

**Frustrated Lewis Pair Chemistry of Carbon, Nitrogen and Sulfur Oxides**

Journal:	<i>Chemical Science</i>
Manuscript ID:	SC-MRV-02-2014-000395.R1
Article Type:	Minireview
Date Submitted by the Author:	02-Mar-2014
Complete List of Authors:	Stephan, Douglas; University of Toronto, Department of Chemistry Erker, G; Westfälische Wilhelms Universität, Organisch-Chemisches Institut;

## ARTICLE

Cite this:  
10.1039/x0xx00000x

DOI: **Frustrated Lewis Pair Chemistry of Carbon, Nitrogen and Sulfur Oxides**

Douglas W. Stephan<sup>a\*</sup> and Gerhard. Erker<sup>b\*</sup>

Received 00th January 2012,  
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Frustrated Lewis pairs have been used to activate a variety of small molecules. In this review we focus on the recent chemistry of FLPs with CO<sub>2</sub>, CO, N<sub>2</sub>O, NO and SO<sub>2</sub>. While FLP capture of these small molecule is achieved in all of these cases, subsequent applications of the products include stoichiometric and catalytic reductions of CO<sub>2</sub>, C-O bond scission of CO and use of FLP-NO radicals in polymerization

## Introduction

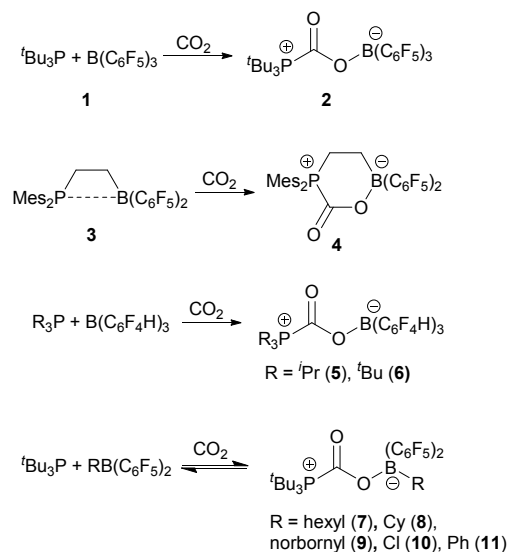
The ability of frustrated Lewis pairs (FLPs), the combination of sterically encumbered donors and acceptors, to reversibly activate H<sub>2</sub><sup>1</sup> has drawn much attention. This finding has led to the development of metal-free protocols for catalytic hydrogenations.<sup>2-5</sup> Both intra- and intermolecular FLPs have exhibited such reactivity, while the steric and electronic features of Lewis acid/base combinations has also been broadened dramatically in recent years.<sup>6</sup> Despite the continuing interest in metal-free reductions, the first reactions of FLPs with a small molecule other than H<sub>2</sub> was the P/B addition to olefins.<sup>7</sup> Subsequent to this report, the reactivity of FLPs with a wide variety of small molecules has been explored. Indeed, FLP have been shown to react with alkynes, B-H bonds, disulfides, CO<sub>2</sub>, CO, N<sub>2</sub>O, NO and SO<sub>2</sub> and to effect the ring-opening of a variety of species including THF, cyclopropanes, some cyclic ethers, and lactide. In this paper, we review the reactivity of FLPs with the simple element oxides, CO<sub>2</sub>, CO, N<sub>2</sub>O, NO and SO<sub>2</sub>, discussing the ability of FLPs to capture these species. In addition, the utility and subsequent stoichiometric and in some cases catalytic reactivity of the FLP species is reviewed.

## Reactions of CO<sub>2</sub> with FLPs

### Capture of CO<sub>2</sub>

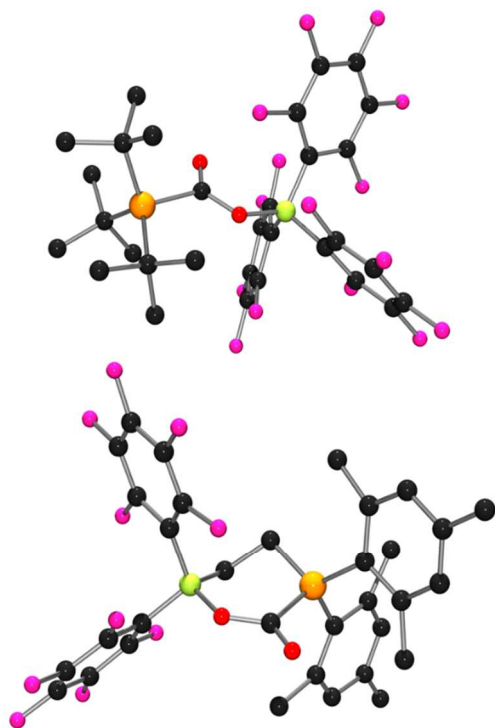
In our early work we had shown that FLPs add readily to CO<sub>2</sub>.<sup>8</sup> In this work, the addition reactions of the intermolecular P/B FLP <sup>t</sup>Bu<sub>3</sub>P/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (**1**) or the intramolecular ethylene-bridged Mes<sub>2</sub>P(CH<sub>2</sub>)<sub>2</sub>B(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> (**3**) with CO<sub>2</sub> was described. The former forms the rather stable addition product **2**, the latter gives the heterocyclic adduct **4** in a reversible reaction. However, compound **4** could be isolated at -35 °C and characterized. Both **2** and **4** were characterized by X-ray crystallography (Figure 1) revealing P-C and B-O bonds that were found to be 1.893(1) Å and 1.547(2) Å in **2** and 1.900(3) Å and 1.550(4) Å in **4**. Interestingly the thermal stability of **2** is significantly greater than

that of **4**: as **2** liberates CO<sub>2</sub> at 80 °C, whereas **4** loses CO<sub>2</sub> above ca. -20 °C. These data are consistent with DFT calculations that the loss of CO<sub>2</sub> from **4** has a barrier of 18.2 kcal/mol whereas the barrier to loss of CO<sub>2</sub> from **2** is 35.0 kcal/mol.

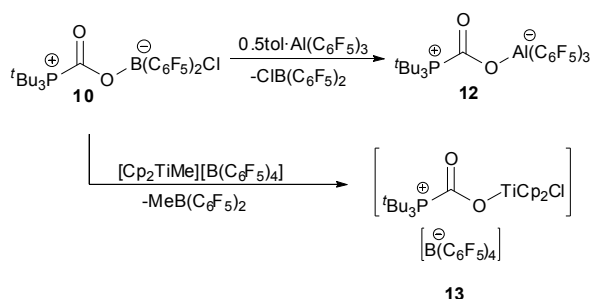


Scheme 1 Synthesis of CO<sub>2</sub>-products.

The corresponding FLPs derived from B(C<sub>6</sub>F<sub>4</sub>H)<sub>3</sub> and either <sup>i</sup>Pr<sub>3</sub>P or <sup>t</sup>Bu<sub>3</sub>P have also been shown to bind CO<sub>2</sub> affording the species R<sub>3</sub>P(CO<sub>2</sub>)B(C<sub>6</sub>F<sub>4</sub>H)<sub>3</sub> (R = <sup>i</sup>Pr (**5**), <sup>t</sup>Bu (**6**)). Similarly, the boranes, RB(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> (R = hexyl, Cy, norbornyl), ClB(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> or PhB(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> and <sup>t</sup>Bu<sub>3</sub>P and CO<sub>2</sub> generate the species <sup>t</sup>Bu<sub>3</sub>P(CO<sub>2</sub>)BR(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> (R = hexyl (**7**), Cy (**8**), norbornyl (**9**), Cl (**10**), Ph (**11**); Scheme 1).<sup>9, 10</sup> In a subsequent study, **10** was shown to react with Me<sub>3</sub>SiOSO<sub>2</sub>CF<sub>3</sub> to cleanly produce <sup>t</sup>Bu<sub>3</sub>P(CO<sub>2</sub>)B(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(OSO<sub>2</sub>CF<sub>3</sub>).<sup>11</sup> Compound **10** also was shown to undergo Lewis acid exchange reactions. For example, reaction with (0.5tol)•Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> gave <sup>t</sup>Bu<sub>3</sub>P(CO<sub>2</sub>)Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (**12**), while the corresponding reaction with [Cp<sub>2</sub>TiMe][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] afforded the species [<sup>t</sup>Bu<sub>3</sub>P(CO<sub>2</sub>)TiCp<sub>2</sub>Cl][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (**13**) (Scheme 2).<sup>11</sup>



**Figure 1** POV-ray Depiction of top: **2**, bottom: **4** P: orange; O: red; F: pink; C: black; B: yellow-green. H-atoms omitted for clarity.

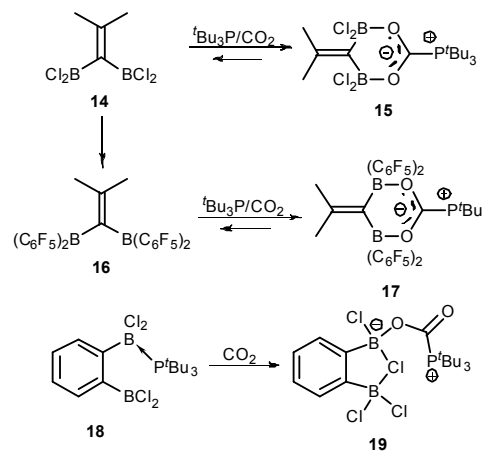


**Scheme 2** Synthesis of **12** and **13**.

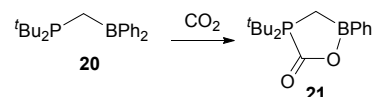
The ability of *bis*-boranes and phosphines to capture CO<sub>2</sub> have also been explored. The combination of Me<sub>2</sub>C=C(BCl<sub>2</sub>)<sub>2</sub><sup>12</sup> with <sup>t</sup>Bu<sub>3</sub>P and 1 atm CO<sub>2</sub> resulted in the formation of the product Me<sub>2</sub>C=C(BCl<sub>2</sub>)<sub>2</sub>O<sub>2</sub>CP<sup>t</sup>Bu<sub>3</sub> (**15**) (Scheme 3).<sup>13</sup> In a similar fashion, the analog complex Me<sub>2</sub>C=C(B(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>)<sub>2</sub>O<sub>2</sub>CP<sup>t</sup>Bu<sub>3</sub> (**17**) was also prepared (Scheme 3). These compounds are found to give rise to an IR absorption at 1608 and 1617 cm<sup>-1</sup> for the  $\tilde{\nu}(\text{C}=\text{O})$  modes respectively. More recently, the reaction of the *bis*-borane C<sub>6</sub>H<sub>4</sub>(BCl<sub>2</sub>)<sub>2</sub> with <sup>t</sup>Bu<sub>3</sub>P (**18**) and CO<sub>2</sub> has been described.<sup>14</sup> In this case, in contrast to **15**, the product binds to CO<sub>2</sub> through a single boron center while a Cl atom bridges to the second B atom affording C<sub>6</sub>H<sub>4</sub>[BCl<sub>2</sub>(Cl)BCl(O<sub>2</sub>CP<sup>t</sup>Bu<sub>3</sub>)] (**19**). This species is thermally robust being stable at 80 °C for over 24 h.

Lammertsma and coworkers<sup>15</sup> have recently developed the synthesis of the germinal phosphine-borane species <sup>t</sup>Bu<sub>2</sub>PCH<sub>2</sub>BPh<sub>2</sub> (**20**). Despite the fact that the boron center in this species is much less Lewis acidic than FLPs described above, this

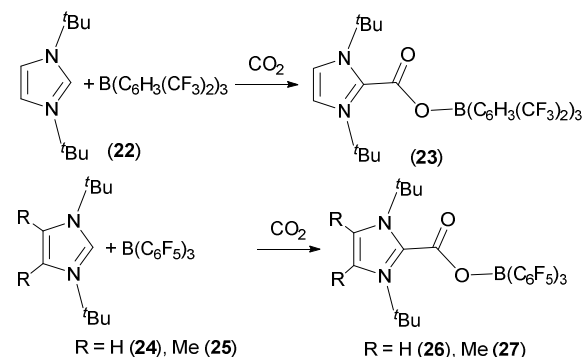
species appears to be pre-organized to act as an FLP as it reacts with CO<sub>2</sub> resulting in the formation of <sup>t</sup>Bu<sub>2</sub>PCH<sub>2</sub>BPh<sub>2</sub>(CO<sub>2</sub>) (**21**) (Scheme 4). Computational studies support a concerted interaction of P/B with the CO fragment of CO<sub>2</sub> en route to the product. This affirms that FLP chemistry does not always require electron withdrawing substituents on B.



**Scheme 3** Reactions of bis-boranes with CO<sub>2</sub>.



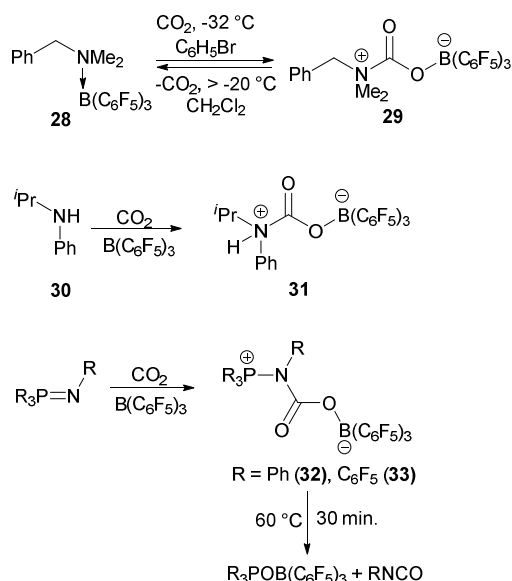
**Scheme 4** Reactions of germinal phosphine-borane with CO<sub>2</sub>.



**Scheme 5** Reactions of carbene-borane FLPs with CO<sub>2</sub>.

N-heterocyclic carbenes (NHCs) are known to bind and react with CO<sub>2</sub> to generate zwitterionic adducts.<sup>16, 17</sup> Subsequent addition of borane results in binding of the CO<sub>2</sub> fragment to B affording complexes of the general formula (C<sub>3</sub>H<sub>2</sub>(NR)<sub>2</sub>)CO<sub>2</sub>BR<sub>3</sub>. Interestingly, Tamm and co-workers have shown that the carbene-borane adduct (C<sub>3</sub>H<sub>2</sub>(N*t*Bu)<sub>2</sub>)/B(C<sub>6</sub>H<sub>3</sub>(CF<sub>3</sub>)<sub>2</sub>)<sub>3</sub> (**22**) behaves as an FLP reacting with CO<sub>2</sub> to give (C<sub>3</sub>H<sub>2</sub>(N*t*Bu)<sub>2</sub>)CO<sub>2</sub>B(C<sub>6</sub>H<sub>3</sub>(CF<sub>3</sub>)<sub>2</sub>)<sub>3</sub> (**23**).<sup>18</sup> In a similar fashion, the FLP (C<sub>3</sub>R<sub>2</sub>(N*t*Bu)<sub>2</sub>)/B(C<sub>6</sub>H<sub>3</sub>(CF<sub>3</sub>)<sub>2</sub>)<sub>3</sub> (R = H (**24**), Me (**25**)) derived from NHC and CO<sub>2</sub>B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> affords a synthetic route to the analogous species (C<sub>3</sub>R<sub>2</sub>(N*t*Bu)<sub>2</sub>)CO<sub>2</sub>B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (R = H (**26**), Me (**27**)) (Scheme 5).<sup>19</sup> Computational studies show that these products are significantly more thermodynamically stable than the carbene-CO<sub>2</sub> adducts.

In a similar sense, primary and secondary amines are known to react with CO<sub>2</sub> to generate carbamates,<sup>20-22</sup> PhCH<sub>2</sub>NMe<sub>2</sub> is unreactive with CO<sub>2</sub>.<sup>23-25</sup> However, the FLP derived from the adduct (PhCH<sub>2</sub>NMe<sub>2</sub>)B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (**28**) reacts with CO<sub>2</sub> to give the FLP adduct PhCH<sub>2</sub>NMe<sub>2</sub>(CO<sub>2</sub>)B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (**29**).<sup>26</sup> The resulting N-C and B-O bond lengths are 1.545(2) Å and 1.550(2) Å, respectively and **29** gives rise to an IR  $\tilde{\nu}(\text{C}=\text{O})$  stretching band of 1822 cm<sup>-1</sup>, markedly lower than the corresponding band for free CO<sub>2</sub> (2345 cm<sup>-1</sup>). In a similar strategy, *N*-isopropylaniline (**30**) and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> reacts with CO<sub>2</sub> to give PhHN<sup>i</sup>PrCO<sub>2</sub>B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (**31**) (Scheme 6) while the related product 1,4-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>NH<sup>i</sup>Bu)(CH<sub>2</sub>N<sup>i</sup>BuCO<sub>2</sub>B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>) was prepared in employing the corresponding diamine.<sup>26</sup>

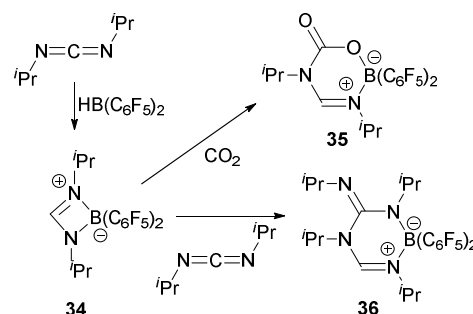


Scheme 6 Reactions of N-bases, B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> and CO<sub>2</sub>.

In a related fashion the combinations of the sterically hindered phosphinimine Lewis bases Ph<sub>3</sub>PN(R) and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> also bind CO<sub>2</sub> to yield the adducts Ph<sub>3</sub>PN(R)CO<sub>2</sub>B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (R = Ph (**32**), C<sub>6</sub>F<sub>5</sub> (**33**); Scheme 6).<sup>27</sup> Compounds **32** and **33** are converted to Ph<sub>3</sub>P=OB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> and RNCO upon warming to 60 °C for 30 minutes (Scheme 4). The analogous reaction is also known for phosphinimines with CO<sub>2</sub> on their own.<sup>28</sup>

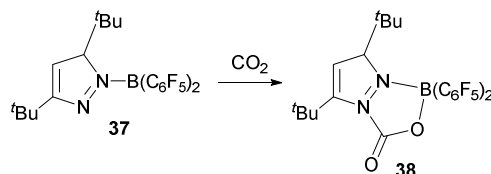
While FLPs are readily generated by the combination of sterically encumbered donors and acceptors, ring strain can also generate similar reactivity. The B-amidinates HC(RN)<sub>2</sub>B(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> were prepared by reaction of HB(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> and carbodiimides.<sup>29</sup> These species are four membered rings and show no evidence of thermally induced ring-opening. Nonetheless, the species HC(<sup>i</sup>PrN)<sub>2</sub>B(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> (**34**) reacts with CO<sub>2</sub> to give HC(<sup>i</sup>PrN)<sub>2</sub>(CO<sub>2</sub>)B(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> (**35**) in 96% yield (Scheme 5). X-ray data confirmed the insertion of the CO<sub>2</sub> fragment into the B–N bond affording a six-membered heterocycle. In an analogous fashion, treatment of HC(<sup>i</sup>PrN)<sub>2</sub>B(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> with excess carbodiimide affords the insertion to give HC(<sup>i</sup>PrN)<sub>2</sub>C(<sup>i</sup>PrN)<sub>2</sub>B(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> (**36**) (Scheme 7).<sup>29</sup> The mechanism of these insertions is thought to involve an equilibrium in which one of the N atoms dissociates from B, affording intramolecular

unquenched Lewis acidity at B and a nucleophilic pendant N-atom. This transient FLP acts to activate the substrate, CO<sub>2</sub>.



Scheme 7 Reactions of B-amidinate with CO<sub>2</sub> and carbodiimide.

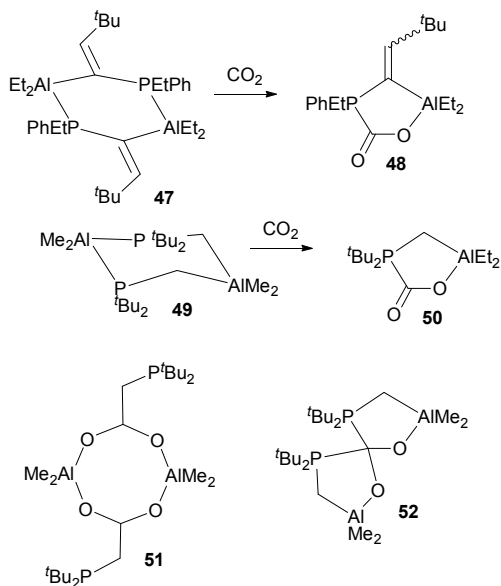
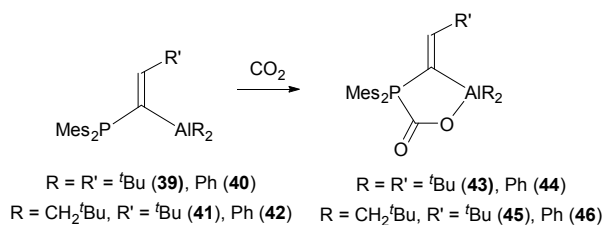
In an interesting design, Tamm and coworkers have reported the pyrazole-borane (C<sub>3</sub>H<sub>7</sub>Bu<sub>2</sub>N<sub>2</sub>)B(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> (**37**) which captures CO<sub>2</sub> affording the intramolecular N/B bound CO<sub>2</sub> adduct (C<sub>3</sub>H<sub>7</sub>Bu<sub>2</sub>N<sub>2</sub>)B(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(CO<sub>2</sub>) (**38**) (Scheme 8). This species is highly stable and computations reveal its formation is strongly exothermic and is formed with a low energy barrier of *ca.* 7.3 kcal mol<sup>-1</sup>.<sup>30</sup>



Scheme 8 Reactions of B-pyrazolate with CO<sub>2</sub>.

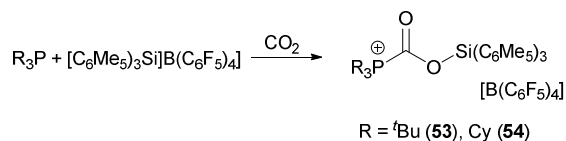
Use of FLPs based on other Lewis acids have also been used to capture of CO<sub>2</sub>. FLPs based on Al-Lewis acids have led to CO<sub>2</sub> capture and subsequent reduction.<sup>31-35</sup> Such work is described in the following sections (*vide infra*). Intramolecular Al-P systems for CO<sub>2</sub> capture have also been prepared and described by Uhl and coworkers. In these efforts, hydroalumination by R<sub>2</sub>AlH (<sup>t</sup>Bu, CH<sub>2</sub><sup>t</sup>Bu) of the alkynyl-phosphine Mes<sub>2</sub>PCCR' to give the germinal FLPs Mes<sub>2</sub>PC(CHR')AlR<sub>2</sub> (R = R' = <sup>t</sup>Bu (**39**), Ph (**40**), R CH<sub>2</sub><sup>t</sup>Bu, R' = <sup>t</sup>Bu (**41**), Ph (**42**)). This species react with CO<sub>2</sub> to afford the five-membered ring in which CO<sub>2</sub> is C-bound to P and O-bound to Al in the species Mes<sub>2</sub>PC(CHR')AlR<sub>2</sub>(CO<sub>2</sub>) (R = R' = <sup>t</sup>Bu (**43**), Ph (**44**), R CH<sub>2</sub><sup>t</sup>Bu, R' = <sup>t</sup>Bu (**45**), Ph (**46**)). ((Scheme 9).<sup>36</sup> The analogous hydroalumination of aryldialkynylphosphines RP(CC<sup>t</sup>Bu)<sub>2</sub> (R = Ph, Mes) with Et<sub>2</sub>AlH afforded mixed alkenyl-alkynyl cyclic dimers which react further with Et<sub>3</sub>Al to give a chair-like Al<sub>2</sub>C<sub>2</sub>P<sub>2</sub> heterocycles (EtPhPC(CH<sup>t</sup>Bu)AlEt<sub>2</sub>)<sub>2</sub> (**47**). This species reacts with CO<sub>2</sub> to give an isomeric mixture of *cis* and *trans* five-membered ring species EtPhPC(CH<sup>t</sup>Bu)AlEt<sub>2</sub>(CO<sub>2</sub>) (**48**) (Scheme 9).<sup>37</sup> In a closely related system, the six-membered heterocycle (<sup>t</sup>Bu<sub>2</sub>PCH<sub>2</sub>AlMe<sub>2</sub>)<sub>2</sub> (**49**) reacts with CO<sub>2</sub> to give <sup>t</sup>Bu<sub>2</sub>PCH<sub>2</sub>AlMe<sub>2</sub>(CO<sub>2</sub>) (**50**).<sup>37</sup> While Uhl and coworkers found this species is stable,<sup>37</sup> Fontaine and coworkers reported that this species rearranges to give the carboxylate bridged dimer (<sup>t</sup>Bu<sub>2</sub>PCH<sub>2</sub>CO<sub>2</sub>AlMe<sub>2</sub>)<sub>2</sub> (**51**) In addition, Fontaine et al also reported the reaction of the Al/P

species with one equivalent of CO<sub>2</sub> to give the spirocyclic species (tBu<sub>2</sub>PCH<sub>2</sub>AlMe<sub>2</sub>)<sub>2</sub>(CO<sub>2</sub>) (**52**) (Scheme 9).<sup>38</sup>



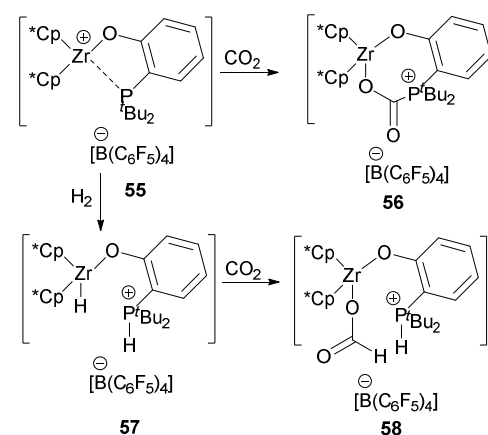
Scheme 9 Reactions of intramolecular Al-P FLPs with CO<sub>2</sub>.

In an alternative Lewis acid system, Mueller and his team have described reactions of FLPs derived from silylium cation [(C<sub>6</sub>Me<sub>5</sub>)<sub>3</sub>Si][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] with phosphines. In the case where steric demands generate FLPs, such systems capture CO<sub>2</sub> affording the species [R<sub>3</sub>PCO<sub>2</sub>Si(C<sub>6</sub>Me<sub>5</sub>)<sub>3</sub>]<sup>+</sup> (R = tBu (**53**), Cy (**54**)) (Scheme 10).<sup>39</sup>



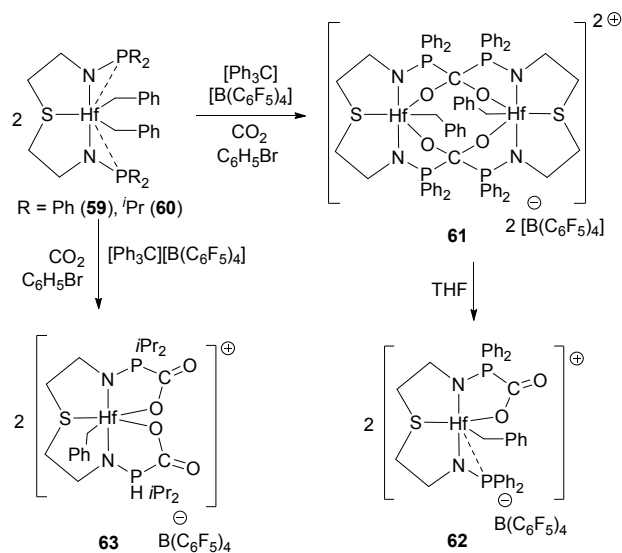
Scheme 10 Reactions of Silylium-cation/Phosphine FLPs with CO<sub>2</sub>.

An alternative approach to FLPs involving the use of Lewis acidic metal centers was undertaken by Wass and coworkers<sup>40, 41</sup> and subsequently by the Erker group.<sup>42, 43</sup> They demonstrated that the species [Cp\*<sub>2</sub>ZrOC<sub>6</sub>H<sub>4</sub>P'Bu<sub>2</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (**55**) acts as an intramolecular FLP to react with CO<sub>2</sub> affording [Cp\*<sub>2</sub>ZrOC<sub>6</sub>H<sub>4</sub>P'Bu<sub>2</sub>CO<sub>2</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (**56**) in which CO<sub>2</sub> is bound between the pendant phosphine and the oxophilic metal center. It was also shown that initial activation of H<sub>2</sub> generates [Cp\*<sub>2</sub>ZrHOC<sub>6</sub>H<sub>4</sub>P'Bu<sub>2</sub>H][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (**57**) which also reacts with CO<sub>2</sub> to give the corresponding formate species [Cp\*<sub>2</sub>Zr(O<sub>2</sub>CH)OC<sub>6</sub>H<sub>4</sub>P'Bu<sub>2</sub>H][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (**58**) (Scheme 11).



Scheme 11 Reactions of Zr complex cations with CO<sub>2</sub>.

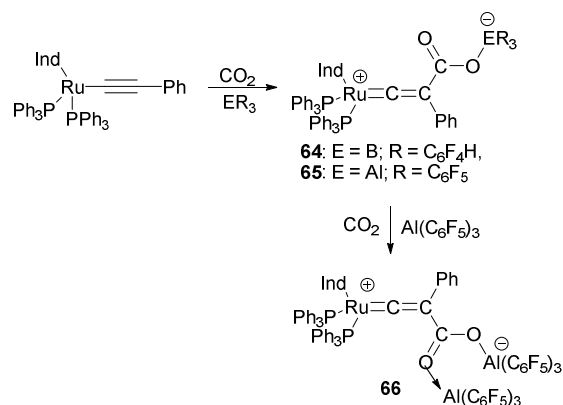
In a related approach, we have shown that the complex S(CH<sub>2</sub>CH<sub>2</sub>NPPH<sub>2</sub>)<sub>2</sub>Hf(CH<sub>2</sub>Ph)<sub>2</sub> (**59**) reacts with [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] to generate the corresponding cationic species by benzyl abstraction.<sup>44</sup> This species reacts with CO<sub>2</sub> to give a twofold symmetric bimetallic species [S(CH<sub>2</sub>CH<sub>2</sub>NPPH<sub>2</sub>)<sub>2</sub>Hf(CH<sub>2</sub>Ph)(CO<sub>2</sub>)<sub>2</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sub>2</sub> (**61**) (Scheme 12).<sup>44</sup> In this case, two CO<sub>2</sub> molecules are bound between two pendant phosphines and two Hf centers. Exposure of a solution of this species in THF to 1 atm of CO<sub>2</sub> prompted quantitative formation of a new product consistent with the uptake of a second equivalent of CO<sub>2</sub> to give [S(CH<sub>2</sub>CH<sub>2</sub>NPPH<sub>2</sub>(CO<sub>2</sub>)Hf(CH<sub>2</sub>Ph)][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (R = Ph (**62**)). The corresponding treatment of the precursor [S(CH<sub>2</sub>CH<sub>2</sub>N<sup>i</sup>Pr<sub>2</sub>)<sub>2</sub>Hf(CH<sub>2</sub>Ph)<sub>2</sub>] (**60**) with [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] also results in the capture of CO<sub>2</sub> yielding the analog [S(CH<sub>2</sub>CH<sub>2</sub>N<sup>i</sup>Pr<sub>2</sub>(CO<sub>2</sub>)<sub>2</sub>Hf(CH<sub>2</sub>Ph)][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (**63**) (Scheme 12).<sup>44</sup>



Scheme 12 Reactions of Hf complex cations with CO<sub>2</sub>.

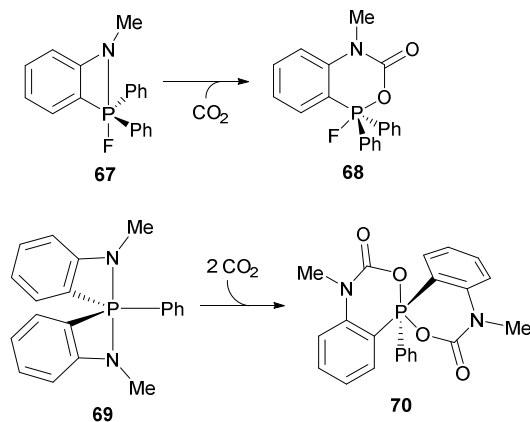
More recently we have exploited transition metal species as bases in FLP-type capture of CO<sub>2</sub>. As it is known that Ru-acetylides are nucleophilic at the *beta*-carbon, these species act as

bases in combination with  $B(C_6F_4H)_3$  or  $Al(C_6F_5)_3$  to generate an FLP. Exposure to  $CO_2$  results in the formation of species (Indenyl)Ru( $PPh_3$ ) $_2(=C=C(Ph)(CO_2ER_3))$  ( $ER_3 = B(C_6F_4H)_3$ ) (**64**),  $Al(C_6F_5)_3$  (**65**) and (Indenyl)Ru( $PPh_3$ ) $_2(=C=C(Ph)(C(OAl(C_6F_5)_3)_2))$  (**66**), respectively (Scheme 13).<sup>45</sup>



**Scheme 13** Reactions of Ru-acetylides/Lewis acids with  $CO_2$ . (one isomer of **38-40** are shown).

In recent work we have also described the use of P(V) centers as Lewis acids. For example, the four-membered ring species  $C_6H_4(NMe)PPh_2$  (**67**) was prepared by treatment of the corresponding amino-difluorophosphorane with  $tBuLi$ .<sup>46</sup> The strained species captures  $CO_2$  to give the species  $C_6H_4(NMe)(CO_2)PPh_2$  (**68**). This is reminiscent of the reactivity of the chemistry of the boron-amidates,<sup>29</sup> however in this case the P(V) centers act as the Lewis acid. In an analogous fashion the species  $(C_6H_4(NMe)_2)PPh$  (**69**) captures two equivalents of  $CO_2$  to give  $[C_6H_4NMe(CO_2)]_2PPh$  (**70**) (Scheme 14).<sup>47</sup>



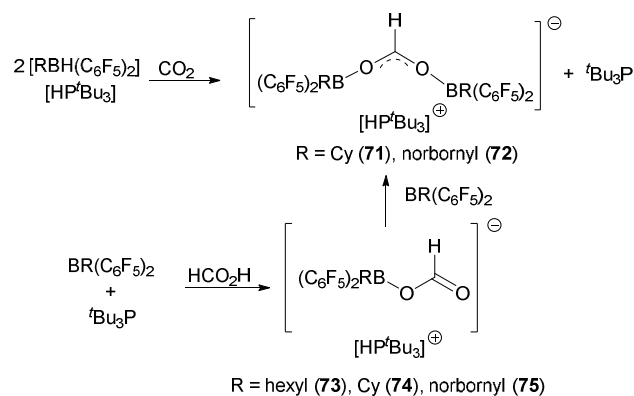
**Scheme 14** Reactions of amido-phosphoranes with  $CO_2$ .

### Stoichiometric Reductions of $CO_2$ by FLP Systems

While the above systems offer a variety of FLP approaches for the capture of  $CO_2$ , it was the report of O'Hare and Ashley<sup>48</sup> in 2009, that first demonstrated the potential of such systems to effect reduction of  $CO_2$ . In their seminal work, these researchers showed that addition of  $CO_2$  to a 1:1 mixture of tetramethylpiperidine (TMP)/ $B(C_6F_5)_3$  in toluene under a  $H_2$  atmosphere resulted in the quantitative conversion into

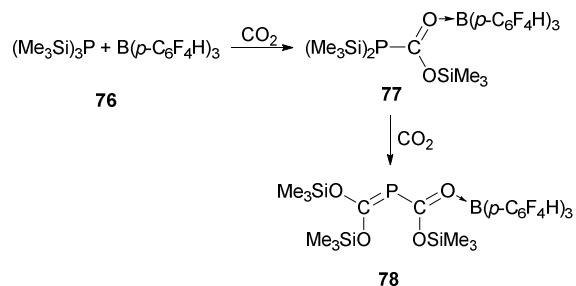
$CH_3OB(C_6F_5)_2$  after 6 days at  $160\text{ }^\circ\text{C}$ . A subsequent vacuum distillation of the solvent ( $100\text{ }^\circ\text{C}$ ) led to the isolation of  $CH_3OH$  in 17-25% yield, presumably a result of protonation by  $[TMPH]^+$ .

In a related study Piers and coworkers<sup>49</sup> showed that TMP and  $B(C_6F_5)_3$  activate  $CO_2$  and in the presence of triethylsilane, affords a silyl carbamate and the known ion pair  $[TMPH][HB(C_6F_5)_3]$  which is subsequently converted to the formate  $[TMPH][HCO_2B(C_6F_5)_3]$ . Further addition of excess  $B(C_6F_5)_3$  and triethylsilane, effect the catalytic hydrosilation of formatosilane to  $CH_4$  and  $(Et_3Si)_2O$ .<sup>49</sup> In similar reactions involving initial FLP activation of  $H_2$ , the compounds  $[tBu_3PH][RBH(C_6F_5)_2]$  ( $R = Cy$ , norbornyl) were shown to react with  $CO_2$  affording the species  $[tBu_3PH][(C_6F_5)_2BR)_2(\mu-HCO_2)]$  ( $R = Cy$  (**71**), norbornyl (**72**)). The related species  $[tBu_3PH][(C_6F_5)_2BR(O_2CH)]$  ( $R = hexyl$  (**73**),  $Cy$  (**74**), norbornyl (**75**)) (Scheme 15) were prepared by reaction of the corresponding borane,  $tBu_3P$  and formic acid (Scheme 10). Subsequent addition of borane to **74** or **75** provides a second synthetic route to (**71**) and (**72**), respectively.



**Scheme 15** Reactions of boranes and borate salts with  $CO_2$ .

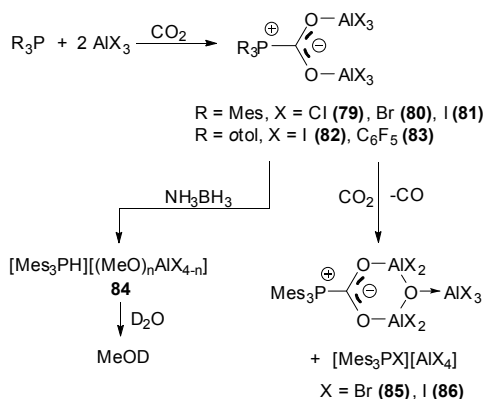
The FLP comprised of  $(Me_3Si)_3P$  and  $B(p-C_6F_4H)_3$ , (**76**) reacts in pentane with  $CO_2$  to give  $((Me_3Si)_2P-C(OSiMe_3)O)B(p-C_6F_4H)_3$  (**77**).<sup>50</sup> The corresponding reaction in  $CH_2Cl_2$  results in the formation of the *bis*-insertion product  $((Me_3SiO)_2C=P-C(OSiMe_3)=O)B(p-C_6F_4H)_3$  (**78**) (Scheme 16). These reactions are thought to proceed via initial formation of a P/B  $CO_2$  adduct analogous to **2** followed by silyl group migration.



**Scheme 16** Reactions of  $(Me_3Si)_3P$  and  $B(p-C_6F_4H)_3$  with  $CO_2$ .

Mixtures of  $PMes_3$  and  $AlX_3$  ( $X = Cl, Br$ ) have been shown to form only weak adducts. These FLPs react with  $CO_2$  cleanly when 1:2 mixtures of  $PMes_3:AlX_3$  are used to give products of the

form  $\text{Mes}_3\text{P}(\text{CO}_2)(\text{AlX}_3)_2$  ( $X = \text{Cl}$  (**79**);  $\text{Br}$  (**80**);  $\text{I}$  (**81**)) (Scheme 17).<sup>32</sup> In these products both oxygen atoms of  $\text{CO}_2$  are bound to  $\text{AlX}_3$  units yielding O-Al distances of 1.807(5) Å and 1.808(6) Å, and 1.829(4) Å and 1.803(3) Å in (**79**) and (**80**), respectively. In contrast to the P/B  $\text{CO}_2$  complexes described above, these compounds are stable to loss of  $\text{CO}_2$  even on heating to 80 °C under vacuum. Nonetheless, these species do react with  $\text{H}_3\text{NBH}_3$  in less than 15 minutes to generate new species. The isotopologues,  $^{13}\text{C}$ -(**79**) and  $^{13}\text{C}$ -(**80**),  $^{13}\text{C}$  NMR data showed consumption of the  $\text{CO}_2$  signal and the appearance of 4 quartet resonances attributable to Al-methoxy species (**84**). In addition, the species  $[\text{Mes}_3\text{PH}]$  is also formed as a by-product, albeit in low yield. Quenching the reaction with  $\text{D}_2\text{O}$ , afforded the  $\text{CH}_3\text{OD}$  in  $\text{D}_2\text{O}$  in yields of 37-51%.<sup>32</sup> While one O-atom is thought to be incorporated into Al by-products, this chemistry demonstrates the FLP-mediated reduction of  $\text{CO}_2$  to  $\text{CH}_3\text{OH}$ . It is also interesting that treatment of P/B- $\text{CO}_2$  complex **12** with  $\text{H}_3\text{NBH}_3$  also effect a similar reduction, affording methanol upon hydrolysis.<sup>14</sup>



Scheme 17 Reactions of Al/P FLPs with  $\text{CO}_2$ .

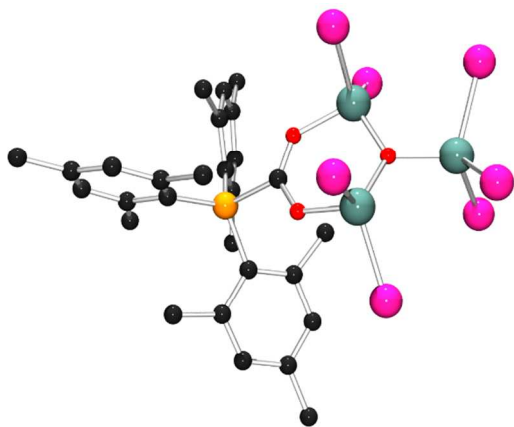
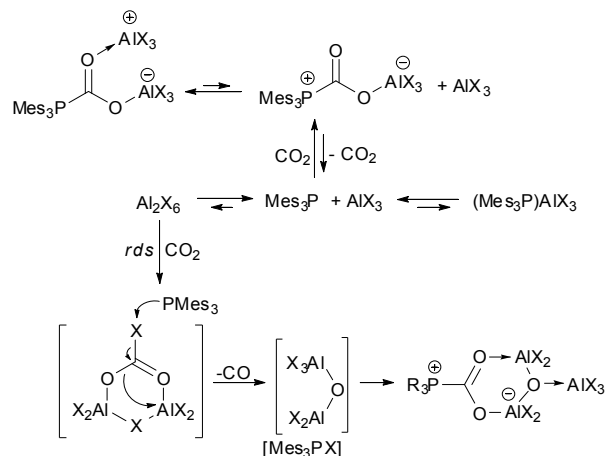


Figure 2 POV-ray Depiction of **86**, P: orange; O: red; I: pink; C: black; Al: teal. H-atoms omitted for clarity.

The related compound,  $\text{Mes}_3\text{PC}(\text{OAlI}_3)_2$  (**81**) could also be prepared and isolated, however on exposure for 16 h to  $\text{CO}_2$  the products  $\text{Mes}_3\text{PC}(\text{OAlI}_2)_2\text{OAlI}_3$  (**86**) (Figure 2) and  $[\text{Mes}_3\text{PI}][\text{AlI}_4]$  were obtained with the concurrent liberation of  $\text{CO}$  (Scheme 17).<sup>31, 34</sup> While the corresponding products **85** and

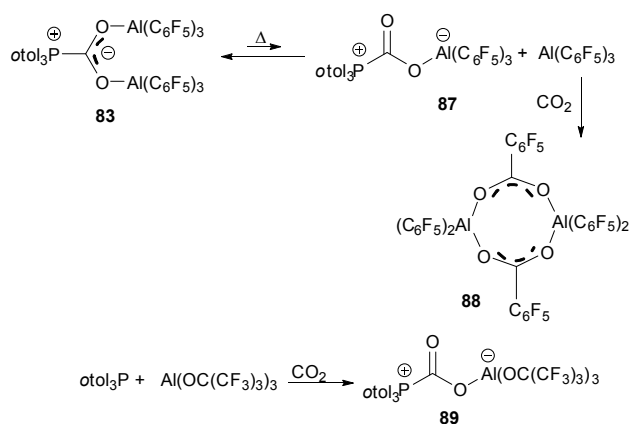
$[\text{Mes}_3\text{PBr}][\text{AlBr}_4]$  were also observed for the  $\text{AlBr}_3$  derivatives the reaction required 48 h. In the case of the  $\text{AlCl}_3$ , the reaction seemed to proceed in a similar fashion although it was significantly slower.



Scheme 18 Proposed reaction pathway for  $\text{CO}_2$  reduction to  $\text{CO}$  by Al/P FLPs.

Probing the mechanism (Scheme 18) of these reactions revealed that while solutions of  $\text{Mes}_3\text{P}/\text{AlX}_3$  generate some adduct and some radical cation, addition of  $\text{CO}_2$  results in loss of color and disappearance of any EPR signal, precluding an open-shell mechanism for the reduction of  $\text{CO}_2$ .<sup>31</sup> Kinetic experiments demonstrate first order dependences on **81** and  $\text{CO}_2$  with the activation parameters:  $\Delta H^\ddagger = 85(5) \text{ kJ/mol}$  and  $\Delta S^\ddagger = -45(15) \text{ J/(mol}\cdot\text{K)}$ . Interestingly kinetics in the presence of cyclohexene showed an inverse first-order dependence on the concentration of cyclohexene. This observation is consistent with competitive binding of the olefin to  $\text{AlX}_3$  and characterization of the cyclohexene adduct  $\text{Al}(\text{C}_6\text{F}_5)_3(\mu^2\text{-C}_6\text{H}_{10})$ .<sup>31</sup>

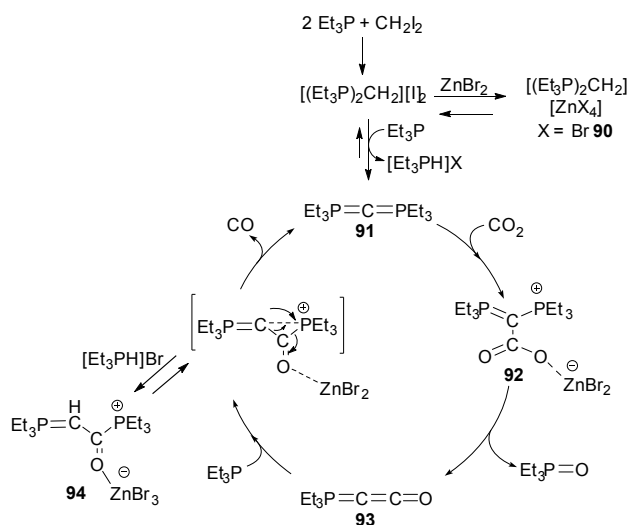
The reactions affording  $\text{CO}_2$  reduction are thus thought to proceed through a dissociative process in which solvent-induced dissociation of  $\text{AlX}_3$  from (**79-83**) initiate the reduction of  $\text{CO}_2$  to  $\text{CO}$  (Scheme 19). This is supported by the observation that  $[\text{Mes}_3\text{PMe}][\text{AlI}_4]$  enhances the reaction rate by promoting dissociation of  $\text{AlI}_3$  generating the halide-bridged species  $[\text{I}_3\text{Al}(\mu\text{-I})\text{AlI}_3]$ . Alane dissociation is also consistent with the absence of reaction of the analogous species  $(\text{otol})_3\text{PC}(\text{OAl}(\text{C}_6\text{F}_5)_3)_2$  (**83**)<sup>20</sup> under  $\text{CO}_2$  (1 atm) at 25 °C; presumably a result of the greater Lewis acidity of  $\text{Al}(\text{C}_6\text{F}_5)_3$ .<sup>31</sup> However, on heating to 90 °C, the species  $(\text{otol})_3\text{PCO}_2\text{Al}(\text{C}_6\text{F}_5)_3$  (**87**) and  $[(\text{C}_6\text{F}_5)\text{CO}_2\text{Al}(\text{C}_6\text{F}_5)_2]_2$  (**88**) are produced (Scheme 14). While **87** was not isolable, the analog  $(\text{otol})_3\text{PCO}_2\text{Al}(\text{OC}(\text{CF}_3)_3)_3$  (**89**) was prepared and fully characterized.<sup>31</sup> These data support a mechanism in which a series of dissociative equilibria generate  $\text{AlX}_3$ , the analog of **2**, and free phosphine permitting an associative insertion reaction of  $\text{CO}_2$  with  $[\text{Al}_2\text{X}_6]$  (Scheme 19). Subsequent nucleophilic attack by phosphine is thought to yield the halophosphonium cation/cyclic anion pair in a barrierless process that liberates  $\text{CO}$  from the cyclic anion.



Scheme 19 Reactions of other Al/P FLPs with CO<sub>2</sub>.

### Catalytic Reductions of CO<sub>2</sub>

Seeking to develop a catalytic reduction of CO<sub>2</sub>, related systems exploiting less oxophilic Lewis acid has been explored. Combination of Et<sub>3</sub>P, CO<sub>2</sub> in the presence of a catalytic amount of CH<sub>2</sub>I<sub>2</sub> and ZnBr<sub>2</sub> resulted in the catalytic oxidation of the phosphine and liberation of CO.<sup>51</sup> This catalysis proceeds via initial generation of an equilibrium mixture of [(Et<sub>3</sub>P)<sub>2</sub>CH<sub>2</sub>][ZnBr<sub>4</sub>] (**90**) and [(Et<sub>3</sub>P)<sub>2</sub>C] (**91**). The latter species reacts with CO<sub>2</sub> generating ((Et<sub>3</sub>P)<sub>2</sub>CCO<sub>2</sub>)(ZnBr<sub>2</sub>) (**92**) and this eliminates Et<sub>3</sub>PO to give the phosphoranylideneketene Et<sub>3</sub>P=C=C=O (**93**). This species is attacked by additional Et<sub>3</sub>P and ZnBr<sub>2</sub> to prompt loss of CO and the regeneration of the *bis*-ylide. This latter point was supported by the isolation of [Et<sub>3</sub>P=CH(PET<sub>3</sub>)(COZnBr<sub>3</sub>)] (**94**), which is best described as P/Zn addition to the phosphaketene which has been protonated by [Et<sub>3</sub>PH][Br] present in the reaction mixture. Literature precedent for some of the proposed intermediates as well as DFT calculations support this mechanism (Scheme 20).<sup>51</sup>



Scheme 20 Catalytic reduction of CO<sub>2</sub> by phosphine/zinc combinations.

Further exploiting metals in FLP chemistry, the complex [(N((CH<sub>2</sub>)<sub>2</sub>NHP<sup>i</sup>Pr<sub>2</sub>)((CH<sub>2</sub>)<sub>2</sub>NP<sup>i</sup>Pr<sub>2</sub>)(CHCH<sub>2</sub>NHP<sup>i</sup>Pr<sub>2</sub>))RuH] (**95**) has been shown to capture CO<sub>2</sub> between the pendant phosphine fragment and the metal center affording [(N((CH<sub>2</sub>)<sub>2</sub>NHP<sup>i</sup>Pr<sub>2</sub>)((CH<sub>2</sub>)<sub>2</sub>NP<sup>i</sup>Pr<sub>2</sub>)(CO<sub>2</sub><sup>i</sup>Pr<sub>2</sub>))Ru][BPh<sub>4</sub>] (**96**) (Figure 3)<sup>52</sup> and an observed IR absorption at 1651 cm<sup>-1</sup>. The P-C, C-O and C=O bond lengths are 1.908(6), 1.239(6) and 1.244(6) Å respectively, reminiscent of the bond lengths seen in main group FLP-CO<sub>2</sub> complexes. The Ru-O bond length of 2.207(3) Å is consistent with the reduced oxophilicity at Ru.<sup>52</sup> Although this species proved to be thermally robust, on heating to 80 °C for over a week this species was found to catalytically reduce CO<sub>2</sub> in the presence of excess HBpin generating MeOBpin and O(Bpin)<sub>2</sub> (Scheme 21). In a similar fashion, HBcat or 9-BBN could be used as the reducing agent. Affording the corresponding products MeOBcat, O(Bcat)<sub>2</sub> and MeOBBN, O(BBN)<sub>2</sub>, respectively. The mechanism involves successive hydroborations of the CO<sub>2</sub> as spectral evidence supports the generation of an initial intermediate. A proposed formaldehyde intermediate **97** is supported by the isolation and structure characterization of benzaldehyde analog [(N((CH<sub>2</sub>)<sub>2</sub>NHP<sup>i</sup>Pr<sub>2</sub>)((CH<sub>2</sub>)<sub>2</sub>NP<sup>i</sup>Pr<sub>2</sub>)(PhCHO)<sup>i</sup>Pr<sub>2</sub>))Ru][BPh<sub>4</sub>].

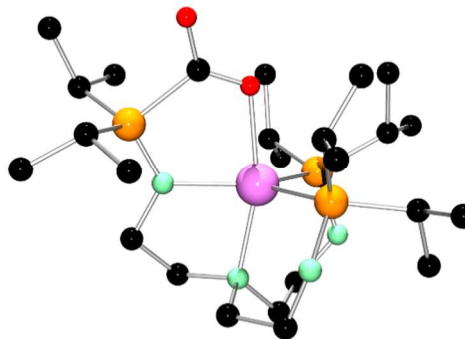
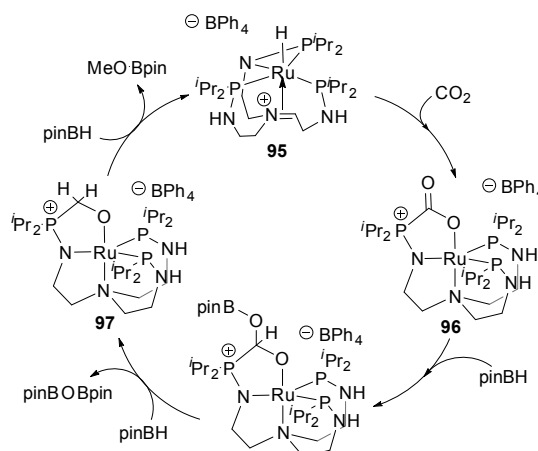


Figure 3 POV-ray Depiction of the cation of (**96**); C; black, N; aquamarine, P; orange, Ru; scarlet. H-atoms omitted for clarity.



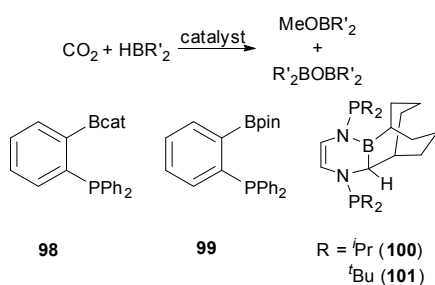
Scheme 21 Catalytic Reduction of CO<sub>2</sub> by Ru-pendant phosphine/system.

In a very recent development, the Fontaine group<sup>53</sup> has been able to achieve related borane reduction of CO<sub>2</sub> employing the FLP system, Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>B(O<sub>2</sub>C<sub>6</sub>H<sub>4</sub>) (**98**) as a catalyst (Scheme 22). Indeed using 1 mol% of **98** in the presence of HB(O<sub>2</sub>C<sub>2</sub>Me<sub>4</sub>) and



CO<sub>2</sub> (1 atm) results in the catalytic production of MeOB(O<sub>2</sub>C<sub>2</sub>Me<sub>4</sub>) and O(B(O<sub>2</sub>C<sub>2</sub>Me<sub>4</sub>)<sub>2</sub>) with turnover frequencies up to 973 h<sup>-1</sup> and TONs up to 2950 at 70 °C. It is noteworthy that no adduct formation was observed between **98** and CO<sub>2</sub>, demonstrating that a weak interaction with an ambiphilic catalyst is sufficient to initiate reduction with boranes to MeOBR<sub>2</sub>. Interestingly, preliminary results show that Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>B(O<sub>2</sub>C<sub>2</sub>Me<sub>4</sub>) (**99**) (Scheme 22) is also an active catalyst for the CO<sub>2</sub> reduction in the presence of BH<sub>3</sub>·SMe<sub>2</sub>.<sup>53</sup>

In a related study we showed that the N-heterocyclic carbenes C<sub>3</sub>H<sub>2</sub>(NPR<sub>2</sub>)<sub>2</sub> react with 9-BBN to effect the ring-opening of the carbene affording insertion of the carbene into the B-C bond yielding C<sub>3</sub>H<sub>2</sub>(NPR<sub>2</sub>)<sub>2</sub>BC<sub>8</sub>H<sub>14</sub> (**100**, **101**) (Scheme 22).<sup>54</sup> These molecules are intramolecular FLPs and also catalyse the reduction of CO<sub>2</sub> in the presence of boranes including HBpin, HBCat and BH<sub>3</sub>·SMe<sub>2</sub> to give methoxy-boranes and BOB species.



Scheme 22 Catalytic reduction of CO<sub>2</sub> by B/P species and boranes.

## Reactions of FLPs and SO<sub>2</sub>

The reactions of FLPs with CO<sub>2</sub> prompted analogous reactions with SO<sub>2</sub>. These led to considerably more stable FLP addition products. The intermolecular FLP **1** rapidly added SO<sub>2</sub> at room temperature in bromobenzene solution.<sup>55</sup> The product **102** was isolated in 80% yield from the reaction mixture (Scheme 23). The zwitterionic compound **102** shows heteronuclear magnetic resonance signals at δ 67.8 (<sup>31</sup>P) and δ 0.3 (<sup>11</sup>B), respectively. In contrast to the planar coordination environment of the C(O)-O-moiety in the FLP CO<sub>2</sub> addition products, the sulfur atom in the respective [P]-S(O)-O-[B] products show a non-planar coordination geometry and, consequently, represents a centre of chirality. In the X-ray crystal structure analysis of compound **102**, the sum of bond angles at sulfur is 314.6°, with the individual bond lengths amounting to 1.572(1) Å (S1-O1 single bond), 1.465(1) Å (S1-O2 double bond) and 2.275(1) Å (P1-S1) [B1-O1: 1.565(2) Å] (Scheme 18, Figure 4).

The intramolecular vicinal P/B FLP **103** contains a pair of carbon chirality centers.<sup>56</sup> From the synthesis of **103** by HB(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> hydroboration of dimesitylcyclohexenylphosphine their relative stereochemistry is determined, both the C-P and the C-B vectors are *trans*-diequatorially oriented at the central six-membered carbocycle. Compound **77** cleanly adds SO<sub>2</sub> to give **104** (Scheme 23). Compound **104** contains a sulfur chirality centre and, consequently, the formation of two diastereomeric products (**104** and **104'**) was observed. In the crystal both have been found in a 3:1 ratio. (Figure 4, bottom shows the major isomer). In solution the isolated product contains the diastereoisomers in a 1:1.3 ratio.

In addition, equilibrating conformational structures of these cyclic FLP SO<sub>2</sub> addition products were observed and analyzed by temperature dependent dynamic NMR spectroscopy.<sup>55</sup>

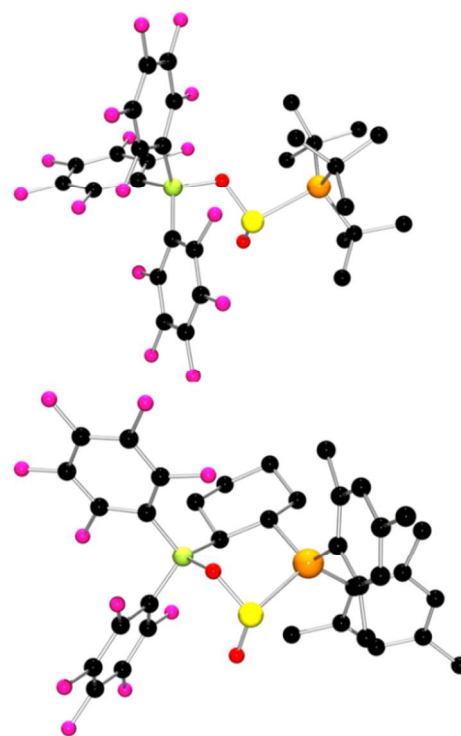
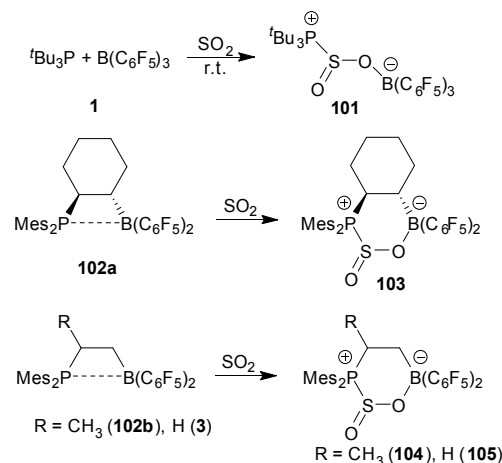


Figure 4 POV-ray depictions of **102** (top) and **104** (major diastereoisomer) (bottom). P: orange; O: red; F: pink; C: black; B: yellow-green. H-atoms omitted for clarity.

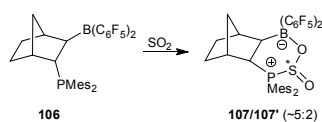


Scheme 23 Synthesis of FLP-SO<sub>2</sub> complexes

The vicinal P/B FLPs **103** and **3** (Scheme 23) were also treated with SO<sub>2</sub>. The reaction of the chiral system **103** with sulfur dioxide gave a mixture of two diastereomeric addition products (**104**, **104'**: 84/16) as well. One of these [*rac*-(1*R*,<sup>S</sup>)-**104**] was characterized by X-ray diffraction.<sup>56</sup> It shows a mixture of two conformers in the solid state. In contrast, the outcome of the reaction of the ethylene-bridged P/B FLP with sulfur dioxide is simpler as only one product (**105**) is formed. Due to the sulfur chirality centre it features pairs of diastereotopic C<sub>6</sub>F<sub>5</sub>-substituents at boron and mesityl groups at phosphorus. The

heteronuclear magnetic resonance signals of compound **105** occur at  $\delta$  33.3 ( $^{31}\text{P}$ ) and  $\delta$  1.2 ( $^{11}\text{B}$ ), respectively.

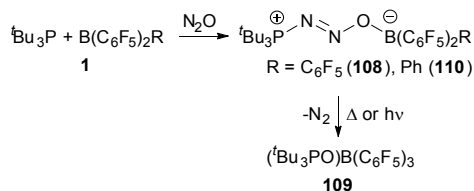
The intramolecular FLP **106**,<sup>57</sup> was synthesized by  $\text{HB}(\text{C}_6\text{F}_5)_2$  hydroboration of 2-dimesitylphosphinonorborene. As this species features the  $\text{PMe}_2$  Lewis base in the 2-endo and the  $\text{B}(\text{C}_6\text{F}_5)_2$  Lewis acid in the 3-exo-position, compound **106** is a non-interacting intramolecular FLP [ $^{11}\text{B}$  NMR:  $\delta$  75.0 (solution), 75.2 (solid state),  $^{31}\text{P}$  NMR:  $\delta$  -21.8 (solution), -22.4 (solid state)]. Compound **106** reacted rapidly with  $\text{SO}_2$  at 25 °C to form the addition product **107**. In solution, a mixture of two (racemic) epimers (**107**, **107'**) was found in a ca. 5:2 molar ratio [ $^{31}\text{P}$  NMR:  $\delta$  59.5 (major),  $\delta$  53.6 (minor)] (Scheme 24). Compound **107** was characterized by X-ray diffraction. In the crystal the P-S (2.404(2) Å) and B-O (1.573(5) Å) bonded FLP/ $\text{SO}_2$  addition product is observed. It features a trigonal-pyramidal geometry at sulfur with a ca. 5:2 disorder of the S=O oxygen atom over two positions.<sup>57</sup>



Scheme 24 Synthesis of FLP- $\text{SO}_2$  complexes, **107/107'**

## Reactions of $\text{N}_2\text{O}$ with FLPs

The FLP **1** ( $\text{R} = \text{C}_6\text{F}_5$ ) reacts with  $\text{N}_2\text{O}$  to give  ${}^t\text{Bu}_3\text{P}(\text{N}_2\text{O})\text{B}(\text{C}_6\text{F}_5)_3$  (**108**) in good yield (Scheme 20).<sup>58</sup> The nature of the species was characterized by  $^{31}\text{P}$ ,  $^{11}\text{B}$  and  $^{19}\text{F}$  NMR spectroscopy. In addition, employing  $^{15}\text{N}_2\text{O}$  the isotopomeric product was prepared.  $^{15}\text{N}$  NMR signals at 566.6 and 381.7 ppm showed N-P coupling of 58.7 and 19.6 Hz, respectively, and a  ${}^1J_{\text{NN}} = 15.6$  Hz consistent with inequivalent nitrogen atoms and with a dissymmetric capture of  $\text{N}_2\text{O}$ . Indeed a crystal structure determination confirmed the nature of this product (Figure 5) in which the N-N and N-O bonds were found to be 1.257(2) and 1.336(2) Å, respectively and the P-N bond is 1.709(2) Å. The  ${}^t\text{Bu}_3\text{P}$  and  $\text{OB}(\text{C}_6\text{F}_5)_3$  fragments are *transoid* with respect to the  $\text{N}=\text{N}$  double bond. Computational studies suggest N-N and N-O infrared frequencies should be observed at 1483 and 1257  $\text{cm}^{-1}$ , respectively, which is in agreement with experimental observations. The species **108** was shown to evolve  $\text{N}_2$  on heating to 135 °C for 2 days affording  $({}^t\text{Bu}_3\text{P}=\text{O})\text{B}(\text{C}_6\text{F}_5)_3$  (**109**) (Scheme 25). Similarly this could also be achieved by photolysis in 5 minutes. It was suggested that isomerization about the  $\text{N}=\text{N}$  bond is required to place the P and O *cis* to one another and to liberate  $\text{N}_2$ .



Scheme 25 Reactions of the FLP **1** and  $\text{N}_2\text{O}$ .

Use of weaker bases in analogous reactions was generally unsuccessful. In contrast, use of weaker Lewis acids was tolerated. For example, reaction of  ${}^t\text{Bu}_3\text{P}$ ,  $\text{B}(\text{C}_6\text{F}_5)_2\text{Ph}$  and  $\text{N}_2\text{O}$  gave the analogous species  ${}^t\text{Bu}_3\text{P}(\text{N}_2\text{O})\text{B}(\text{C}_6\text{F}_5)_2\text{Ph}$  (**110**).<sup>59</sup> The structural features are similar with  $\text{B}(\text{C}_6\text{F}_5)_3$ , although the P-N and N-N bonds are slightly longer and the N-O bond distance is slightly shorter, consistent with the diminished Lewis acidity of the borane.

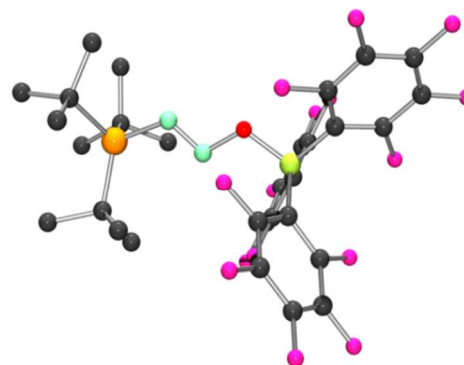
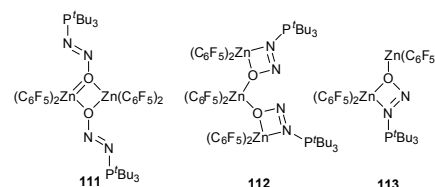


Figure 5 POV-ray depiction of **108** P: orange; O: red; N: pale-green; F: pink; C: black; B: yellow-green. H-atoms omitted for clarity.

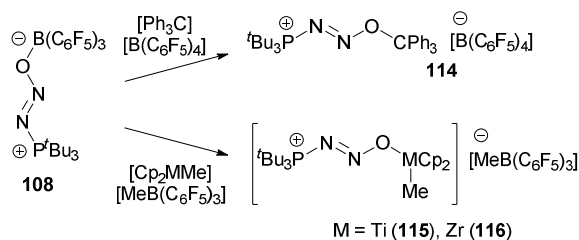


Scheme 26 Products of the reactions of  ${}^t\text{Bu}_3\text{PN}_2\text{OB}(\text{C}_6\text{F}_4\text{H})_3$  with  $\text{Zn}(\text{C}_6\text{F}_5)_2$ .

The ability of these  $\text{N}_2\text{O}$ -FLP compounds to tolerate weaker Lewis acids prompted an examination of exchange reactions. The species  ${}^t\text{Bu}_3\text{PN}_2\text{OB}(\text{C}_6\text{H}_4\text{F})_3$  was prepared as the species above and then reacted with  $\text{Zn}(\text{C}_6\text{F}_5)_2$  to give the centrosymmetric and dimer [ ${}^t\text{Bu}_3\text{PN}_2\text{OZn}(\text{C}_6\text{F}_5)_2$ ]<sub>2</sub> (**111**). Adjusting the stoichiometry to 1:1.5  ${}^t\text{Bu}_3\text{PN}_2\text{OB}(\text{C}_6\text{H}_4\text{F})_3$ :  $\text{Zn}(\text{C}_6\text{F}_5)_2$  gave  $({}^t\text{Bu}_3\text{PN}_2\text{OZn}(\text{C}_6\text{F}_5)_2)_2\text{Zn}(\text{C}_6\text{F}_5)_2$  (**112**) while 1:2 ratio of reagents gave  ${}^t\text{Bu}_3\text{PN}_2\text{O}(\text{Zn}(\text{C}_6\text{F}_5)_2)_2$  (**113**) (Scheme 26).<sup>60</sup> These compounds were the first metal complexes in which the binding mode of  $\text{N}_2\text{O}$  was unambiguously established.

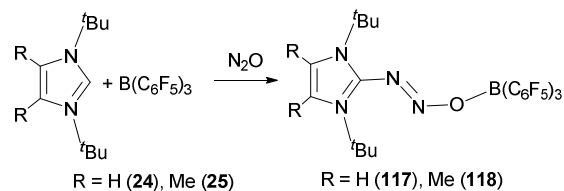
In a similar fashion,  ${}^t\text{Bu}_3\text{PN}_2\text{OB}(\text{C}_6\text{H}_4\text{F})_3$  was used to effect exchange of the weak Lewis acid for other more electrophilic boranes.<sup>59</sup> For example, treatment with a variety of boranes including  $\text{BR}_2\text{R}'$  ( $\text{R} = \text{C}_6\text{F}_5$ ,  $\text{R}' = \text{Mes}$ ;  $\text{R} = \text{C}_6\text{F}_5$ ,  $\text{R}' = \text{OC}_6\text{F}_5$ ;  $\text{R} = \text{R}' = \text{C}_6\text{F}_4$ -*p*-H) and *bis*-borane  $(\text{C}_6\text{F}_5)_2\text{B}(\text{C}_6\text{F}_4)\text{B}(\text{C}_6\text{F}_5)_2$  afforded the exchange products. In the latter case, two equivalents of  $\text{PN}_2\text{OB}$  species afford  ${}^t\text{Bu}_3\text{P}(\text{N}_2\text{O})\text{B}(\text{C}_6\text{F}_5)_2\text{C}_6\text{F}_4(\text{C}_6\text{F}_5)_2\text{B}(\text{ON}_2)\text{P}{}^t\text{Bu}_3$ . In a similar fashion, treatment with Lewis acid  $[\text{CPh}_3][\text{B}(\text{C}_6\text{F}_5)_4]$  afforded the species  $[{}^t\text{Bu}_3\text{P}(\text{N}_2\text{O})\text{CPh}_3][\text{B}(\text{C}_6\text{F}_5)_4]$  (**114**) while reaction with the highly acidic  $[\text{Cp}_2\text{MMe}][\text{MeB}(\text{C}_6\text{F}_5)_3]$  ( $\text{M} = \text{Ti}$ ,  $\text{Zr}$ ) generated  $[{}^t\text{Bu}_3\text{P}(\text{N}_2\text{O})\text{MCp}_2\text{Me}][\text{MeB}(\text{C}_6\text{F}_5)_3]$  ( $\text{M} = \text{Ti}$  (**115**),  $\text{Zr}$  (**116**)) (Scheme 27).<sup>59</sup> It is interesting to note that attempts to make the Zr species above directly from  $[\text{Cp}_2\text{ZrMe}][\text{MeB}(\text{C}_6\text{F}_5)_3]$ ,  $\text{N}_2\text{O}$  and phosphine were not successful, however using the zirconocene methoxide cation  $[\text{Cp}^*_2\text{Zr}(\text{OMe})][\text{B}(\text{C}_6\text{F}_5)_4]$ , the product

$[\text{Bu}_3\text{P}(\text{N}_2\text{O})\text{ZrCp}^*_2(\text{OMe})][\text{B}(\text{C}_6\text{F}_5)_4]$  was obtained.<sup>59</sup> The mechanism of Lewis acid exchange reactions was illuminated by NMR experiments of the reaction of  $\text{Bu}_3\text{P}(\text{N}_2\text{O})\text{B}(\text{C}_6\text{F}_5)_3$  (**108**) and free  $\text{B}(\text{C}_6\text{F}_5)_3$ . Variable temperature studies revealed the activation parameters of the exchange process as  $\Delta H^\ddagger = 71.2(9)$   $\text{kJ}\cdot\text{mol}^{-1}$  and  $\Delta S^\ddagger = 32(3)$   $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ . The observation of the small, positive  $\Delta S^\ddagger$  suggests that the B-O linkage is weakened before the incoming borane binds.



**Scheme 27** Products of the Lewis acid exchange reactions.

The above requirement of a strong donor for  $\text{N}_2\text{O}$  capture by an FLP is further consistent with the isolation of  $\text{N}_2\text{O}$  adduct derived from the FLP based on the NHCs and borane,  $\text{C}_3\text{R}_2(\text{N}t\text{Bu})_2/\text{B}(\text{C}_6\text{F}_5)_3$  (R = H (**24**), Me (**25**)) affording  $(\text{C}_3\text{R}_2(\text{N}t\text{Bu})_2)\text{N}_2\text{OB}(\text{C}_6\text{F}_5)_3$  (R = H (**117**), Me (**118**)).<sup>19</sup> It is noteworthy, that the carbene reacts with  $\text{N}_2\text{O}$  in the absence of borane to effect oxidation of the carbene to the urea derivative,<sup>61, 62</sup> the use of the FLP permits capture of intact  $\text{N}_2\text{O}$ .

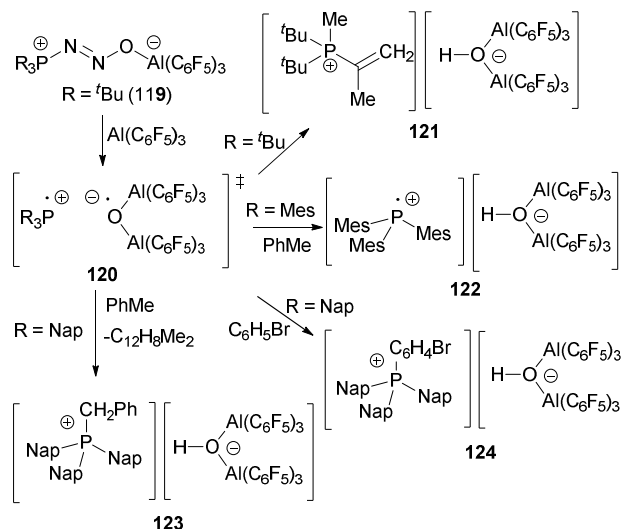


**Scheme 28** Products of the carbene-borane FLPs with  $\text{N}_2\text{O}$ .

Alteration of the above FLP chemistry to combination of phosphines and  $\text{Al}(\text{C}_6\text{F}_5)_3$  was also probed. Similar to the above chemistry, the stoichiometric reaction of  $\text{Bu}_3\text{P}$ ,  $\text{Al}(\text{C}_6\text{F}_5)_3$  and  $\text{N}_2\text{O}$  afforded the isolation of  $\text{Bu}_3\text{P}(\text{N}_2\text{O})\text{Al}(\text{C}_6\text{F}_5)_3$  (**119**).<sup>63</sup> A crystallographic study revealed the O-Al bond length to be 1.820(2) Å, significantly longer than the O-B bond length of 1.543(2) Å<sup>27</sup> in the B analog. However, in contrast to the borate analog, this species reacts further with additional Lewis acid. Thus modification of the stoichiometry to two equivalents of  $\text{Al}(\text{C}_6\text{F}_5)_3$  resulting in the liberation of  $\text{N}_2$  and prompting the generation of a transient “frustrated radical pair (FRP)” that is proposed to be  $[\text{R}_3\text{P}\cdot]^+[(\mu\text{-O}\cdot)(\text{Al}(\text{C}_6\text{F}_5)_3)_2]^-$  (**120**) (Scheme 23). Such FRPs rapidly effect alkyl and aryl C-H bond activations. For example, exposure of a combination of a 1:2 ratio of  $\text{Bu}_3\text{P}$  and  $\text{Al}(\text{C}_6\text{F}_5)_3\cdot\text{tol}$  to  $\text{N}_2\text{O}$  resulted in the formation of  $[\text{Bu}_2\text{PMe}(\text{C}(\text{CH}_2)\text{Me})][(\mu\text{-OH})(\text{Al}(\text{C}_6\text{F}_5)_3)_2]$  (**121**).<sup>63</sup> In this case, the FRP effected the C-H activation of one of the *t*-butyl groups of the phosphine affording the hydroxyl-bridged anion and prompting methyl-migration in the cation.

In an analogous fashion, a 1:2 solution of  $\text{Mes}_3\text{P}$  and  $\text{Al}(\text{C}_6\text{F}_5)_3\cdot\text{tol}$  exposed to  $\text{N}_2\text{O}$  resulted in an intensely deep purple solution and the isolation of  $[\text{Mes}_3\text{P}\cdot][(\mu\text{-HO})(\text{Al}(\text{C}_6\text{F}_5)_3)_2]$  (**122**) (Scheme 23).<sup>63</sup> The presence of the radical cation was evident from the absence of a  $^{31}\text{P}$  NMR signal and the observation of an EPR doublet at  $g = 2.0056$ , with electron-P coupling of 239 G. The  $^{19}\text{F}\{^1\text{H}\}$  and  $^1\text{H}$  NMR spectroscopy were consistent with the presence of the diamagnetic anion. X-ray diffraction studies confirmed the formation of this rare example of a structurally characterized phosphoniumyl radical cation salt.<sup>28</sup> The origin of the H atom in the anion was unambiguously confirmed to be the solvent toluene as GC-MS revealed the presence of radical coupling dimers from toluene. In addition, the corresponding reaction of  $\text{PMes}_3\text{-d}_{27}$  (95% deuteration), showed about 10% deuterated anion suggesting hydrogen from the cation is limited.

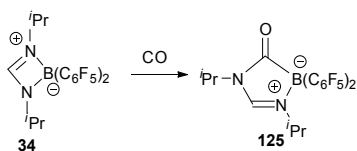
Interestingly, the corresponding reaction of  $(\text{Nap})_3\text{P}$ ,  $\text{Al}(\text{C}_6\text{F}_5)_3\cdot\text{tol}$  and  $\text{N}_2\text{O}$  gave the product  $[(\text{Nap})_3\text{PCH}_2\text{Ph}][(\mu\text{-OH})(\text{Al}(\text{C}_6\text{F}_5)_3)_2]$  (**123**) in which toluene C-H bond activation has occurred. In contrast, performing the analogous reaction of a 1:2 mixture of  $(\text{Nap})_3\text{P}$  and  $\text{Al}(\text{C}_6\text{F}_5)_3\cdot\text{PhH}$  in  $\text{C}_6\text{D}_5\text{Br}$  with  $\text{N}_2\text{O}$  affording the species  $[(\text{Nap})_3\text{PC}_6\text{H}_4\text{Br}][(\mu\text{-HO})(\text{Al}(\text{C}_6\text{F}_5)_3)_2]$  (**124**) where aryl C-H activation results (Scheme 23).<sup>63</sup> The identification of these C-H bond cleavage products further support the view that highly reactive FRPs are generated from combinations of phosphines,  $\text{Al}(\text{C}_6\text{F}_5)_3$  and  $\text{N}_2\text{O}$



**Scheme 29** Products of Al/P FLPs with  $\text{N}_2\text{O}$ .

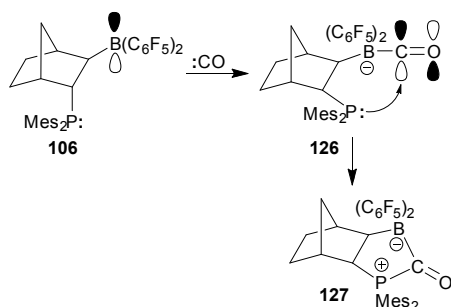
## Cooperative FLP Addition Reactions to CO and NO

The capture of CO by the B-amidinate **34** affords the species  $(\text{HC}(t\text{PrN})_2(\text{CO})\text{B}(\text{C}_6\text{F}_5)_2)$  (**125**) (Scheme 24).<sup>29</sup> As with the capture of  $\text{CO}_2$ , this reaction is thought to proceed by ring-opening of the amidinate generating an intramolecular B/N FLP. This FLP acts in concerted donor acceptor fashion to capture CO. Characterization of **125** revealed that the B-C, C-N and C-O bond lengths were 1.637(1) 1.423(1) and 1.217(1) Å, respectively.



Scheme 30 Reactions of B-amidinate with CO.

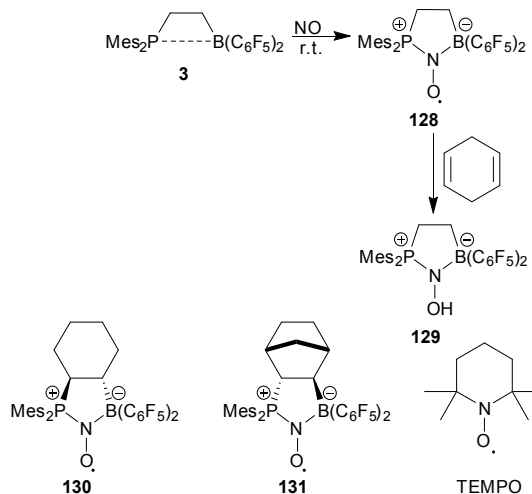
The FLP **106** was co-condensed with CO in an argon matrix at 10 K leading to the observation of both the unreacted system **106** and free CO ( $\tilde{\nu} = 2138 \text{ cm}^{-1}$ ) by IR spectroscopy. Upon slowly warming to ca. 35 K the borane carbonyl product **126** gave rise to a typical IR absorption at  $2196 \text{ cm}^{-1}$ . This feature is at higher wavenumbers than the corresponding absorption for free CO.<sup>64-71 72-79</sup> In contrast, FLP **106** reacts with CO in solution to give the P/B/CO addition product **127** in good yield (Scheme 25).<sup>80, 81</sup> The reaction is reversible at temperatures above ca. 240 K, and thus the product was isolated and characterized at low temperature [NMR:  $\delta$  224.7 ( $^{13}\text{C}$ ,  $^1J_{\text{PC}} = 111 \text{ Hz}$ ),  $\delta$  -12.9 ( $^{11}\text{B}$ ),  $\delta$  -6.4 ( $^{31}\text{P}$ ); IR:  $\tilde{\nu}(\text{CO}) = 1791 \text{ cm}^{-1}$ ]. Compound **127** was characterized by X-ray diffraction (Figure 6). It shows a trigonal planar coordination environment at the carbonyl carbon atom (C-O: 1.174(2) Å, B-C<sub>co</sub>: 1.684(2) Å). The P-C<sub>co</sub> bond is rather long (2.104(2) Å) and the C=O moiety is markedly leaning over toward the phosphorus side (angle B-C-O: 135.3(2)°).

Scheme 31 Formation of the CO complexes **126** and **127**.Figure 6 POV-ray Depiction of **127**. P: orange, C: black, F: pink, B: yellow-green, O: red, hydrogen atoms are omitted for clarity.

The interaction of the FLP **106** with CO is reminiscent of the interaction of a transition metal with CO. In both cases, CO acts as a  $\sigma$ -donor and a  $\pi$ -acceptor. However in the case of the FLP the acceptor and donor sites lie on the B and P atoms respectively. Nonetheless, the  $\sigma$ -donation to B and the P-donation to the CO

$\pi^*$ -orbital is analogous to the situation described by the Dewar-Chatt-Duncanson model of metal coordination chemistry.<sup>82, 83</sup>

A variety of reactive vicinal P/B FLPs react similarly with nitric oxide. A typical example is the cooperative N,N-addition of both the borane Lewis acid and the phosphine Lewis base of **3** to NO to form the persistent FLP-NO radical **128** (Scheme 32).<sup>84</sup> Pale blue crystals of the aminoxyl radical were obtained. The X-ray crystal structure of **128** showed the five-membered heterocyclic core with P-N and B-N distances of 1.713(1) Å and 1.592(2) Å, respectively. The exocyclic N-O linkage is rather short at 1.296(1) Å but, of course much longer than that in free NO (1.151 Å). Compound **128** is EPR active; with a complex resonance centred at  $g = 2.0089$  with hyperfine coupling constants of  $A(^{14}\text{N}) = 18.5 \text{ MHz}$ ,  $A(^{31}\text{P}) = 48.5 \text{ MHz}$  and  $A(^{11}\text{B}) = 9.1 \text{ MHz}$ . These data indicate that **128** is a more oxygen centred radical than TEMPO (Scheme 26), where the  $A(^{14}\text{N})$  is 43.5 MHz. The Mulliken spin density population was calculated by DFT methods to be 0.54  $e^-$  at oxygen and 0.34  $e^-$  at nitrogen for **128**. This stands in contrast to TEMPO, where the analogous calculations show 0.50 and 0.44  $e^-$  at O and N, respectively. The persistent FLP-NO radical rapidly undergoes typical H atom abstraction reactions from 1,4-cyclohexadiene to give the diamagnetic FLP-NOH compound **129** in which the N-O bond is 1.422(2) Å. The calculated (DFT) O-H bond dissociation energy of **129** is 77.2 kcal·mol<sup>-1</sup> whereas for TEMPOH the energy is calculated to be 67.2 kcal·mol<sup>-1</sup>, very close to the experimentally determined value of 65.2 kcal·mol<sup>-1</sup>. This renders the FLP-NO radical about 10 kcal·mol<sup>-1</sup> less thermodynamically stable and consequently more reactive.<sup>85</sup> A variety of reactive vicinal phosphine/borane FLPs were used to prepare persistent FLP-NO aminoxyl radicals (Scheme 32) in straightforward syntheses. Most of these were characterized crystallographically (eg. **130**: Figure 7).<sup>86</sup>



Scheme 32 Reactions and structural formulae of FLP-NO complexes

The FLP-NO radicals also abstracts H atom from benzylic positions of toluene to generate the respective FLP-NOH products and the very reactive carbon centered benzylic radicals. The latter combine readily with the free persistent radical **130** to form the respective FLP-NO-benzyl compound **133**.

Consequently, a mixture of **132** and **133** was obtained by reacting **130** with toluene at 70 °C (Scheme 33). The FLP-NO-benzyl O-C linkage is cleaved at ca. 120-130 °C to reversibly generate the FLP-NO radical and the respective benzylic radical. This chemistry was used for NO mediated polymerisation of styrene. With the system [FLP-NO-CH(CH<sub>3</sub>)Ph] (**133a**) living styrene polymerisation could be achieved at 130 °C to give polystyrene with a polydispersity index of ca. 1.30.<sup>86</sup>

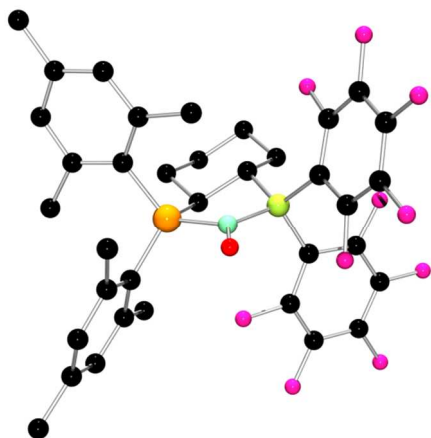
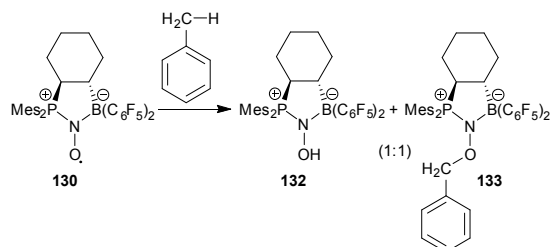


Figure 7 POV-ray Depiction of **130**. P: orange, C: black, F: pink, B: yellow-green, O: red, hydrogen atoms are omitted for clarity.



Scheme 33 Reaction of FLP-NO complex **130** in toluene.

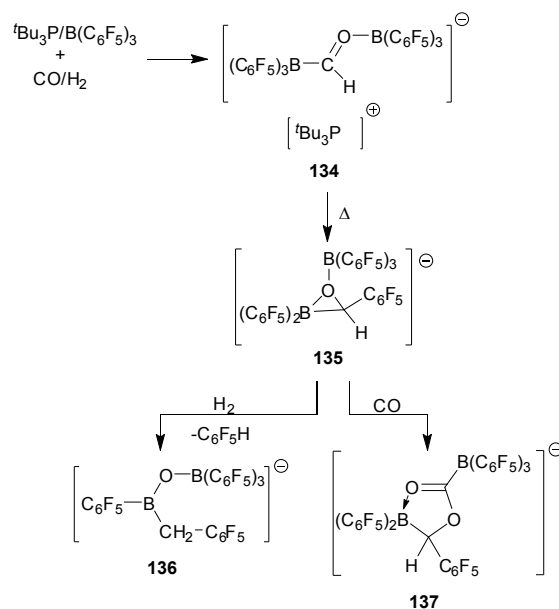
A thorough kinetic/mechanistic study was carried out on the reaction of the norbornene derived FLP **106** with NO.<sup>87</sup> The reaction was shown to be kinetically first order in both the FLP and NO. In combination with a DFT study, a pathway of the formation of the persistent FLP-NO radical **128** by a rapid reversible NO addition to the boryl Lewis acid functionality followed by rate determining intramolecular phosphine addition to the nitrogen atom of the borane bound NO was proposed. In contrast, phosphines typically react with NO following a third order rate law, first order in phosphine and second order in NO to generate N<sub>2</sub>O and phosphine oxide.<sup>88-90</sup> This latter reactivity is also seen for the reaction of the intermolecular FLP **1** with NO, affording <sup>t</sup>Bu<sub>3</sub>PO and N<sub>2</sub>O.<sup>58</sup> The latter product was trapped in as the species <sup>t</sup>Bu<sub>3</sub>P(N<sub>2</sub>O)B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (**108**) which was described above.<sup>40</sup>

## CO Reduction at an FLP Template

Trialkylboranes react with CO effecting C-C coupling. H. C. Brown *et al.* had developed this reaction to a synthetic procedure, followed by oxidative workup, to prepare tertiary alcohols, while

variants of this chemistry led to ketones or aldehydes.<sup>73</sup> These reactions proceed via boron-acyl species. Piers *et al.* has recently described a scandocene Lewis acid stabilized formylborate anion.<sup>91-93</sup> The conceptually related B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> stabilized formylborate salt (**134**) was formed by treatment of the intermolecular FLP <sup>t</sup>Bu<sub>3</sub>P/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (**1**) with syn-gas (Scheme 28). Similar to Piers' [Sc]-O=CHB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> system compound **134** undergoes a C<sub>6</sub>F<sub>5</sub> shift to the carbonyl carbon atom to give **135**.<sup>94</sup> This species can be further reduced by treatment with H<sub>2</sub> generating the species **136** while **135** also reacts with excess CO to give a rare example of an alkylcarboxylato-borate species (**137**).

[B]H boranes are known to react differently with CO, yielding borane carbonyl compounds.<sup>72-79</sup> In 1937 Schlesinger *et al.* described the formation of borane-carbonyl [H<sub>3</sub>B-CO] by the reaction of B<sub>2</sub>H<sub>6</sub> with CO under forcing conditions. The resulting low boiling liquid dissociates upon lowering the CO pressure. More recently, reaction of Piers' borane HB(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub><sup>95-97</sup> was shown to form the analogous borane-carbonyl product (C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>B(H)-CO (**138**) which could be isolated at low temperature (-40 °C) An X-ray diffraction study (Figure 8)<sup>98</sup> shows B-C and C-O bond lengths of 1.601(2) Å and 1.107(2) Å, respectively. It is noteworthy that the Piers group has also described a borane-carbonyl derived from an antiaromatic, and highly Lewis acidic, pentaarylboreole compound.<sup>71</sup>



Scheme 34 Reactions of Syn-gas with FLP **1**, (all cations are [<sup>t</sup>Bu<sub>3</sub>PH]<sup>+</sup>).

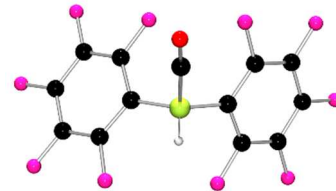
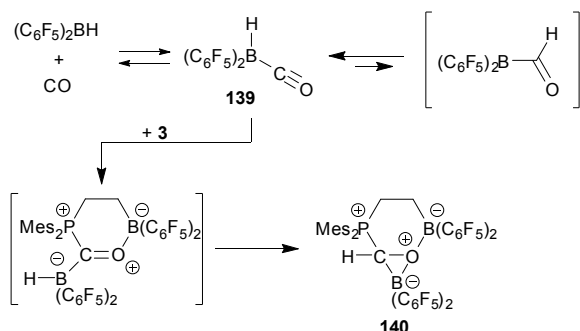


Figure 8 POV-ray Depiction of **138**. C: black, F: pink, B: yellow-green, O: red, hydrogen atoms are omitted for clarity.

A 1,2-hydride shift from B to the carbonyl carbon of CO is thermodynamically disfavored and thus formyl-borane products are not readily accessible. A recent DFT calculation has shown that the conversion of  $(\text{C}_6\text{F}_5)_2\text{B}(\text{H})\text{-CO}$  (**138**) to  $(\text{C}_6\text{F}_5)_2\text{B-CHO}$  is markedly endergonic by ca. 17 kcal mol<sup>-1</sup>. However, the reaction of the ethylene-bridged FLP **3** with CO and Piers' borane,  $\text{HB}(\text{C}_6\text{F}_5)_2$ , proceeds cleanly under mild conditions at 25 °C yielding the “ $\eta^2$ -formyl-borane” at the P/B FLP template. This product **139** was isolated in >80% yield and characterized by X-ray diffraction revealing B-C, B-O and C-O bond lengths of 1.588(4) Å, 1.533(3) Å and 1.465(3) Å, respectively (Scheme 29). The reaction path appears to involve the cooperative P/B addition of the FLP to the transient borane-carbonyl intermediate, followed by hydride shift affording **139** (Scheme 35).<sup>80</sup>



Scheme 35 Formation of **140** from **139**.

Analogs of **139** have been derived from the corresponding reactions of other vicinal P/B FLPs. For example, compound **140** (see Figure 9), derived from **106**/CO and  $\text{HB}(\text{C}_6\text{F}_5)_2$ . This “ $\eta^2$ -formyl-borane” moiety at this FLP template is further reduced by exposure to  $\text{H}_2$  (60 bar) at 25 °C to yield **144**, the product of reductive CO splitting.<sup>98</sup> It appears that reversible cleavage of the lateral B-O bond of **141** generates an O/B FLP (**142**) that heterolytically splits  $\text{H}_2$  to give **143**. Subsequent intramolecular nucleophilic attack by hydride then leads to ring-opening with formation of **144** (Scheme 36).

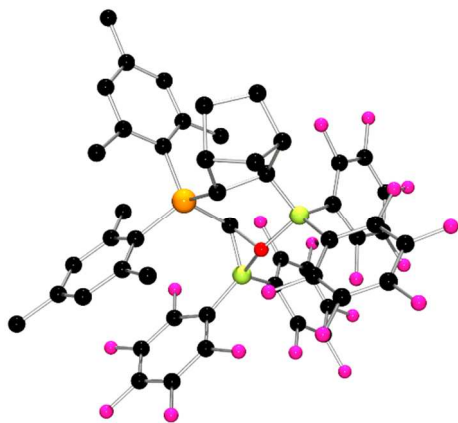
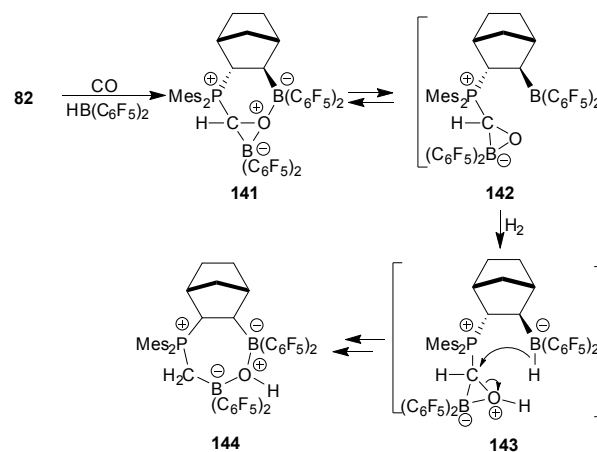


Figure 9 POV-ray Depiction of **141**. P: orange, C: black, F: pink, B: yellow-green, O: red, hydrogen atoms are omitted for clarity.

The facile opening of the lateral B-O bond in these systems was supported by the isolation of the respective pyridine trapping product **145** derived from **140** (Scheme 37). Treatment of compound **141** with excess pyridine resulted in a complete removal of the newly formed formylborane from the FLP, and formation of the pyridine stabilized formylborane product  $(\text{C}_6\text{F}_5)_2\text{B-CHO}$  (**147**) and the pyridine adduct of **106**, **146**. Spectroscopic characterization of the formyl-borane fragment showed <sup>1</sup>H and <sup>13</sup>C resonances at 11.24 and 233.1 ppm respectively and a <sup>11</sup>B signal at -5.1 ppm. X-ray diffraction confirmed the structure with B-C and C-O distances of 1.649(3) Å and 1.210(2) Å, respectively. (Figure 10). Subsequent reactions of **147** in reduction or Wittig olefination reveal a typical organic carbonyl reactivity of this boryl carbaldehyde.<sup>98</sup>



Scheme 36 Reaction Pathway to **144**.

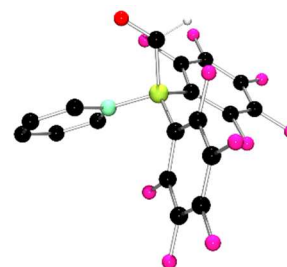
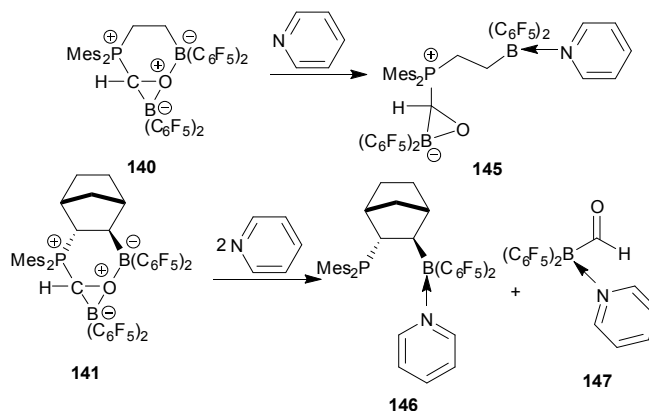


Figure 10 POV-ray Depiction of **147**. N: blue-green; C: black, F: pink, B: yellow-green, O: red, hydrogen atoms are omitted for clarity



Scheme 37 Reactions of **135** and **136** with pyridine.

## Conclusions

The advent of FLP have yielded a unique approach to the binding, activation and reactivity of small molecules. In this review we have described the reactions of FLPs with the oxides of C, N and S. In the case of CO<sub>2</sub> the chemistry has evolved from CO<sub>2</sub> capture to stoichiometric reduction to CO or methanol. Employing a similar FLP strategy but moving to less oxophilic Lewis acids has yielded a system capable of the catalytic reduction of CO<sub>2</sub>. While this rapid development has been interesting, the challenge of uncovering systems which effect similar catalytic reductions, but employ an oxygen atom acceptor that is of high value remains.

Analogous binding of SO<sub>2</sub> and N<sub>2</sub>O can also be achieved with FLPs. While these products are interesting, the subsequent reactivity has received limited attention. In the case of N<sub>2</sub>O, exchange reactions were used to uncover a variety of metal binding modes. Nonetheless, the utility of FLP-N<sub>2</sub>O of SO<sub>2</sub> species as reactants affording either oxygen delivery or further oxidation of S are subjects of on-going interests.

The studies on FLP reactions with CO and NO point out the behavior of FLPs that is reminiscent of transition metal systems. The cooperative action of the Lewis acid and base on CO or NO can formally be described by a scheme similar to the Dewar-Chatt-Duncanson description for binding in metal carbonyl or nitrosyl complexes.<sup>99</sup> The reduction of CO described in the final portion of this account further underlines the potential of FLPs for small molecule activation. In these cases, the CO is reduced, novel intermediates have been isolated and C-O bond scission has been effected.

While FLP chemistry has opened numerous fronts for new reactivity, the examples described herein illustrate that the activation of CO<sub>2</sub>, SO<sub>2</sub>, N<sub>2</sub>O, NO and CO is one of the areas of FLP chemistry that has grown rapidly in recent years. It is noteworthy that the majority of these early studies have focused on the use of FLP systems incorporating electrophilic boranes and strongly basic donors. These combinations have allowed the illumination of new reactivity and afforded the isolation of interesting products. Nonetheless, the future of FLP chemistry lies in the potential for the discovery of new FLPs that are less oxophilic and less basic allowing capture reaction and release of small molecule reduction products. Despite the flurry of activity in FLP chemistry in recent years, the true potential of this strategy to small molecule activation, reactivity and metal-free catalysis remains untapped. Nonetheless, the findings to date, suggest that extensions and broaden applications of the concept of FLPs will lead to new strategies to effect the chemistry of both the oxides of C, N and S as well as other small molecules of interest.

## Acknowledgements

The authors are grateful to the teams of outstanding students and postdoctoral fellows in Münster and Toronto for their contributions to the research discussed herein and they are also grateful to the collaborators elsewhere for their many important contributions to this chemistry. It has been a pleasure to work

with them on these addressed topics. GE gratefully acknowledges the financial support of his work by the Deutsche Forschungsgemeinschaft (DFG), the European Research Council (ERC) and the Alexander von Humboldt-Stiftung and DWS thanks NSERC of Canada for financial support and the award of a Canada Research Chair and the Alexander von Humboldt-Stiftung for a senior research award re-invitation.

## Notes and references

<sup>a</sup> Department of Chemistry, University of Toronto, 80 St George St, Toronto, Ontario, Canada, M5S3H6; Tel: 01-416-946-3294; [dstephan@chem.utoronto.ca](mailto:dstephan@chem.utoronto.ca)

<sup>b</sup> Organisch-Chemisches Institut, Westfälische Wilhelms-Universität 48149 Münster, Corrensstr. 40, Germany  
[erker@uni-muenster.de](mailto:erker@uni-muenster.de)

1. G. C. Welch, R. R. S. Juan, J. D. Masuda and D. W. Stephan, *Science*, 2006, **314**, 1124-1126.
2. P. A. Chase, G. C. Welch, T. Jurca and D. W. Stephan, *Angew. Chem. Int. Ed.*, 2007, **46**, 8050-8053.
3. P. A. Chase, T. Jurca and D. W. Stephan, *Chem. Commun.*, 2008, 1701-1703.
4. P. Spies, S. Schwendemann, S. Lange, G. Kehr, R. Fröhlich and G. Erker, *Angew. Chem. Int. Ed.*, 2008, **47**, 7543-7546.
5. D. Chen and J. Klankermayer, *Chem. Commun.*, 2008, 2130-2131.
6. D. W. Stephan and G. Erker, *Angew. Chem. Int. Ed.*, 2010, **49**, 46-76.
7. J. S. J. McCahill, G. C. Welch and D. W. Stephan, *Angew. Chem. Int. Ed.*, 2007, **46**, 4968-4971.
8. C. M. Mömning, E. Otten, G. Kehr, R. Fröhlich, S. Grimme, D. W. Stephan and G. Erker, *Angew. Chem. Int. Ed.*, 2009, **48**, 6643-6646.
9. I. Peuser, R. C. Neu, X. X. Zhao, M. Ulrich, B. Schirmer, J. A. Tannert, G. Kehr, R. Fröhlich, S. Grimme, G. Erker and D. W. Stephan, *Chem-Eur J*, 2011, **17**, 9640-9650.
10. M. Harhausen, R. Fröhlich, G. Kehr and G. Erker, *Organometallics*, 2012, **31**, 2801-2809.
11. R. C. Neu, G. Menard and D. W. Stephan, *Dalton Trans.*, 2012, **41**, 9016-9018.
12. W. Siebert, M. Hildenbrand, P. Hornbach, G. Karger and H. Pritzkow, *Z. Naturforsch.*, 1989, **44b**, 1179-1186.
13. X. X. Zhao and D. W. Stephan, *Chem. Commun.*, 2011, **47**, 1833-1835.
14. M. J. Sgro, J. Domer and D. W. Stephan, *Chem. Commun.*, 2012, **48**, 7253-7255.
15. F. Bertini, V. Lyaskoyskyy, B. Timmer, F. de Kanter, M. Lutz, A. Ehlers, J. Slootweg and K. Lammertsma, *J. Am. Chem. Soc.*, 2012, **134**, 201-204.
16. M. Feroci, I. Chiarotto, S. V. Cipriotti and A. Inesi, *Electrochim. Acta*, 2013, **109**, 95-101.
17. J. D. Holbrey, W. M. Reichert, I. Tkatchenko, E. Bouajila, O. Walter, I. Tommasi and R. D. Rogers, *Chem. Commun. (Cambridge, U. K.)*, 2003, 28-29.
18. E. L. Kolychev, T. Bannenberg, M. Freytag, C. G. Daniliuc, P. G. Jones and M. Tamm, *Chem. Eur. J.*, 2012, **18**, 16938-16946.
19. E. Theuergarten, T. Bannenberg, M. D. Walter, D. Holschumacher, M. Freytag, C. G. Daniliuc, P. G. Jones and M. Tamm, *Dalton Trans.*, 2014, **43**, 1651-1662.
20. Y. Liu, G. P. Jessop, M. Cunningham, C. A. Eckert and C. L. Liotta, *Science*, 2006, **313**, 958-960.
21. P. G. Jessop, D. H. Heldebrant, X. Li, C. A. Eckert and C. L. Liotta, *Nature*, 2005, **436**, 1102.
22. D. A. Dickie, M. V. Parkes and R. A. Kemp, *Angew. Chem. Int. Ed.*, 2008, **47**, 9955-9957.
23. F. Fichter and B. Becker, *Chem. Ber.*, 1911, 3481-3485.
24. E. A. Werner, *J. Chem. Soc.*, 1920, **117**, 1046-1053.
25. D. Belli Dell'Amico, F. Calderazzo, L. Labella, F. Marchetti and G. Pampaloni, *Chem. Rev.*, 2003, **103**, 3857-3897.
26. T. Voss, T. Mahdi, E. Otten, R. Fröhlich, G. Kehr, D. W. Stephan and G. Erker, *Organometallics*, 2012, **31**, 2367-2378.
27. C. F. Jiang and D. W. Stephan, *Dalton Trans.*, 2013, **42**, 630-637.
28. P. Molina, M. Alajarin and A. Arques, *Synthesis*, 1982, 596.

29. M. A. Dureen and D. W. Stephan, *J. Am. Chem. Soc.*, 2010, **132**, 13559-13568.
30. E. Theuergarten, J. Schlosser, D. Schluns, M. Freytag, C. G. Daniliuc, P. G. Jones and M. Tamm, *Dalton Trans.*, 2012, **41**, 9101-9110.
31. G. Menard, T. M. Gilbert, J. A. Hatnean, A. Kraft, I. Krossing and D. W. Stephan, *Organometallics*, 2013, **32**, 4416-4422.
32. G. Ménard and D. W. Stephan, *J. Am. Chem. Soc.*, 2010, **132**, 1796-1797.
33. G. Menard and D. W. Stephan, *Dalton Trans.*, 2013, **42**, 5447-5453.
34. G. Menard and D. W. Stephan, *Angew. Chem. Int. Ed.*, 2011, **50**, 8396-8399.
35. G. Ménard and D. W. Stephan, *Angew. Chem. Int. Ed.*, 2011, **50**, 8396-8399.
36. C. Appelt, H. Westenberg, F. Bertini, A. W. Ehlers, J. C. Slootweg, K. Lammertsma and W. Uhl, *Angew. Chem. Int. Ed.*, 2011, **50**, 3925-3928.
37. S. Roters, C. Appelt, H. Westenberg, A. Hepp, J. Slootweg, K. Lammertsma and W. Uhl, *Dalton Trans.*, 2012, **41**, 9033-9045.
38. J. Boudreau, M. A. Courtmanche and F. G. Fontaine, *Chem. Commun.*, 2011, **47**, 11131-11133.
39. M. Reissmann, A. Schafer, S. Jung and T. Muller, *Organometallics*, 2013, **32**, 6736-6744.
40. A. M. Chapman, M. F. Haddow and D. F. Wass, *J. Am. Chem. Soc.*, 2011, **133**, 8826-8829.
41. A. M. Chapman, M. F. Haddow and D. F. Wass, *J. Am. Chem. Soc.*, 2011, **133**, 18463-18478.
42. X. Xu, G. Kehr, C. G. Daniliuc and G. Erker, *J. Am. Chem. Soc.*, 2013, **135**, 6465-6476.
43. S. Fromel, G. Kehr, R. Fröhlich, C. G. Daniliuc and G. Erker, *Dalton Trans.*, 2013, **42**, 14531-14536.
44. M. J. Sgro and D. W. Stephan, *Chem. Commun.*, 2013, **49**, 2610-2612.
45. M. P. Boone and D. W. Stephan, *Organometallics*, 2014, **33**, 387-393.
46. X. Pan, X. Chen, T. Li, Y. Li and X. Wang, *J. Am. Chem. Soc.*, 2013, **135**, 3414-3417.
47. L. J. Hounjet, C. B. Caputo and D. W. Stephan, *Angew. Chem. Int. Ed.*, 2012, **51**, 4714-4717.
48. A. E. Ashley, A. L. Thompson and D. O'Hare, *Angew. Chem. Int. Ed.*, 2009, **48**, 9839-9843.
49. A. Berkefeld, W. E. Piers and M. Parvez, *J. Am. Chem. Soc.*, 2010, **132**, 10660-10661.
50. K. Takeuchi and D. W. Stephan, *Chem. Commun.*, 2012, **48**, 11304-11306.
51. R. Dobrovetsky and D. W. Stephan, *Angew. Chem. Int. Ed.*, 2013, **52**, 2516-2519.
52. M. J. Sgro and D. W. Stephan, *Angew. Chem. Int. Ed.*, 2012, **51**, 11343-11345.
53. M. A. Courtmanche, M. A. Legare, L. Maron and F. G. Fontaine, *J. Am. Chem. Soc.*, 2013, **135**, 9326-9329.
54. T. Wang and D. W. Stephan, *Chem. Eur. J.*, 2014, DOI: 10.1002/chem.201304870.
55. M. Sajid, A. Klose, B. Birkmann, L. Y. Liang, B. Schirmer, T. Wiegand, H. Eckert, A. J. Lough, R. Fröhlich, C. G. Daniliuc, S. Grimme, D. W. Stephan, G. Kehr and G. Erker, *Chem. Sci.*, 2013, **4**, 213-219.
56. K. Axenov, C. Mommig, G. Kehr, R. Fröhlich and G. Erker, *Chem. Eur. J.*, 2010, **16**, 14069-14073.
57. M. Sajid, A. Klose, B. Birkmann, L. Y. Liang, B. Schirmer, T. Wiegand, H. Eckert, A. J. Lough, R. Fröhlich, C. G. Daniliuc, S. Grimme, D. W. Stephan, G. Kehr and G. Erker, *Chem. Sci.*, 2013, **4**, 213-219.
58. E. Otten, R. C. Neu and D. W. Stephan, *J. Am. Chem. Soc.*, 2009, **131**, 9918-9919.
59. R. C. Neu, E. Otten, A. Lough and D. W. Stephan, *Chem. Sci.*, 2012, **2**, 170.
60. R. C. Neu, E. Otten and D. W. Stephan, *Angew. Chem. Int. Ed.*, 2009, **48**, 9709-9712.
61. A. G. Tskhovrebov, E. Solari, M. D. Wodrich, R. Scopelliti and K. Severin, *J. Am. Chem. Soc.*, 2012, **134**, 1471-1473.
62. T. A.G., V. B., S. E., S. R. and S. K., *J Am Chem Soc.*, 2013, **135**, 9486-9492.
63. G. Menard, J. A. Hatnean, H. J. Cowley, A. J. Lough, J. M. Rawson and D. W. Stephan, *J. Am. Chem. Soc.*, 2013, **135**, 6446-6449.
64. P. L. Timms, *J. Am. Chem. Soc.*, 1967, **89**, 1629.
65. W. H. Knoth, J. C. Sauer, J. H. Balthis, H. C. Miller and E. L. Muetterties, *J. Am. Chem. Soc.*, 1967, **89**, 4842.
66. H. Jacobsen, H. Berke, S. Döring, G. Kehr, G. Erker, R. Fröhlich and O. Meyer, *Organometallics*, 1999, **18**, 1724-1735.
67. J. C. Jeffery, N. C. Norman, J. A. J. Pardoe and P. L. Timms, *Chem. Commun.*, 2367-2368.
68. A. Terheiden, E. Bernhardt and H. Willner, *Angew. Chem. Int. Ed.*, 2002, **41**, 799.
69. M. Finze, E. Bernhardt, H. Willner and C. W. Lehmann, *Inorg. Chem.*, 2006, **45**, 669.
70. M. Gerken, G. Pawelke, E. Bernhardt and H. Willner, *Chem. Eur. J.*, 2010, **16**, 7527.
71. A. Fukazawa, J. L. Dutton, C. Fan, L. G. Mercier, A. Y. Houghton, Q. Wu, W. E. Piers and M. Parvez, *Chem. Sci.*, 2012, **3**, 1814-1818.
72. A. B. Burg and H. I. Schlesinger, *J. Am. Chem. Soc.*, 1937, **59**, 780-787.
73. H. C. Brown, *Acc. Chem. Res.*, 1969, **2**, 65.
74. J. Gebicki and J. Liang, *J. Mol. Struct.*, 1984, **117**, 283.
75. E. J. Sluys and v. d. B. J. Veken, *J. Am. Chem. Soc.*, 1996, **118**, 440.
76. M. A. McAllister, J. L. Hubbard and M. P. Castellani, *J. Mol. Struct.*, 2000, **496**, 41.
77. J. C. Carter, A. L. Moyé and G. W. Luther III, *J. Am. Chem. Soc.*, 1974, **96**, 3071.
78. L. J. Malone and R. W. Parry, *J. Am. Chem. Soc.*, 1965, **87**, 2354.
79. L. J. Malone and R. W. Parry, *Inorg. Chem.*, 1967, **6**, 176.
80. M. Sajid, L.-M. Elmer, C. Rosorius, C. G. Daniliuc, S. Grimme, G. Kehr and G. Erker, *Angew. Chem. Int. Ed.*, 2013, **52**, 1-5.
81. M. Sajid, A. Lawzer, W. S. Dong, C. Rosorius, W. Sander, B. Schirmer, S. Grimme, C. G. Daniliuc, G. Kehr and G. Erker, *J. Am. Chem. Soc.*, 2013, **135**, 18567-18574.
82. J. Chatt and L. A. Duncanson, *J Chem Soc*, 1953, 2939-2947.
83. M. Dewar, *Bull. Chim. Soc. Fr.*, 1951, **18**, C71.
84. A. Cardenas, B. Culotta, T. Warren, S. Grimme, A. Stute, R. Fröhlich, G. Kehr and G. Erker, *Angew. Chem. Int. Ed.*, 2011, **50**, 7567-7571.
85. L. Tebben and A. Studer, *Angew. Chem., Int. Ed.*, 2011, **50**, 5034.
86. M. Sajid, A. Stute, A. J. P. Cardenas, B. J. Culotta, J. A. M. Hepperle, T. H. Warren, B. Schirmer, S. Grimme, A. Studer, C. G. Daniliuc, R. Fröhlich, J. L. Petersen, G. Kehr and G. Erker, *J. Am. Chem. Soc.*, 2012, **134**, 10156-10168.
87. C. M. Pereira, M. Sajid, G. Kehr, A. M. Wright, B. Schirmer, Z. W. Qu, S. Grimme, G. Erker and P. C. Ford, *J. Am. Chem. Soc.*, 2014, **136**, 513.
88. M. D. Lim, I. L. Lorkovic and P. C. Ford, *Inorg. Chem.*, 2002, **41**, 1026.
89. A. Bakac, M. Schouten, A. Johnson, W. Song, O. Pestovsky and E. Szajna-Fuller, *Inorg. Chem.*, 2009, **48**, 6979.
90. J. L. Heinecke, C. Khin, J. C. M. Pereira, S. A. Suarez, A. V. Iretskii, F. Doctorovich and P. C. Ford, *J. Am. Chem. Soc.*, 2013, **135**, 4007.
91. A. Berkefeld, W. E. Piers, M. Parvez, L. Castro, L. Maron and O. Eisenstein, *J. Am. Chem. Soc.*, 2012, **134**, 10843-10851.
92. S. Anderson, J. C. Jeffery, Y. H. Liao, D. F. Mullica, E. L. Sappenfield and F. G. A. Stone, *Organometallics*, 1997, **16**, 958.
93. A. A. Markov, G. F. Sharifullina, S. P. Dolin, N. I. Moiseeva, A. E. Gekhman and I. I. Moiseev, *Russ. Chem. Bull.*, 2011, **60**, 2175.
94. R. Dobrovetsky and D. W. Stephan, *J. Am. Chem. Soc.*, 2013, **135**, 4974-4977.
95. D. J. Parks, R. E. V. H. Spence and W. E. Piers, *Angew. Chem. Int. Ed.*, 1995, **34**, 809-811.
96. D. J. Parks, W. E. Piers and G. P. A. Yap, *Organometallics*, 1998, **17**, 5492-5503.
97. W. E. Piers and T. Chivers, *Chem Soc Rev*, 1997, **26**, 345-354.
98. M. Sajid, G. Kehr, C. G. Daniliuc and G. Erker, *Angew. Chem. Int. Ed.*, 2014, **53**, 1118-1121.
99. O. Ekkert, G. G. Miera, T. Wiegand, H. Eckert, B. Schirmer, J. L. Petersen, C. G. Daniliuc, R. Fröhlich, S. Grimme, G. Kehr and G. Erker, *Chem. Sci.*, 2013, **4**, 2657-2664.