Exploring Tetracoordinate Silicon Lewis Acids for Frustrated Lewis Pair Chemistry

by

Sarah Anne Weicker

A thesis submitted in conformity with the requirements for the degree of Master of Science
Department of Chemistry
University of Toronto

© Copyright by Sarah A. Weicker 2015
Exploring Tetracoordinate Silicon Lewis Acids for Frustrated Lewis Pair Chemistry

Sarah Anne Weicker

Master of Science

Department of Chemistry
University of Toronto

2015

Abstract

Although hundreds of papers have been published on frustrated Lewis pair (FLP) chemistry since 2006, only a small number of them have examined the use of silicon as a Lewis acid. Herein, we detail our efforts in employing tetracoordinate silicon Lewis acids (SLAs) in FLP chemistry. The synthesis of SLAs in the forms \( R_{4-n}Si(OSO_2CF_3)_n \) \((n = 1, 2)\), \( R_3SiN(SO_2CF_3)_2 \), and \( RSi(C_6F_5)_3 \) is described as well as investigations into their reactivity with a variety of small molecules. Silyl triflates are shown to activate carbon dioxide when paired with a secondary amine base to yield silyl carbamates. Sequestration of \( CO_2 \) by silyl triflates and triflimides with trialkylphosphines is also described, as well as investigations into \( CO_2 \) reduction.
Acknowledgments

First and foremost, I would like to thank my supervisor Professor Doug Stephan for all of his support, guidance, and patience. Thank you Doug for your enthusiasm towards chemistry and for giving me the freedom to explore new directions for my project.

I am extremely grateful to the members of the Stephan group for their helpful discussions and for creating a fun and pleasant environment to work in. Thanks to Dr. Manuel Pérez Vázquez and Dr. Roman Dobrovetsky for their assistance in the lab and their willingness to help me with my chemistry. I am very grateful to all the crystallographers of the group including Ian Mallov, Conor Pranckevicius, Lauren Longobardi, Chris Caputo, Judy Tsao, Dr. Fatme Dahcheh, and Eliar Mosaferi. Special thanks to Judy, Conor, Ian, and Dr. Alan Lough for their help with solving structures. I am indebted to the NMR staff Dr. Darcy Burns, Dmitry Pichugin, and Dr. Sergiy Nokhrin for all their assistance with silicon and variable temperature NMR experiments. Thank you to Dr. Timothy Burrow and Levy Cao for their help and advice with running EPR experiments. I am also grateful to Giordana Riccitelli, Alexandra Morrissey, and Rose Balazs for running samples for elemental analysis. Thanks to Julie Roy for being my waste train buddy and an awesome roomie.

Thanks to those of you who helped me to edit this thesis – Nick Hein, Judy Tsao, Ian Mallov, Rashi Hiranandani, and Dr. Manuel Pérez Vázquez. In addition, thanks to Prof. Doug Stephan and Prof. Datong Song for reading this thesis and their final edits.

I owe a huge thanks to Rashi for being a terrific friend both in and out of the lab. My time in Toronto would not have been the same without you. I would also like to thank my parents, Ted and Rachelle, and my brother Dylan for their support and encouragement with my academic endeavours.
# Table of Contents

Abstract ........................................................................................................................................... ii

Acknowledgments ............................................................................................................................. iii

Table of Contents ............................................................................................................................... iv

List of Tables .................................................................................................................................. vi

List of Figures .................................................................................................................................. vii

List of Schemes ................................................................................................................................. ix

List of Abbreviations and Symbols ................................................................................................. xi

1 Introduction ................................................................................................................................. 1

1.1 Overview of Frustrated Lewis Pairs ....................................................................................... 1

1.2 Beyond Boron: Modulating the Identity of the Lewis Acid .................................................. 4

1.2.1 Group 15 Lewis Acids ........................................................................................................ 5

1.2.2 Group 14 Lewis Acids ........................................................................................................ 5

1.3 Scope of Thesis ......................................................................................................................... 7

2 Synthesis and Reactivity of Four-Coordinate Silicon Lewis Acids ........................................ 8

2.1 Introduction ........................................................................................................................... 8

2.1.1 Silicon: Properties and Differences from Carbon ............................................................... 8

2.1.2 Applications of Silicon Lewis Acids .................................................................................. 8

2.2 Results and Discussion ........................................................................................................... 9

2.2.1 Synthesis of Four-Coordinate Silicon Lewis Acids ........................................................... 9

2.2.2 Gutmann-Beckett Quantification of Lewis Acidity ............................................................. 13

2.2.3 Exploring the Reactivity of Four-Coordinate Silicon Lewis Acids .................................. 14

2.2.4 Coordination Complexes of Formal Ph2Si2+ .................................................................. 18

2.3 Conclusions ............................................................................................................................ 21

2.4 Experimental .......................................................................................................................... 21

2.4.1 General Considerations ......................................................................................................... 21

2.4.2 Syntheses ............................................................................................................................. 22

2.4.3 Reactions ............................................................................................................................. 25

2.4.4 X-Ray Data Collection, Reduction, Solution, and Refinement ........................................ 26
3 Activation of Carbon Dioxide by Silicon-Based Frustrated Lewis Pairs .................. 28

3.1 Introduction .............................................................................................................. 28

3.2 Results and Discussion .......................................................................................... 31

3.2.1 Activation of Carbon Dioxide Employing a Secondary Amine Base .............. 31

3.2.2 Activation of Carbon Dioxide Employing PEt₃ ................................................. 37

3.2.3 Activation of Carbon Dioxide Employing P′Bu₃ .............................................. 43

3.2.4 Investigations into Carbon Dioxide Reduction ............................................... 48

3.3 Conclusions ........................................................................................................... 50

3.4 Experimental ......................................................................................................... 51

3.4.1 General Considerations ....................................................................................... 51

3.4.2 General Procedure for CO₂ Reactions ............................................................... 51

3.4.3 Reactions of Silyl Triflates with Tetramethylpiperidine and CO₂ .................... 51

3.4.4 Reactions of Silicon Lewis Acids with PEt₃ and Carbon Dioxide ...................... 54

3.4.5 Reactions of Silicon Lewis Acids with P′Bu₃ and Carbon Dioxide ...................... 58

3.4.6 Reaction of 3-17 with Me₂NHBH₃ .................................................................... 62

3.4.7 X-Ray Data Collection, Reduction, Solution, and Refinement ......................... 63

4 Conclusion .............................................................................................................. 65

4.1 Thesis Summary ..................................................................................................... 65

4.2 Future Work ........................................................................................................... 65

References .................................................................................................................. 67
List of Tables

Table 2.1 Lewis acidity test data determined via the Gutmann-Beckett method.......................... 13

Table 2.2 Friedel-Crafts dimerization of diphenylethylene by Si Lewis acid catalysts.............. 15

Table 2.3 Crystallographic data for compounds 2-1, 2-2, 2-7, and 2-11 .............................. 27

Table 3.1 Select NMR data and crystallographic bond lengths and angles for compounds 3-2-3-5 .............................................................................................................................................. 36

Table 3.2 Summary of CO$_2$ binding by silicon Lewis acids and PEt$_3$ at 25 °C................ 42

Table 3.3 Summary of CO$_2$ binding by silicon Lewis acids and P$^t$Bu$_3$ ......................... 47

Table 3.4 Crystallographic data for compounds 3-1 – 3-4......................................................... 64
### List of Figures

**Figure 1.1** Frontier molecular orbital depictions of a) a classic Lewis acid-base adduct and b) a frustrated Lewis pair .................................................................................................................................................. 2

**Figure 2.1** POV-Ray depiction of the molecular structure of 2-1................................................................. 10

**Figure 2.2** POV-Ray depiction of the molecular structure of 2-2................................................................. 11

**Figure 2.3** POV-Ray depiction of the molecular structure of 2-7................................................................. 12

**Figure 2.4** Lewis acidity determination with the Gutmann-Beckett method.............................................. 13

**Figure 2.5** Experimental EPR Spectrum of 2-9 in toluene (blue) at 25 °C and simulated EPR spectrum (red)........................................................................................................................................ 17

**Figure 2.6** POV-Ray depiction of the molecular structure of 2-11................................................................. 19

**Figure 2.7** $^{31}$P/$^1$H NMR spectra depicting donor exchange following reaction of 2 eq. OPEt$_3$ with [Ph$_2$Si(OPPh$_3$)$_2$][OTf]$_2$........................................................................................................................................ 20

**Figure 3.1** Selected examples of CO$_2$ sequestration by FLPs................................................................. 29

**Figure 3.2** POV-Ray depiction of the molecular structure of 3-1................................................................. 32

**Figure 3.3** POV-Ray depiction of the molecular structure of 3-2................................................................. 33

**Figure 3.4** Resonances forms of 3-2 ............................................................................................................. 33

**Figure 3.5** POV-Ray depiction of the molecular structure of 3-3................................................................. 35

**Figure 3.6** POV-Ray depiction of the molecular structure of 3-4................................................................. 35

**Figure 3.7** Variable temperature $^{31}$P/$^1$H NMR study depicting the conversion between 3-6 and 3-7 in a $^{13}$CO$_2$ filled NMR tube ......................................................................................................................... 38

**Figure 3.8** $^{31}$P/$^1$H NMR spectra depicting the activation of $^{13}$CO$_2$ by Ph$_2$Si(OTf)$_2$ and different stoichiometric equivalents of PEt$_3$........................................................................................................................................ 40
Figure 3.9 $^1$H NMR spectrum at -40 °C of reaction between Ph$_2$Si(OTf)$_2$, 3 eq. PEt$_3$, and CO$_2$ in CD$_2$Cl$_2$...

Figure 3.10 $^1$H and $^{31}$P{$^1$H} NMR spectra of mixture of Me$_3$SiOTf with P$^t$Bu$_3$ before (bottom) and after (top) $^{13}$CO$_2$ addition at 25 °C...

Figure 3.11 Variable temperature $^{31}$P{$^1$H} NMR spectra of 1:2 stoichiometric mixtures of Ph$_2$Si(OTf)$_2$ and P$^t$Bu$_3$ pressurized with $^{13}$CO$_2$...

Figure 3.12 $^{31}$P{$^1$H} NMR spectra of reaction between Et$_3$SiNTf$_2$, 2 HP$^t$Bu$_2$, and CO$_2$ in CD$_2$Cl$_2$...

Figure 4.1 Increasing Lewis acidity by silacycle ring strain...

viii
List of Schemes

**Scheme 1.1** Early examples of non-classical reactivity of Lewis acids and bases.......................... 2

**Scheme 1.2** Hydrogen activation by FLPs; a) the first example of reversible metal-free H₂ activation and b) the proposed mechanism of FLP-mediated catalytic imine hydrogenation....... 3

**Scheme 1.3** Selected examples of a) alkyne, b) carbon dioxide, and c) nitrous oxide activation by B/P FLP systems................................................................................................................................. 4

**Scheme 1.4** a) Nucleophilic aromatic substitution of the trityl cation with sterically hindered phosphines and b) activation of ether α C-H bonds by a cyclohexadienyl-phosphonium cation... 6

**Scheme 1.5** a) Disulfide cleavage by a carbon-based FLP and b) dihydrogen activation with a N-methylacridinium Lewis acid........................................................................................................... 6

**Scheme 1.6** Examples of silicon Lewis acids in FLP chemistry................................................................. 7

**Scheme 2.1** Preparation of silyl triflates by metathesis with AgOTf or protodesilylation.............. 9

**Scheme 2.2** Preparation of compounds 2-6 and 2-7.................................................................................. 12

**Scheme 2.3** Friedel Crafts cyclization of 1,1-diphenylethylene................................................................. 14

**Scheme 2.4** Attempted FLP chemistry with 2-6 and 2-7 ................................................................. 16

**Scheme 3.1** Stoichiometric reduction of CO₂ to formic acid and methanol by a silylium cation 29

**Scheme 3.2** Stoichiometric CO₂ reduction with amine-boranes utilizing a) a bis-borane and b) an alane FLP system .................................................................................................................................... 30

**Scheme 3.3** FLP catalyzed CO₂ reduction with a) Et₃SiH and b) HBcat.............................................. 31

**Scheme 3.4** Proposed mechanism of CO₂ activation by silyl triflates and TMP ...................... 34

**Scheme 3.5** CO₂ activation employing PEt₃ and Me₃SiOTf.................................................................. 37
Scheme 3.6 CO₂ activation employing PEt₃ and silicon Lewis acids in the form of R₃SiX (X=OTf, NTf₂) ................................................................. 39

Scheme 3.7 Proposed stepwise single and double activation of CO₂ with Ph₂Si(OTf)₂ and PEt₃ 41

Scheme 3.8 Previous examples of FLP-type “double” activation of small molecules ............... 42

Scheme 3.9 CO₂ activation employing P₃Bu₃ and silicon Lewis acids in the form of R₃SiX (X=OTf, NTf₂) ....................................................................................................................... 45

Scheme 3.10 Proposed decomposition of 3-18 by reaction with P₃Bu₃ ..................................... 46

Scheme 3.11 Proposed stepwise single and double activation of CO₂ at low temperature with Ph₂Si(OTf)₂ and P₃Bu₃ .............................................................................................................. 46

Scheme 3.12 Formation of 3-20 using P₃Bu₃ or HP₃Bu₂ .......................................................... 49

Scheme 3.13 Reaction of 3-17 with excess Me₂NHBH₃ ............................................................. 50
List of Abbreviations and Symbols

Å Ångstrom (10^{-10} m)
a hyperfine coupling constant
abs coeff absorption coefficient, \( \mu \) (mm^{-1})
anal. calc. calculated (elemental) analysis
atm atmosphere (1.013 x 10^5 Pa)
Ar aryl
9-BBN 9-Borabicyclo[3.3.1]nonane
br broad
Bu \( n \)-butyl (-CH\(_2\)(CH)\(_2\)CH\(_3\))
calc calculated
cat catalyst, catechol
C Celcius
Cy cyclohexyl (-C\(_6\)H\(_{11}\))
d doublet
d (calc) density calculated (g cm\(^{-3}\))
DCM dichloromethane (CH\(_2\)Cl\(_2\))
dd doublet of doublets
def2TZV a basis set
DFT density functional theory
DMAP 4-dimethylaminopyridine
dppe 1,2-bis(diphenylphosphino)ethane
EA elemental analysis
EPC electrophilic phosphonium cation
EPR electron paramagnetic resonance
eq. equivalents
Et ethyl (-CH₂CH₃)
FLP frustrated Lewis pair
g grams
HOMO highest occupied molecular orbital
HMBC heteronuclear multiple bond correlation
Hz Hertz (s⁻¹)
I nuclear spin
i ipso
IDipp 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene
¹Pr isopropyl (-CH(CH₃)₂)
J coupling constant (Hz)
K Kelvin
kJ/mol kilojoule per mole
L Lewis base; neutral donor
LA Lewis acid
LUMO lowest unoccupied molecular orbital
m meta
M molar (mol L⁻¹)
m multiplet
Me methyl (-CH₃)
Mes mesityl (-C₆H₂(CH₃)₃)
mg milligram (10⁻³ g)
MHz megahertz (10⁶ Hz)
mL millilitre (10⁻³ L)
mol mole (6.022 x 10⁻²³)
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>NBO</td>
<td>natural bond orbital</td>
</tr>
<tr>
<td>NHC</td>
<td>N-heterocyclic carbene</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>NR</td>
<td>no reaction</td>
</tr>
<tr>
<td>NTf$_2$</td>
<td>bis(trifluoromethane)sulfonamide; triflimide (-N(SO$_2$CF$_3$)$_2$)</td>
</tr>
<tr>
<td>Nu</td>
<td>nucleophile</td>
</tr>
<tr>
<td>o</td>
<td>ortho</td>
</tr>
<tr>
<td>OTf</td>
<td>trifluoromethanesulfonate; triflate (-OSO$_2$CF$_3$)</td>
</tr>
<tr>
<td>OTs</td>
<td>tosylate (-OSO$_2$C$_6$H$_4$CH$_3$)</td>
</tr>
<tr>
<td>p</td>
<td>para</td>
</tr>
<tr>
<td>Ph</td>
<td>phenyl (C$_6$H$_5$)</td>
</tr>
<tr>
<td>POV-Ray</td>
<td>Persistence of Vision Raytracer</td>
</tr>
<tr>
<td>ppm</td>
<td>parts per million</td>
</tr>
<tr>
<td>q</td>
<td>quartet</td>
</tr>
<tr>
<td>R</td>
<td>substituent</td>
</tr>
<tr>
<td>reflns</td>
<td>reflections</td>
</tr>
<tr>
<td>RT</td>
<td>room temperature</td>
</tr>
<tr>
<td>s</td>
<td>singlet; second</td>
</tr>
<tr>
<td>sept</td>
<td>septet</td>
</tr>
<tr>
<td>SIMes</td>
<td>1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene</td>
</tr>
<tr>
<td>SLA</td>
<td>silicon Lewis acid</td>
</tr>
<tr>
<td>tBu</td>
<td>tert-butyl (-C(CH$_3$)$_3$)</td>
</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran (C$_4$H$_8$O)</td>
</tr>
<tr>
<td>TMP</td>
<td>2,2,6,6-tetramethylpiperidine (C$<em>9$H$</em>{19}$N)</td>
</tr>
<tr>
<td>trityl</td>
<td>triphenylmethyl (CPh$_3$)</td>
</tr>
<tr>
<td>V</td>
<td>volume ($\AA^3$)</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>----------------------------</td>
</tr>
<tr>
<td>wB97XD</td>
<td>a functional for DFT</td>
</tr>
<tr>
<td>wt</td>
<td>weight</td>
</tr>
<tr>
<td>X</td>
<td>anion or substituent (e.g., Cl, Br, OTf, NTf₂)</td>
</tr>
<tr>
<td>Z</td>
<td>formula units</td>
</tr>
<tr>
<td>δ</td>
<td>chemical shift (ppm)</td>
</tr>
<tr>
<td>Δ</td>
<td>change</td>
</tr>
<tr>
<td>κⁿ</td>
<td>denticity</td>
</tr>
<tr>
<td>μ</td>
<td>bridging</td>
</tr>
<tr>
<td>°</td>
<td>degree</td>
</tr>
<tr>
<td>†</td>
<td>transition state</td>
</tr>
<tr>
<td>%</td>
<td>percent</td>
</tr>
<tr>
<td>~</td>
<td>approximately</td>
</tr>
</tbody>
</table>
1 Introduction

1.1 Overview of Frustrated Lewis Pairs

In 1923, Gilbert Lewis described acids and bases as species that can act as electron pair acceptors or donors respectively.\(^1\) Classical reactivity models of Lewis acids and bases predict the interaction of the electrons in the highest occupied molecular orbital (HOMO) of the Lewis base with the lowest unoccupied molecular orbital (LUMO) of the Lewis acid to form a dative bond. An example of this is the simple coordination complex \(\text{H}_3\text{NBH}_3\), which is formed by donation of ammonia’s lone pair of electrons to the vacant p-orbital of BH\(_3\). Dative bonding provides stabilization by quenching the reactivity of the Lewis acid and base components and producing a donor-acceptor adduct with a lower energy HOMO (Figure 1.1a). This concept of Lewis acids and bases is key in our understanding of much of modern transition metal and main group chemistry.\(^2,3\)

Over the course of the 20\(^{th}\) century, deviations from this reactivity model were observed. In 1942, H. C. Brown reported that no adduct formation was observed between BMe\(_3\) and lutidine.\(^4\) This stood in contrast to the anticipated donor-acceptor adduct, which forms for similar but less sterically encumbered systems such as BF\(_3\) and lutidine (Scheme 1.1a). Subsequent work by Wittig and Rückert in 1950 noted that when [Na][CPh\(_3\)] was added to the THF adduct of triphenylborane, ring-opening of THF occurred rather than adduct formation (Scheme 1.1b).\(^5\) In 1966, Tochtermann reported that the trityl anion and triphenylborane could undergo 1,2-addition to 1,3-butadiene (Scheme 1.1c).\(^6\)

These observations marked the beginnings of “frustrated Lewis pair” chemistry, a term later coined by Stephan and coworkers to describe combinations of sterically hindered Lewis acids and bases which are unable to form adducts.\(^7\) Such systems can exploit the unquenched LUMO and HOMO of the Lewis acid and base components to effect non-classical reactivity (Figure 1.1b).\(^8\)
Scheme 1.1 Early examples of non-classical reactivity of Lewis acids and bases

In the mid-2000s, Stephan and coworkers demonstrated that the unquenched reactivity of FLPs could be applied in the activation of small molecules. In 2006, it was reported that the linked phosphine-borane species Mes₂P(C₆F₄)B(C₆F₅)₂ could heterolytically cleave dihydrogen to yield Mes₂PH(C₆F₄)BH(C₆F₅)₂ (Scheme 1.2a). This zwitterionic salt was found to release hydrogen gas when heated to elevated temperatures, representing the first example of metal-free reversible
hydrogen activation. Since this landmark discovery, H\textsubscript{2} activation has been extended to a number of other FLP systems and has even been used for the catalytic hydrogenation of unsaturated substrates such as olefins, enamines, silyl enol ethers, ketones, N-protected nitriles, and imines (Scheme 1.2b).\textsuperscript{10-15} Of particular note is the stoichiometric FLP-mediated hydrogenation of the aromatic rings of anilines to cyclohexylammonium derivatives.\textsuperscript{16}

![Scheme 1.2 Hydrogen activation by FLPs; a) the first example of reversible metal-free H\textsubscript{2} activation and b) the proposed mechanism of FLP-mediated catalytic imine hydrogenation](image)

Further studies into frustrated Lewis pair systems have revealed a requirement that the relative acidity and basicity of the pair must fall within a range of tolerance; the use of a weaker Lewis acid may necessitate a stronger Lewis base partner to observe comparable reactivity towards small molecules and \textit{vice versa}.\textsuperscript{17} It should also be noted that in certain cases, classical Lewis pairs can exhibit FLP reactivity; this is usually attributed to weak or reversible adduct formation as well as solvent-induced adduct dissociation.\textsuperscript{18,19} A notable example of this is reversible hydrogen activation by B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} and diethyl ether.\textsuperscript{20}

In a manner similar to transition metals, an FLP can activate hydrogen through the dual role of its constituents which can simultaneously donate and accept electron density.\textsuperscript{8} Studies by the
groups of Papai\textsuperscript{8,21} and Grimme\textsuperscript{22} have demonstrated that the heterolytic cleavage of H\textsubscript{2} proceeds via the initial polarization of the dihydrogen molecule in an “encounter complex.” This is followed by donation of the \(\sigma_{\text{H}_2}\) electron pair to the vacant orbital of the Lewis acid, while the filled HOMO of the Lewis base donates in to \(\sigma_{\text{H}_2}^*\), resulting in H-H bond cleavage.\textsuperscript{23} This “ambiphilic” activation motif is not limited to only dihydrogen; indeed, the unquenched donor/acceptor abilities of FLPs also allow for activation of other small molecules including N\textsubscript{2}O,\textsuperscript{24} CO\textsubscript{2},\textsuperscript{25} alkenes,\textsuperscript{26} and alkynes\textsuperscript{27} (Scheme 1.3).

![Scheme 1.3](image)

**Scheme 1.3** Selected examples of a) alkyne, b) carbon dioxide, and c) nitrous oxide activation by B/P FLP systems

### 1.2 Beyond Boron: Modulating the Identity of the Lewis Acid

Numerous Lewis bases have been employed in FLP chemistry, including alkyl amines,\textsuperscript{28} anilines,\textsuperscript{16} phosphines,\textsuperscript{9,17} carbenes,\textsuperscript{29} ethers,\textsuperscript{20} ketones,\textsuperscript{30} sulfides,\textsuperscript{31} and telluroethers\textsuperscript{32} as well as more exotic bases such as carbodiphosphoranes,\textsuperscript{33} silylenes,\textsuperscript{34} and boron anions.\textsuperscript{35} The breadth of Lewis acids explored, however, has been more limited. To date, the majority of FLP chemistry has utilized group 13 Lewis acids, most notably the commercially available Lewis acid B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} as well as related derivatives. Aluminum-based FLPs have also been applied in the activation of hydrogen, carbon dioxide, olefins, and nitrous oxide.\textsuperscript{36-39}
1.2.1 Group 15 Lewis Acids

Of recent interest in our group is the expansion of FLP chemistry to also include group 15-centred Lewis acids. In 2012, Hounjet et al. demonstrated the utility of phosphorus as a Lewis acid for small molecule activation.\(^{40}\) It was reported that the P-N bonds of strained amidophosphoranes could sequester CO\(_2\) by a formal insertion process. This reactivity was compared to a frustrated Lewis pair, as the amidophosphoranes contained both acidic and basic P,N functionalities. More recently, the highly electrophilic phosphonium cations (EPCs) \([\text{C}_6\text{F}_5_3\text{PF}]^+\) and \([\text{(SIMes)}\text{PPh}_2\text{F}]^{2+}\) have been shown to be effective Lewis acid catalysts for the hydrodefluorination of fluoroalkanes and the hydrosilylation or transfer-hydrogenation of olefins and alkynes.\(^{41-44}\) Studies into their further use for small molecule activation and FLP-type transformations are currently underway. The remarkable Lewis acidity of these EPCs can be attributed to strongly electron-withdrawing substituents as well as an energetically low-lying \(\sigma^*_{(P-F)}\) orbital. Since these initial reports, Gabbai and coworkers have also expanded this chemistry to include the air-stable, Lewis acidic stibonium cation \([\text{Sb(C}_6\text{F}_5)_4]^+\) which can activate C-F bonds and perform catalytic hydrodefluorination of fluoroalkanes.\(^{45}\)

1.2.2 Group 14 Lewis Acids

Within group 14, an obvious carbon-based analogue of \(\text{B(C}_6\text{F}_5)_3\) is the isoelectronic trityl cation \([\text{CPh}_3]^+\), which is strongly Lewis acidic and hydridophilic at the central carbon atom. Studies conducted by Stephan and coworkers in 2006 revealed that the trityl cation forms the anticipated donor-acceptor adducts with small bases, such as PMe\(_3\) and PPh\(_3\); however, with bulkier phosphines, nucleophilic attack is observed at the \(para\) position to yield cyclohexadienyl-phosphonium cations \([\text{R}_3\text{P}-(\text{C}_6\text{H}_5)\text{CPh}_2]^+\). When \(R = \text{iPr}\), rearrangement of this species is observed to allow for rearomatization (Scheme 1.4a).\(^{46}\) Recently, it has been noted by Holthausen et al. that the cyclohexadienyl-phosphonium cation \([\text{Bu}_2\text{PH}-(\text{C}_6\text{H}_5)\text{CPh}_2]^+\) can still behave as an FLP and reacts with ethers to activate the \(\alpha\) C-H bond (Scheme 1.4b).\(^{47}\)
Scheme 1.4  a) Nucleophilic aromatic substitution of the trityl cation with sterically hindered phosphines and b) activation of ether $\alpha$ C-H bonds by a cyclohexadienyl-phosphonium cation

Other group 14-centered Lewis acids have also been successfully employed in FLP-type transformations. Alcarazo and coworkers demonstrated that an electron-poor allene could serve as the Lewis acid partner for the heterolytic S-S bond cleavage of disulfides (Scheme 1.5a).\(^{48}\)

The Ingleson group has also very recently described hydrogen activation by N-methylacridinium salts as well as their use in the catalytic reduction of imines (Scheme 1.5b).\(^{49}\)

Scheme 1.5  a) Disulfide cleavage by a carbon-based FLP and b) dihydrogen activation with a N-methylacridinium Lewis acid

The application of silicon Lewis acids (SLAs) in frustrated Lewis pair chemistry has predominantly focused on silylium ions: trivalent silicon cations that are valence isoelectronic
with boranes. In 2013, the Müller group demonstrated that the bulky silylium cation [(C₆Me₅)₃Si][B(C₆F₅)₄] could cleave dihydrogen with triaryl or trialkyl phosphines as the Lewis base partner. Similarly, mixtures of [(C₆Me₅)₃Si][B(C₆F₅)₄] and sterically hindered trialkylphosphines could be used to activate carbon dioxide (Scheme 1.6a). Further investigations by Ashley and coworkers have shown that silylium-phosphine adducts can also display frustrated behavior, with hydrogen activation being possible upon solvent-assisted adduct dissociation at high temperatures.

To our knowledge, only one previous example exists of four-coordinate SLAs being applied in FLP-type chemistry. In 2010, the Manners group reported that combinations of trimethylsilyl triflate (Me₃SiOTf) and sterically hindered amine or pyridine bases could be used to dehydrogenate amine–borane and phosphine–borane adducts (Scheme 1.6b). These combinations of Lewis acids and bases, however, were not found to react with hydrogen.

Scheme 1.6 Examples of silicon Lewis acids in FLP chemistry

1.3 Scope of Thesis

Aside from trivalent silylium cations, the use of SLAs for FLP chemistry has remained largely unexplored. As will be described in this thesis, the objective of this work was to further investigate the ability of tetracoordinate SLAs to effect FLP-type transformations. Four-coordinate species were of particular interest as they exhibit greater stability than their silylium counterparts. Furthermore, a four-coordinate framework allows for the preparation of more structurally diverse Lewis acids. The synthesis and reactivity of tetracoordinate silicon Lewis acids in the forms of RSi(C₆F₅)₃ (R= H, F) and R₄-nSiXₙ (X = OTf, NTf₂, n= 1 or 2) is described.
2 Synthesis and Reactivity of Four-Coordinate Silicon Lewis Acids

2.1 Introduction

2.1.1 Silicon: Properties and Differences from Carbon

Silicon is a non-toxic, cheap, and abundant element, composing 27.7% of the earth’s crust. Although silicon and carbon are both group 14 elements, silicon-centred species display different chemical properties than their lighter carbon congeners. Silicon is a more electropositive element than carbon, with an electronegativity of 1.90 on the Pauling scale (c.f. C: 2.55 and H: 2.20). As a result, $\delta^+\text{Si}^--\text{C}\delta^-$ and $\delta^+\text{Si}^--\text{H}\delta^-$ bonds are polarized such that silicon experiences partial positive charge. Silicon’s larger atomic radius relative to carbon yields longer Si-C bonds compared to C-C bonds and also results in less effective orbital overlap. Electron deficiency at silicon is not effectively stabilized by hyperconjugation or p-conjugation, which are known to provide stabilization for cationic carbon centres. Consequently, silicon Lewis acids often display increased electrophilicity compared to their carbon-based analogues.

Much of the chemistry of organosilicon species is governed by silicon’s ability to become hypervalent; complexes of five or six coordinate silicon are not uncommon, and in some cases even higher coordination numbers have been reported. Nucleophilic substitution reactions at silicon proceed via association mechanisms, with five coordinate intermediates often being isolable. This stands in contrast to $\text{S}_2\text{2}$ reactions with at carbon centres which proceed via five-coordinate [Nu--CR$_3$--X]$^+$ transition states. Silicon chemistry is also greatly influenced by the strong oxophilicity and fluorophilicity of silicon (bond strengths: Si-F 565 kJ/mol; Si-O 452 kJ/mol); this allows for the formation of these bonds to act as thermodynamic driving forces.

2.1.2 Applications of Silicon Lewis Acids

While trivalent silylium cations have only been realized in recent decades, four-coordinate silicon Lewis acids have played an important role in organic chemistry throughout the 20th century. SLAs such as silyl chlorides and silyl triflates are useful silylating reagents and synthetic building blocks for the preparation of organosilicon compounds. Additionally, SLAs have been used as catalysts for a number of organic carbon-carbon bond forming reactions; examples include the Diels-Alder reaction, Mukaiyama aldol, and couplings.
of acetals or acetal-like compounds with nucleophiles. Upon activation by Lewis bases to form five-coordinate siliconate species, organosilicon compounds can also be utilized to transfer organic substituents such as allyl, -CF<sub>3</sub>, and -C<sub>6</sub>F<sub>5</sub> to electrophiles.

In the case of neutral SLAs in the form R<sub>3</sub>SiX, the identity of X strongly impacts the observed Lewis acidic properties. The qualitative acidity of commonly used SLAs is as follows: R<sub>3</sub>SiCl < R<sub>3</sub>SiOTs < R<sub>3</sub>SiBr < R<sub>3</sub>SiOTf < R<sub>3</sub>SiI < R<sub>3</sub>SiNTf<sub>2</sub>. This ranking closely relates to the coordinating ability of X, whereby more weakly coordinating anions give rise to more Lewis acidic silicon centres. In the research presented, Lewis acids in the forms R<sub>3</sub>SiOTf and R<sub>3</sub>SiNTf<sub>2</sub> are explored due to their relatively high Lewis acidity; furthermore, the OTf and NTf<sub>2</sub> substituents proved to be convenient handles to monitor by <sup>19</sup>F NMR spectroscopy.

The synthesis and reactivity of electron deficient silanes of the form RSi(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (R= H, F) is also described. The tendency of silicon to expand its coordination number to form hypervalent species is enhanced by the presence of multiple electron-withdrawing substituents. Consequently, it was of interest to investigate if these SLAs could activate small molecules via associative five-coordinate species.

### 2.2 Results and Discussion

#### 2.2.1 Synthesis of Four-Coordinate Silicon Lewis Acids

Two methodologies were employed for the synthesis of silyl triflates. These were (1) metathesis of silver triflate (AgOTf) with the corresponding silyl chloride and (2) protodesilylation using triflic acid (HOTf) (Scheme 2.1).

![Scheme 2.1 Preparation of silyl triflates by metathesis with AgOTf or protodesilylation](image)

Protodesilylation is a well-established method of preparing silyl triflates. It allows for the generation of Lewis acids in the form of R<sub>3</sub>SiOTf by selective bond cleavages of R<sub>3</sub>Si-Y with HOTf. The ease of cleavage of Y by strong Brønsted acids decreases in the order Y= allyl >
phenyl $>$ C1$>$ H $>>$ alkyl.\textsuperscript{72} As phenyl groups have a high propensity to undergo protodesilylation relative to other substituents, metathesis with AgOTf proved to be a useful approach for the preparation of phenyl-containing silyl triflates.

A solution of Ph\textsubscript{2}SiCl\textsubscript{2} was added to two stoichiometric equivalents of AgOTf. After stirring in the dark for 24 hours, the resulting suspension was filtered to remove the AgCl byproduct and the volatiles were removed \textit{in vacuo} to yield a white solid. Single crystals suitable for X-ray diffraction analysis revealed the identity of this species to be the bis-triflate Ph\textsubscript{2}Si(OTf)\textsubscript{2} (\textbf{2-1}), which was obtained as a powder in 92% yield (\textbf{Figure 2.1}).

\textbf{Figure 2.1} POV-Ray depiction of the molecular structure of \textbf{2-1}. C: black, O: red, F: pink, Si: aquamarine, S: yellow. H atoms omitted for clarity.

The Lewis acid Ph\textsubscript{3}Si(OTf) was synthesized by a modified literature preparation.\textsuperscript{73} A suspension of AgOTf in CH\textsubscript{2}Cl\textsubscript{2} was treated with one stoichiometric equivalent of Ph\textsubscript{3}SiCl. This mixture was stirred for 12 hours and, following workup, Ph\textsubscript{3}Si(OTf) (\textbf{2-2}) was obtained as a white solid in 78% yield. The solid-state molecular structure is displayed in \textbf{Figure 2.2}. The \textsuperscript{1}H NMR spectra of \textbf{2-1} and \textbf{2-2} exhibit the anticipated phenyl resonances, while the \textsuperscript{19}F\\{\textsuperscript{1}H\} NMR spectra display signals indicative of a bound triflate at $\delta_F = -76.10$ and $\delta_F = -76.87$ respectively.
Figure 2.2 POV-Ray depiction of the molecular structure of 2-2. C: black, O: red, F: pink, Si: aquamarine. H atoms omitted for clarity.

The 1:2 stoichiometric reaction of HSiPhCl$_2$ with AgOTf proceeded in an analogous fashion, affording HSiPh(OTf)$_2$ (2-3), a yellow oil, in 81% yield. The $^1$H NMR spectrum of 2-3 displays a distinctive Si-H resonance at $\delta_H = 5.74$ with $^{29}$Si satellites ($^1J_{HSi} = 310$ Hz) and the $^{19}$F{$^1$H} NMR spectrum shows a resonance corresponding to a bound triflate at $\delta_F = -76.16$.

The protodesilylation approach was utilized for the synthesis of the Lewis acids (C$_6$F$_5$)$_3$Si(OTf) and Et$_3$SiNTf$_2$. For (C$_6$F$_5$)$_3$Si(OTf) (2-4), the previously reported literature preparation from PhSi(C$_6$F$_5$)$_3$ and HOTf was followed.$^{74}$ Et$_3$SiNTf$_2$ (2-5) was prepared by treatment of the strong acid HNTf$_2$ with an excess of neat HSiEt$_3$. After reaction completion and removal of excess silane in vacuo, Et$_3$SiNTf$_2$ was isolated as a colourless oil in 98% yield.

The $^1$H NMR spectrum of Et$_3$SiNTf$_2$ (2-5) in CD$_2$Cl$_2$ was complex and displayed multiple sets of ethyl resonances, while the $^{19}$F{$^1$H} NMR spectrum displayed two broad triflimide resonances. The complexity of these spectra can be attributed to interactions of 2-5 with the solvent. This, however, did not preclude the use of dichloromethane as a solvent for subsequent reactions, as this solvent interaction was not observed in the presence of other donors. When 2-5 was examined by NMR spectroscopy in C$_6$D$_5$Br, the spectra were much simpler, displaying only the anticipated ethyl resonances as well as a single $^{19}$F{$^1$H} NMR triflimide resonance. The
The synthesis of another silyl triflimide, Ph$_3$SiNTf$_2$, was attempted by the 1:1 stoichiometric reaction of Ph$_3$Si(allyl) with HNTf$_2$; this, however, yielded a mixture of products.

The electron-deficient silanes HSi(C$_6$F$_5$)$_3$ (2-6) and FSi(C$_6$F$_5$)$_3$ (2-7) were also synthesized. Compound 2-6 was prepared by the known literature procedure using a Grignard reagent and HSiCl$_3$ (Scheme 2.2a).$^{75}$ Although compound 2-7 was also previously reported,$^{76}$ it was prepared by a different method; (C$_6$F$_5$)$_3$Si(OTf) was treated with the fluoride source [NBu$_4$][BF$_4$] (Scheme 2.2b). The solid-state structure of 2-7 displayed in Figure 2.3.

![Scheme 2.2 Preparation of compounds 2-6 and 2-7](image)

![Figure 2.3 POV-Ray depiction of the molecular structure of 2-7. C: black, F: pink, Si: aquamarine.](image)
2.2.2 Gutmann-Beckett Quantification of Lewis Acidity

One of the most commonly applied methodologies to assess Lewis acidity is the Gutmann-Beckett method.\textsuperscript{77,78} This method involves the coordination of triethylphosphine oxide (OPEt\textsubscript{3}) to the Lewis acid of interest. The resulting adduct is then examined by \textsuperscript{31}P NMR spectroscopy and its chemical shift is compared to that of free OPEt\textsubscript{3} (δ\textsubscript{P} = 50.4 in CD\textsubscript{2}Cl\textsubscript{2}). A greater downfield shift in the \textsuperscript{31}P resonance typically confers greater Lewis acidity.

![Figure 2.4](image)

**Figure 2.4** Lewis acidity determination with the Gutmann-Beckett method

Gutmann-Beckett Lewis acidity tests were conducted in CD\textsubscript{2}Cl\textsubscript{2} for a variety of silicon Lewis acids. A 3:1 Lewis acid:OPEt\textsubscript{3} ratio was utilized to ensure full complexation of OPEt\textsubscript{3}. The results are summarized in Table 2.1.

<table>
<thead>
<tr>
<th>Lewis Acid</th>
<th>δ\textsubscript{P}</th>
<th>Δδ\textsubscript{P}</th>
</tr>
</thead>
<tbody>
<tr>
<td>FSi(C\textsubscript{6}F\textsubscript{5})\textsubscript{3}</td>
<td>54.8 (br)</td>
<td>4.4</td>
</tr>
<tr>
<td>HSi(C\textsubscript{6}F\textsubscript{5})\textsubscript{3}</td>
<td>58.4 (br)</td>
<td>8.0</td>
</tr>
<tr>
<td>(C\textsubscript{6}F\textsubscript{5})\textsubscript{3}Si(OTf)</td>
<td>106.4</td>
<td>56.0</td>
</tr>
<tr>
<td>Me\textsubscript{3}Si(OTf)</td>
<td>91.4</td>
<td>41.0</td>
</tr>
<tr>
<td>Ph\textsubscript{3}Si(OTf)</td>
<td>95.9</td>
<td>45.5</td>
</tr>
<tr>
<td>Ph\textsubscript{2}Si(OTf)\textsubscript{2}</td>
<td>104.2</td>
<td>53.8</td>
</tr>
<tr>
<td>PhHSi(OTf)\textsubscript{2}</td>
<td>96.5</td>
<td>46.2</td>
</tr>
<tr>
<td>Et\textsubscript{3}SiNTf\textsubscript{2}</td>
<td>90.3</td>
<td>39.9</td>
</tr>
<tr>
<td>[Et\textsubscript{3}Si][B(C\textsubscript{6}F\textsubscript{5})\textsubscript{4}]\textsuperscript{a}</td>
<td>88.4</td>
<td>40.3</td>
</tr>
<tr>
<td>B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3}</td>
<td>77.0</td>
<td>26.6</td>
</tr>
<tr>
<td>[FP(C\textsubscript{6}F\textsubscript{5})\textsubscript{3}][B(C\textsubscript{6}F\textsubscript{5})\textsubscript{4}]</td>
<td>90.8</td>
<td>40.4</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Measurement performed in C\textsubscript{6}D\textsubscript{5}Br due to instability in DCM, Δδ\textsubscript{P} relative to chemical shift of OPEt\textsubscript{3} in C\textsubscript{6}D\textsubscript{5}Br (δ\textsubscript{P} = 48.1)
Using the Lewis acidity of B(C₆F₅)₃ as a point of reference (Δδₚ = 26.6), the measured Δδₚ values for the silanes FSi(C₆F₅)₃ (Δδₚ = 4.4) and HSi(C₆F₅)₃ (Δδₚ = 8.0) imply relatively weak Lewis acidities. In contrast, the large changes in chemical shift (Δδₚ) observed for the silyl triflates and Et₃SiNTf₂ suggest they are stronger Lewis acids than B(C₆F₅)₃ and even [FP(C₆F₅)₃][B(C₆F₅)₄] in some cases. These counterintuitive results can be attributed to the lability of the triflate and triflimide anions, which can dissociate from silicon upon coordination of a donor. ¹⁹F{¹H} NMR spectroscopy provides support for this; the -CF₃ resonances of both Me₃SiOTf and Et₃SiNTf₂ shift upfield upon binding of OPEt₃, which is consistent with anion dissociation.

The measured Δδₚ values are comparable between Me₃SiOTf (2-8), Et₃SiNTf₂, and [Et₃Si][B(C₆F₅)₄], despite known differences in the Lewis acidities of these compounds. The lack of dependence on anion identity can once again be rationalized by anion dissociation. As a consequence, the measured Δδₚ values for silyl triflates and triflimides are more representative of the Lewis acidity of their corresponding silylium cations. As the Gutmann-Beckett method assigns artificially large measurements of Lewis acidity to silyl triflates and triflimides, this precludes the meaningful comparison of these measurements to other Lewis acids, such as boranes or phosphonium cations, which do not contain labile substituents.

2.2.3 Exploring the Reactivity of Four-Coordinate Silicon Lewis Acids

2.2.3.1 Friedel-Crafts Dimerization of 1,1-Diphenylethylene

To gain further insights into the Lewis acidic properties of these compounds, Lewis acids 2-1 - 2-8 were examined for their effectiveness as catalysts for the Friedel-Crafts type dimerization of diphenylethylene (Scheme 2.3). This cyclization reaction is known to occur in the presence of strong Lewis acids such as B(C₆F₅)₃ and [FP(C₆F₅)₃][B(C₆F₅)₄].
Addition of these catalysts (5 mol%) to a CD₂Cl₂ solution of 1,1-diphenylethylenne at room temperature afforded varying yields of the indene-type product (Table 2.2).

**Table 2.2** Friedel-Crafts dimerization of diphenylethylenne by Si Lewis acid catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Time (h)</th>
<th>Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-1 Ph₂Si(OTf)₂</td>
<td>6</td>
<td>&gt;99</td>
</tr>
<tr>
<td>2-2 Ph₃Si(OTf)</td>
<td>48</td>
<td>94</td>
</tr>
<tr>
<td>2-4 (C₆F₅)₃Si(OTf)</td>
<td>6</td>
<td>&gt;99</td>
</tr>
<tr>
<td>2-5 Et₃SiNTf₂</td>
<td>24</td>
<td>67</td>
</tr>
<tr>
<td>2-6 HSi(C₆F₅)₃</td>
<td>24</td>
<td>0</td>
</tr>
<tr>
<td>2-7 FSi(C₆F₅)₃</td>
<td>24</td>
<td>0</td>
</tr>
<tr>
<td>2-8 Me₃Si(OTf)</td>
<td>48</td>
<td>20</td>
</tr>
</tbody>
</table>

Ph₂Si(OTf)₂ and (C₆F₅)₃Si(OTf) proved to be the most effective catalysts for this transformation, achieving complete conversion in under 6 hours. Catalysts 2-2, 2-5, and 2-8 gave incomplete conversion after 24 hours. In the case of Et₃SiNTf₂, this can be attributed to decomposition of the catalyst in solution. For Ph₃Si(OTf), the catalysis is slow with higher conversions (94%) being observed after 48 hours. When FSi(C₆F₅)₃ and HSi(C₆F₅)₃ were used as the catalysts for the Friedel-Crafts dimerization, no conversion to the cyclization product was observed after 24 hours at ambient temperature. These solutions remained colourless, showing no evidence of the bright green carbocation intermediate of the dimerization reaction.

### 2.2.3.2 Preliminary Reactions with Small Molecules

#### 2.2.3.2.1 Reactions Employing HSi(C₆F₅)₃ and FSi(C₆F₅)₃

Combinations of SLAs and sterically hindered bases were probed for reactivity towards small molecules typical of FLP chemistry. When HSi(C₆F₅)₃ (2-6) or FSi(C₆F₅)₃ (2-7) was put under 4 atm of H₂ gas with one equivalent of P₃Bu₃ or tetramethylpiperidine (TMP), or an excess of tBuNCHPh, no reaction was observed. Similarly, no reaction occurred when 1:1 mixtures of 2-6 or 2-7 and P₃Bu₃ were exposed to CO₂, N₂O, or phenylacetylene (Scheme 2.4).
This lack of reactivity of 2-6 and 2-7 is consistent with the weak Lewis acidity indicated by the Gutmann-Beckett method. These examined Lewis pairs likely do not fall into the range of acidity/basicity required for small molecule activation.

In probing stronger Lewis base partners, it was found that treatment of 2-6 with the carbene SIMes led to the immediate formation of a deep blue-green solution. The $^{19}$F NMR spectrum of this solution displayed numerous broad resonances, unidentifiable decomposition products, and C$_6$F$_5$H resonances. EPR spectroscopy analysis revealed a signal, indicating the presence of a radical species (2-9) (Figure 2.5).
Numerous attempts to crystalize 2-9 were unsuccessful; thus, the structure of this radical has not been elucidated. The EPR spectra of 2-9 were consistently broad, regardless of the solvent used, concentration, or temperature. EPR simulations suggest that the unpaired electron has a g-value of 2.0068 and couples to a $I=1$ nucleus (a = 14.2 MHz) and a $I=1/2$ nucleus (a = 25.9 MHz). Given the composition of the starting materials, these nuclei are proposed to be $^{14}$N and $^{19}$F or $^1$H respectively. 2-9 is both air- and light-sensitive, with decomposition indicated by the rapid disappearance of the deep blue colour. When compound 2-9 is stored in the dark under inert atmosphere, it is indefinitely stable.

2.2.3.2.2 Reactions Employing Ph$_2$Si(OTf)$_2$ and (C$_6$F$_5$)$_3$Si(OTf)

The silyl triflates Ph$_2$Si(OTf)$_2$ (2-1) and (C$_6$F$_5$)$_3$Si(OTf) (2-4) were also examined for reactivity towards small molecules in the presence of sterically hindered bases. No reactivity was observed under 4 atm of H$_2$ gas when employing TMP, P$^t$Bu$_3$, or an excess of $^t$BuNCHPh as the Lewis base. Similarly, no reaction occurred between 2-1 or 2-4 with phenylacetylene and P$^t$Bu$_3$. These silyl triflates did, however, display reactivity towards CO$_2$ with sterically hindered Lewis bases; these findings will be described in depth in Chapter 3 of this thesis.

Exposure of 1:1 mixtures of 2-1 and trialkylphosphines (P$^t$Bu$_3$, PEt$_3$) to N$_2$O gas, resulted in partial conversion to the corresponding phosphine oxide adducts [Ph$_2$Si(OPR$_3$)(OTf)][OTf]. These were identified by resonances in the $^{31}$P NMR spectra at $\delta_p = 109.9$ and $\delta_p = 104.2$ for the
OP°Bu₃ and OPEt₃ adducts respectively. There was no evidence of intermediates containing a R₃P-(NNO) moiety as is observed for N₂O activation with borane/phosphine Lewis pairs.²⁴ For analogous B/P systems, thermolysis or photolysis is required for conversion of the isolable R₃P-(NNO)-B moiety to the borane-phosphine oxide adduct.

As slow oxidation of electron-rich phosphines by nitrous oxide has been previously noted,⁸⁰,⁸¹ it is believed that these reactions employing Ph₂Si(OTf)₂ proceed via simple oxidation of the phosphine and subsequent phosphine oxide coordination rather than generation of a transient N₂O sequestered species. Consequently, reactions with N₂O were not pursued further.

### 2.2.4 Coordination Complexes of Formal Ph₂Si²⁺

One approach to generating highly Lewis acidic species is the incorporation of positive charge. Cationic species often exhibit enhanced Lewis acidity relative to their neutral analogues. This is exemplified by the remarkable Lewis acidity of borenium,⁸²,⁸³ silylium,⁵⁵ and phosphonium cations.⁴¹ Looking beyond trivalent silylium cations, cationic silicon (IV) species can also be generated by coordination of neutral donors to four-coordinate silicon. Coordination complexes of Si(IV) commonly adopt coordination numbers of up to six; however, if anion dissociation occurs from these silicon donor-acceptor complexes, formally cationic species can be generated. For instance, reaction of silyl triflates (R₃SiOTf) with neutral Lewis bases (L) can yield either neutral hypervalent silicon complexes (R₃LₙSiOTf) (n= 1, 2) or base-stabilized silylium cations ([R₃SiLₙ][OTf]), depending on the strength of the donor and the sterics of the various substituents.⁸⁴,⁸⁵ We were interested in examining if dicationic Si(IV) complexes could be accessed from Ph₂Si(OTf)₂ by the replacement of the triflate substituents with neutral donors. A similar approach has previously been reported by Burford and coworkers to generate pnictogen (V) dications.⁸⁶

We initially investigated phosphines as neutral donors for Si(IV) as they represent a ubiquitous and versatile class of ligands for both transition metals and main group complexes. Our initial attempts in coordinating phosphines to Ph₂Si(OTf)₂ were unsuccessful; no adduct formation was observed using PMes₃ (Tolman cone angle of 212°), PPh₃ (145°), or even the less sterically encumbered phosphines PEt₃ (132°) and dppe (125°).⁸⁷ Consequently, less hindered donors were examined. Treatment of Ph₂Si(OTf)₂ with two equivalents of OPPh₃ led to the clean formation of a new product (2-10), as evidenced by a single resonance in ³¹P{¹H} NMR spectrum at δ_P = 58.9.
This resonance is downfield from free OPPh\(_3\) and indicates donor coordination to silicon. Additionally, the \(^{19}F\) NMR spectrum displays a single peak at \(\delta_F = -78.69\), indicative of a dissociated triflate anion, and the \(^{29}\text{Si}\{^1\text{H}\}\) resonance at \(\delta_{\text{Si}} = -28.0\) is consistent with four-coordinate silicon.\(^{88}\) These data support the formulation of 2-10 as the dication \([\text{Ph}_2\text{Si}(\text{OPPh}_3)_2][\text{OTf}]_2\), isolated in 99% yield.

Reaction of \(\text{Ph}_2\text{Si(OTf)}_2\) with two stoichiometric equivalents of \(\text{OPEt}_3\) proceeds in a similar manner. The \(^{31}\text{P}\) NMR spectrum of the reaction mixture displays a single product (2-11) with a signal at \(\delta_P = 101.8\). The \(^{19}F\) (\(\delta_F = -78.81\)) and \(^{29}\text{Si}\) NMR resonances (\(\delta_{\text{Si}} = -32.6\)) also indicate the presence of a four-coordinate silicon centre with dissociated triflate anions. Single crystal X-ray diffraction analysis confirmed the identity of 2-11 as \([\text{Ph}_2\text{Si(\text{OPEt}_3)_2}][\text{OTf}]_2\), obtained as a powder in 97% yield (Figure 2.7).

![Figure 2.6](image.png)

**Figure 2.6** POV-Ray depiction of the molecular structure of 2-11. C: black, O: red, F: pink, Si: aquamarine, P: orange; S: yellow. H atoms omitted for clarity.

The solid-state structure of 2-11 is consistent with the solution phase NMR data. Silicon is four-coordinate with a tetrahedral geometry. The two triflate counterions are fully dissociated from the silicon centre. Of note are the P-O and Si-O bond lengths of 1.563(4) Å and 1.659(5) Å respectively. This Si-O bond length is consistent with a single bond, while the P-O bond is
elongated from a formal double bond; this suggests that the +2 positive charge is distributed across both the phosphorus atoms and silicon.

To further probe the nature of the charge distribution, DFT calculations were undertaken with the help of Dr. Roman Dobrovetsky. Both the NBO and the Mulliken charges of the dicationic model complex [Ph₂Si(OPMe₃)]²⁺ were examined at the wB97XD/def2TZV level of theory. For both methods, it was found that both silicon and phosphorus atoms possess positive charge, with silicon possessing a greater magnitude of charge per atom (Si: 1.300 Mulliken charges, 2.076 NBO charges; P: 0.971 Mulliken charges per atom, 1.700 NBO charges per atom).

A donor exchange experiment was conducted to better understand the bonding between the phosphine oxide donors and the silicon centres in compounds 2-10 and 2-11 (Figure 2.8). A CD₂Cl₂ solution of 2-10 was treated with two equivalents of OPEt₃. The ³¹P{¹H} NMR spectrum of the reaction mixture revealed immediate formation of 2-11 and liberation of OPPh₃. The resonances attributable to 2-11 and OPPh₃ appear slightly broadened relative to pure samples of these species, suggesting a weak interaction in solution. This experiment highlights the lability of the phosphine oxide donors. Viewed through a dative bonding model, the weaker donor (OPPh₃) is exchanged for the stronger sigma donor (OPEt₃).

![Figure 2.7](image.png)

**Figure 2.7** ³¹P{¹H} NMR spectra depicting donor exchange following reaction of 2 eq. OPEt₃ with [Ph₂Si(OPPh₃)₂][OTf]₂
Base stabilized \( \text{Ph}_2\text{Si}^{2+} \) fragments can also be readily accessed by treatment of \( \text{Ph}_2\text{Si(OTf)}_2 \) with other neutral donors. For instance, the 1:2 stoichiometric of \( \text{Ph}_2\text{Si(OTf)}_2 \) and 4-dimethylaminopyridine (DMAP) affords \([\text{Ph}_2\text{Si(DMAP)}_2][\text{OTf}]_2 \) (2-12) in near quantitative yield. The \( ^{19}\text{F} \) NMR spectrum of 2-12 displays a single resonance at \( \delta_{\text{F}} = -78.73 \), implying displacement of both triflate anions. The \( ^{29}\text{Si} \) NMR chemical shift of 2-12 (\( \delta_{\text{Si}} = -4.6 \)) is also consistent with four-coordinate silicon. This dicationic complex is extremely moisture sensitive and readily hydrolyzes to yield the cyclic trimer \((\text{Ph}_2\text{SiO})_3\) and the pyridinium triflate salt \([\text{DMAP-H}][\text{OTf}]\), which were both identified crystallographically.

2.3 Conclusions

Four-coordinate silicon Lewis acids were prepared and examined for use in FLP chemistry. The Lewis acids \( \text{RSi(C}_6\text{F}_5)_3 \) (\( \text{R} = \text{H, F} \)) were found to be only weakly Lewis acidic by the Guttman-Beckett method. No reactivity towards small molecules typical of FLP chemistry was observed when employing combinations of these Lewis acids and sterically hindered bases. Silyl triflates displayed greater Lewis acidic properties; however, still no reactivity towards dihydrogen was observed for any of the Lewis acid-base pairs investigated.

The bis-triflate \( \text{Ph}_2\text{Si(OTf)}_2 \) was found to be a suitable precursor to dicationic adducts, which can be accessed by coordination of neutral donors (OPEt\(_3\), OPPh\(_3\), DMAP) to silicon. The reactivity of these complexes towards small molecules has yet to be investigated and can serve as an area of future work.

2.4 Experimental

2.4.1 General Considerations

All preparations and manipulations were carried out under an anhydrous \( \text{N}_2 \) atmosphere using standard glovebox and Schlenk-line techniques. Glassware was oven-dried and cooled under vacuum prior to use. Unless specified, all reagents were used as received without further purifications. Solvents (\( \text{CH}_2\text{Cl}_2 \), toluene, and pentane) were dried using an Innovative Technologies solvent purification system, degassed, and stored over molecular sieves. \( \text{CD}_2\text{Cl}_2 \) was dried over CaH\(_2\), degassed, and stored over activated molecular sieves. \( \text{C}_6\text{D}_5\text{Br} \) was degassed and stored over activated molecular sieves. NMR spectra were obtained on a Bruker Avance III-400 MHz, Varian 400 MHz, Agilent DD2 500 MHz, Agilent DD2 600 MHz, or
Varian Mercury 300 MHz spectrometer. All NMR experiments were conducted at a temperature of 25 °C. $^1$H, $^{13}$C, $^{19}$F, $^{29}$Si, and $^{31}$P NMR spectra were referenced using (residual) solvent resonances relative to SiMe$_4$ ($^1$H and $^{13}$C) or relative to an external standard ($^{19}$F: CFCl$_3$, $^{29}$Si: SiMe$_4$, $^{31}$P: 85% H$_3$PO$_4$). Chemical shifts are reported in ppm and coupling constants as scalar values in Hz. Combustion analyses were performed by ANALEST at the University of Toronto with a Perkin-Elmer CHN Analyzer.

Electron paramagnetic resonance studies were conducted at the University of Toronto using a Bruker continuous wave system, operating at 9.5 GHz (X band). EPR simulations were performed by Dr. Timothy Burrow with EasySpin software.

### 2.4.2 Syntheses

($C_6F_5)_3$Si(OTf) and HSi($C_5F_3$)$_3$ were prepared by the previously reported methods.$^{74,75}$ Compounds 2-1, 2-2, 2-3, and 2-7 were previously reported in the literature but were synthesized by different procedures and/or had not been fully characterized.$^{89,73,90,76}$ The modified preparation and characterization of these compounds is described below.

#### Preparation of 2-1:
A solution of Ph$_2$SiCl$_2$ (534 mg, 2.11 mmol, 1.0 eq) in CH$_2$Cl$_2$ (2 mL) was added to a suspension of AgOTf (1.084 g, 4.22 mmol, 2.0 eq) in CH$_2$Cl$_2$ (3 mL). The resulting mixture was left stirring at room temperature in the dark for 24 hours. The AgCl precipitate was removed by filtration and the solvent was removed in vacuo. The resulting solid was washed with minimal pentane (1 mL) to give a white powder. Yield: 930 mg, 92%. Crystals suitable for X-ray diffraction were grown from a concentrated CH$_2$Cl$_2$ solution at room temperature. The product can also be recrystallized from pentane in the freezer at -35 °C. $^1$H NMR (400.0 MHz, CD$_2$Cl$_2$): $\delta_H = 7.61$ (dd, 4H, $^3J_{HH} = 8$ Hz, $^3J_{HH} = 8$ Hz, $m$-C$_6$H$_5$); 7.76 (tt, 2H, $^3J_{HH} = 8$ Hz, $^4J_{HH} = 1$ Hz, $p$-C$_6$H$_5$); 7.83 (dd, 4H, $^3J_{HH} = 8$ Hz, $^4J_{HH} = 1$ Hz, o-C$_6$H$_5$). $^{13}$C$\{^1$H} NMR (75.4 MHz, CD$_2$Cl$_2$): $\delta_C = 118.60$ (q, $^1J_{CF} = 318$ Hz, CF$_3$); 122.73 (s, i-C$_6$H$_5$); 129.47 (s, m-C$_6$H$_5$); 134.75 (s, p-C$_6$H$_5$); 135.60 (s, o-C$_6$H$_5$). $^{19}$F$\{^1$H} NMR (376.4 MHz, CD$_2$Cl$_2$): $\delta_F = -76.10$ (s, CF$_3$). $^{29}$Si NMR (79.5 MHz, CD$_2$Cl$_2$): $\delta_{Si} = -24.6$ (s).

**Anal. Calc.** for $C_{14}H_{16}F_6O_6S_2Si$: C, 35.00; H, 2.10. Found: C, 34.57; H, 2.39.
Preparation of 2-2: A solution of Ph₃SiCl (460 mg, 1.56 mmol, 1.0 eq) in CH₂Cl₂ (2 mL) was added to a suspension of AgOTf (400 mg, 1.56 mmol, 1.0 eq) in CH₂Cl₂ (3 mL). The resulting mixture was stirred in the dark for 12 hours. The AgCl precipitate was removed by filtration and the solvent was removed in vacuo, affording a white solid. Yield: 495 mg, 78%. Single crystals suitable for X-ray diffraction were grown from a concentrated pentane solution at room temperature. ¹H NMR (400.0 MHz, CD₂Cl₂): δ_H = 7.53 (dd, 6H, ḟ_JHH = 8 Hz, ḟ_JH = 8 Hz, m-C₆H₅); 7.63 (t, 3H, ḟ_JHH = 8 Hz, p-C₆H₅); 7.75 (d, 6H, ḟ_JHH = 8 Hz, o-C₆H₅). ¹³C{¹H} NMR (100.6 MHz, CD₂Cl₂): δ_C = 118.86 (q, ḟ_JCF = 318 Hz, CF₃); 129.11 (s, m-C₆H₅); 129.91 (s, i-C₆H₅); 132.46 (s, p-C₆H₅); 136.03 (s, o-C₆H₅). ¹⁹F{¹H} NMR (376.4 MHz, CD₂Cl₂): δ_F = -76.87 (s, CF₃). ²⁹Si{¹H} NMR (79.5 MHz, CD₂Cl₂): δ_Si = 1.7 (s). Anal. Calc. for C₁₉H₁₅F₃O₃SSi: C, 55.87; H, 3.70. Found: C, 55.84; H, 3.92.

Preparation of 2-3: A solution of HSiPhCl₂ (228 mg, 1.29 mmol, 1.0 eq) in CH₂Cl₂ (2 mL) was added to a suspension of AgOTf (661 mg, 2.57 mmol, 2.0 eq) in CH₂Cl₂ (3 mL). The resulting mixture was left standing overnight in the dark. The AgCl precipitate was removed by filtration and the solvent was removed in vacuo, yielding a clear yellow oil. Yield: 425 mg, 81%. ¹H NMR (400.0 MHz, CD₂Cl₂): δ_H = 5.74 (s, 1H, ḟ_JHSi = 310 Hz, Si-H); 7.63 (dd, 2H, ḟ_JHH = 8 Hz, ḟ_JH = 8 Hz, m-C₆H₅); 7.78 (tt, 1H, ḟ_JHH = 8 Hz, ḟ_JH = 1 Hz, p-C₆H₅); 7.84 (d, 2H, ḟ_JHH = 8 Hz, o-C₆H₅). ¹³C{¹H} NMR (100.6 MHz, CD₂Cl₂): δ_C = 118.79 (q, ḟ_JCF = 318 Hz, CF₃); 122.49 (s, i-C₆H₅); 129.92 (s, m-C₆H₅); 134.69 (s, o-C₆H₅); 135.47 (s, p-C₆H₅). ¹⁹F{¹H} NMR (376.4 MHz, CD₂Cl₂): δ_F = -76.16 (s, CF₃). ²⁹Si{¹H} NMR (79.5 MHz, CD₂Cl₂): δ_Si = -28.2 (s). Satisfactory elemental analysis values could not be obtained due to decomposition of 2-3 in the EA glove bag.

Preparation of 2-5: To a 20 mL scintillation vial containing HNTf₂ (244 mg, 0.868 mmol, 1.0 eq), an excess of neat HSiEt₃ (450 mg, 3.86 mmol, 4.5 eq) was added. The resulting mixture was left standing overnight and accompanied by the evolution of hydrogen gas. The excess silane was removed in vacuo, affording a colourless oil. Yield: 335 mg, 98%. ¹H NMR (400.0 MHz, C₆D₅Br): δ_H = 0.68 (qm, 6H, ḟ_JHH = 7 Hz, Si-CH₂); 0.81 (tm, 9H, ḟ_JHH = 7 Hz, CH₃). ¹³C{¹H} NMR (100.6 MHz, C₆D₅Br): δ_C = 4.37 (s, CH₂); 4.98 (s, CH₃); 118.49 (q, ḟ_JCF = 321 Hz, CF₃) ¹⁹F{¹H} NMR (376.4 MHz, C₆D₅Br): δ_F = -78.57 (br,
\(29^7\text{Si}^1\text{H} \) NMR (79.5 MHz, \(C_6D_5\text{Br}\)): \(\delta_{\text{Si}} = 55.6 \) (s). **Anal. Calc.** for \(C_{8}H_{13}F_{6}NO_{4}S_{2}\text{Si} \): C, 24.30; H, 3.82; N, 3.54. Found: C, 23.87; H, 4.09; N, 3.52.

**Preparation of 2-7:** A CH\(_2\)Cl\(_2\) solution of \((C_6F_5)_3\text{Si(OTf)}\) (210 mg, 0.310 mmol, 1.0 eq, 2 mL) was treated with a CH\(_2\)Cl\(_2\) solution of [NBu\(_4\)][BF\(_4\)] (102 mg, 0.310 mmol, 1.0 eq, 1 mL). The mixture was allowed to stir at room temperature for 45 minutes and then the solvent was removed in vacuo. The residue was dissolved in pentane (7 mL) and then filtered to remove the salt by-product. The filtrate was dried in vacuo, yielding a white solid. Yield: 144 mg, 85%. Single crystals suitable for X-ray diffraction were grown in pentane at -35 °C. \(^{13}\text{C}^1\text{H} \) NMR (125.73 MHz, CD\(_2\)Cl\(_2\)): \(\delta_{C} = 103.01\) (m, \(i-C_6F_5\)); 138.12 (dm, \(J_{CF} = 256 \) Hz, \(m-C_6F_5\)); 145.26 (dm, \(J_{CF} = 256 \) Hz, \(p-C_6F_5\)); 149.84 (dm, \(J_{CF} = 248 \) Hz, \(o-C_6F_5\)). \(^{19}\text{F}^1\text{H} \) NMR (376.4 MHz, CD\(_2\)Cl\(_2\)): \(\delta_{F} = -127.50\) (m, 6F, \(o-C_6F_5\)); -144.75 (tt, 3F, \(J_{FF} = 19.9 \) Hz, \(J_{CH} = 5.3 \) Hz, \(p-C_6F_5\)); -158.16 (sept, 1 F, \(J_{FF} = 5.3 \) Hz, Si-F); -159.55 (m, 6F, \(m-C_6F_5\)). **Anal. Calc.** for \(C_{18}F_{16}\text{Si} \): C, 39.43. Found: C, 39.48.

**Preparation of 2-10:** A CH\(_2\)Cl\(_2\) solution of OPPh\(_3\) (52 mg, 0.187 mmol, 2.0 eq, 2 mL) was added to a CH\(_2\)Cl\(_2\) solution of Ph\(_2\)Si(OTf)\(_2\) (45 mg, 0.0937 mmol, 1.0 eq, 2 mL). The mixture was allowed to stir at room temperature for 10 minutes and the solvent was removed in vacuo. The resulting oil was triturated in pentane (3 mL) and dried in vacuo to give a white solid. Yield: 96 mg, 99%. \(^1\text{H} \) NMR (400.0 MHz, CD\(_2\)Cl\(_2\)): \(\delta_{H} = 7.32\) (m, 4H, Ar-H); 7.38 (t, 4 H, \(J_{HH} = 8 \) Hz, Ar-H); 7.48 (m, 12 H, Ar-H); 7.64 (m, 14 H, Ar-H); 7.90 (t, 6H, \(J_{HH} = 8 \) Hz, Ar-H). \(^{13}\text{C}^1\text{H} \) NMR (100.6 MHz, CD\(_2\)Cl\(_2\)): \(\delta_{C} = 119.61\) (d, \(J_{CP} = 113 \) Hz, \(i-Pc_6H_5\)); 121.36 (q, \(J_{CF} = 323 \) Hz, CF\(_3\)); 123.56 (s, \(i-SiC_6H_5\)); 130.05 (s, \(m-SiC_6H_5\)); 131.06 (d, \(J_{CP} = 14 \) Hz, P-C\(_6H_5\)); 133.50 (d, \(J_{CF} = 13 \) Hz, P-C\(_6H_5\)); 134.81 (s, \(p-SiC_6H_5\)); 134.97 (s, \(o-SiC_6H_5\)); 137.39 (s, \(PhC_6H_5\)). \(^{19}\text{F}^1\text{H} \) NMR (376.4 MHz, CD\(_2\)Cl\(_2\)): \(\delta_{F} = -78.69\) (s, CF\(_3\)). \(^{29}\text{Si} \) NMR (79.5 MHz, CD\(_2\)Cl\(_2\)): \(\delta_{Si} = -28.0\) (s). \(^{31}\text{P}^1\text{H} \) NMR (161.9 MHz, CD\(_2\)Cl\(_2\)): \(\delta_{p} = 58.9\) (s). **Anal. Calc.** for \(C_{50}H_{40}F_{6}O_{8}P_{2}S_{2}\text{Si} \): C, 57.91; H, 3.89. Found: C, 57.22; H, 3.39.

**Preparation of 2-11:** A CH\(_2\)Cl\(_2\) solution of OPEt\(_3\) (25 mg, 0.187 mmol, 2.0 eq, 2 mL) was added to a CH\(_2\)Cl\(_2\) solution of Ph\(_2\)Si(OTf)\(_2\) (45 mg, 0.0937 mmol, 1.0 eq, 2 mL). The mixture was stirred at room temperature for 10 minutes and then the solvent was removed in vacuo. The resulting oily solid
was washed with pentane (3 mL) to afford a white powder. Yield: 68 mg, 97%. Single crystals suitable for X-ray diffraction were grown from a concentrated toluene solution at room temperature. $^1$H NMR (400.0 MHz, CD$_2$Cl$_2$): $\delta_H = 1.14$ (dt, 18H, $^3J_{HP} = 20$ Hz, $^3J_{HH} = 8$ Hz, CH$_3$); 2.44 (dq, 12H, $^2J_{HP} = 13$ Hz, $^3J_{HH} = 8$ Hz, CH$_2$); 7.67 (dd, 4H, $^3J_{HH} = 8$ Hz, $^3J_{HH} = 8$ Hz, m-C$_6$H$_5$); 7.78 (t, 2H, $^3J_{HH} = 8$ Hz, p-C$_6$H$_5$); 7.94 (d, 4H, $^3J_{HH} = 8$ Hz, o-C$_6$H$_5$). $^{13}$C($^1$H) NMR (100.6 MHz, CD$_2$Cl$_2$): $\delta_C = 5.28$ (d, $^2J_{CF} = 5$ Hz, CH$_3$); 17.44 (d, $^1J_{CF} = 59$ Hz, CH$_2$); 121.05 (q, $^1J_{CF} = 320$ Hz, CF$_3$); 125.17 (s, i-C$_6$H$_5$); 130.13 (s, m-C$_6$H$_5$); 134.70 (s, p-C$_6$H$_5$); 135.39 (s, o-C$_6$H$_5$). $^{19}$F($^1$H) NMR (376.4 MHz, CD$_2$Cl$_2$): $\delta_F = -78.81$ (s, CF$_3$). $^{29}$Si NMR (79.5 MHz, CD$_2$Cl$_2$): $\delta_{Si} = -32.6$ (s). $^{31}$P($^1$H) NMR (161.9 MHz, CD$_2$Cl$_2$): $\delta_p = 101.8$ (s). Anal. Calc. for C$_{26}$H$_40$F$_6$O$_8$P$_2$S$_2$: C, 41.71; H, 5.38. Found: C, 41.37; H, 5.19.

**Preparation of 2-12:** A CH$_2$Cl$_2$ solution of 4-dimethylaminopyridine (22 mg, 0.183 mmol, 2.0 eq, 2 mL) was added to a CH$_2$Cl$_2$ solution of Ph$_2$Si(OTf)$_2$ (44 mg, 0.0916 mmol, 1.0 eq, 2 mL). The mixture was allowed to stir at room temperature for 10 minutes and the solvent was removed in vacuo. The resulting solid was triturated in pentane (3 mL) to give a white powder. Yield: 65 mg, 98%. $^1$H NMR (400.0 MHz, CD$_2$Cl$_2$): $\delta_H = 3.32$ (s, 12 H, N-CH$_3$); 7.06 (d, 4H, $^3J_{HH} = 8$ Hz, DMAP Ar-H); 7.68 (dd, 4H, $^3J_{HH} = 7$ Hz, $^3J_{HH} = 7$Hz, m-C$_6$H$_5$); 7.74 (d, 4H, $^3J_{HH} = 7$ Hz, o-C$_6$H$_5$); 7.81 (t, 2H, $^3J_{HH} = 7$ Hz, p-C$_6$H$_5$); 7.97 (d, 4H, $^3J_{HH} = 8$ Hz, DMAP Ar-H). $^{13}$C($^1$H) NMR (100.6 MHz, CD$_2$Cl$_2$): $\delta_C = 40.93$ (s, N-CH$_3$); 110.16 (s, DMAP Ar); 120.98 (s, i-C$_6$H$_5$); 121.13 (q, $^1J_{CF} = 322$ Hz, CF$_3$); 130.43 (s, m-C$_6$H$_5$); 135.04 (s, p-C$_6$H$_5$); 135.39 (s, o-C$_6$H$_5$); 136.68 (s, o-C$_6$H$_5$); 143.03 (s, DMAP Ar); 158.05 (s, DMAP Ar). $^{19}$F($^1$H) NMR (376.4 MHz, CD$_2$Cl$_2$): $\delta_F = -78.73$ (s, CF$_3$). $^{29}$Si NMR (79.5 MHz, CD$_2$Cl$_2$): $\delta_{Si} = -4.6$ (s). Anal. Calc. for C$_{28}$H$_{30}$F$_6$N$_4$O$_8$S$_2$: C, 46.40; H, 4.17; N, 7.73. Found: C, 45.90; H, 4.44; N, 7.62.

**2.4.3 Reactions**

**Friedel Crafts Cyclization of 1,1-Diphenylethylene:** 1,1-diphenylethylene (27 mg, 0.147 mmol) was added to a solution of the appropriate catalyst (0.007 mmol, 5 mol%) in CD$_2$Cl$_2$ (1 mL). The reaction progress was monitored by $^1$H NMR spectroscopy. When using catalysts 2-1 or 2-4, quantitative conversion to the cyclization product was observed after 6 hours. For these mixtures,
the volatiles were removed in vacuo and pentane was added to the residue. This mixture was filtered and the solvent was removed in vacuo affording 1-methyl-1,3,3-triphenyl-2,3-dihydro-1H-indene as a colorless solid. Yield: 25 mg, 93%. \textsuperscript{1}H NMR (400.0 MHz, C\textsubscript{6}D\textsubscript{5}Br): \(\delta_H = 1.41\) (s, 3H, CH\textsubscript{3}); 2.93 (d, 1H, \(^2J_{HH} = 13\) Hz, -CH\textsubscript{2}); 3.26 (d, 1H, \(^2J_{HH} = 13\) Hz, -CH\textsubscript{2}); 6.85-7.25 (m, 19H, ArH).

\textsuperscript{13}C\{\textsuperscript{1}H\} NMR (100.6 MHz, C\textsubscript{6}D\textsubscript{5}Br): \(\delta_C = 28.42\) (s); 50.58 (s); 60.41 (s); 60.73 (s); 124.52(s); 125.14 (s); 125.21 (s); 125.53 (s); 126.38 (s); 126.40 (s); 126.82 (s); 127.05 (s); 127.44 (s); 127.49 (s); 128.18 (s); 128.28 (s); 147.01 (s); 148.05 (s); 148.05 (s); 148.31 (s); 148.72 (s); 149.99 (s).

**Reaction of 2-10 with OPEt\textsubscript{3}:** An NMR tube was charged with [Ph\textsubscript{2}Si(OPPh\textsubscript{3})\textsubscript{2}][OTf\textsubscript{2}] (2-10) (32 mg, 0.0312 mmol, 1.0 eq). In a vial, OPEt\textsubscript{3} (8 mg, 0.0624 mmol, 2.0 eq) was weighed and dissolved in 1 mL of CD\textsubscript{2}Cl\textsubscript{2}. The OPEt\textsubscript{3} solution was then transferred to the NMR tube via pipette. The \textsuperscript{31}P\{\textsuperscript{1}H\} NMR spectrum of the resulting mixture revealed donor exchange, with the formation of Ph\textsubscript{2}Si(OPEt\textsubscript{3})\textsubscript{2}[OTf\textsubscript{2}] and OPPh\textsubscript{3}. The \textsuperscript{31}P NMR signals corresponding to [Ph\textsubscript{2}Si(OPEt\textsubscript{3})\textsubscript{2}][OTf\textsubscript{2}] (2-11) and OPPh\textsubscript{3} were slightly broadened, likely due to a weak interaction between the two species. \textsuperscript{31}P\{\textsuperscript{1}H\} NMR (161.9 MHz, CD\textsubscript{2}Cl\textsubscript{2}): \(\delta_P = 29.0\) (s;br, OPPh\textsubscript{3}); 101.8 (s;br, [Ph\textsubscript{2}Si(OPEt\textsubscript{3})\textsubscript{2}][OTf\textsubscript{2}]).

**2.4.4 X-Ray Data Collection, Reduction, Solution, and Refinement**

Single crystals were coated with Paratone-N oil and mounted under a cold nitrogen stream. Data sets were collected on a Bruker Kappa Apex II CCD diffractometer using a graphite monochromater with MoK\textalpha radiation (\(\lambda = 0.71073\) Å). Data reduction was performed using the Bruker SMART software package. Data sets were corrected for absorption effects using SADABs. The structures were solved by direct methods using XS and refined by full-matrix least-squares on \(F^2\) using XL as implemented in the SHELXTL suite of programs. All non-hydrogen atoms were refined anisotropically unless noted otherwise. Hydrogen atoms were placed in calculated positions using an appropriate riding model and coupled isotropic temperature factors.
<table>
<thead>
<tr>
<th>Crystal</th>
<th>2-1</th>
<th>2-2</th>
<th>2-7</th>
<th>2-11</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C₁₄H₁₀F₆O₆S₂S</td>
<td>C₁₀H₁₁F₃O₃SSi</td>
<td>C₁₈F₁₆Si</td>
<td>C₂₆H₄₀F₆O₈P₂S₂Si</td>
</tr>
<tr>
<td>Formula wt</td>
<td>480.45</td>
<td>408.46</td>
<td>548.27</td>
<td>748.75</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Orthorhombic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P₂₁/c</td>
<td>P₂₁/c</td>
<td>Pna₂₁</td>
<td>P₂₁</td>
</tr>
<tr>
<td>a (Å)</td>
<td>11.918(2)</td>
<td>10.277(3)</td>
<td>9.4747(5)</td>
<td>9.435(3)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>7.6223(15)</td>
<td>9.030(2)</td>
<td>17.6143(9)</td>
<td>11.290(3)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>20.083(4)</td>
<td>20.194(5)</td>
<td>10.7498(5)</td>
<td>16.739(5)</td>
</tr>
<tr>
<td>α (deg)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>β (deg)</td>
<td>92.120(6)</td>
<td>91.540(12)</td>
<td>90</td>
<td>101.808(12)</td>
</tr>
<tr>
<td>γ (deg)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>1823.1(6)</td>
<td>1873.3(8)</td>
<td>1794.04(16)</td>
<td>2419.80(17)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>T (K)</td>
<td>149(2)</td>
<td>150(2)</td>
<td>149(2)</td>
<td>149(2)</td>
</tr>
<tr>
<td>d (calc) gcm⁻³</td>
<td>1.750</td>
<td>1.448</td>
<td>2.030</td>
<td>1.425</td>
</tr>
<tr>
<td>Abs coeff, µ, mm⁻¹</td>
<td>0.449</td>
<td>0.282</td>
<td>0.299</td>
<td>0.354</td>
</tr>
<tr>
<td>Data collected</td>
<td>17169</td>
<td>13967</td>
<td>13767</td>
<td>25165</td>
</tr>
<tr>
<td>R int</td>
<td>0.0986</td>
<td>0.0232</td>
<td>0.0304</td>
<td>0.1427</td>
</tr>
<tr>
<td># of indpndt reflns</td>
<td>3196</td>
<td>3304</td>
<td>4062</td>
<td>6140</td>
</tr>
<tr>
<td>Reflns F₀ ≥ 2.0 σ(F₀)</td>
<td>1891</td>
<td>2950</td>
<td>3468</td>
<td>3324</td>
</tr>
<tr>
<td>Variables</td>
<td>262</td>
<td>244</td>
<td>316</td>
<td>413</td>
</tr>
<tr>
<td>R (&gt;2σ)</td>
<td>0.0794</td>
<td>0.0278</td>
<td>0.0346</td>
<td>0.0656</td>
</tr>
<tr>
<td>wR²</td>
<td>0.2241</td>
<td>0.0741</td>
<td>0.0801</td>
<td>0.1210</td>
</tr>
<tr>
<td>Goodness of fit</td>
<td>1.055</td>
<td>1.041</td>
<td>1.027</td>
<td>0.987</td>
</tr>
</tbody>
</table>
3 Activation of Carbon Dioxide by Silicon-Based Frustrated Lewis Pairs

3.1 Introduction

Nature delicately balances carbon dioxide levels through the processes of photosynthesis, cellular respiration, and organic decomposition. In the past two centuries, however, this global carbon cycle has been disrupted by human activities.\textsuperscript{91} Anthropogenic carbon dioxide emissions, most significantly from fossil fuel combustion, have resulted in increased atmospheric CO\textsubscript{2} concentrations and have been a strong contributor to global climate change.\textsuperscript{92} As atmospheric CO\textsubscript{2} levels continue to rise, international political initiatives have implored countries to mitigate climate change by reducing emissions and shifting away from fossil fuels towards renewable energy sources.\textsuperscript{92} Others have advocated for adaptations such as CO\textsubscript{2} sequestration or using CO\textsubscript{2} as a C\textsubscript{1} feedstock to generate high value, industrially-relevant chemicals or fuels.\textsuperscript{93,94}

One such example of using CO\textsubscript{2} to produce fuel is the proposed Olah methanol economy.\textsuperscript{95} While fossil fuel combustion generates “new” atmospheric carbon, utilizing methanol or dimethyl ether generated from the reduction of CO\textsubscript{2} would be preferable as it would recycle preexisting carbon from the troposphere. Such a process would enable CO\textsubscript{2} to serve as a valuable and renewable carbon source, allowing for the environmentally neutral use of carbon-based fuels and hydrocarbon products.\textsuperscript{96} In order to make a methanol economy feasible, further investigations into systems that can activate and reduce CO\textsubscript{2} are required.

A number of transition metal catalysts have been reported that activate CO\textsubscript{2} and reduce it to formic acid, carbon monoxide, methanol, and methane. Many of these processes use silanes,\textsuperscript{97,98} boranes,\textsuperscript{99,100} or H\textsubscript{2} as the reductant\textsuperscript{101-103} and commonly involve CO\textsubscript{2} insertion into a metal-hydride bond.\textsuperscript{104} There are fewer examples of main group species that can activate and reduce CO\textsubscript{2}.\textsuperscript{104} One notable example is CO\textsubscript{2} sequestration by N-heterocyclic carbenes (NHCs); this occurs by nucleophilic attack on CO\textsubscript{2} to generate imidazolium carboxylates.\textsuperscript{105} In 2009, it was demonstrated that NHCs could catalytically reduce CO\textsubscript{2} to Ph\textsubscript{2}Si(OMe)\textsubscript{2}, a methanol precursor, using diphenylsilane as the reductant.\textsuperscript{106} Silylium cations have also been shown to stoichiometrically reduce CO\textsubscript{2} using hydrosilanes to yield formic acid and methanol after an aqueous quench (Scheme 3.1).\textsuperscript{107}
Scheme 3.1 Stoichiometric reduction of CO₂ to formic acid and methanol by a silylium cation

Other main group systems, such as frustrated Lewis pairs, have taken advantage of the ambiphilic nature of carbon dioxide. While CO₂ is an overall non-polar molecule, the internal dipoles along the C-O bonds result in an electrophilic central carbon and basic oxygen atoms. This enables FLPs to activate CO₂ by simultaneous nucleophilic attack of the Lewis base at carbon and binding of the Lewis acid to oxygen. Examples of activation products are displayed in Figure 3.1. The reversibility of the CO₂ activation is highly dependent on the FLP system used and the strength of binding.

Figure 3.1 Selected examples of CO₂ sequestration by FLPs

With activation possible, there was interest in exploring if such species were amenable to reduction at the CO₂ moiety. To date, there have been several examples of stoichiometric and catalytic CO₂ reduction by FLPs. Stoichiometric CO₂ reduction has predominantly focused on ammonia borane or related derivatives as the reductant. In two separate publications, Stephan and coworkers reported the reduction of CO₂ to methanol with bis-borane and Al-based FLPs.
using dimethylamine-borane and ammonia-borane respectively as the reducing agents (Scheme 3.2).\textsuperscript{110,37}

Scheme 3.2 Stoichiometric CO\textsubscript{2} reduction with amine-boranes utilizing \textbf{a}) a bis-borane and \textbf{b}) an alane FLP system

Notable examples of FLP-mediated catalytic reduction have utilized boranes or silanes as reductants. Building upon the direct CO\textsubscript{2} hydrogenation work of Ashley and O’Hare,\textsuperscript{111} the Piers group reported tandem FLP/Lewis acid-catalyzed reduction of CO\textsubscript{2} to methane.\textsuperscript{112} This process involves insertion of CO\textsubscript{2} into a B-H bond of a hydridoborate salt followed by B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} catalyzed dioxgenative hydrosilylation of the CO\textsubscript{2} moiety (Scheme 3.3a). The Fontaine group has also demonstrated catalytic CO\textsubscript{2} reduction with linked B-P systems in which HBcat is the reductant and oxygen scavenger (Scheme 3.3b).\textsuperscript{113} In 2014, our group reported a similar reaction in which phosphines catalyze the reduction of CO\textsubscript{2} using 9-BBN dually as the Lewis acid and sacrificial reductant.\textsuperscript{114}
It was of interest to explore if four-coordinate SLAs could also be applied in the activation of CO₂. In this chapter, the activation of CO₂ employing both amine and phosphine Lewis base partners is discussed as well as forays into CO₂ reduction.

### 3.2 Results and Discussion

#### 3.2.1 Activation of Carbon Dioxide Employing a Secondary Amine Base

A CD₂Cl₂ solution of Ph₂Si(OTf)₂ was added to one equivalent of tetramethylpiperidine (TMP) in a J-Young NMR tube. The ¹H NMR spectrum of this mixture appeared unchanged from the starting materials, indicating that an adduct was not formed. The NMR tube was degassed and backfilled with carbon dioxide gas. Following this, a white solid (3-1) began to precipitate from solution.

Analysis of the CD₂Cl₂ soluble components by ¹H NMR spectroscopy revealed two sets of aromatic resonances in an approximate 1:1 ratio, corresponding to a mixture of free Ph₂Si(OTf)₂ and a new compound containing phenyl substituents (3-2). The resonance attributable to the tetramethylpiperidine N-H proton was absent from the ¹H NMR spectrum, implying complete consumption of TMP. The presence of unreacted Ph₂Si(OTf)₂ suggests that the stoichiometry of this reaction is not 1:1 with respect to the Lewis acid and Lewis base. Thus, 2:1 mixtures of TMP and Ph₂Si(OTf)₂ were prepared and exposed to CO₂. These reactions yielded the same white
precipitate (3-1) and the previously observed CD$_2$Cl$_2$ soluble product (3-2) with no evidence of residual Ph$_2$Si(OTf)$_2$.

The precipitate was removed by filtration and dissolved in CD$_3$CN. Proton NMR spectroscopy revealed a broad downfield 1:1:1 triplet at $\delta_{H}= 6.53$ ($J_{HN}= 12$ Hz) and aliphatic proton signals, while the $^{19}$F spectrum exhibited a single free triflate resonance at $\delta_{F} = -79.39$. These observations suggested the assignment of 3-1 as the ammonium triflate salt [TMPH][OTf]. This formulation was also confirmed by X-ray crystallographic studies (Figure 3.2).

![Figure 3.2 POV-Ray depiction of the molecular structure of 3-1. C: black, N: blue, O: red, F: pink, S: yellow. H atoms omitted for clarity.](image)

The $^{13}$C{$^1$H} NMR spectrum of 3-2 displays a resonance at $\delta_{C} = 165.02$, attributable to a carbonyl carbon. Repeating this reaction again using $^{13}$CO$_2$ resulted in augmentation of the resonance at $\delta_{C} = 165.02$, confirming incorporation of carbon dioxide into the product. While the spectroscopic data for 3-2 were consistent with the formulation C$_9$H$_{18}$NCO$_2$SiPh$_2$(OTf), the identity of this species was ultimately confirmed by X-ray crystallographic studies (Figure 3.3). 3-2 was isolated as a white solid in 88% yield.
Figure 3.3 POV-Ray depiction of the molecular structure of 3-2 C: black, N: blue, O: red, F: pink, Si: aquamarine, S: yellow. H atoms and disorder in the TMP moiety omitted for clarity.

The solid-state molecular structure of 3-2 reveals a five-coordinate silicon centre with a distorted trigonal bipyramidal geometry. Interestingly, the CO$_2$ moiety is bound to silicon in a $\kappa^2$ fashion. The Si1-O1 and Si1-O2 bond lengths are not equal in magnitude, with values of 1.747(3) Å and 1.938(3) Å respectively. Additionally, the Si1-O3 bond length of 1.823(3) Å is elongated relative to the Si-O bond in Ph$_2$Si(OTf)$_2$ (1.6792(2) Å). The C19-O2 bond length of 1.283(5) Å is consistent with a C-O bond order of less than 2, while the O1-C19-O2 angle of 107.5(3)$^\circ$ is significantly smaller than the idealized carbonyl bond angle of 120$^\circ$. Based on these metric parameters, Figure 3.4 proposes two resonance forms for 3-2.

Figure 3.4 Resonances forms of 3-2

To further probe CO$_2$ activation employing SLAs, the silyl triflates Ph$_3$Si(OTf), (C$_6$F$_5$)$_3$Si(OTf), and Me$_3$Si(OTf) were combined in an analogous fashion with two equivalents of TMP. No adducts were observed by NMR spectroscopy. In all cases, exposure of these mixtures to CO$_2$
gas led to the formation of a white precipitate. These reactions appeared to be analogous to that observed using Ph₂Si(OTf)₂ as the Lewis acid. Following reaction termination and removal of the salt by-product, silyl carbamates 3-3, 3-4, and 3-5 were isolated in yields of 86%, 95%, and 83% respectively. Attempts to perform the analogous reaction using the less sterically hindered Lewis acid HSiPh(OTf)₂ were unsuccessful, instead resulting in a reaction directly between the Lewis acid and TMP.

Compounds 3-1 - 3-5 are proposed to form via transient generation of a CO₂ sequestered species, followed by deprotonation by a second equivalent of base (Scheme 3.4).

Scheme 3.4 Proposed mechanism of CO₂ activation by silyl triflates and TMP; κ² binding of CO₂ moiety in compound 3-2 is not depicted for clarity.

No release of CO₂ is observed when these silyl carbamates are placed under vacuum. This stands in contrast to a similar reaction reported by Piers and coworkers in 2010; it was found that B(C₆F₅)₃ reacts with two equivalents of tetramethylpiperidine and CO₂ to yield a tetramethylpiperidinium carbamatoborate salt;¹¹² however, the activation of carbon dioxide by this B/N system was reversible, with CO₂ being liberated upon drying under vacuum. The increased stability of silyl carbamates 3-2 – 3-5 is likely a consequence of the precipitation of the salt by-product, which prevents the reverse reaction.

Single crystals suitable for X-ray diffraction analysis of 3-3 and 3-4 were obtained by slow evaporation of pentane solutions. The solid-state molecular structures are displayed below in
Figures 3.6 and 3.7. A comparison of selected NMR data and crystallographic bond lengths and angles (where applicable) is given for compounds 3-2 – 3-5 in Table 3.1.

Figure 3.5 POV-Ray depiction of the molecular structure of 3-3. C: black, N: blue, O: red, F: pink, Si: aquamarine. H atoms omitted for clarity.

Figure 3.6 POV-Ray depiction of the molecular structure of 3-4. C: black, N: blue, O: red, Si: aquamarine. H atoms omitted for clarity.
Table 3.1 Select NMR data and crystallographic bond lengths and angles for compounds 3-2-3-5

<table>
<thead>
<tr>
<th></th>
<th>δ C(NCO₂)</th>
<th>δ Si</th>
<th>Si1-O1 (Å)</th>
<th>Si1-O2 (Å)</th>
<th>C19-O1 (Å)</th>
<th>C19-O2 (Å)</th>
<th>O1-C19-O2 (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-2</td>
<td>165.02</td>
<td>-72.0</td>
<td>1.747(3)</td>
<td>1.938(3)</td>
<td>1.345(5)</td>
<td>1.283(5)</td>
<td>107.5(3)</td>
</tr>
<tr>
<td>3-3</td>
<td>157.67</td>
<td>-49.9</td>
<td>1.669(1)</td>
<td>2.390(1)</td>
<td>1.366(2)</td>
<td>1.237(2)</td>
<td>114.2(1)</td>
</tr>
<tr>
<td>3-4</td>
<td>155.92</td>
<td>-12.1</td>
<td>1.6824(1)</td>
<td>2.8280(1)</td>
<td>1.3613(1)</td>
<td>1.2200</td>
<td>119.44</td>
</tr>
<tr>
<td>3-5</td>
<td>156.36</td>
<td>19.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

The solid-state molecular structures of 3-3 and 3-4 display tetrahedral geometries about silicon. In contrast to the structure of 3-2, the CO₂ moieties are not bound in a chelating fashion. In fact, the Si1-O2 contact distances for 3-3 and 3-4 are quite long, with distances of 2.390(1) Å and 2.8280(1) Å respectively. This suggests only weak donation from the carbonyl oxygen to silicon in 3-3, while there is no evidence for such interaction in 3-4. The C19-O2 bond length and O1-C19-O2 angle for 3-3 show slight deviations from typical carbamate metric parameters; however, those for 3-4 are quite consistent with a C=O double bond and very close to the idealized sp² hybridized carbon angle of 120°. The degree of the Si1-O2 interaction in 3-2 – 3-4 appears to be strongly dependent on the electrophilicity of the silicon centre.

A comparison of the NMR data reveals that the ²⁹Si signal for compound 3-2 (δ Si = -72.0) is more upfield than those of 3-4, 3-5, and 3-6. This is true even when compared to the parent Lewis acid Ph₂SiOTf₂ (δ Si = -24.6). An upfield shift in the ²⁹Si NMR signal is usually consistent with five coordinate silicon and suggests the κ² binding of CO₂ is still present for 3-2 in solution. Furthermore, the more downfield ¹³C carbonyl resonance of 3-2 is also consistent with a different CO₂ binding motif than in 3-3, 3-4, and 3-5.
3.2.2 Activation of Carbon Dioxide Employing PEt₃

In the activation of CO₂ by SLAs and TMP, the precipitation of the salt 3-1 acts as a driving force for the reaction by preventing reversibility. Consequently, there was interest in exploring systems in which deprotonation of the CO₂ sequestered product could not occur. Such systems could provide a comparison of the relative CO₂ binding strengths for different SLAs. Our studies began using the tertiary phosphine PEt₃ as the Lewis base partner.

Treatment of commercially available Me₃SiOTf with one stoichiometric equivalent of PEt₃ resulted the formation of an adduct [Me₃SiPEt₃][OTf] (3-6), as evidenced by a sharp singlet in the ³¹P{¹H} NMR spectrum at δₚ = -11.5. Interestingly, the ²⁹Si spectrum of this adduct did not display Si-P coupling, suggesting that the adduct dissociates reversibly on the NMR time scale. This mixture was exposed to CO₂ gas in a J-Young NMR tube. Examination of the ³¹P{¹H} NMR spectrum of the reaction mixture after 20 minutes revealed two broad singlets at δₚ = -15.5 (3-6, shifted due to equilibrium) and δₚ = 38.4 (3-7). Repetition of this experiment with isotopically enriched ¹³CO₂ gas resulted in the same broad singlet at δₚ = -15.5 as well as a doublet at δₚ = 38.4 (¹JₚC = 115 Hz) in the ³¹P{¹H} NMR spectrum. The ¹³C NMR spectrum displayed a corresponding broad doublet at δₐ = 163.14 with a matching coupling constant (¹JₚC = 115) Hz. This one bond P-C coupling suggests reversible insertion of CO₂ into the Si-P adduct 3-6 (Scheme 3.5). Insertion of CO₂ in to weak Lewis acid-base adducts is known, as has been reported for PMes₃/AlX₃ (X=Cl, Br) adducts. ³⁷

\[
\begin{align*}
\text{Et₃P-Si}_{\text{Me}}_{\text{Me}}_{\text{Me}} \text{[OTf]} & \rightleftharpoons \text{Me}_{\text{Si}}_{\text{Me}}_{\text{Me}} \text{[OTf]} + \text{PEt₃} \\
\text{Et₃P-Si}_{\text{Me}}_{\text{Me}}_{\text{Me}} \text{[OTf]} & \rightleftharpoons \text{Et₃P-CO-O-Si}_{\text{Me}}_{\text{Me}}_{\text{Me}} \text{[OTf]} \\
\end{align*}
\]

**Scheme 3.5** CO₂ activation employing PEt₃ and Me₃SiOTf

Variable temperature NMR experiments using labeled ¹³CO₂ demonstrate that lower temperatures promote the insertion of CO₂ into the Si-P adduct. At -20 °C, full conversion to the CO₂ captured product 3-7 is observed (Figure 3.7).
Figure 3.7 Variable temperature $^{31}$P{$^1$H} NMR study depicting the conversion between 3-6 and 3-7 in a $^{13}$CO$_2$ filled NMR tube. * denotes [HPEt$_3$]$^+$ impurity arising from moisture in the CO$_2$ gas.

The $^{31}$P chemical shift of the Si-P adduct is strongly dependent on the equilibrium conditions as well as temperature. In contrast, the resonance attributable to 3-7 only sharpens and increases in intensity upon cooling. Unfortunately due to the reversible nature of the CO$_2$ activation, compound 3-7 was not isolable; however, all NMR spectroscopic data supports the formulation of 3-7 as [Et$_3$PCO$_2$SiMe$_3$][OTf].

The analogous stoichiometric reaction of Ph$_3$Si(OTf) with PEt$_3$ yields a weak adduct, [Ph$_3$SiPEt$_3$][OTf] (3-8). This is evidenced by the singlet in the $^{31}$P NMR spectrum at $\delta_p = -16.4$ which is slightly downfield from free PEt$_3$. Addition of CO$_2$ to this adduct results in the rapid formation of an equilibrium between the Si-P donor-acceptor adduct and a new species 3-9 at $\delta_p = 41.0$. The $^{13}$C NMR spectrum of this mixture displays a characteristic doublet at $\delta_C = 163.49$ exhibiting a P-C coupling of 112 Hz as well as resonances for constituent silicon and phosphorus fragments. This spectroscopic data supports the reversible formation of a similar CO$_2$ insertion product [Et$_3$PCO$_2$SiPh$_3$][OTf] (3-9) (Scheme 3.6); attempts to isolate 3-9 were unsuccessful due to gradual loss of CO$_2$ under a nitrogen atmosphere.
In a parallel fashion, the silyl triflimide \( \text{Et}_3\text{SiNTf}_2 \) was treated with one equivalent of \( \text{PET}_3 \). Analysis of the \(^{31}\text{P} \) NMR spectrum revealed a single resonance at \( \delta = -4.9 \), corresponding to the adduct \([\text{Et}_3\text{SiPET}_3][\text{NTf}_2] \) (3-10). Upon exposure of 3-10 to \( \text{CO}_2 \), slow conversion to a \( \text{CO}_2 \) insertion product 3-11 (\( \delta = 38.5 \)) was observed over the course of 48 hours. The reduced rate of \( \text{CO}_2 \) capture for this system can be attributed to the greater Si-P bond strength of 3-10, which necessitates increased times for adduct dissociation. 3-11 was found to be stable under vacuum and was isolated as a colourless oil. While the oil-like nature of 3-11 may be attributable to trace impurities, alkylphosphonium triflimide ionic liquids are known, with some examples even containing ester functionalities.\(^{118}\)

**Scheme 3.6** \( \text{CO}_2 \) activation employing \( \text{PET}_3 \) and silicon Lewis acids in the form of \( \text{R}_3\text{SiX} \) (\( \text{X}=\text{OTf}, \text{NTf}_2 \))

We then turned to the bis-triflate \( \text{Ph}_2\text{Si(OTf)}_2 \) to explore further reactivity towards \( \text{CO}_2 \). Treatment of \( \text{Ph}_2\text{Si(OTf)}_2 \) with one stoichiometric equivalent of \( \text{PET}_3 \) did not result in adduct formation, as evidenced by the unchanged \(^{31}\text{P} \) NMR spectrum from that of free \( \text{PET}_3 \). Following addition of \( \text{CO}_2 \), the \(^{31}\text{P}\{}^1\text{H}\} \) NMR spectrum revealed two new resonances at \( \delta = 43.9 \) (3-12, major) and \( \delta = 41.7 \) (3-13, minor). Repetition of this reaction with \(^{13}\text{CO}_2 \) gas revealed that both new signals in the \(^{31}\text{P} \) NMR spectrum couple to \(^{13}\text{C} \) nuclei with similar coupling constants of \( J_{\text{PC}} = \text{112 Hz} \) (3-12) and \( J_{\text{PC}} = \text{119 Hz} \) (3-13). Changing the relative ratio of the \( \text{Ph}_2\text{Si(OTf)} \) and \( \text{PET}_3 \) reactants has a significant effect on the ratio of 3-12 and 3-13 in solution (**Figure 3.9**).
**Figure 3.8** $^{31}\text{P}\{^1\text{H}\}$ NMR spectra depicting the activation of $^{13}\text{CO}_2$ by $\text{Ph}_2\text{Si(OTf)}_2$ and different stoichiometric equivalents of $\text{PEt}_3$; **3-12**: blue; **3-13**: purple; $\text{PEt}_3$: orange; * denotes $[\text{HPEt}_3]^+$ impurity arising from moisture in the $\text{CO}_2$ gas.

With 0.5 stoichiometric equivalents of $\text{PEt}_3$, **3-12** is the predominant species in solution; however, with 4.0 equivalents of $\text{PEt}_3$, the major species, **3-13**, appears to be in equilibrium with free phosphine, giving rise to a broadened $^{31}\text{P}\{^1\text{H}\}$ spectrum.

The $^{13}\text{C}$ NMR spectra of these reaction mixtures reveal that the carbonyl carbon resonances of **3-12** and **3-13** have nearly identical chemical shifts of $\delta_C = 162.83$ and $\delta_C = 162.65$. For each reaction, the $^{19}\text{F}$ NMR spectrum displays only one triflate signal at room temperature. As a greater amount of $\text{PEt}_3$ is utilized, this $^{19}\text{F}$ NMR resonance shifts upfield. At 0.5 equivalents of $\text{PEt}_3$, the triflate signal appears at $\delta_F = -76.57$, whereas with 4.0 equivalents the resonance appears at $\delta_F = -78.78$ (cf. $\delta_F = -76.10$ for $\text{Ph}_2\text{Si(OTf)}_2$). A more upfield resonance is consistent with a greater degree of dissociation of the triflate anion.\textsuperscript{79,85} These chemical shifts suggest the dissociation of a single triflate in **3-12** and both triflate anions in **3-13**. Thus, it is proposed that **3-12** and **3-13** correspond to stepwise $\text{CO}_2$ activation products in which one or two molecules of $\text{CO}_2$ are captured (**Scheme 3.7**).
Scheme 3.7 Proposed stepwise single and double activation of CO$_2$ with Ph$_2$Si(OTf)$_2$ and PEt$_3$

This is further supported by the low temperature NMR spectrum of the reaction between Ph$_2$Si(OTf)$_2$, excess PEt$_3$, and CO$_2$. At low temperatures, the P-Et resonances of 3-13 and free PEt$_3$ decoalesce in the $^1$H NMR spectrum. Although still broad, integration of the CH$_2$-PCO$_2$ resonance relative to the aromatic signals reveals a ratio of two PEt$_3$ moieties per equivalent of Lewis acid (Figure 3.10).

![NMR spectrum](image)

Figure 3.9 $^1$H NMR spectrum at -40 °C of reaction between Ph$_2$Si(OTf)$_2$, 3 eq. PEt$_3$, and CO$_2$ in CD$_2$Cl$_2$; 3-13: purple; PEt$_3$: orange

There are limited examples of double activation of small molecules by FLP systems. In 2011, Stephan and coworkers reported that the bis-borane $(C_6F_5)_2B(C_6F_4)B(C_6F_5)_2$ could activate two molecules of nitrous oxide using two equivalents of P$^t$Bu$_3$ to afford the bis-zwitterionic compound $^t$Bu$_3$P(N$_2$O)B(C$_6$F$_5$)$_2$C$_6$F$_4$B(C$_6$F$_5$)$_2$B(ON$_2$)P$^t$Bu$_3$ (Scheme 3.8a).$^{119}$ For this system, it is proposed that N$_2$O activation occurs in a stepwise fashion.

In 2012, the Stephan group also reported the double activation of CO$_2$ using a diamidophosphorane.$^{40}$ This process occurs by the insertion of two molecules of CO$_2$ into the P-N bonds to yield a bis(carbamato)phosphorane (Scheme 3.8b). In contrast to the bis-borane
system, which contains two different Lewis acidic centres, the diamidophosphorane uses a single phosphorus Lewis acidic centre for the double activation process.

Scheme 3.8 Previous examples of FLP-type double activation of small molecules

In a similar manner to the diamidophosphorane, it is proposed that the single silicon centre of \( \text{Ph}_2\text{Si(OTf)}_2 \) can act as the Lewis acid for the activation of two \( \text{CO}_2 \) molecules. This process is facilitated by the lability of the triflate substituents, which dissociate upon coordination of a donor to silicon. The initial \( \text{CO}_2 \) activation step yields species 3-12, a silyl triflate with a pendant phosphonium moiety. This formally cationic substituent is believed to further enhance the Lewis acidity at silicon, thus promoting the activation of a second \( \text{CO}_2 \) molecule. This may explain why small amounts of 3-13 are observed even when only 0.5 equivalents of \( \text{PEt}_3 \) are used.

Table 3.2 Summary of \( \text{CO}_2 \) binding by silicon Lewis acids and \( \text{PEt}_3 \) at 25 °C

<table>
<thead>
<tr>
<th>Lewis Acid</th>
<th>( \delta_\text{P} ) Si-P Adduct</th>
<th>( \delta_\text{P} ) PCO(_2)</th>
<th>( \delta_\text{C} ) PCO(_2)</th>
<th>( ^1J_{PC} ) (Hz)</th>
<th>Complexation(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Me}_3\text{SiOTf} )</td>
<td>-11.5</td>
<td>38.4</td>
<td>163.14</td>
<td>115</td>
<td>70%</td>
</tr>
<tr>
<td>( \text{Ph}_3\text{SiOTf} )</td>
<td>-16.4</td>
<td>41.0</td>
<td>163.49</td>
<td>112</td>
<td>70%</td>
</tr>
<tr>
<td>( \text{Et}_3\text{SiNTf}_2 )</td>
<td>-4.9</td>
<td>38.5</td>
<td>162.51</td>
<td>115</td>
<td>90%</td>
</tr>
<tr>
<td>( \text{Ph}_2\text{Si(OTf)}_2 )</td>
<td>n/a</td>
<td>43.9</td>
<td>162.83</td>
<td>112</td>
<td>n/a</td>
</tr>
</tbody>
</table>

\(^{a}\) Average amount (%) of \( \text{CO}_2 \) complexation observed relative to residual phosphine or Si-P adduct; note: % complexation is dependent on \( \text{CO}_2 \) pressure
3.2.3 Activation of Carbon Dioxide Employing $\text{P}^\text{t}\text{Bu}_3$

The results in the previous section demonstrated the successful application of $\text{PEt}_3$ in the activation of $\text{CO}_2$ with silyl triflates and $\text{Et}_3\text{SiNTf}_2$. To further expand this chemistry, it was of interest to probe if analogous reactivity could be observed by employing other phosphines. In particular, sterically hindered phosphines were examined as these could reduce the likelihood of adduct formation with the Lewis acid. Initial attempts in using $\text{PMe}_{3}$ (Tolman cone angle of 212°)$^{87}$ as the Lewis base along with silyl triflates did not result in any observed reactivity towards $\text{CO}_2$, perhaps due to insufficient basicity. Following this, $\text{P}^\text{t}\text{Bu}_3$ was examined as a base for $\text{CO}_2$ activation due to its comparable basicity to $\text{PEt}_3$ but significantly larger steric parameters (Tolman cone angle of 182° vs 132°).$^{87}$

Upon treatment of $\text{Me}_3\text{SiOTf}$ with $\text{P}^\text{t}\text{Bu}_3$, no Lewis acid/base interaction was observed by NMR spectroscopy. This mixture was then exposed to $^{13}\text{CO}_2$ gas in a sealed J-Young NMR tube. Monitoring the reaction by NMR spectroscopy revealed an interaction between $\text{Me}_3\text{SiOTf}$, $\text{P}^\text{t}\text{Bu}_3$, and $\text{CO}_2$ at room temperature. The phosphine resonances in the $^{31}\text{P}$ and $^1\text{H}$ NMR spectra appeared significantly broadened as compared to free $\text{P}^\text{t}\text{Bu}_3$; however, no phosphorus-carbon coupling was observed (Figure 3.10). The $^{13}\text{C}$ NMR spectrum of the reaction mixture exhibited a broadened free $\text{CO}_2$ resonance as well as an extremely broad signal in the baseline from $\delta_\text{C} = 158 – 166$, suggesting very weak $\text{CO}_2$ binding by $\text{Me}_3\text{SiOTf}$ and $\text{P}^\text{t}\text{Bu}_3$.

![Figure 3.10](image-url) $^1\text{H}$ and $^{31}\text{P}^\{^1\text{H}\}$ NMR spectra of mixture of $\text{Me}_3\text{SiOTf}$ with $\text{P}^\text{t}\text{Bu}_3$ before (bottom) and after (top) $^{13}\text{CO}_2$ addition at 25°C
To further probe this reaction, a variable temperature NMR experiment was conducted. Cooling of the reaction mixture led to a dramatically different appearance of the $^{31}$P NMR spectrum. At 0 °C, a very broad doublet (due to $^{31}$P-$^{13}$C coupling) is visible at $\delta_P = 51.6$ and appears to be in equilibrium with free $\text{P}^3\text{Bu}_3$. Cooling the sample further to -40 °C, results in the disappearance of the free $\text{P}^3\text{Bu}_3$ resonance and yields a spectrum with a sharp doublet at $\delta_P = 50.2$ ($^{1}J_{CP} = 87$ Hz) corresponding to a CO$_2$ captured species (3-14). The $^{13}$C{^1}H} NMR spectrum displays the expected resonances for the constituent silicon and phosphorus fragments, as well as a doublet at $\delta_P = 161.45$ with a matching P-C coupling of 87 Hz. This spectroscopic data allows for the proposed formulation of 3-14 as [$^3\text{Bu}_3\text{PCO}_2\text{SiMe}_3][\text{OTf}]$ (Scheme 3.9).

It is interesting that 3-14 is only observable in solution at low temperature. By contrast, CO$_2$ capture by Me$_3$SiOTf and PEt$_3$ readily occurs at room temperature. As P$^3$Bu$_3$ is actually a slightly stronger donor than PEt$_3$ (Tolman electronic parameters: PEt$_3$ 2061.7 cm$^{-1}$, P$^3$Bu$_3$ 2056.1 cm$^{-1}$), this difference in reactivity must be attributable to steric effects. It is proposed that the weak and reversible adduct formation between Me$_3$SiOTf and PEt$_3$ allows for pre-association of the Lewis acid and base components and facilitates CO$_2$ activation. At room temperature, pre-organization of more hindered Lewis bases, such as P$^3$Bu$_3$, with tetrahedral Lewis acids may be less favorable due to increased steric congestion.

In an analogous fashion, a 1:1 stoichiometric mixture of Ph$_3$Si(OTf) and P$^3$Bu$_3$ was prepared; analysis of this mixture by NMR spectroscopy indicated no adduct formation. Upon addition of $^{13}$CO$_2$ gas, NMR spectroscopy revealed minor conversion (~10%) to a new CO$_2$ captured species [$^3\text{Bu}_3\text{PCO}_2\text{SiPh}_3][\text{OTf}]$ (3-15) as evidenced by a small doublet in in the $^{31}$P{^1}H} spectrum $\delta_P = 57.5$ ($^{1}J_{PC} = 85$ Hz) and a corresponding doublet in the $^{13}$C spectrum at $\delta_C = 162.93$. Allowing this mixture to stand for a day at room temperature led to no change in composition, with free P$^3$Bu$_3$ still remaining as the predominant species in solution. Again, it is noteworthy that utilization of P$^3$Bu$_3$ as the Lewis base tends to favor the free starting materials over CO$_2$ binding. On the other hand, the analogous system employing PEt$_3$ as the Lewis base yields greater amounts of CO$_2$ incorporation at equilibrium conditions.

Treatment of Et$_3$SiNTf$_2$ with one equivalent of P$^3$Bu$_3$ led to the formation of a classical Lewis acid-base adduct (3-16), giving rise to a sharp resonance in the $^{31}$P{^1}H} NMR spectrum at $\delta_P = 37.2$. Exposure of this adduct to CO$_2$ gas resulted in the rapid formation of
[tBu₃P(CO₂)SiEt₃][NTf₂] (3-17). This was evidenced by a resonance in the ³¹P{¹H} NMR spectrum at δₚ = 53.1 and a characteristic doublet in the ¹³C NMR spectrum at δ_c = 162.34, exhibiting a P-C coupling constant of 87 Hz. 3-17 was found to be stable under vacuum and was isolated as a white solid in 71% yield.

It is notable that carbon dioxide insertion into adduct 3-16 occurs much more readily than for [Et₃SiPEt₃][NTf₂] (3-10). This can be attributed to the different strengths of these adducts, with 3-16 being weaker due to the larger steric parameters of P°Bu₃.

![Scheme 3.9](image)

**Scheme 3.9** CO₂ activation employing P°Bu₃ and silicon Lewis acids in the form of R°SiX (X=OTf, NTf₂)

Treatment of Ph₂Si(OTf)₂ with one stoichiometric equivalent of P°Bu₃ did not result in adduct formation; this mixture was degassed and ¹³CO₂ was added. The ³¹P{¹H} NMR spectrum of the resulting mixture displayed a broadened P°Bu₃ resonance and a broad doublet corresponding to a CO₂ captured product (δₚ = 57.5, ¹J_PC = 80 Hz) [tBu₃P(CO₂)SiPh₂(OTf)][OTf₂] (3-18). At room temperature, there is no evidence for a double CO₂ activation product, which had been previously observed when employing PEt₃.

Over time, decomposition of 3-18 occurs at room temperature. The major decomposition species can be identified by a doublet in the ¹³C NMR spectrum at δ_c = 181.61 (¹J_PC = 45 Hz) and a corresponding signal in the ³¹P NMR spectrum at δₚ = 49.7. Resonances arising from isobutylene are also observable in the ¹H NMR spectrum. Thus, the major decomposition product is proposed to be a phosphinoformate species, which forms by the deprotonation of a tert-butyl substituent of 3-18 (Scheme 3.10).
Scheme 3.10 Proposed decomposition of 3-18 by reaction with P^tBu_3

As solutions of 3-18 had broad spectra and typically begun to decompose before full spectroscopic characterization could be obtained, low temperature NMR spectra of 3-18 were acquired. Cooling a 1:1 mixture of Ph_2Si(OTf)_2 and P^tBu_3 in a ^13CO_2 filled J-Young to -40 °C gave rise to very different NMR spectra from those observed at room temperature. The ^31P{^1H} NMR spectrum exhibited two sharp doublets at δ_P = 55.8 (major, J_{PC} = 81 Hz) and δ_P = 56.3 (minor, J_{PC} = 80 Hz), while the ^13C{^1H} spectrum displayed corresponding doublets at δ_C = 162.54 and δ_C = 163.33. These two species are proposed to correspond to the products of mono-(3-18) and bis-CO_2 (3-19) activation respectively (Scheme 3.11).

Scheme 3.11 Proposed stepwise single and double activation of CO_2 at low temperature with Ph_2Si(OTf)_2 and P^tBu_3

Variable temperature ^31P NMR studies of 1:2 stoichiometric mixtures of Ph_2Si(OTf)_2 and P^tBu_3 pressurized with ^13CO_2 provide further support for this. As this mixture is cooled, consumption of P^tBu_3 and 3-18 is observed along with a concurrent increase in the intensity of the resonance attributable to 3-19 (Figure 3.11). At -30 °C, full consumption of the phosphine is observed along with near complete conversion to a single bis-CO_2 activation product.
Figure 3.11 Variable temperature $^{31}$P$_1^1$H} NMR spectra of 1:2 stoichiometric mixtures of Ph$_2$Si(OTf)$_2$ and PtBu$_3$ pressurized with $^{13}$CO$_2$

Table 3.3 Summary of CO$_2$ binding by silicon Lewis acids and PtBu$_3$

<table>
<thead>
<tr>
<th>Lewis Acid</th>
<th>T (°C)</th>
<th>$\delta_P$ Si-P Adduct</th>
<th>$\delta_P$ PCO$_2$</th>
<th>$\delta_C$ PCO$_2$</th>
<th>$^1$J$_{PC}$ (Hz)</th>
<th>Complexation$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me$_3$SiOTf</td>
<td>25</td>
<td>n/a</td>
<td>62.5(br)</td>
<td>158-166</td>
<td>n/a</td>
<td>&lt;1%</td>
</tr>
<tr>
<td></td>
<td>-40</td>
<td>n/a</td>
<td>50.2</td>
<td>161.45</td>
<td>87</td>
<td>100%</td>
</tr>
<tr>
<td>Ph$_3$SiOTf</td>
<td>25</td>
<td>n/a</td>
<td>57.5</td>
<td>162.93</td>
<td>85</td>
<td>10%</td>
</tr>
<tr>
<td>Et$_3$SiNTf$_2$</td>
<td>25</td>
<td>37.2</td>
<td>53.1</td>
<td>162.34</td>
<td>87</td>
<td>100%</td>
</tr>
<tr>
<td>Ph$_2$Si(OTf)$_2$</td>
<td>25</td>
<td>n/a</td>
<td>57.5</td>
<td>162.96</td>
<td>80</td>
<td>50%$^b$</td>
</tr>
<tr>
<td></td>
<td>-40</td>
<td>n/a</td>
<td>55.8</td>
<td>162.54</td>
<td>81</td>
<td>n/a</td>
</tr>
</tbody>
</table>

65.3 163.33 80

a) Average amount (%) of CO$_2$ complexation observed relative to residual phosphine or Si-P adduct. Note: % complexation is dependent on CO$_2$ pressure.

b) for 1:1 stoichiometric ratio of Ph$_2$Si(OTf)$_2$: PtBu$_3$
3.2.4 Investigations into Carbon Dioxide Reduction

With the demonstration that CO₂ activation was possible by Si/P FLP systems, the next logical step was to investigate the reduction of the CO₂ moiety to a substance of greater value, such as methanol or formic acid. The use of silanes as a reductant for CO₂ has been demonstrated for several main group systems, usually proceeding via hydrosilylation of the CO₂ moiety. This approach was initially of interest as the silanes could be introduced to the reaction mixtures prior to CO₂ addition. This could potentially allow for the reduction of non-isolable CO₂ captured species. Other reductants, such as ammonia borane and its derivatives, are known to react directly with silyl triflate/phosphine Lewis pairs and thus would not be suitable as in situ reducing agents.

A variety of silanes (HSiEt₃, HSiPh₃, H₂SiPh₂, H₃SiPh) were added in excess (10 eq) to 1:1 mixtures of silyl triflates and P₃Bu₃. After ensuring no reaction occurred, ¹³CO₂ was added to these mixtures. At room temperature, no CO₂ reduction was observed for any of the reactions. In some cases, the presence of silane even appeared to prevent CO₂ activation altogether. Heating these reactions typically led to a mixture of decomposition products, with no clear evidence of reduction.

In a similar fashion, a 1:1 mixture of Et₃SiNTf₂ and P₃Bu₃ was added to an excess of HSiEt₃ (10 eq). Upon addition of ¹³CO₂ to this mixture, rapid formation of the CO₂ activated product 3-17 occurred; however, no further reactivity was observed so the mixture was heated to 80 °C. After 2 days, partial conversion to a new species (3-20) occurred, indicated by the appearance of a downfield doublet in the ¹³C NMR spectrum at δC = 181.29 (¹JC = 31 Hz) and doublet in the ³¹P NMR spectrum at δP = 47.2 with a matching coupling constant. Unfortunately, these resonances are indicative of the formation of a phosphinoformate species rather than a CO₂ reduction product. Indeed, this same product (3-20) can be formed in the absence of triethylsilane by treating Et₃SiNTf₂ with two equivalents of P₃Bu₃ or HP₃Bu₂ in a CO₂ filled vessel (Scheme 3.11).
Scheme 3.12 Formation of 3-20 using P^tBu_3 or HP^tBu_2; colours correspond to Figure 3.12

Figure 3.12 $^{31}$P-$^1$H NMR spectra of reaction between Et$_3$SiNTf$_2$, 2 HP^tBu_2, and CO$_2$ in CD$_2$Cl$_2$

Due to the lack of desired reactivity observed with silanes, dimethylamine-borane was explored as a reductant. Ammonia-borane and its derivatives are known to be a good source of H$_2$ due to their protic N-H and hydridic B-H fragments. Reaction of isolated 3-17 with an excess (3.0 eq) of Me$_2$NH BH$_3$ leads to the rapid formation of HSiEt$_3$ and [HP^tBu_3][NTf$_2$]. This is evidenced by the distinctive Si-H resonance ($\delta_H$ = 3.60) in the $^1$H NMR spectrum which has $^{29}$Si satellites, as well as the single resonance in the $^{31}$P-$^1$H NMR spectrum at $\delta_P$ = 55.4. A free CO$_2$ peak can also be observed in the $^{13}$C-$^1$H spectrum, implying loss of CO$_2$ from 3-17. Examination of the $^{11}$B NMR spectrum reveals the presence of several boron-containing species, with the major resonances being assignable to unreacted Me$_2$NH BH$_3$, the dimeric species (Me$_2$NBH$_2$)$_2$, and H$_2$B($\mu$-H)(\mu-NMe$_2$)BH$_2$ (Scheme 3.12).
Scheme 3.13 Reaction of 3-17 with excess Me₂NHBH₃

3.3 Conclusions

Silyl triflates and tetramethylpiperidine are shown to react with CO₂ to yield silyl carbamates in the form of C₉H₁₈N(CO₂)SiR₃ and the ammonium triflate salt [TMPH][OTf]. In these carbamate products, the CO₂ moiety was found to bind to silicon in either a κ¹ or κ² fashion depending on the electrophilicity of the silicon centre. Silyl triflates and triflimides are also shown to be active in the complexation of CO₂ in combination with PE₃ or P₃Bu₃ to yield species of the general form [R₃P(CO₂)SiR₃][X]. When X=OTf, these species are unstable with respect to CO₂ liberation; however when X=NTf₂, these species are stable under an N₂ atmosphere or vacuum and can be isolated. When employing PE₃ or P₃Bu₃ as the Lewis base partner, Ph₂Si(OTf)₂ has been proposed to activate either one or two molecules of CO₂ depending on the stoichiometric equivalents of phosphine used as well as the temperature. Preliminary attempts to reduce Si/P CO₂ activation products with dimethylamine-borane or hydrosilanes were unsuccessful, resulting in either loss of CO₂ or no reaction respectively.
3.4 Experimental

3.4.1 General Considerations

All preparations and manipulations were carried out under an anhydrous N\textsubscript{2} atmosphere using standard glovebox and Schlenk-line techniques. Glassware was oven-dried and cooled under vacuum prior to use. Unless specified, all reagents were used as received without further purifications. 2,2,6,6-Tetramethylpiperidine was distilled from CaH\textsubscript{2} prior to use. Solvents (CH\textsubscript{2}Cl\textsubscript{2}, toluene, and pentane) were dried using an Innovative Technologies solvent purification system, degassed, and stored over molecular sieves. CD\textsubscript{2}Cl\textsubscript{2} was dried over CaH\textsubscript{2}, degassed, and stored over activated molecular sieves. C\textsubscript{6}D\textsubscript{5}Br was degassed and stored over activated molecular sieves. NMR spectra were obtained on a Bruker Avance III-400 MHz, Varian 400 MHz, Agilent DD2 500 MHz, or Varian Mercury 300 MHz spectrometer. All NMR experiments were conducted at a temperature of 25 °C unless otherwise noted. \textsuperscript{1}H, \textsuperscript{11}B, \textsuperscript{13}C, \textsuperscript{19}F, \textsuperscript{29}Si, and \textsuperscript{31}P NMR spectra were referenced using (residual) solvent resonances relative to SiMe\textsubscript{4} (\textsuperscript{1}H and \textsuperscript{13}C) or relative to an external standard (\textsuperscript{11}B: (Et\textsubscript{2}O)BF\textsubscript{3}, \textsuperscript{19}F: CF\textsubscript{3}Cl, \textsuperscript{29}Si: SiMe\textsubscript{4}, \textsuperscript{31}P: 85% H\textsubscript{3}PO\textsubscript{4}). Chemical shifts are reported in ppm and coupling constants as scalar values in Hz. Combustion analyses were performed by ANALEST at the University of Toronto with a Perkin-Elmer CHN Analyzer.

3.4.2 General Procedure for CO\textsubscript{2} Reactions

A J-Young NMR tube was charged with the appropriate reagents under an N\textsubscript{2} atmosphere. The NMR tube was then attached via a three-way adaptor to a vacuum line and a CO\textsubscript{2} cylinder equipped with a regulator. After thorough evacuation of the system and the regulator space, the J-Young contents were frozen in liquid nitrogen, degassed, and then sealed under vacuum. The regulator was filled with CO\textsubscript{2} gas and then closed off from the cylinder. 10 PSI of CO\textsubscript{2} gas was then vacuum transferred from the regulator space into the J-Young NMR tube. To our best estimate, this provides initial pressures of approximately 2-3 atm of CO\textsubscript{2}.

3.4.3 Reactions of Silyl Triflates with Tetramethylpiperidine and CO\textsubscript{2}

**General Synthesis of C\textsubscript{9}H\textsubscript{18}N(CO\textsubscript{2})SiR\textsubscript{3}:** A J-Young NMR tube was charged with the appropriate silyl triflate (1.0 eq) and 2,2,6,6-tetramethylpiperidine (2.0 eq) in 1 mL CD\textsubscript{2}Cl\textsubscript{2}. The J-Young was degassed and filled with CO\textsubscript{2}. Upon warming to room temperature, a white solid
started to precipitate from solution. The progress of the reaction was monitored by $^1$H NMR spectroscopy; complete conversion to the product typically occurred in less than one hour, with the exception of the reaction of Ph$_3$Si(OTf) with TMP and CO$_2$ which required a reaction time of 12 hours. Upon reaction completion, the contents of the J-Young were transferred to a vial and 3 mL of pentane was added. The mixture was filtered to remove the precipitate. Volatiles were removed from the filtrate in vacuo, affording C$_9$H$_{18}$N(CO$_2$)SiR$_3$. The $^{13}$C isotopomers were synthesized in an analogous fashion using $^{13}$CO$_2$. In each case, the use of $^{13}$C-labeled carbon dioxide resulted in increased signal intensity of the resonance attributable to the carbamate carbon in the $^{13}$C NMR spectrum.

**Characterization of 3-1:** The precipitate from the syntheses of 3-2 – 3-5 was isolated by filtration of the reaction mixtures. The white solid was washed with CH$_2$Cl$_2$ and pentane (5 mL) and then dried in vacuo. NMR spectroscopy and X-ray diffraction identified this species as [TMPH][OTf]. Single crystals suitable for X-ray diffraction were grown at room temperature from CH$_2$Cl$_2$. $^1$H NMR (400.0 MHz, CD$_3$CN): $\delta$H = 1.41 (s, 12H, CH$_3$); 1.65 (m, 4H, CH$_2$); 1.74 (m, 2H, CH$_2$); 6.53 (t br, 2H, $^1$J$_{HH}$ = 12 Hz, NH). $^{13}$C$^1$H NMR (75.4 MHz, CD$_3$CN): $\delta$C = 16.71 (CH$_2$, s); 27.39 (CH$_3$, s); 35.36 (CH$_2$, s); 59.04 (C-Me$_2$, s); 121.78 (q, $^1$J$_{CF}$ = 320 Hz, CF$_3$). $^{19}$F$^1$H NMR (376.4 MHz, CD$_3$CN): $\delta$F = -79.39 (s, CF$_3$).

**Characterization of 3-2:** Scale: Ph$_3$Si(OTf)$_2$ (34 mg, 0.0708 mmol, 1.0 eq), 2,2,6,6-tetramethylpiperidine (20 mg, 0.142 mmol, 2.0 eq). The product is a white solid which can be recrystallized from pentane or CH$_2$Cl$_2$/pentane solutions at -30 °C. Yield: 32 mg, 88%. Single crystals suitable for X-ray diffraction were grown by slow evaporation of a pentane solution. $^1$H NMR (400.0 MHz, CD$_2$Cl$_2$): $\delta$H = 1.58 (s, 12H, CH$_3$); 1.66 (m, 2H, CH$_2$); 1.76 (m, 4H, CH$_2$); 7.45 (ddm, 4H, $^3$J$_{HH}$ = 7 Hz, $^3$J$_{HH}$ = 7 Hz, m-C$_6$H$_5$); 7.51 (tt, 2H, $^3$J$_{HH}$ = 8 Hz, $^4$J$_{HH}$ = 2 Hz, p-C$_6$H$_5$); 7.84 (ddd, 4H, $^3$J$_{HH}$ = 7 Hz, $^4$J$_{HH}$ = 1 Hz, $^4$J$_{HH}$ = 1 Hz, o-C$_6$H$_5$). $^{13}$C$^1$H NMR (100.6 MHz, CD$_2$Cl$_2$): $\delta$C = 16.14 (s, CH$_2$); 29.16 (s, CH$_3$); 41.52 (CH$_2$, s); 61.22 (C-Me$_2$, s); 119.29 (q, $^1$J$_{CF}$ = 318 Hz, CF$_3$); 128.49 (s, m-C$_6$H$_5$); 131.42 (s, p-C$_6$H$_5$); 132.84 (s, i-C$_6$H$_5$); 135.53 (s, o-C$_6$H$_5$); 165.02 (s, NCO$_2$). $^{19}$F$^1$H NMR (376.4 MHz, CD$_2$Cl$_2$): $\delta$F = -77.77 (s, CF$_3$). $^{29}$Si NMR (79.5 MHz, CD$_2$Cl$_2$): $\delta$Si = -72.0 (s). Anal. Calc. for C$_{23}$H$_{28}$F$_3$NO$_5$SSi: C, 53.58; H, 5.47; N, 2.72. Found: C, 53.88; H, 5.69; N, 3.23.
Characterization of 3-3: Scale: \((\text{C}_6\text{F}_5)_3\text{Si(OTf)}\) (20 mg, 0.0295 mmol, 1.0 eq), 2,2,6,6-tetramethylpiperidine (8 mg, 0.0590 mmol, 2.0 eq). The product is a white solid. Yield: 20 mg, 95%. Single crystals suitable for X-ray diffraction were grown by slow evaporation of a pentane solution. \(^1\text{H NMR}\) (500.0 MHz, CD\(_2\)Cl\(_2\)): \(\delta_H = 1.41\) (s, 12H, CH\(_3\)); 1.61 (m, 2H, CH\(_2\)); 1.68 (t, 4H, \(^3\)J\(_{HH} = 6\) Hz, CH\(_2\)). \(^{13}\text{C}\{^1\text{H}\}\) NMR (125.73 MHz, CD\(_2\)Cl\(_2\)): \(\delta_C = 16.10\) (s, CH\(_2\)); 29.37 (s, CH\(_3\)); 41.36 (s, CH\(_2\)); 58.89 (s, C-Me\(_2\)); 106.99 (t, \(^2\)J\(_{CF} = 28\) Hz, i-C\(_6\)F\(_5\)); 137.81 (dm, \(^1\)J\(_{CF} = 253\) Hz, m-C\(_6\)F\(_5\)); 142.78 (dm, \(^1\)J\(_{CF} = 257\) Hz, p-C\(_6\)F\(_5\)); 149.19 (dm, \(^1\)J\(_{CF} = 245\) Hz, o-C\(_6\)F\(_5\)); 157.67 (s, NCO\(_2\)). \(^{19}\text{F}\{^1\text{H}\}\) NMR (376.4 MHz, CD\(_2\)Cl\(_2\)): \(\delta_F = -128.35\) (d, 6F, \(^3\)J\(_{FF} = 18.1\) Hz, o-C\(_6\)F\(_5\)); -149.22 (t, 3F, \(^3\)J\(_{FF} = 19.9\) Hz, p-C\(_6\)F\(_5\)); -161.16 (m, 6F, m-C\(_6\)F\(_5\)). \(^{29}\text{Si NMR}\) (79.5 MHz, CD\(_2\)Cl\(_2\)): \(\delta_{Si} = -49.9\) (s). \textbf{Anal. Calc.} for C\(_{28}\)H\(_{18}\)F\(_{15}\)NO\(_2\)Si: C, 47.13; H, 2.54; N, 1.96. Found: C, 46.89; H, 2.26; N, 2.00.

Characterization of 3-4: Scale: Ph\(_3\)SiOTf (30 mg, 0.0734 mmol, 1.0 eq), 2,2,6,6-tetramethylpiperidine (21 mg, 0.147 mmol, 2.0 eq). The product is a white solid. Yield: 27 mg, 83%. \(^1\text{H NMR}\) (400.0 MHz, CD\(_2\)Cl\(_2\)): \(\delta_H = 1.47\) (s, 12H, C-CH\(_3\)); 1.64 (m, 2H, CH\(_2\)); 1.71 (t, 4H, \(^3\)J\(_{HH} = 6\) Hz, CH\(_2\)); 7.39 (dd, 6H, \(^3\)J\(_{HH} = 7\) Hz, \(^3\)J\(_{HH} = 7\) Hz, m-C\(_6\)H\(_5\)); 7.45 (t, 3H, \(^3\)J\(_{HH} = 7\) Hz, p-C\(_6\)H\(_5\)); 7.66 (d, 6H, \(^3\)J\(_{HH} = 7\) Hz, o-C\(_6\)H\(_5\)). \(^{13}\text{C}\{^1\text{H}\}\) NMR (125.73 MHz, CD\(_2\)Cl\(_2\)): \(\delta_C = 15.95\) (s, CH\(_3\)); 29.94 (s, CH\(_3\)); 40.40 (s, CH\(_2\)); 57.06 (s, C-Me\(_2\)); 128.13 (s, m-C\(_6\)H\(_5\)); 130.39 (s, p-C\(_6\)H\(_5\)); 134.23 (s, i-C\(_6\)H\(_5\)); 136.04 (s, o-C\(_6\)H\(_5\)); 155.92 (s, NCO\(_2\)). \(^{29}\text{Si NMR}\) (79.5 MHz, CD\(_2\)Cl\(_2\)): \(\delta_{Si} = -12.1\) (s). \textbf{Anal. Calc.} for C\(_{13}\)H\(_{27}\)NO\(_2\)Si: C, 75.80; H, 7.50; N, 3.16. Found: C, 76.49; H, 7.50; N, 2.97.

Characterization of 3-5: Scale: Me\(_3\)SiOTf (30 mg, 0.135 mmol, 1.0 eq), 2,2,6,6-tetramethylpiperidine (38 mg, 0.270 mmol, 2.0 eq). The product is a colourless oil. Yield: 30 mg, 86%. \(^1\text{H NMR}\) (500.0 MHz, CD\(_2\)Cl\(_2\)): \(\delta_H = 0.26\) (s, 9H, Si-CH\(_3\)); 1.39 (s, 12H, C-CH\(_3\)); 1.58 (m, 2H, CH\(_2\)); 1.64 (t, 4H, \(^3\)J\(_{HH} = 6\) Hz, CH\(_2\)). \(^{13}\text{C}\{^1\text{H}\}\) NMR (125.73 MHz, CD\(_2\)Cl\(_2\)): \(\delta_C = 0.24\) (s, Si-CH\(_3\)); 16.25 (s, CH\(_2\)); 29.94 (s, C-CH\(_3\)); 41.11 (s, CH\(_2\)); 56.53 (s, C-Me\(_2\)); 156.36 (s, NCO\(_2\)). \(^{29}\text{Si NMR}\) (79.5 MHz, CD\(_2\)Cl\(_2\)): \(\delta_{Si} = 19.2\) (s). \textbf{Anal. Calc.} for C\(_{13}\)H\(_{27}\)NO\(_2\)Si: C, 60.65; H, 10.57; N, 5.44. Found: C, 60.05; H, 11.01; N, 6.13.
3.4.4 Reactions of Silicon Lewis Acids with PEt₃ and Carbon Dioxide

**General Procedure:** A J-Young NMR tube was charged with the appropriate silyl triflate or triflimide (1.0 eq) and PEt₃ (1.0 eq, unless specified) in CD₂Cl₂ (1 mL). The reaction mixture was then examined for adduct formation by multinuclear NMR spectroscopy. Following this, the J-Young NMR tube was degassed and CO₂ gas was added. In each case, NMR spectra obtained after one hour revealed the formation of a CO₂ sequestered species. ¹³C isotopomers of these species were also synthesized in an analogous fashion using ¹³CO₂. With the exception of 3-11, the CO₂ captured species were not isolable and thus were characterized in a CO₂-filled J-Young NMR tube. In the reaction mixtures containing CO₂, hydrolysis products such as [HPEt₃]⁺ and R₃SiOSiR₃ are present due to moisture from the CO₂ gas.

**Reaction of Me₃SiOTf and PEt₃:** Scale: Me₃SiOTf (30 mg, 0.135 mmol, 1.0 eq), PEt₃ (10 mg, 0.135 mmol, 1.0 eq). Examining the reaction mixture by multinuclear NMR spectroscopy prior to CO₂ addition revealed adduct formation.

Adduct (3-6): ¹H NMR (400.0 MHz, CD₂Cl₂): δ_H = 0.53 (s, 9H, Si-CH₃); 1.16 (dt, 9H, J_HP = 16 Hz, P-CH₂CH₃); 1.83 (m, 6H, P-CH₂). ¹³C{¹H} NMR (100.6 MHz, CD₂Cl₂): δ_C = 0.53 (s, Si-CH₃); 8.26 (s, P-CH₂CH₃); 14.81 (br, P-CH₂). ¹⁹F{¹H} NMR (376.4 MHz, CD₂Cl₂): δ_F = -78.09 (s, CF₃). ²⁹Si NMR (79.5 MHz, CD₂Cl₂): δ_Si = 30.9 (s). ³¹P{¹H} NMR (161.9 MHz, CD₂Cl₂): δ_P = -11.5 (s).

**Addition of CO₂:** Upon addition of CO₂, an equilibrium was observable between the phosphine adduct (3-6) and the carbon dioxide captured product (3-7).
Reaction Mixture (25 °C): $^1$H NMR (400.0 MHz, CD$_2$Cl$_2$): $\delta_H = 0.48$ (s, Si-CH$_3$); 1.16-1.42 (br, 3-7 P-Et); 1.54-1.80 (br, 3-6 P-Et); 2.25-2.40 (br, 3-6 P-Et); 2.40-2.90 (br, 3-7 P-Et). $^{13}$C$^1$H NMR (100.6 MHz, CD$_2$Cl$_2$): $\delta_C = -0.10$ (s, Si-CH$_3$); 6.36 (br, P-CH$_2$CH$_3$); 12.45 (br, P-CH$_3$); 12.06 (q, $^1$J$_{CF}$ = 319 Hz, CF$_3$); 125.28 (br, free CO$_2$); 163.14 (d/br, $^1$J$_{CP}$ = 115 Hz, P-CO$_2$). $^{19}$F$^1$H NMR (376.4 MHz, CD$_2$Cl$_2$): $\delta_F = -78.39$ (s, CF$_3$). $^{29}$Si$^1$H NMR (HMBC) (99.3 MHz, CD$_2$Cl$_2$): $\delta_Si = 40.3$ (br). $^{31}$P$^1$H NMR (161.9 MHz, CD$_2$Cl$_2$): $\delta_P = -13.9$ (br, 3-6); 38.4 (br, 3-7).

Reaction of Ph$_3$SiOTf and PEt$_3$: Scale: Ph$_3$SiOTf (22 mg, 0.0539 mmol, 1.0 eq), PEt$_3$ (4 mg, 0.0539 mmol, 1.0 eq). Examining the reaction mixture by multinuclear NMR spectroscopy prior to CO$_2$ addition revealed adduct formation.

Adduct (3-8): $^1$H NMR (400.0 MHz, CD$_2$Cl$_2$): $\delta_H = 1.04$ (dt, 9H, $^3$J$_{HP}$=15 Hz, $^2$J$_{HH}$= 8 Hz, CH$_3$); 1.53 (qd, 6H, $^2$J$_{HH}$= 8 Hz, $^2$J$_{HP}$=2 Hz, P-CH$_2$); 7.52 (ddm, 6H, $^3$J$_{HH}$= 7 Hz, $^3$J$_{HH}$= 7 Hz, m-C$_6$H$_3$); 7.62 (tm, 3H, $^3$J$_{HH}$= 7 Hz, p-C$_6$H$_5$); 7.69 (dm, 6H, $^3$J$_{HH}$= 7 Hz, o-C$_6$H$_5$). $^{13}$C$^1$H NMR (100.6 MHz, CD$_2$Cl$_2$): $\delta_C = 9.01$ (d, $^1$J$_{CP}$= 8 Hz, P-CH$_2$); 17.41 (s, P-CH$_2$CH$_3$); 119.40 (q, $^1$J$_{CF}$ = 318 Hz, CF$_3$); 128.24 (s/br, i-C$_6$H$_5$); 129.13 (s, m-C$_6$H$_5$); 132.58 (s, p-C$_6$H$_5$); 136.13 (s, o-C$_6$H$_5$). $^{19}$F$^1$H NMR (376.4 MHz, CD$_2$Cl$_2$): $\delta_F = -77.32$ (s, CF$_3$). $^{29}$Si$^1$H NMR (HMBC) (99.3 MHz, CD$_2$Cl$_2$): $\delta_Si = -1.0$ (s). $^{31}$P$^1$H NMR (161.9 MHz, CD$_2$Cl$_2$): $\delta_P = -16.4$ (s).

Addition of CO$_2$: Upon addition of CO$_2$ gas, an equilibrium was observable between the phosphine adduct (3-8) and a carbon dioxide captured product (3-9).

Reaction Mixture: $^1$H NMR (400.0 MHz, CD$_2$Cl$_2$): $\delta_H = 1.04$ (m/br, 3-8 P-CH$_2$CH$_3$); 1.28 (dt, $^3$J$_{HP}$=20 Hz, $^2$J$_{HH}$= 8 Hz, 3-9 P-CH$_2$CH$_3$); 1.48 (m/br, 3-8 P-CH$_2$); 2.62 (dq, $^2$J$_{HP}$= 14 Hz, $^3$J$_{HH}$= 8 Hz, 3-9 P-CH$_2$); 7.51 (br, m-C$_6$H$_5$); 7.60 (br, p-C$_6$H$_5$); 7.68 (br, o-C$_6$H$_5$). $^{13}$C$^1$H NMR (100.6 MHz, CD$_2$Cl$_2$): $\delta_C = 6.24$ (d, $^2$J$_{PC}$= 6 Hz, 3-9 P-CH$_2$CH$_3$); 9.05 (br, 3-8 P-CH$_2$CH$_3$); 12.62 (d,
reaction mixtures are strongly dependent on the number of equivalents of PEt

was observed between Ph

consistently low on carbon due to

32.31; H, 5.42; N, 2.51

31

(HMBC) (99.3 MHz, CD2Cl2): δSi = -0.5 (s, 3-8); 0.5 (s, 3-9). 31P{1H} NMR (161.9 MHz, CD2Cl2): δp = -15.2 (s, 3-8); 41.0 (s, 3-9).

Preparation of 3-11: Scale: Et3SiNTf2 (28 mg, 0.0711 mmol, 1.0 eq), PEt3 (5 mg, 0.0711 mmol, 1.0 eq). Examining the 31P{1H} NMR spectra prior to CO2 addition revealed adduct formation (3-10). (δp = -4.9). This mixture then degassed and was exposed to CO2.

Over the course of 2 days, the resonance attributable to the adduct disappeared and the formation of 3-11 could be observed at δp = 38.5. Upon completion of the reaction, the contents of the J-Young were transferred to a vial and the solvent was removed in vacuo, yielding a colourless oil. The oil was washed with pentane. The supernatant was decanted and the resultant colourless oil was dried under vacuum. Yield: 24 mg, 62%. 1H NMR (400.0 MHz, CD2Cl2): δH = 0.93 (m, 6H, Si-CH2); 1.02 (t, 9H, 3JHH = 7 Hz, Si-CH2CH3); 1.35 (dt, 9H, 3JHP = 20 Hz, 3JHH = 8 Hz, P-CH2CH3); 2.47 (dq, 6H, 2JHP = 13 Hz, 3JHH = 8 Hz, P-CH2). 13C{1H} NMR (100.6 MHz, CD2Cl2): δC = 4.72 (s, Si-CH2); 6.08 (d, 3JCP = 6 Hz, P-CH2CH3); 6.33 (s, Si-CH2CH3); 12.30 (d, 1JCP = 43 Hz, P-CH2); 120.24 (q, 1JCF = 321 Hz, CF3); 162.51 (d, 1JCP = 115 Hz, POCO). 19F{1H} NMR (376.4 MHz, CD2Cl2): δF = -79.24(s, CF3). 29Si NMR (79.5 MHz, CD2Cl2): δSi = 40.5(s). 31P{1H} NMR (161.9 MHz, CD2Cl2): δp = 38.5 (s). Anal. Calc. for C13H30F6NO6PS2Si: C, 32.31; H, 5.42; N, 2.51. Found: C, 30.94; H, 4.81; N, 2.94. Elemental analysis values were consistently low on carbon due to a minor, inseparable [HPEt3][NTf2] impurity.

Reactions of Ph2Si(OTf)2 with PEt3 and CO2: A J-Young NMR tube was charged with Ph2Si(OTf)2 (1.0 eq) and PEt3 (0.5, 1.0, 2.0, or 4.0 eq) in CD2Cl2 (1 mL). No adduct formation was observed between Ph2Si(OTf)2 and PEt3 by 31P NMR spectroscopy. The J-Young NMR tube was degassed and CO2 gas was added. The relative amounts of 3-12 and 3-13 observed in the reaction mixtures are strongly dependent on the number of equivalents of PEt3 used.
With 0.5 equivalents of PEt₃: Scale: Ph₂Si(OTf)₂ (29 mg, 0.0604 mmol, 1.0 eq), PEt₃ (2 mg, 0.0302 mmol, 0.5 eq).

**Reaction Mixture:** $^1$H NMR (400.0 MHz, CD₂Cl₂): $\delta_H = 1.35$ (m, 3-12 PCH₂CH₃); 2.69 (m/br, 3-12 P-CH₂); 7.61 (dd/br, $^3J_{HH} = 8$ Hz, $^3J_{HH} = 8$ Hz, m-C₆H₅); 7.76 (tt, $^3J_{HH} = 8$ Hz, $^4J_{HH} = 2$ Hz, p-C₆H₅); 7.83 (dm, $^3J_{HH} = 8$ Hz, o-C₆H₅). $^{13}$C$^1$H NMR (100.6 MHz, CD₂Cl₂): $\delta_C = 6.15$ (d, $^2J_{PC} = 6$ Hz, 3-12 P-CH₂CH₃); 12.66 (d, $^1J_{PC} = 42$ Hz, 3-12 P-CH₂); 118.97 (q, $^1J_{CF} = 318$ Hz, CF₃); 122.84 (s, i-C₆H₅); 125.30 (s, free CO₂); 129.52 (s, m-C₆H₅); 134.79 (s, p-C₆H₅); 135.65 (s, o-C₆H₅); 162.83 (d, $^1J_{PC} = 112$ Hz, 3-12 P-CO₂). $^{19}$F$^1$H NMR (376.4 MHz, CD₂Cl₂): $\delta_F = -76.57$ (s, CF₃). $^{29}$Si NMR (79.5 MHz, CD₂Cl₂): $\delta_{Si} = -24.6$ (s, 3-12). $^{31}$P$^1$H NMR (161.9 MHz, CD₂Cl₂): $\delta_P = 41.7$ (br, trace, 3-13); 43.9 (s, 3-12).

With 4.0 equivalents of PEt₃: Scale: Ph₂Si(OTf)₂ (29 mg, 0.603 mmol, 1.0 eq), PEt₃ (18 mg, 0.241 mmol, 4.0 eq).

**Reaction Mixture:** $^1$H NMR (400.0 MHz, CD₂Cl₂): $\delta_H = 0.90-1.50$ (br, overlapping PEt₃ and 3-13 P-Et); 2.40-2.80 (br, 3-13 P-CH₂CH₃); 7.59 (dd, $^3J_{HH} = 7$ Hz, $^3J_{HH} = 7$ Hz, m-C₆H₅); 7.69 (t, $^3J_{HH} = 7$ Hz, p-C₆H₅); 7.83 (dd, $^3J_{HH} = 7$ Hz, $^4J_{HH} = 1$ Hz, o-C₆H₅). $^{13}$C$^1$H NMR (100.6 MHz, CD₂Cl₂): $\delta_C = 6.00$ (br, 3-13 P-CH₂CH₃); 9.30 (br, PEt₃ P-CH₂CH₃); 12.24 (br, 3-13 P-CH₂); 18.48 (br, PEt₃ P-CH₂); 121.14 (q, $^1J_{CF} = 320$ Hz, CF₃); 124.56 (s, i-C₆H₅); 125.25 (br, free CO₂); 129.33 (s, m-C₆H₅); 133.92 (s, p-C₆H₅); 135.66 (s, o-C₆H₅); 162.65 (d/b r, $^1J_{PC} = 119$ Hz, PCO₂). $^{19}$F$^1$H NMR (376.4 MHz, CD₂Cl₂): $\delta_F = -78.78$ (s, CF₃). $^{29}$Si NMR (79.5 MHz, CD₂Cl₂): $\delta_{Si} = -21.0$ (s, 3-13). $^{31}$P$^1$H NMR (161.9 MHz, CD₂Cl₂): $\delta_P = -18.6$ (br, PEt₃); 41.7 (br, 3-13); 43.9 (br, trace, 3-12).
3.4.5 Reactions of Silicon Lewis Acids with \( \text{PH}^3\text{Bu}_3 \) and Carbon Dioxide

**General Procedure:** A J-Young NMR tube was charged with the appropriate silyl triflate or triflimide (1.0 eq) and \( \text{PH}^3\text{Bu}_3 \) (1.0 eq, unless specified) in CD\(_2\)Cl\(_2\) (1 mL). The reaction mixture was then examined for adduct formation by multinuclear NMR spectroscopy. The J-Young NMR tube then was degassed and backfilled with CO\(_2\). In each case, NMR spectra obtained after one hour revealed the formation of a CO\(_2\) sequestered species. \(^{13}\)C isotopomers of these species were also synthesized in an analogous fashion using \(^{13}\)CO\(_2\). With the exception of 3-17 and 3-20, the CO\(_2\) captured species were not isolable and thus were characterized in a CO\(_2\) filled J-Young NMR tube. In the reaction mixtures, hydrolysis products such as [HP\(^3\)Bu\(^3\)]\(^+\) and R\(_2\)SiOSiR\(_3\) are present due to moisture in the CO\(_2\) gas.

**Reaction of Me\(_3\)SiOTf with \( \text{PH}^3\text{Bu}_3 \) and \(^{13}\)CO\(_2\):** Scale: Me\(_3\)SiOTf (22 mg, 0.0990 mmol, 1.0 eq), \( \text{PH}^3\text{Bu}_3 \) (20 mg, 0.0990 mmol, 1.0 eq). Examining the reaction mixture by multinuclear NMR spectroscopy prior to CO\(_2\) addition revealed no adduct formation. \(^{13}\)CO\(_2\) was then added to the J-Young NMR tube. This resulted in broadening of the \( \text{PH}^3\text{Bu}_3 \) resonances at room temperature; complete conversion to the CO\(_2\) activation product was observed at -40 °C.

![Reaction Scheme](image)

**Room Temperature (25 °C):** \(^1\)H NMR (400.0 MHz, 25 °C, CD\(_2\)Cl\(_2\)): \( \delta_H = 0.49 \) (s, 9H, Si-CH\(_3\)\); 1.19-1.50 (br, 27 H, PC(CH\(_3\))\(_3\)). \(^{13}\)C\(^{1}\)H NMR (100.6 MHz, 25 °C, CD\(_2\)Cl\(_2\)): \( \delta_C = 0.32 \) (s, Si-CH\(_3\)); 32.36 (br, PC(CH\(_3\))\(_3\)); 34.70 (br, P-C); 119.54 (q, \( J_{CF} = 319 \) Hz, CF\(_3\)); 161.97 (br, P-CO\(_2\)). \(^{19}\)F\(^{1}\)H NMR (376.4 MHz, CD\(_2\)Cl\(_2\)): \( \delta_F = -77.86 \) (s, CF\(_3\)). \(^{29}\)Si\(^{1}\)H NMR (HMBC) (99.3 MHz, CD\(_2\)Cl\(_2\)): \( \delta_Si = 43.7 \) (s). \(^{31}\)P\(^{1}\)H NMR (161.9 MHz, 25 °C, CD\(_2\)Cl\(_2\)): \( \delta_P = 62.5 \) (s/br).

**Low Temperature (-40 °C), 3-14:** \(^1\)H NMR (500.0 MHz, -40 °C, CD\(_2\)Cl\(_2\)): \( \delta_H = 0.44 \) (s, 9H, Si-CH\(_3\)); 1.65 (d, 27 H, \( J_{HF} = 15 \) Hz, PC(CH\(_3\))\(_3\)). \(^{13}\)C\(^{1}\)H NMR (100.6 MHz, -40 °C, CD\(_2\)Cl\(_2\)): \( \delta_C = -0.67 \) (s, Si-CH\(_3\)); 29.86 (s, PC(CH\(_3\))\(_3\)); 40.99 (d, \( J_{CP} = 18 \) Hz, P-C); 120.49 (q, \( J_{CF} = 321 \) Hz, CF\(_3\)); 161.45 (d, \( J_{CP} = 87 \) Hz, P-CO\(_2\)). \(^{19}\)F\(^{1}\)H NMR (376.4 MHz, CD\(_2\)Cl\(_2\)): \( \delta_F = -79.07 \) (s, CF\(_3\)). \(^{29}\)Si\(^{1}\)H NMR (HMBC) (99.3 MHz, CD\(_2\)Cl\(_2\)): \( \delta_Si = 38.2 \) (s). \(^{31}\)P\(^{1}\)H NMR (202.4 MHz, -40 °C, CD\(_2\)Cl\(_2\)): \( \delta_P = 50.23 \) (d, \( J_{CP} = 87 \) Hz).
Reaction of Ph₃Si(OTf) with P₃Bu₃ and CO₂: Scale: Ph₃Si(OTf) (30 mg, 0.0734 mmol, 1.0 eq), P₃Bu₃ (15 mg, 0.0734 mmol, 1.0 eq). Examining the reaction mixture by multinuclear NMR spectroscopy prior to CO₂ addition revealed no adduct formation. ¹³CO₂ was then added to the J-Young NMR tube.

Reaction Mixture: ¹H NMR (400.0 MHz, CD₂Cl₂): δ_H = 1.31 (d, ³J_HP= 10 Hz, free P₃Bu₃); 1.66 (d, ³J_HP= 15 Hz, 3-15 P-C(CH₃)₃); 7.51 (dd/br, ³J_HH= 7 Hz, ³J_HH= 7 Hz, m-C₆H₅); 7.61 (t/br, ³J_HH= 7 Hz, p-C₆H₅); 7.71 (d/br, ³J_HH= 7 Hz, o-C₆H₅). ¹³C ¹H NMR (100.6 MHz, CD₂Cl₂): δ_C = 30.69 (br, P-C); 32.61 (d, ³J_CP= 13 Hz, P-C(CH₃)₃); 119.43 (q, ¹J_CF= 321 Hz, CF₃); 125.32 (s, free CO₂); 128.91 (s, m-C₆H₅); 129.09 (s, i-C₆H₅); 132.44 (s, p-C₆H₅); 136.02 (s, o-C₆H₅); 162.93 (d/br, ¹J_CP= 85 Hz, 3-15 P-CO₂). ¹⁹F ¹H NMR (376.4 MHz, 25 °C, CD₂Cl₂): δ_F = -77.42 (s, CF₃). ²⁹Si NMR (HMBC) (99.3 MHz, CD₂Cl₂): δ_Si = 1.6 (s). ³¹P ¹H NMR (161.9 MHz, CD₂Cl₂): δ_P = 57.5 (s/br, 3-15); 62.5 (s/br, free P₃Bu₃).

Preparation of 3-17: Scale: Et₃SiNTf₂ (32 mg, 0.0809 mmol, 1.0 eq), P₃Bu₃ (16 mg, 0.0809 mmol, 1.0 eq). Examining the ¹H and ³¹P ¹H spectra prior to CO₂ addition revealed adduct formation (3-16, δ_P= 37.2). This mixture was exposed to CO₂. After one hour, ³¹P NMR spectroscopy revealed conversion to a new species. The contents of the J-Young tube were then transferred to a vial and the solvent was removed in vacuo, yielding a colourless oil. The oil was triturated in pentane. The supernatant was decanted and the resultant white solid was dried under vacuum. Yield: 37 mg, 71%. ¹H NMR (600.0 MHz, CD₂Cl₂): δ_H = 0.97 (m, 6H, Si-CH₂CH₂Si); 1.05 (m, 9H, Si-CH₂CH₂Si); 1.73 (d, 27H, ³J_HP= 15 Hz, PC(CH₃)₃). ¹³C ¹H NMR (150.9 MHz, CD₂Cl₂): δ_C = 4.77 (s, Si-Et); 6.46 (s, Si-Et); 30.61 (s, PC(CH₃)₃); 41.83 (d, ¹J_CP= 18 Hz, P-C(CH₃)₃); 120.34 (q, ¹J_CF= 322 Hz, CF₃); 162.31 (d, ²J_CP= 87 Hz, P-CO₂). ¹⁹F ¹H NMR (376.4 MHz, CD₂Cl₂): δ_F = -79.48 (s, CF₃). ²⁹Si ¹H NMR (119.2 MHz, CD₂Cl₂): δ_Si = 41.0 (s). ³¹P ¹H NMR (161.9 MHz, CD₂Cl₂): δ_P = 53.1 (s). Anal. Calc. for C₂₁H₄₂F₆NO₆PS₂Si: C, 39.30; H, 6.60; N, 2.18. Found: C, 38.74; H, 6.79; N, 2.53.
Reaction of Ph2Si(OTf)2 with P1Bu3 (1:1) and CO2: Scale: Ph2Si(OTf)2 (30 mg, 0.0624 mmol, 1.0 eq), P1Bu3 (13 mg, 0.0624 mmol, 1.0 eq). Examining the reaction mixture by multinuclear NMR spectroscopy prior to CO2 addition revealed no adduct formation. 13CO2 was then added to the J-Young NMR tube.

Room Temperature (25 °C): 1H NMR (400.0 MHz, CD2Cl2): δH = 1.30 (br, free P1Bu3); 1.70 (br, 3–18 P-C(CH3)3); 7.62 (dd/br, JHH = 8 Hz, JHP = 8 Hz, m-C6H5); 7.76 (t/br, JHH = 8 Hz, p-C6H5); 7.81 (dd, JHH = 8 Hz, JHP = 1 Hz, o-C6H5). 13C{1H} NMR (125.7 MHz, CD2Cl2): δC = 30.58 (br); 32.51 (br); 34.63 (d/br, JCP = 30 Hz, P-C); 42.76 (d/br, JCP = 12 Hz, P-C); 119.41 (q, JCF = 319 Hz, CF3); 122.80 (s/br, i-C6H5); 122.89 (s/br, i-C6H5); 125.29 (s/br, free CO2); 129.51 (s/br, m-C6H5); 129.75 (s/br, m-C6H5); 134.80 (s, overlapping p-C6H5); 135.58 (s/br, overlapping o-C6H5); 162.96 (d/br, JCP = 80 Hz, P-CO2). 19F{1H} NMR (376.4 MHz, CD2Cl2): δF = -77.32 (s, CF3). 29Si{1H} NMR (HMBC) (99.3 MHz, CD2Cl2): δSi = -24.6 (s, Ph2Si(OTf)2); -20.7 (s, 3–18). 31P{1H} NMR (161.9 MHz, CD2Cl2): δP = 57.5 (s/br, 3–18); 62.5 (s/br, free P1Bu3).

Reaction of Ph2Si(OTf)2 with P1Bu3 (1:2) and 13CO2: Scale: Ph2Si(OTf)2 (29 mg, 0.0603 mmol, 1.0 eq), P1Bu3 (24 mg, 0.121 mmol, 2.0 eq). 13CO2 was added to the J-Young NMR tube. At room temperature 3–18 and free P1Bu3 were observed; however, upon cooling to -30 °C, NMR spectroscopic data indicated conversion to 3–19.

Low Temperature (-30 °C); 1H NMR (500.0 MHz, CD2Cl2): δH = 1.64 (d, 54H, JHP = 16 Hz, P-C(CH3)3); 7.62 (dd, 4H, JHH = 8 Hz, JHP = 8 Hz, m-C6H5); 7.76 (m, 6H, overlapping p-C6H5 o-C6H5). 13C{1H} NMR (125.7 MHz, CD2Cl2): δC = 29.91 (s, P-C(CH3)3); 45.04 (d, JCP = 16 Hz, P-C(CH3)3); 112.80 (s, P-C(CH3)3); 126.96 (d, JCP = 16 Hz, P-C(CH3)3); 141.36 (q, JCF = 321 Hz, CF3); 148.79 (s, overlapping m-C6H5); 156.29 (s/br, free CO2); 162.96 (d/br, JCP = 80 Hz, P-CO2).
Preparation of 3-20

Method 1: A J-Young NMR tube was charged with Et₃SiNTf₂ (32 mg, 0.0809 mmol, 1.0 eq) and P'Bu₃ (33 mg, 0.162 mmol, 2.0 eq) in C₆D₅Br (1 mL). Adduct formation could be observed by ³¹P NMR spectroscopy. The J-Young NMR tube then was degassed and backfilled with CO₂, yielding a mixture of 3-17 and free P'Bu₃. The J-Young NMR tube was then heated at 80°C for 3 days, forming 3-20 and a [HP'Bu₃][NTf₂] salt by-product. Complete conversion was observed by NMR spectroscopy.

Method 2: A J-Young NMR tube was charged with Et₃SiNTf₂ (41 mg, 0.103 mmol, 1.0 eq) and HP'Bu₂ (30 mg, 0.206 mmol, 2.0 eq) in CD₂Cl₂ (1 mL). Adduct formation could be observed by ³¹P NMR spectroscopy (δ_p = 3.9). The J-Young NMR tube then was degassed and backfilled with CO₂ (approx. 2 atm). The contents of the J-Young were emptied into a vial in the glovebox and toluene (5 mL) was added to precipitate out a white solid, identified as [H₂P'Bu₂][NTf₂]. The precipitate was removed by filtration. Volatiles were removed from the filtrate in vacuo, affording a colourless oil 3-20. Yield: 24 mg, 77%.

¹H NMR (400.0 MHz, CD₂Cl₂): δ_H = 0.82 (q/br, 6H, ³J_HH = 8 Hz, Si-CH₂); 1.00 (t, 9H, ³J_HH = 8 Hz, Si-CH₂CH₃); (d, 18H, ³J_HP = 128 Hz, P-C(CH₃)₃). ¹³C{¹H} NMR (100.6 MHz, CD₂Cl₂): δ_C = 5.23 (s, Si-Et); 6.75 (s/br, Si-Et); 30.32 (d, ²J_CP = 13 Hz, P-C(CH₃)₃); 33.20 (d, ²J_CP = 22 Hz, P-C); 181.29 (d, ²J_CP = 31 Hz, P-CO₂). ³¹P{¹H} NMR (161.9 MHz, CD₂Cl₂): δ_p = 47.2 (s). ²⁹Si NMR (HMBC) (79.5 MHz, CD₂Cl₂): δ_Si = 26.0. Satisfactory elemental analysis values could not be obtained after repeated attempts due to a minor Et₃SiOSiEt₃ impurity and persistent residual toluene.

Characterization of [HP'Bu₃][NTf₂]: The precipitate from the synthesis of 3-20 (method 1) was isolated by filtration of the reaction mixture. The white solid was washed with toluene and dried in vacuo. NMR spectroscopy identified this species as [HP'Bu₃][NTf₂]. ¹H NMR (400.0 MHz,
CD₂Cl₂): δ_H = 1.65 (d, 27H, ³_J_HP = 16 Hz, CH₃); 5.61 (d, 1H, ¹_J_HP = 447 Hz, P-H). ¹³C{¹H} NMR (100.6 MHz, CD₂Cl₂): δ_C = 30.36 (s, CH₃); 37.47 (d, ¹_J_CP = 28 Hz, P-C); 120.33 (q, ¹_J_CF = 323 Hz, CF₃). ¹⁹F{¹H} NMR (376.4 MHz, CD₂Cl₂): δ_F = -79.41 (s, CF₃). ³¹P{¹H} NMR (161.9 MHz, CD₂Cl₂): δ_P = 55.2 (s).

**Characterization of [H₂P'Bu₂][NTf₂]:** The precipitate from the preparation of 3-20 (method 2) was isolated by filtration. The white solid was washed with toluene and dried *in vacuo*. NMR spectroscopy identified this species as [H₂P'Bu₂][NTf₂]. ¹H NMR (400.0 MHz, CD₂Cl₂): δ_H = 1.56 (d, 18H, ³_J_HP = 18 Hz, CH₃); 5.97 (d, 2H, ¹_J_HP = 464 Hz, P-H). ¹³C{¹H} NMR (100.6 MHz, CD₂Cl₂): δ_C = 27.71 (d, ²_J_CP = 2 Hz, CH₃); 32.01 (d, ¹_J_CP = 33 Hz, P-C); 120.25 (q, ¹_J_CF = 321 Hz, CF₃). ¹⁹F{¹H} NMR (376.4 MHz, CD₂Cl₂): δ_F = -79.41 (s, CF₃). ³¹P{¹H} NMR (161.9 MHz, CD₂Cl₂): δ_P = 24.6 (s).

### 3.4.6 Reaction of 3-17 with Me₂NHBH₃

An NMR tube was charged with [¹Bu₃¹³CO₂SiEt₃][NTf₂] (3-17) (32 mg, 0.0683 mmol, 1.0 eq). In a vial, Me₂NHBH₃ (12 mg, 0.205 mmol, 3.0 eq) was weighed and dissolved in 1 mL of CD₂Cl₂. The Me₂NHBH₃ solution was then transferred to the NMR tube via pipette. The resulting mixture was examined by NMR spectroscopy after 30 minutes.

**Reaction Mixture:** ¹H NMR (400.0 MHz, CD₂Cl₂): δ_H = 0.59 (qd, ³_J_HH = 8 Hz, ³_J_HH = 3 Hz, Si-CH₃); 0.97 (t, ³_J_HH = 8 Hz, Si-CH₂CH₃); 1.48 (q/br, ¹_J_BH = 96 Hz, Me₂NHB-H₃); 1.64 (d, ³_J_PH = 15 Hz, [HP¹Bu₃]⁺ P-C(CH₃)₃); 2.28 (br); 2.43 (br); 2.50 (d, ³_J_HH = 6 Hz, (CH₃)₂-NHB₃H); 2.57 (d, ³_J_HH = 6 Hz, N-(CH₃)₂); 2.60 (d/br, ³_J_HH = 6 Hz, N-(CH₃)₂); 3.60 (sept, ³_J_HH = 3 Hz, Si-H); 3.93 (br); 5.57 (d, ¹_J_HP = 446 Hz, [H²P'Bu₃⁺]). ¹¹B NMR (128.3 MHz, CD₂Cl₂): δ_B = -17.6 (td, ¹_J_BH = 130 Hz, ¹_J_BH = 24 Hz, H₂B(μ-H)(μ-NMe₂)BH₂); -13.6 (q, ¹_J_BH = 96 Hz, Me₂NHB₃H); -2.2 (br/t, ¹_J_BH = 99 Hz); 2.2 (t, ¹_J_BH = 110 Hz); 5.2 (t, ¹_J_BH = 112 Hz, (Me₂NHB₃H)₂). ¹³C{¹H} NMR (100.6 MHz, CD₂Cl₂): δ_C = 2.79 (s, SiCH₂); 6.86 (d, J = 21 Hz); 8.30 (s, SiCH₂CH₃); 30.32 (s, PC(CH₃)₃); 37.77 (d, ¹_J_CP = 28 Hz, PC); 42.04 (s); 43.87 (s); 44.78 (s, Me₂NHB₃H); 51.96 (s);
52.26 (s); 120.28 (q, J_{CF} = 319 Hz, CF$_3$); 125.28 (liberated CO$_2$). $^{19}$F{$^1$H} NMR (376.4 MHz, CD$_2$Cl$_2$): $\delta_F = -78.73$ (s, CF$_3$). $^{31}$P{$^1$H} NMR (161.9 MHz, CD$_2$Cl$_2$): $\delta_P = 55.4$ (s, [HP$^3$Bu$_3$]$^+$).

### 3.4.7 X-Ray Data Collection, Reduction, Solution, and Refinement

Single crystals were coated with Paratone-N oil and mounted under a cold nitrogen stream. Data sets were collected on a Bruker Kappa Apex II CCD diffractometer using a graphite monochromater with MoK$\alpha$ radiation ($\lambda = 0.71073$ Å). Data reduction was performed using the Bruker SMART software package. Data sets were corrected for absorption effects using SADABS. The structures were solved by direct methods using XS and refined by full-matrix least-squares on F$^2$ using XL as implemented in the SHELXTL suite of programs. All non-hydrogen atoms were refined anisotropically unless noted otherwise. Hydrogen atoms were placed in calculated positions using an appropriate riding model and coupled isotropic temperature factors.

In the case of 3-2, this structure was both twinned and disordered. The TMP moiety is disordered over two positions with a s.o.f. (site occupancy factor) of 50 : 50. The disordered portion of the structure was refined isotropically, while the remaining non-hydrogen atoms were refined anisotropically.
Table 3.4 Crystallographic data for compounds 3-1 – 3-4

<table>
<thead>
<tr>
<th>Crystal</th>
<th>3-1</th>
<th>3-2</th>
<th>3-3</th>
<th>3-4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C₁₀H₂₀F₃NO₃S</td>
<td>C₂₃H₂₈F₃NO₅SSi</td>
<td>C₂₈H₁₈F₁₅NO₂Si</td>
<td>C₂₈H₃₃NO₂Si</td>
</tr>
<tr>
<td>Formula wt</td>
<td>291.33</td>
<td>515.62</td>
<td>713.52</td>
<td>443.64</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Orthorhombic</td>
<td>Monoclinic</td>
<td>Triclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>Pbca</td>
<td>C2/c</td>
<td>P-1</td>
<td>P2₁/n</td>
</tr>
<tr>
<td>a (Å)</td>
<td>8.6532(4)</td>
<td>34.968(3)</td>
<td>10.681(2)</td>
<td>11.2388(5)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>16.4198(7)</td>
<td>7.7242(6)</td>
<td>11.263(3)</td>
<td>15.1696(6)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>19.1367(8)</td>
<td>18.4219(16)</td>
<td>12.109(2)</td>
<td>14.6794(6)</td>
</tr>
<tr>
<td>α (deg)</td>
<td>90</td>
<td>90</td>
<td>78.187(10)</td>
<td>90</td>
</tr>
<tr>
<td>β (deg)</td>
<td>90</td>
<td>94.395(5)</td>
<td>76.213(10)</td>
<td>107.785(2)</td>
</tr>
<tr>
<td>γ (deg)</td>
<td>90</td>
<td>90</td>
<td>77.935(11)</td>
<td>90</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>2719.0(2)</td>
<td>4961.2(7)</td>
<td>1365.0(5)</td>
<td>2419.80(17)</td>
</tr>
<tr>
<td>Z</td>
<td>8</td>
<td>8</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>T (K)</td>
<td>149(2)</td>
<td>150(2)</td>
<td>149(2)</td>
<td>150(2)</td>
</tr>
<tr>
<td>d (calc) gcm⁻³</td>
<td>1.423</td>
<td>1.354</td>
<td>1.736</td>
<td>1.218</td>
</tr>
<tr>
<td>Abs coeff, µ, mm⁻¹</td>
<td>0.274</td>
<td>0.235</td>
<td>0.220</td>
<td>0.122</td>
</tr>
<tr>
<td>Data collected</td>
<td>19418</td>
<td>4341</td>
<td>19524</td>
<td>18326</td>
</tr>
<tr>
<td>R int</td>
<td>0.0266</td>
<td>0.0000</td>
<td>0.0335</td>
<td>0.0356</td>
</tr>
<tr>
<td># of indpndt reflns</td>
<td>2390</td>
<td>4341</td>
<td>4785</td>
<td>4267</td>
</tr>
<tr>
<td>Reflns Fₒ ≥ 2.0 σ (Fₒ)</td>
<td>2081</td>
<td>3525</td>
<td>4061</td>
<td>3402</td>
</tr>
<tr>
<td>Variables</td>
<td>167</td>
<td>298</td>
<td>424</td>
<td>289</td>
</tr>
<tr>
<td>R (&gt;2σ)</td>
<td>0.0289</td>
<td>0.0498</td>
<td>0.0303</td>
<td>0.0427</td>
</tr>
<tr>
<td>wR²</td>
<td>0.0755</td>
<td>0.1177</td>
<td>0.0814</td>
<td>0.1080</td>
</tr>
<tr>
<td>Goodness of fit</td>
<td>0.937</td>
<td>1.069</td>
<td>1.024</td>
<td>1.016</td>
</tr>
</tbody>
</table>
4 Conclusion

4.1 Thesis Summary

This thesis has described studies examining tetracoordinate silicon Lewis acids for FLP chemistry. This field remains relatively unexplored as compared to traditional group 13-based frustrated Lewis pairs. In this work, two general types of silicon Lewis acids were studied: (1) neutral silanes with strongly electron withdrawing substituents $\text{RSi}(\text{C}_6\text{F}_5)_3$ and (2) four-coordinate Si species with labile substituents $\text{R}_4\text{SiX}_n$ ($\text{X}=\text{NTf}_2$ $n=1$, $\text{X}=\text{OTf}$ $n=1, 2$).

SLAs in form (1) were found to be unreactive towards small molecules when paired with sterically hindered amines and phosphines typical of FLP chemistry. No reactions were observed with $\text{CO}_2$, $\text{N}_2\text{O}$, $\text{H}_2$, and alkyne substrates. Lewis acidity measurements obtained employing the Gutmann-Beckett method suggest that the compounds $\text{RSi}(\text{C}_6\text{F}_5)_3$ ($\text{R}=\text{H, F}$) exhibit only a fraction of the Lewis acidity of $\text{B}(\text{C}_6\text{F}_5)_3$ which is likely why the activation of small molecules was unsuccessful.

Lewis acids of form (2) were successfully employed in the FLP-type activation of $\text{CO}_2$. Combinations of silyl triflates and tetramethylpiperidine react with $\text{CO}_2$ to afford silyl carbamates $\text{C}_9\text{H}_{18}\text{N}(\text{CO}_2)\text{SiR}_3$ and an ammonium triflate salt. When paired with $\text{PEt}_3$ or $\text{P}^\text{t}\text{Bu}_3$, silyl triflates or $\text{Et}_3\text{SiNTf}_2$ were found to capture $\text{CO}_2$ to yield species in the form $[\text{R}_3\text{P}(\text{CO}_2)\text{SiR}_3][\text{X}]$ ($\text{X}=\text{OTf}$, $\text{NTf}_2$). When $\text{X}=\text{NTf}$, these $\text{CO}_2$ adducts display increased stability with respect to $\text{CO}_2$ liberation; this is presumably due to the weaker coordinating ability of the triflimide anion relative to triflate. Reactions employing $\text{Ph}_2\text{Si}(\text{OTf})_2$ as the Lewis acid have been proposed to yield the species $[\text{R}_3\text{P}(\text{CO}_2)\text{SiPh}_2(\text{OTf})][\text{OTf}]$ and $[(\text{R}_3\text{PCO}_2)_2\text{SiPh}_2][\text{OTf}]_2$ in which one or two molecules of $\text{CO}_2$ are captured. Formation of the bis-$\text{CO}_2$ activation products appears to be favoured at low temperatures or by the presence of excess phosphine. Attempts thus far to reduce Si/P $\text{CO}_2$ activation products with hydrosilanes and dimethylamine-borane have been unsuccessful, but future work can examine the use of other SLAs or reducing agents for these means.

4.2 Future Work

The work described demonstrates that four-coordinate SLAs can be utilized for FLP-type transformations. Continued work can examine the synthesis of new Si-based Lewis acids to
further expand this chemistry. Several approaches could be employed to develop new tetracoordinate silicon species with increased Lewis acidic properties. The incorporation of positive charge into the substituents to increase electrophilicity at silicon is one possibility. This was the rationale behind the synthesis of the dicationic adducts [Ph₂Si(L)₂][OTf]₂ (L= OPEt₃, OPPh₃, DMAP); however, the reactivity of these species towards small molecules has yet to be fully examined. Another method is to tether substituents on silicon to generate ring strain. This strain can be relieved upon adopting a five-coordinate geometry, thus promoting interactions with small molecules (Figure 4.1). This strained silacycle approach has been previously exploited to increase the Lewis acidity of four-coordinate silicon species,¹²¹,¹²² but its application in Si-based FLP chemistry has yet to be explored.

![Figure 4.1 Increasing Lewis acidity by silacycle ring strain](image)

Although reduction of CO₂ was not achieved in this work, further investigations are warranted. Silicon-centred species have shown utility as both Lewis acids and reducing agents for CO₂. Additional studies could allow for the development of a system in which silanes can act both as the Lewis acid and the reductant.
References


(121) Denmark, S. E.; Jacobs, R. T.; Dai-Ho, G.; Wilson, S. Organometallics 1990, 9, 3015.