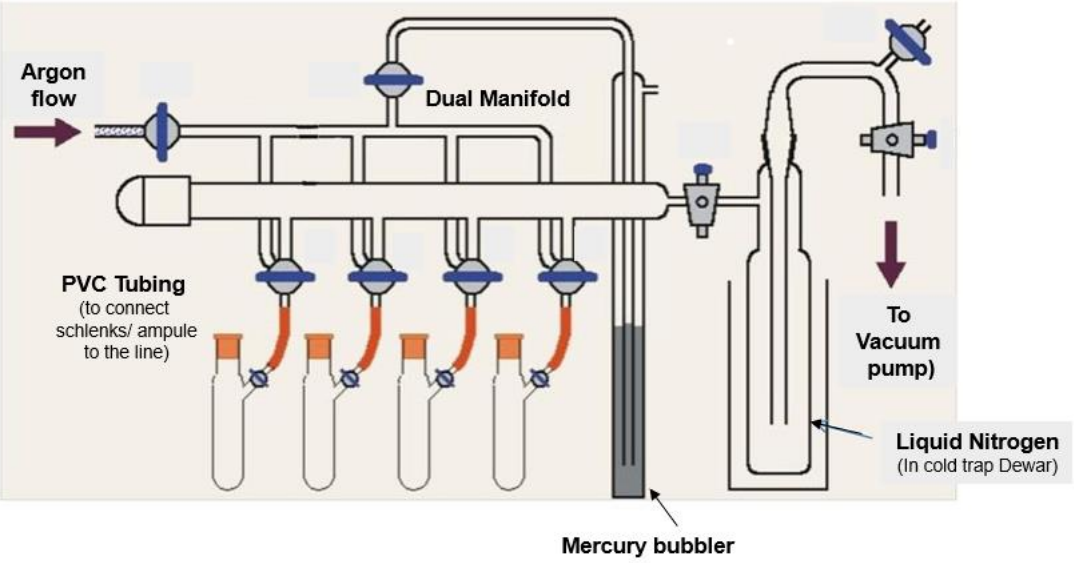


Figure 2.1 The Schlenk line set up used in this investigation.[1]

The reaction chemistry carried out using a Schlenk line employed special glassware (Schlenk tubes) which consist of a flask featuring an additional side arm to allow for connection to the manifold via rubber tubing. In order to ensure that the environment inside the glassware is as free from air and moisture as possible, these flasks were evacuated to *ca.* 10^{-2} Torr, and backfilled with inert gas three times prior to use. During the final evacuation cycle, traces of moisture on the inner walls of the glassware were removed by heating the glassware using a Bunsen burner under vacuum. All ground-glass joints were greased with high vacuum grease to secure an air-tight seal prior to use. Solvents and liquids were transferred between one flask and another using cannulae or syringes, thereby minimizing exposure to air.

2.1.1.2 Glove box techniques

A glove box is a sealed container filled (in the case of this study) with nitrogen gas, that is designed for the handling and storage of air- and/or moisture sensitive solids. Neoprene gloves are built into the sides of the box in order to allow access, and compounds/equipment are able to enter *via* an antechamber, which is evacuated to *ca.* 10^{-2} Torr and backfilled with inert gas three times before entering the box.[2] The atmosphere inside the box is constantly purified by passing through molecular sieves and a copper catalyst to remove traces of water and oxygen, respectively.

2.2 Spectroscopic techniques

2.2.1 NMR spectroscopy

NMR spectra were measured on Bruker Avance III HD nanobay 400 MHz NMR spectrometer equipped with 9.4 T magnet, or a Bruker Avance III 500 MHz NMR spectrometer equipped with 11.75 T magnet and a ^{13}C detect cryoprobe. For ^{1}H, ^{13}C and ^{29}Si spectra, resonances and are reported relative to tetramethylsilane (δ = 0 ppm), ^{31}P resonances are referenced externally to H_3PO_4 (85 %), ^{19}F chemical shifts to CF_3COOH, ^{11}B chemical shifts to $BF_3{\cdot}Et_2O$, and ^{7}Li chemical shifts to 1 M LiCl in D_2O. All ^{13}C NMR spectra were measured with proton decoupling. COSY, HMBC and HSQC experiments were used to aid the assignment of ^{1}H and ^{13}C NMR spectra. Chemical shifts are quoted in δ (ppm) and coupling constants in Hz. NMR spectra were measured in benzene-d_6 (dried over potassium), dichloromethane-d_2 (dried over CaH_2), or toluene-d_8 (dried over potassium), with the solvent then being distilled under reduced pressure and stored under

argon in a Teflon valve ampoule prior to use. NMR samples of air/moisture sensitive materials were prepared under inert gas in 5 mm Wilmad 507-PP tubes fitted with J. Young Teflon valves.

2.2.2 X-Ray crystallography

Single-crystal X-ray diffraction data were collected at 150 K on an Oxford Diffraction/Agilent SuperNova diffractometer with Cu-Kα (λ = 1.54184 Å) radiation, equipped with a nitrogen gas Oxford Cryosystems cryostream unit.[3] Raw frame data were reduced using CrysAlisPro.[4] The structures were solved using SHELXT[5] and refined to convergence on F^2 and against all independent reflections by full-matrix least-squares using SHELXL[6] in combination with the SHELXLE[7] program. Structure solution and refinement was carried out by Dr Evgeny Kolychev, Dr Maria Ángeles-Fuentes, Dr Jamie Hicks, Andreas Heilmanm or Caitilín McManus using Superflip,[8] and refined using the CRYSTALS program suite on F^2.[9,10]

2.2.3 Elemental microanalysis

Elemental microanalyses were carried out for all novel compounds reported in this thesis at London Metropolitan University. In some cases, accurate results could not be obtained despite multiple attempts, and in these cases the absence of microanalytical data is noted in the experimental section.

2.2.4 Quantum chemical calculations

All computational work reported in this thesis was carried out by Dr Petra Vasko, and utilized Density Functional Theory (DFT) within the Gaussian09 (Revision D.01)

package.[11] Geometry optimizations were performed with the PBE1PBE exchange-correlation functional using a def-TZVP basis set.[12] The nature of all stationary points found (minimum or saddle point) was confirmed by full frequency calculations.

2.3 Preparation and purification of starting materials

2.3.1 Solvents

Solvents used in the work described in this thesis were dried, purified and degassed before use. Generally, these were dried by passing through a column of an appropriate drying agent, using the in-house MBRAUN Solvent Purification system (MB-SPS). Dichloromethane (CH_2Cl_2), acetonitrile, pentane, benzene, hexane and toluene were obtained directly from the SPS and were stored over 4 Å sieves molecular sieves (CH_2Cl_2, acetonitrile) or a potassium mirror (toluene, benzene, hexane, pentane). Diethyl ether was pre-dried over KOH pellets for a minimum of one week before being dried further by distillation from benzophenone and sodium wire. It was then stored in an ampoule over a potassium mirror. THF was dried by distillation from sodium wire and stored in an ampoule over a sodium mirror. Deuterated solvents were dried over potassium (C_7D_8) or CaH_2 ($CDCl_3$, CD_2Cl_2 or C_6D_6) and distilled under reduced pressure. They were subsequently degassed by the freeze-pump-thaw method and stored over 4 Å molecular sieves ($CDCl_3$, CD_2Cl_2) or a potassium mirror (C_6D_6, C_7D_8).

2.3.2 Starting materials

Unless otherwise stated, starting materials were purchased from commercially available sources, and used without further purification. 9,9-dimethylxanthene was purchased from Sigma Aldrich or ArkPharm. Thioxanthene-9-one, *n*BuLi (1.5 M or 2.5 M solutions in hexane), *s*BuLi (1.4 M solution in cyclohexane), methyl iodide, 2-chloro-2-methylpropane, tri-*tert*-butylphosphine, palladium acetate ($Pd(OAc)_2$), pinacolborane (HBpin), phenyl silane ($PhSiH_3$), triphenyltin hydride (Ph_3SnH) and tributyltin hydride (tBu_3SnH) were purchased from Sigma Aldrich. Bromine, 5-methyl-2-aminobenzoic acid, chlorodi(p-tolyl)phosphine ($ClP(ptol)_2$), caesium carbonate and diphenyl silane were purchased from Alfa Aesar. Dimethyltin dichloride and chlorodiphenylphsophine ($ClPPh_2$) were purchased from either Sigma Aldrich or Alfa Aesar. *N*,*N*,*N′*,*N′*-tetramethylethylenediamine (TMEDA) was purchased from either Sigma Aldrich or Alfa Aesar, dried over sodium, distilled and stored in an ampoule over molecular sieves prior to use. $FBMes_2$ was synthesized by Yan Hui Guo and Anna Booth according to a method reported by Soos *et al.*;[12] $[Ph_3C][BAr^F{}_4]$, $[HNEt_3][BPh_4]$ and SiH_4 were synthesized by Dr Andrey Protchenko following the procedure of Barth *et al.*[13] and Sears *et al.*, respectively.[14] 4-(Diphenylphosphino)-9,9-dimethylxanthene,[15] $B(C_6F_5)_3$,[16] $ClPMes_2$,[17] ClBpin,[18] ClBcat,[19] $PhB(C_6F_5)_2$[20] and $ClB(C_6F_5)_2$[21,22] were synthesized according to the literature procedures.

2.3.2.1 Preparation of dibromothioxanthene precursor 2.1

The synthesis of **2.1** followed a procedure similar to that reported by Emslie *et al.*[21] Glacial acetic acid was added in a Schlenk tube containing a solution of 2,7-di-tert-butyl-9,9-dimethylthioxanthene[22] (15.0 g, 44.3 mmol) in dichloromethane under a flow of argon.

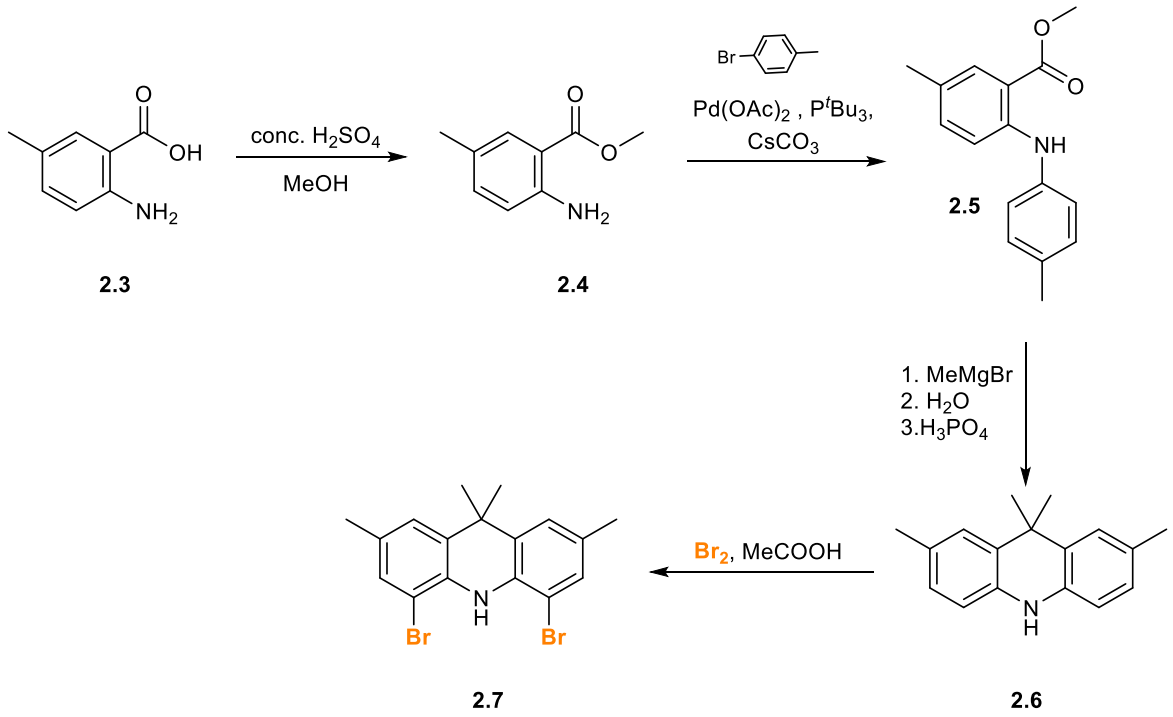
The reaction mixture was then cooled to 273 K and Br_2 (9.0 mL, 177.0 mmol) added. The mixture was warmed slowly to room temperature and stirred further for another 48 h, whereupon H_2O (600 mL) and dichloromethane were added. The dichloromethane layer was then separated, and the water layer extracted with dichloromethane until it was almost colourless. The crude organic extract was washed with H_2O (3 x 500 mL) to remove any traces of remaining acetic acid. The organic extract was then dried with $Na_2S_2O_3$ solution until the solution became colourless. It was then washed with H_2O, then brine, and dried over $MgSO_4$. After filtration it was dried *in vacuo* to give a pale pink solid. The crude material was recrystallized from boiling hexane (ca. 750 mL) to give 12.6 g of pale pink crystals, which were dried *in vacuo*. The mother liquor was concentrated to one third of its original volume to yield 3.3 g of additional crystals. Total yield: 15.9 g (72%) The ^1H NMR data matched literature values.[21]

2.3.2.2 Preparation of bromo(phosphino)thioxanthene precursor 2.2

The synthesis of **2.2** followed a modified procedure similar to that reported by Emslie *et al*.[21] *n*BuLi in hexane (1.90 mL of 1.6 M solution, 3.02 mmol) was added dropwise at 195 K into a Schlenk tube containing a solution of **2.1** (1.5 g, 3.02 mmol) in diethyl ether (20 mL). The reaction mixture was stirred for 1 h at 195 K, and at room temperture for another 2 h, resulting in a colourless solution. Ph_2PCl (0.56 mL, 3.12 mmol) was then added dropwise at 195 K, and the resulting mixture stirred at that temperature for 15 min before warming to room temperature. After 12 h of stirring at room temperature, volatiles were removed *in vacuo* and the oily residue sonicated in hexane for 5-10 min. The insoluble LiCl was removed by filtration and the solvent removed *in vacuo* to leave an air-sensitive pale yellow powder. Recrystallization from warm acetonitrile yielded pure **2.2** as pale fawn

coloured crystals. Yield: 1.26 g (67 %). The ^{1}H and ^{31}P NMR data matched literature values. [21]

2.3.2.3 Preparation of acridan precursors 2.4-2.7



Scheme 2.1 Preparation of starting material **2.4-2.7**.

2.3.2.4 Preparation of 2.4

The synthesis of **2.4** (**Scheme 2.1**) followed a procedure similar to that reported by Westwood *et al.*[23] H_2SO_4 (15 mL) was added slowly to a solution of 5-methyl-2-aminobenzoic acid (**2.3**) (10.0 g, 66.2 mmol) in methanol (150 mL) and the reaction mixture heated at 358 K for 90 h. After cooling and concentration under reduced pressure, the residue was washed with $NaHCO_3$ (250 mL) and the product extracted with ethyl acetate (3 x 100 mL). The organic layer was dried over $MgSO_4$, filtered, and volatiles were

removed *in vacuo* to give **2.4** as a brown solid. Yield: 9.94 g (91%). The ^{1}H NMR data matched literature values.[23]

2.3.2.5 Preparation of 2.5

The synthesis of **2.5** (**Scheme 2.1**) followed a procedure similar to that reported by Emslie *et al*.[21] A solution of 4-bromotoluene (10.4 g, 61.7 mmol) and **2.4** (10.0 g, 60.5 mmol) in toluene (60 mL) was added to a mixture of $Pd(OAc)_2$ (0.747 g, 3.33 mmol), P*t*Bu_3 (2.00 g, 9.92 mmol) and Cs_2CO_3 (27.0 g, 82.9 mmol) in toluene (15 mL). The reaction mixture was heated to reflux (at 398 K) for 24 h, yielding a light brown suspension. This was allowed to cool to room temperature and filtered, yielding a light brown filtrate which was concentrated *in vacuo* to give a brown oil. The crude product was purified by silica gel column chromatography (hexane, followed by 50:1 hexane:ethyl acetate) to obtain a yellow oil. Yield: 11.55 g (75%). The ^{1}H NMR data matched literature values.[24]

2.3.2.6 Preparation of 2.6

The synthesis of **2.6** (**Scheme 2.1**) followed a procedure similar to that reported by Emslie *et al.* [22] MeMgBr (25.2 mL of a 3.0 M solution in Et_2O, 75.7 mmol) was added dropwise to a solution of **2.5** (4.6 g, 18 mmol) in THF (90 mL) at 258 K, and the reaction mixture stirred at room temperature overnight to give a green solution. H_2O (280 mL) was added dropwise at 273 K and the resulting yellow solution extracted using Et_2O (2 x 50 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo* to yield a yellow oil. 85% H_3PO_4 (19 mL) was then added, and the mixture heated to 373 K for 2.5 h, during which time the solution turned green. The reaction mixture was allowed to cool to room temperature and H_2O (150 mL) added, resulting in a green solution and a brown solid. The product was extracted into Et_2O (2 x 100 mL), and the aqueous phase neutralised with 1 M NaOH (300

mL) then extracted into Et_2O (2 x 100 mL). The combined organic phases were dried over Na_2SO_4, filtered and concentrated *in vacuo* to give a sticky brown solid. The product was washed with hexane at 273 K and volatiles removed *in vacuo* to give a pale brown solid. Yield: 3.33 g (78%). The ^{1}H NMR data matched literature values.[24]

2.3.2.7 Preparation of 2.7

The synthesis of **2.7** (**Scheme 2.1**) followed a procedure similar to that reported by Liu *et al*.[24] Br_2 (5.81 g, 36.4 mmol) was added dropwise to a solution of **2.6** (3.0 g, 11.8 mmol) in glacial acetic acid (30 mL) at 268 K. The reaction mixture was stirred for 2 h at room temperature, resulting in a dark green solution, which was quenched with a saturated solution of Na_2SO_3 (to remove excess Br_2) and filtered to yield the product as a green solid, which was dried *in vacuo*. Yield: 4.60 g (98%). The ^{1}H NMR data matched literature values.[24]

2.3.2.8 Preparation of 2.8

Compound **2.8** was prepared *in situ* according to a modified literature procedure.[25] A solution of $HB(C_6F_5)_2$ (17.3 mg, 0.05 mmol) in CD_2Cl_2 (0.4 mL) was prepared in a J. Young's NMR tube. Phenylacetylene (5.48 µL, 0.05 mmol) was added to the solution and the mixture shaken vigorously until the colour turned from colourless to dark orange. The reaction was monitored by ^{1}H, ^{11}B, and ^{19}F{^{1}H} NMR measurements until all of the phenylacetylene had reacted to generate compound **2.8**. The ^{1}H NMR data for **2.8** was consistent with literature values. [25]

2.3.2.9 Preparation of 2.9

Compound **2.9** was prepared *in situ* according to a modified literature procedure. [25] A solution of **2.8** (0.05 mmol) in CD_2Cl_2 (0.4 mL) was prepared in a J. Young's NMR tube, pinacolborane (7.3 µL, 0.05 mmol) added to the solution, and the reaction mixture shaken vigorously for 5 min. The progress of the reaction was monitored by ^{1}H, $^{11}B\{^{1}H\}$, and $^{19}F\{^{1}H\}$ NMR measurements until all of the pinacolborane had reacted to form compound **2.9**. ^{1}H, $^{11}B\{^{1}H\}$, and $^{19}F\{^{1}H\}$ data were consistent with literature values.[25]

2.4 References

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