Metal-containing and Metal-free systems for small molecule activation

by

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Metal-containing and metal-free systems toward small molecule activation

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Abstract
The objective of this thesis is to investigate small molecule activation with metal-containing and metal-free systems. Chapter 2 describes a tri-aryl benzene ligand scaffold for multimetallic N₂ activation. A RuCp* complex was synthesized and characterized by NMR and X-ray crystallography. It offered an easy entry to understanding of the ligand coordination environment. Additionally, several multi-iron complexes were also obtained even though they were not the desired products. However, they still demonstrated the feasibility of using this ligand to effect multimetallic chemistry. Chapters 3 to 5 describe a series of compounds with charge-separation feature. These compounds could not only bind CO₂ reversibly, but also catalyze the hydroboration of CO₂ with a wide borane scope. In Chapter 3, a possible intermediate from the catalytic cycle was isolated and it partly revealed the mechanism of the catalytic reaction.
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# Table of Contents

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

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

List of Tables ................................................................................................................ viii

List of Figures ................................................................................................................ ix

List of Schemes ............................................................................................................. xviii

List of Abbreviations and Symbols .............................................................................. xxi

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

1.1 N₂ activation ........................................................................................................ 1

1.1.1 Mo complexes for N₂ activation ...................................................................... 1

1.1.2 N₂ activation by iron systems ......................................................................... 3

1.1.3 Polynuclear systems for multi-electron process ............................................. 6

1.2 CO₂ activation and conversion ............................................................................ 9

1.2.1 Activation of CO₂ in a stoichiometric manner ............................................. 10

1.2.2 Catalytic reduction of CO₂ by metal-free molecules .................................. 17

1.3 4,5-Diazafluorenide ligand chemistry .................................................................. 22

1.4 Scope and objectives ............................................................................................. 24

1.5 References ............................................................................................................ 25

2 Chapter 2 Multimetallic systems towards N₂ activation .................................... 28

2.1 Abstract .............................................................................................................. 28

2.2 Introduction ......................................................................................................... 28

2.3 Results and Discussion ...................................................................................... 30

2.4 Conclusion .......................................................................................................... 35

2.5 Experimental ....................................................................................................... 36

2.5.1 General procedures ....................................................................................... 36
2.5.2 Synthesis of 2.1 ............................................................................................................. 36
2.5.3 Synthesis of 2.2 ............................................................................................................. 38
2.5.4 Synthesis of 2.3 ............................................................................................................. 40
2.5.5 Synthesis of 2.4 ............................................................................................................. 42
2.5.6 Formation of 2.5 .......................................................................................................... 44
2.5.7 Formation of 2.6 .......................................................................................................... 45
2.5.8 Synthesis of 2.7 .......................................................................................................... 45
2.6 References ......................................................................................................................... 48

3 Chapter 3 Catalytic hydroboration of CO$_2$ with a carbon-centered organocatalyst .......... 49
3.1 Abstract .......................................................................................................................... 49
3.2 Introduction ....................................................................................................................... 49
3.3 Results and discussion ..................................................................................................... 50
3.4 Conclusion ........................................................................................................................ 58
3.5 Experimental .................................................................................................................... 59
    3.5.1 General procedures .................................................................................................... 59
    3.5.2 Reaction between 9-BBN and $^{13}$CO$_2$ in the presence of catalyst 3.1 at 70 °C ..... 60
    3.5.3 Reaction between HBcat and $^{13}$CO$_2$ in the presence of catalyst 3.1 at 70 °C ...... 60
    3.5.4 Reaction between 9-BBN and CO$_2$ in the presence of catalyst 3.1 at 25 °C........ 61
    3.5.5 Reaction between 9-BBN and CO$_2$ in the presence of catalyst 3.1 at 70 °C........ 63
    3.5.6 Reaction between HBcat and CO$_2$ in the presence of catalyst 3.1 at 25 °C........... 64
    3.5.7 Reaction between HBcat and CO$_2$ in the presence of catalyst 3.1 at 70 °C......... 66
    3.5.8 Reaction between HBcat and CO$_2$ in the presence of catalyst 3.1 at 70 °C........... 67
    3.5.9 Reaction between HBpin and CO$_2$ in the presence of catalyst 3.1 at 100 °C....... 69
    3.5.10 Reaction between BH$_3$·SMe$_2$ and CO$_2$ in the presence of catalyst 3.1 at 25 °C ... 70
    3.5.11 Reaction between BH$_3$·SMe$_2$ and CO$_2$ in the presence of catalyst 3.1 at 70 °C ... 72
    3.5.12 Synthesis of 3.2 ....................................................................................................... 73
5.4 Conclusion..................................................................................................................115

5.5 Experimental ..............................................................................................................115

5.5.1 General procedures.................................................................................................115

5.5.2 Synthesis of 5.3........................................................................................................116

5.5.3 Synthesis of indenyllithium\(^\text{13}\)........................................................................117

5.5.4 Synthesis of 5.4........................................................................................................118

5.5.5 Synthesis of 5.5........................................................................................................119

5.5.6 Synthesis of 5.1........................................................................................................122

5.5.7 Synthesis of 5.2........................................................................................................124

5.5.8 Reaction between 9-BBN and CO\(_2\) in the presence of catalyst 5.1 at 25 °C......125

5.5.9 Reaction between 9-BBN and CO\(_2\) in the presence of catalyst 5.1 at 70 °C......127

5.5.10 Reaction between BH\(_3\)·SMe\(_2\) and CO\(_2\) in the presence of catalyst 5.1 at 25 °C .129

5.5.11 Reaction between BH\(_3\)·SMe\(_2\) and CO\(_2\) in the presence of catalyst 5.1 at 70 °C .130

5.5.12 Reaction between BH\(_3\)·SMe\(_2\) and 2.5 atm of CO\(_2\) in the presence of catalyst
5.1 at 25 °C .......................................................................................................................132

5.5.13 Reaction between BH\(_3\)·SMe\(_2\) and 5 atm of CO\(_2\) in the presence of catalyst 5.1
at 25 °C .............................................................................................................................133

5.5.14 Reaction between BH\(_3\)·SMe\(_2\) and 10 atm of CO\(_2\) in the presence of catalyst
5.1 at 25 °C ........................................................................................................................135

5.5.15 X-ray crystallography ...........................................................................................136

5.6 References .....................................................................................................................136

6 Chapter 6 Summary ........................................................................................................138

6.1 Abstract .......................................................................................................................138

6.2 Chapter 2 .....................................................................................................................138

6.3 Chapter 3-5 ..................................................................................................................139

6.4 Final remark ................................................................................................................141
List of Tables

Table 2.1 Selected crystallographic data of 2.5: ................................................................. 44
Table 2.2 Selected crystallographic data of 2.7: ................................................................. 47
Table 3.1 Hydroboration of CO\textsubscript{2} by a variety of boranes\textsuperscript{a} with 3.1 as catalyst ........................................ 55
Table 3.2 Selected crystallographic data of 3.2: ................................................................. 76
Table 3.3 Selected crystallographic data of 3.3: ................................................................. 78
Table 4.1 Hydroboration of CO\textsubscript{2} by a variety of boranes\textsuperscript{a} with 4.1 as catalyst ........................................ 88
Table 4.2 Selected crystallographic data of 4.2: ................................................................. 99
Table 5.1 Hydroboration of CO\textsubscript{2} by 9-BBN and BH\textsubscript{3}·SMe\textsubscript{2} with 5.1 as catalyst\textsuperscript{a} ....................... 115
Table 5.2 Selected crystallographic data of 5.2: ................................................................. 125
List of Figures

Figure 1.1 Structure of the iron-molybdenum cofactor......................................................... 1
Figure 1.2 A series of Fe-N₂ complexes from Peters’ group.................................................. 4
Figure 1.3 Multimetallic complexes for OEC mimic. The first one only shows the core structure for clarity. .......................................................................................................................... 7
Figure 1.4 Multi-iron complexes from Betley’s group. .............................................................. 8
Figure 1.5 Cu/Fe cyclophane complexes for N₂ activation. ...................................................... 8
Figure 1.6 [FeFe]-hydrogenase and [NiFe]-hydrogenase mimics. ............................................. 9
Figure 1.7 CO₂ adducts of some cyclophane complexes.......................................................... 11
Figure 1.8 Metal-free catalysts with carbene-like structure for CO₂ reduction ......................... 17
Figure 1.9 Phosphorus derivatives as catalyst for CO₂ conversion. ......................................... 19
Figure 1.10 Some FLP examples for CO₂ reduction................................................................. 20
Figure 1.11 TBD, NHC, and phosphorus bases for CO₂ reduction. .......................................... 21
Figure 1.12 CO₂ adducts of metal-diazafluorenide complexes. .............................................. 23
Figure 2.1 ¹H NMR spectrum of 2.4 in CDCl₃. ......................................................................... 31
Figure 2.2 ¹H NMR spectrum of the reaction between K₃L and FeBr₂(THF)₂. ......................... 32
Figure 2.3 ¹H NMR spectrum of the reaction between 2.4 and Fe(HMDS)₂. ......................... 33
Figure 2.4 X-ray crystal structure of 2.5 with 50% probability ellipsoids. Hydrogen atoms and phenyl atoms on the nitrogen atoms of the side arms around the core are omitted for clarity. The core structure is shown with atoms labelled. Selected bond lengths (Å) and angles (°) for 2.5: Fe1-O4, 1.952(6); Fe1-O5, 2.361(6); Fe1-O6, 2.083(5); Fe2-Fe3, 3.115(2); Fe2-O4, 2.144(6); Fe2-O5, 1.927(5); Fe2-O6, 2.040(6); Fe3-O4, 2.071(6); Fe3-O7, 2.029(6); Fe3-O6, 2.035(6);
Fe1-O4-Fe2, 101.1(2); Fe1-O4-Fe3, 134.0(3); Fe2-O4-Fe3, 95.3(2); Fe1-O5-Fe2, 94.6(3); Fe2- 
O6-Fe3, 99.7(2). ......................................................................................................................... 33

Figure 2.5 X-ray crystal structure of 2.6 with 50% probability ellipsoids. Hydrogen atoms are 
omitted for clarity. Selected bond lengths (Å) and angles (°) for 2.6: Fe1-N1, 2.172; Fe1-N2, 
2.129(4); Fe1-N3, 2.169; Fe1-O1, 1.930(3); Fe1-O2, 1.980(6); Fe1-O3, 1.998. ......................... 34

Figure 2.6 1H NMR spectrum of 2.7 in C6D6. ........................................................................ 35

Figure 2.7 X-ray crystal structure of 2.7 with 50% probability ellipsoids. Hydrogen atoms and 
methyl groups on Cp* are omitted for clarity. Selected bond lengths (Å) and angles (°) for 2.7: 
Ru1-O1, 2.044(6); Ru1-N1, 2.037(8); Ru2-O2, 2.037(7); Ru2-N2, 2.069(7); Ru3-O3, 2.008(6); 
Ru3-N3, 2.053(8); N1-Ru1-O1, 88.6(3); N2-Ru2-O2, 89.1(3); N3-Ru3-O3, 88.3(3). .......... 35

Figure 2.8 1H NMR spectrum of 2.1 in CDCl3 ........................................................................ 37

Figure 2.9 13C NMR spectrum of 2.1 in CDCl3 ........................................................................ 38

Figure 2.10 1H NMR spectrum of 2.2 in CDCl3 ........................................................................ 39

Figure 2.11 13C NMR spectrum of 2.2 in CDCl3 ........................................................................ 40

Figure 2.12 1H NMR spectrum of 2.3 in CDCl3 ........................................................................ 41

Figure 2.13 13C NMR spectrum of 2.3 in CDCl3 ........................................................................ 42

Figure 2.14 1H NMR spectrum of 2.4 in CDCl3 ........................................................................ 43

Figure 2.15 13C NMR spectrum of 2.4 in CDCl3 ........................................................................ 44

Figure 2.16 1H NMR spectrum of 2.7 in C6D6. Note, two humps at 1.36 and 0.92 ppm are from 
grease. ....................................................................................................................................... 46

Figure 2.17 13C NMR spectrum of 2.7 in C6D6. Note, peaks at 137.90, 129.34, 128.57, 125.70 
and 21.44 ppm are from trace amount of toluene. A peak at 30.24 ppm is from grease. ........ 47

Figure 3.1 1H NMR spectrum of the final mixture of the reaction between 3.1, 10 eq. of 9-BBN 
and CO2 at 70 °C. .......................................................................................................................... 51
Figure 3.2 $^{13}$C NMR spectrum of the final mixture of the reaction between 3.1, 10 eq. of 9-BBN and CO$_2$ at 70 °C. ........................................................................................................................................ 52

Figure 3.3 $^1$H NMR spectrum of the final mixture of the reaction between 3.1, 30 eq. of HBcat and CO$_2$ at 70 °C. ........................................................................................................................................ 52

Figure 3.4 $^{13}$C NMR spectrum of the final mixture of the reaction between 3.1, 30 eq. of HBcat and CO$_2$ at 70 °C. ........................................................................................................................................ 53

Figure 3.5 TON vs time plot for the formation of CH$_3$OBcat catalyzed by 3.1. A C$_6$D$_5$Br solution of 3.1 and 100 eq. of HBcat was exposed to 1.5 atm CO$_2$ at 70 °C (•) and 25 °C (○). .......... 53

Figure 3.6 DFT calculations showing the mechanism for the formation of HCOOBcat. Note, the mechanism discussed above is not general, as different boranes and catalysts could give different energetics according to DFT. ........................................................................................................................................ 56

Figure 3.7 X-ray crystal structure of 3.2 with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) for 3.2: O1-B1, 1.410(8); O1-C13, 1.379(4); O2-B1, 1.409(9); O2-C14, 1.384(3); N1-C12, 1.471(4); B1-C8, 1.493(6); C4-C8, 1.434(8); C7-C8, 1.435(2); O1-B1-O2, 109.6(2); O1-B1-C8, 125.3(2); O2-B1-C8, 124.9(9); C4-C8-C7, 104.9(1). ........................................................................................................................................ 57

Figure 3.8 X-ray crystal structure of 3.3 with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) for 3.3: N1-C47, 1.488(3); C7-C37, 1.480(6); C18-C37, 1.499(8); B2-O5, 1.505(5); B2-O6, 1.469(8); B2-O7, 1.493(6); B2-O8, 1.480(7); C7-C37-C18, 102.3(2); O6-B2-O5, 106.8(1); O6-B2-O8, 113.7(7); O5-B2-O7, 108.3(9); O7-B2-O8, 102.6(9). ........................................................................................................................................ 58

Figure 3.9 $^1$H NMR spectrum of the reaction between 9-BBN and CO$_2$ in the presence of catalyst 3.1 at 25 °C. A peak at 2.11 ppm refers to hexamethylbenzene as the internal standard. .......... 62

Figure 3.10 $^{11}$B NMR spectrum of the reaction between 9-BBN and CO$_2$ in the presence of catalyst 3.1 at 25 °C........................................................................................................................................ 62

Figure 3.11 $^1$H NMR spectrum of the reaction between 9-BBN and CO$_2$ in the presence of catalyst 3.1 at 70 °C. A peak at 2.09 ppm refers to hexamethylbenzene as the internal standard. 63
Figure 3.12 $^{11}$B NMR spectrum of the reaction between 9-BBN and CO$_2$ in the presence of catalyst 3.1 at 70 °C. ........................................................................................................................................... 64

Figure 3.13 $^1$H NMR spectra of the reaction between HBcat and CO$_2$ in the presence of catalyst 3.1 at 25 °C from 5 min (bottom) to 6 h (top). ........................................................................................................................................... 65

Figure 3.14 $^{11}$B NMR spectrum of the reaction between HBcat and CO$_2$ in the presence of catalyst 3.1 at 25 °C from 5 min (bottom) to 6 h (top). ........................................................................................................................................... 65

Figure 3.15 $^1$H NMR spectrum of the reaction between HBcat and CO$_2$ in the presence of catalyst 3.1 at 70 °C from 15 min (bottom) to 2 h (top). ........................................................................................................................................... 66

Figure 3.16 $^{11}$B NMR spectrum of the reaction between HBcat and CO$_2$ in the presence of catalyst 3.1 at 70 °C from 15 min (bottom) to 2 h (top). ........................................................................................................................................... 67

Figure 3.17 $^1$H NMR spectrum of the reaction between HBcat and CO$_2$ in the presence of catalyst 3.1 at 70 °C. A peak at 2.10 ppm refers to hexamethylbenzene as the internal standard. 68

Figure 3.18 $^{11}$B NMR spectrum of the reaction between HBcat and CO$_2$ in the presence of catalyst 3.1 at 70 °C. ........................................................................................................................................... 68

Figure 3.19 $^1$H NMR spectrum of the reaction between HBpin and CO$_2$ in the presence of catalyst 3.1 at 100 °C. A peak at 2.23 ppm refers to hexamethylbenzene as the internal standard. ........................................................................................................................................... 69

Figure 3.20 $^{11}$B NMR spectrum of the reaction between HBpin and CO$_2$ in the presence of catalyst 3.1 at 100 °C. ........................................................................................................................................... 70

Figure 3.21 $^1$H NMR spectrum of the reaction between BH$_3$·SM$_2$ and CO$_2$ in the presence of catalyst 3.1 at 25 °C. A peak at 2.10 ppm refers to hexamethylbenzene as the internal standard. 71

Figure 3.22 $^{11}$B NMR spectrum of the reaction between BH$_3$·SM$_2$ and CO$_2$ in the presence of catalyst 3.1 at 25 °C. ........................................................................................................................................... 71

Figure 3.23 $^1$H NMR spectrum of the reaction between BH$_3$·SM$_2$ and CO$_2$ in the presence of catalyst 3.1 at 70 °C. A peak at 2.06 ppm refers to hexamethylbenzene as the internal standard. 72
Figure 3.24 $^{11}$B NMR spectrum of the reaction between BH$_3$·SMe$_2$ and CO$_2$ in the presence of catalyst 3.1 at 70 °C.

Figure 3.25 $^1$H NMR spectrum of 3.2 in C$_6$D$_6$. Note, a peak at 4.27 ppm refers to CH$_2$Cl$_2$. Two humps at 1.36 and 0.92 ppm are from grease.

Figure 3.26 $^{13}$C NMR spectrum of 3.2 in C$_6$D$_6$.

Figure 3.27 $^{11}$B NMR spectrum of 3.2 in C$_6$D$_6$.

Figure 3.28 $^1$H NMR spectrum of the reaction between HBcat and CO$_2$ in the presence of catalyst 3.2 at 25 °C. A peak at 2.22 ppm refers to hexamethylbenzene as the internal standard.

Figure 3.29 $^{11}$B NMR spectrum of the reaction between HBcat and CO$_2$ in the presence of catalyst 3.2 at 25 °C.

Figure 3.30 $^1$H NMR spectrum of 3.3 in CDCl$_3$. Note, the integration of H at 6.4 ppm from B(cat)$_2$ is smaller than expected. A peak at 5.30 ppm refers to CH$_2$Cl$_2$.

Figure 4.1 $^1$H NMR spectrum of 4.2 in DMSO-d$_6$. The peak at 11.02 ppm in the $^1$H NMR spectrum corresponds to a carboxylic acid.

Figure 4.2 $^{13}$C NMR spectrum of 4.2 in DMSO-d$_6$. The $^{13}$C NMR spectrum confirms the formation of a carboxylic acid species with a new peak at 166.37 ppm.

Figure 4.3 IR spectrum of 4.2 in CDCl$_3$.

Figure 4.4 TGA trace of compound 4.2. The 20.88% mass loss between 40 °C and 110 °C matches with the expected weight loss of 21.67%. TGA methods: 1. Ramp 5 °C/min to 40 °C; 2. Isothermal at 40 °C for 5 min; 3. Ramp 5 °C/min to 200 °C.

Figure 4.5 TON vs time plot for the formation of (CH$_3$OBO)$_3$ catalyzed by 4.1. A CDCl$_3$ solution of 4.1 and 100 eq. of BH$_3$·SMe$_2$ was exposed to 1.5 atm of CO$_2$ at 25 °C.

Figure 4.6 $^1$H NMR spectrum of 4.3 in CDCl$_3$.

Figure 4.7 $^{13}$C NMR spectrum of 4.3 in CDCl$_3$. 
Figure 4.8 $^1$H NMR spectrum of 4.4 in CDCl$_3$ ................................................................. 92

Figure 4.9 $^{13}$C NMR spectrum of 4.4 in CDCl$_3$ .................................................................. 93

Figure 4.10 $^1$H NMR spectrum of 4.5 in CDCl$_3$ ................................................................. 94

Figure 4.11 $^{13}$C NMR spectrum of 4.5 in CDCl$_3$ .................................................................. 94

Figure 4.12 $^1$H NMR spectrum of 4.6 in CD$_3$CN ................................................................. 96

Figure 4.13 $^{13}$C NMR spectrum of 4.6 in CD$_3$CN .................................................................. 96

Figure 4.14 $^1$H NMR spectrum of 4.1 in CDCl$_3$ .................................................................. 98

Figure 4.15 $^{13}$C NMR spectrum of 4.1 in CDCl$_3$ .................................................................. 98

Figure 4.16 $^1$H NMR spectrum of the reaction between 9-BBN and CO$_2$ in the presence of catalyst 4.1 at 25 °C. A peak at 2.24 ppm refers to hexamethylbenzene as the internal standard. ................................................................................................................................. 101

Figure 4.17 $^{11}$B NMR spectrum of the reaction between 9-BBN and CO$_2$ in the presence of catalyst 4.1 at 25 °C .................................................................................................................. 101

Figure 4.18 $^1$H NMR spectrum of the reaction between 9-BBN and CO$_2$ in the presence of catalyst 4.1 at 70 °C. A peak at 2.25 ppm refers to hexamethylbenzene as the internal standard. ................................................................................................................................. 102

Figure 4.19 $^{11}$B NMR spectrum of the reaction between 9-BBN and CO$_2$ in the presence of catalyst 4.1 at 70 °C .................................................................................................................. 103

Figure 4.20 $^1$H NMR spectrum of the reaction between HBcat and CO$_2$ in the presence of catalyst 4.1 at 25 °C. A peak at 2.24 ppm refers to hexamethylbenzene as the internal standard ................................................................................................................................. 104

Figure 4.21 $^{11}$B NMR spectrum of the reaction between HBcat and CO$_2$ in the presence of catalyst 4.1 at 25 °C .................................................................................................................. 104
Figure 4.22 $^1$H NMR spectrum of the reaction between HBpin and CO$_2$ in the presence of catalyst 4.1 at 90 °C. A peak at 2.22 ppm refers to hexamethylbenzene as the internal standard.

Figure 4.23 $^{11}$B NMR spectrum of the reaction between HBpin and CO$_2$ in the presence of catalyst 4.1 at 90 °C.

Figure 4.24 $^1$H NMR spectra of the reaction between BH$_3$:SMe$_2$ and CO$_2$ in the presence of catalyst 4.1 at 25 °C from 1 h (bottom) to 7 h (top).

Figure 4.25 $^{11}$B NMR spectrum of the reaction between BH$_3$:SMe$_2$ and CO$_2$ in the presence of catalyst 4.1 at 25 °C above from 1 h (bottom) to 7 h (top).

Figure 5.1 $^1$H NMR spectrum of 5.2 in DMSO-d$_6$. The peak at 9.98 ppm in the $^1$H NMR spectrum corresponds to a carboxylic acid. Note, the peak at 5.75 ppm refers to CH$_2$Cl$_2$. 

Figure 5.2 $^{13}$C NMR spectrum of 5.2 in DMSO-d$_6$. The $^{13}$C NMR spectrum confirms the formation of a carboxylic acid species with a new peak at 166.63 ppm.

Figure 5.3 IR spectrum of 5.2 in nujol.

Figure 5.4 $^1$H NMR spectrum of 5.3 in CDCl$_3$.

Figure 5.5 $^{13}$C NMR spectrum of 5.3 in CDCl$_3$.

Figure 5.6 $^1$H NMR spectrum of 5.4 in CDCl$_3$.

Figure 5.7 $^{13}$C NMR spectrum of 5.4 in CDCl$_3$.

Figure 5.8 $^1$H NMR spectrum of 5.5 in CDCl$_3$.

Figure 5.9 $^{13}$C NMR spectrum of 5.5 in CDCl$_3$.

Figure 5.10 $^1$H NMR spectrum of 5.1 in CDCl$_3$.

Figure 5.11 $^1$H NMR spectrum of 5.1 in DMSO-d$_6$. Note, the peaks from 3.38 and 1.09 ppm are from Et$_2$O.
Figure 5.12 $^{13}$C NMR spectrum of 5.1 in CDCl$_3$ ........................................................................................................... 124

Figure 5.13 The hydrogen bonded pair in the crystal lattice of 5.2. The intermolecular O1–O2 distance is ~2.6 Å .......................................................................................................................... 125

Figure 5.14 $^1$H NMR spectrum of the reaction between 9-BBN and CO$_2$ in the presence of catalyst 5.1 at 25 °C. A peak at 2.24 ppm refers to hexamethylbenzene as the internal standard. .......................................................................................................................... 126

Figure 5.15 $^{11}$B NMR spectrum of the reaction between 9-BBN and CO$_2$ in the presence of catalyst 5.1 at 25 °C .......................................................................................................................... 127

Figure 5.16 $^1$H NMR spectrum of the reaction between 9-BBN and CO$_2$ in the presence of catalyst 5.1 at 70 °C. A peak at 2.25 ppm refers to hexamethylbenzene as the internal standard. .......................................................................................................................... 128

Figure 5.17 $^{11}$B NMR spectrum of the reaction between 9-BBN and CO$_2$ in the presence of catalyst 5.1 at 70 °C .......................................................................................................................... 128

Figure 5.18 $^1$H NMR spectrum of the reaction between BH$_3$·SMe$_2$ and CO$_2$ in the presence of catalyst 5.1 at 25 °C. A peak at 2.15 ppm refers to hexamethylbenzene as the internal standard. .......................................................................................................................... 129

Figure 5.19 $^{11}$B NMR spectrum of the reaction between BH$_3$·SMe$_2$ and CO$_2$ in the presence of catalyst 5.1 at 25 °C .......................................................................................................................... 130

Figure 5.20 $^1$H NMR spectrum of the reaction between BH$_3$·SMe$_2$ and CO$_2$ in the presence of catalyst 5.1 at 70 °C. A peak at 2.14 ppm refers to hexamethylbenzene as the internal standard. .......................................................................................................................... 131

Figure 5.21 $^{11}$B NMR spectrum of the reaction between BH$_3$·SMe$_2$ and CO$_2$ in the presence of catalyst 5.1 at 70 °C .......................................................................................................................... 131

Figure 5.22 $^1$H NMR spectrum of the reaction between BH$_3$·SMe$_2$ and 2.5 atm of CO$_2$ in the presence of catalyst 5.1 at 25 °C. A peak at 2.17 ppm refers to hexamethylbenzene as the internal standard .......................................................................................................................... 132
Figure 5.23 $^{11}$B NMR spectrum of the reaction between BH$_3$·SMe$_2$ and 2.5 atm of CO$_2$ in the presence of catalyst 5.1 at 25 °C.

Figure 5.24 $^1$H NMR spectrum of the reaction between BH$_3$·SMe$_2$ and 5 atm of CO$_2$ in the presence of catalyst 5.1 at 25 °C. A peak at 2.17 ppm refers to hexamethylbenzene as the internal standard.

Figure 5.25 $^{11}$B NMR spectrum of the reaction between BH$_3$·SMe$_2$ and 5 atm of CO$_2$ in the presence of catalyst 5.1 at 25 °C.

Figure 5.26 $^1$H NMR spectrum of the reaction between BH$_3$·SMe$_2$ and 10 atm of CO$_2$ in the presence of catalyst 5.1 at 25 °C. A peak at 2.17 ppm refers to hexamethylbenzene as the internal standard.

Figure 5.27 $^{11}$B NMR spectrum of the reaction between BH$_3$·SMe$_2$ and 10 atm of CO$_2$ in the presence of catalyst 5.1 at 25 °C.

Figure 6.1 Other available versions of the tripodal ligand family. Two of the three side arms are omitted for clarity.

Figure 6.2 Other candidates with the charge-separation feature.
List of Schemes

Scheme 1.1 Dimolybdenum-dinitrogen complex as catalyst for N₂ reduction................................. 2
Scheme 1.2 N₂ reduction on a POCOP Mo pincer complex. ......................................................... 2
Scheme 1.3 N₂ splitting on a tridentate phosphine Mo moiety...................................................... 3
Scheme 1.4 N₂ activation by iron complexes from Holland’s group.............................................. 6
Scheme 1.5 First iron sulfide formate complex. ............................................................................. 10
Scheme 1.6 A diiron formate complex with sulfur bridge. .............................................................. 10
Scheme 1.7 Reaction between CO₂ and ZrCp* complexes........................................................... 11
Scheme 1.8 CO₂ insertion into Ti-C bonds. ..................................................................................... 12
Scheme 1.9 CO₂ insertion into a C-Si bond of Zn complexes......................................................... 12
Scheme 1.10 The synthesis of the first dimetalloxycarbene involving CO₂.................................... 13
Scheme 1.11 CO₂ binding by by silyltriflates and phosphines...................................................... 13
Scheme 1.12 CO₂ insertion into a C-B bond through ring-expansion. ........................................... 14
Scheme 1.13 CO₂ insertion into an N-P bond after binding to carbene carbon............................. 14
Scheme 1.14 Reversible CO₂ binding by electron-rich phosphines. ............................................ 14
Scheme 1.15 CO₂ reduction by a Ru(NADH) model........................................................................ 15
Scheme 1.16 CO₂ reduction by a phosphorus biradical compound............................................. 15
Scheme 1.17 CO₂ reduction to generate a Ru-formate complex. The oxidized product E=O has not been identified................................................................. 16
Scheme 1.18 Metal-ligand cooperation for CO₂ reduction to CO............................................... 16
Scheme 1.19 Stoichiometric cycle for the conversion of CO₂ to carbonyl group......................... 17
Scheme 1.20 Mechanism for methylation of amine with CO$_2$ as C$_1$ source. .......................... 18

Scheme 1.21 CO$_2$ binding on a silylium compound. ........................................................................... 20

Scheme 1.22 Mechanism for catalytic hydroboration of CO$_2$ with a silylium catalyst. .............. 21

Scheme 1.23 Cyclization of o-phenylenediamines with CO$_2$ as C$_1$ source........................................ 21

Scheme 1.24 CO$_2$ binding on TBD. ..................................................................................................... 22

Scheme 1.25 Base-catalyzed CO$_2$ trapping with alkynyl indole. .......................................................... 22

Scheme 1.26 The reaction of a Rh(I) complex and CO$_2$ to the formation of a bimetallic carboxylate compound........................................................................................................ 23

Scheme 2.1 Binding and reduction of N$_2$ by a multi-iron system................................................................. 29

Scheme 2.2 Synthesis of ligand 2.4 .......................................................................................................... 30

Scheme 3.1 Reversible CO$_2$ insertion into a C-H bond ........................................................................... 50

Scheme 3.2 Possible mechanism for the hydroboration of CO$_2$ with 3.1 as catalyst. .............. 55

Scheme 3.3 Synthesis of 3.2 ....................................................................................................................... 57

Scheme 3.4 The reaction between 3.2 and CO$_2$. ..................................................................................... 58

Scheme 4.1 Reversible CO$_2$ binding by 3.1 (R = Me, with the gray portion) and 4.1 (R = n-Pr, without the gray portion). ........................................................................................................ 83

Scheme 4.2 Synthesis of 4.1 ....................................................................................................................... 83

Scheme 4.3 Reversible CO$_2$ reaction with 4.1. The X-ray crystal structure of 4.2. Thermal ellipsoids at 50% probability level. Key bond length[Å] and angles[°]: C7-C11, 1.427(2); C7-C8, 1.409(2); C7-C12, 1.424(2); O1-C12, 1.250(2); O2-C12, 1.338(2); N1-C4, 1.360(2); N1-C3, 1.477(2); N1-C10, 1.362(2); C11-C7-C8, 106.9(1); C11-C7-C12, 125.5(1); C8-C7-C12, 127.5(1)................................................................................................................................. 86

Scheme 4.4 Possible mechanism for insertion of CO$_2$ to C-H bond of 4.1 ........................................... 87
Scheme 5.1 Previous charge separation compounds 3.1 and 4.1 ................................................. 110

Scheme 5.2 Synthesis of compound 5.1 ......................................................................................... 111

Scheme 5.3 Reversible binding of CO₂ (left) and the molecular structure of 5.2 (right). Thermal ellipsoids are shown at 50% probability. All C–H protons are omitted for clarity. Selected bond lengths [Å] and angles [°]: O1–C1 1.248(4), O2–C1 1.331(4), C1–C2 1.420(4), C2–C3 1.425(4), C3–C4 1.369(4), C4–C5 1.440(4), C2–C10 1.435(4), C5–C10 1.437(4), N1–C4 1.486(4), O1–C1–O2 120.5(3), O1–C1–C2 124.4(3), O2–C1–C2 115.1(3), C1–C2–C3 126.1(3), C1–C2–C10 127.2(3), C3–C2–C10 106.6(3) ............................................................................................................. 114

Scheme 6.1 Methylation or formylation of amine with 3.1 as catalyst ........................................ 140

Scheme 6.2 Methylation or formylation of amine with 4.1 as the catalyst .................................... 140

Scheme 6.3 Possible routes for the synthesis of other charge separation compounds ............... 141
List of Abbreviations and Symbols

dme 1,2-dimethoxyethane
dipp 2,6-diisopropylphenyl
OAc Acetate
α/β/γ alpha/beta/gamma (crystallographic unit cell lengths)
Å Angstrom, $10^{-10}$ m
Ar aryl group
atm atmosphere
Bn Benzyl
bpy bipyridine
br Broad
Anal. Calcd calculated elemental analysis based on a formula
δ Chemical shift
Cp cyclopentadienyl (C$_5$H$_5$)
° Degree
DFT density functional theory
DCM dichloromethane
Et$_2$O diethyl ether
DMSO dimethylsulfoxide
eq equivalent
η eta, prefix for contiguous coordinating ligand atoms, (hapticity)
Et Ethyl
FT-IR Fourier transform-infrared
ν frequency, stretching frequency (IR)
FLP frustrated Lewis pair
sept septet (NMR)
hmds hexamethyldisilazane
HOMO highest occupied molecular orbital
iPr iso-propyl
κ kappa, prefix for non-contiguous coordinating atoms
kcal kilocalorie
MS mass spectrometry
Mes mesityl (2,4,6-trimethylphenyl)
Me methyl
μ mu, prefix for a bridging ligand
DMF N$_2$N-dimethylformamide
NHC N-heterocyclic carbene
NMR nuclear magnetic resonance
$J$ nuclear spin-spin coupling constant
ppm parts per million
Cp* pentamethylcyclopentadienyl (C$_5$(CH$_3$)$_5$)
Ph phenyl
π pi orbital
HBpin pinacolborane
HBcat catecholborane
Py pyridine
RT r. t. (room temperature)
σ sigma orbital
s/d/t/m singlet/doublet/triplet/multiplet (NMR)
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
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<tbody>
<tr>
<td>tBu</td>
<td>tert-butyl</td>
</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
</tr>
<tr>
<td>OTf</td>
<td>trifluoromethanesulfonate (trflate)</td>
</tr>
<tr>
<td>UV</td>
<td>ultraviolet</td>
</tr>
<tr>
<td>VT</td>
<td>variable temperature</td>
</tr>
<tr>
<td>λ</td>
<td>wavelength</td>
</tr>
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1 Introduction

1.1 N₂ activation

N₂ is the most abundant molecule in earth’s atmosphere, but it remains a challenge for chemists to activate N₂ due to its thermal and kinetic inertness. However, since nitrogen-containing compounds are important to agriculture and industry, huge efforts have been made to convert N₂ into valuable products. In nature, bacteria employ enzymes, named nitrogenases, to fix N₂ to ammonia. The N₂ reduction on FeMo nitrogenase is based on metal clusters called iron-molybdenum cofactor (FeMoco) (Figure 1.1).¹ The cofactor consists of seven Fe and one Mo, bridged by sulfide atoms around a central carbide. Because of the complexity of the biological systems, the mechanism of N₂ fixation by nitrogenase is still elusive. In industry, the Haber-Bosch process can produce ammonia from N₂ in a large scale with high temperature and high pressure. This process is pivotal for the production of fertilizer to create enough food and support the world’s population. But the precise mechanism for the Haber-Bosch process has not been elucidated.

![Figure 1.1 Structure of the iron-molybdenum cofactor](image)

1.1.1 Mo complexes for N₂ activation

Synthetic chemists are particular interested in the cleavage of N-N triple bond through stoichiometric and catalytic reactions. The model complexes about N₂ activation have been summarized in several review papers.² Traditionally, research focused on using molybdenum as the central atom for N₂ activation. For instance, Chatt’s early work established the now so-called Chatt mechanism for N₂ reduction to ammonia.³ Pickett and co-workers also achieved the conversion of N₂ to NH₃ by an electrochemical method.⁴ Laplaza and Cummins explored the N₂ cleavage on a Mo complex.⁵ In 2003, Yandulov and Schrock reported a Mo system for catalytic...
reduction of N$_2$ with six intermediates isolated and characterized.$^{5b}$ Recently, Nishibayashi and co-workers employed a PNP Mo pincer complex to perform catalytic reduction of N$_2$ into ammonia (Scheme 1.1).$^{5c}$ The dimolybdenum-dinitrogen complex was able to catalyze the conversion of 1 atm of N$_2$ to ammonia with lutidinium triflate as the proton source and cobaltocene as the reductant, reaching a TON of 23.2 eq. of NH$_3$ per catalyst (11.6 eq. of NH$_3$ per Mo atom). The proposed mechanism for the catalytic cycle consists of dissociation of bimetallic N$_2$ species to monometallic Mo-N$_2$ intermediate, the addition of electron and proton to release 1 eq. of ammonia, and the final conversion of Mo nitride moiety back to Mo-N$_2$ intermediate with another eq. of NH$_3$ liberated. One year later, Schrock and co-workers explored the reactivity of another Mo complex of a POCOP ligand (Scheme 1.2).$^6$ Upon addition of Na/Hg, the N-N triple bond was cleaved to generate a terminal Mo nitride species. However, this system was not capable of catalytic transformation as the proton was proposed to bridge between the Mo and one P.

Scheme 1.1 Dimolybdenum-dinitrogen complex as catalyst for N$_2$ reduction.

Scheme 1.2 N$_2$ reduction on a POCOP Mo pincer complex.
Recently, the Mézailles group reported a tridentate phosphine Mo complex that could split N₂ into two terminal nitrides (Scheme 1.3).⁷ The Mo nitride module was formed from the reaction between the Mo-Cl starting material and reducing agent (Na/Hg or NaBEt₃H) under an N₂ atmosphere through a possible bimetallic intermediate with an N₂ bridge. This nitride atom could be functionalized using bis(silane) through double Si-H addition to yield silylamine, which was released from metal center. These results exhibited the potential for a catalytic cycle of N₂ reduction.

\[
\begin{align*}
\text{Ph} & \quad \text{P} \quad \text{Mo} \quad \text{Cl} \quad \text{P} \quad \text{Cl} \quad \text{P} \\
\text{P} & = \text{P(C₅H₅)₂}
\end{align*}
\]

1) 2Na/Hg, NaI, N₂ or 2NaBEt₃H, NaI, N₂

\[
\begin{align*}
\text{Ph} & \quad \text{P} \quad \text{Mo} \quad \text{N=}\text{N} \quad \text{Mo} \quad \text{P} \quad \text{Ph} \\
\text{Ph} & \quad \text{P} \quad \text{Mo} \quad \text{I}
\end{align*}
\]

Scheme 1.3 N₂ splitting on a tridentate phosphine Mo moiety.

1.1.2 N₂ activation by iron systems

In addition to the seminal work with Mo centers, recent evidence has suggested iron as the N₂ binding site in the FeMo-cofactor.² The Peters group has reported a series of trigonal bipyramidal Fe complexes that were capable of N₂ binding and/or even catalytic reduction of N₂ (Figure 1.2).⁸ In 2010, they described a P₃SiFe system in which N₃H₅ intermediates were bound to the iron center.⁸a The Fe-N₂ complex could reach two oxidation states from 0 to +1. Additionally, the conversion of Fe-NH₃ and Fe-N₂H₄ intermediates to Fe-N₂ species resembled the process of N₂ uptake and NH₃ release in the catalytic cycle of the nitrogenase. The N₂ ligand could be silylated to produce the more stable product Fe-N₂SiR₃ than the less stable Fe-N₂H version from protonation. In 2013, they came up with a similar P₃Fe complex capable of binding N₂, NH₂, NH₃, N₂H₄ and OH terminally.⁸b The five-coordinate species adopted S = 3/2 state and were prepared from a four-coordinate S = 3/2 precursor with elimination of the CH₄. The addition of an acid to the Fe-NH₂ intermediate could
generate Fe-NH₃ species and subsequent reduction replaced NH₃ with N₂. This sequence mimicked the N₂ fixation steps in the nitrogenase activity. The model complexes in this work provided key EPR and structural information for the comparison with proposed intermediates in FeMo-cofactor. One year later, they extended the study to put a C atom trans to Fe-N₂ position, resembling the role of interstitial carbide in FeMo-cofactor. The Fe-C interaction in the model complex was more flexible than Fe-Si counterpart. Moreover, the new P₃Fe-N₂ system could produce 4.6 eq. of NH₃ under 1 atm of N₂ at -78 °C and this catalytic performance was comparable to P₃Fe, which had the weakest interaction between the Fe and the central atom. In contrast, the least flexible P₃SiFe gave only a stoichiometric amount of NH₃. Their study showed the carbon atom could take an ionic charge and dissociate from the iron center. Similarly, the inorganic carbide in FeMo-cofactor was also able to hold the ionic charge and mediate its coordination to iron atom to accommodate various nitrogenous ligands. In 2015, a two-coordinate [(CAAC)₂Fe] complex [CAAC = cyclic(alkyl)(amino) carbene] was found to react with N₂ at low temperature (< -80 °C). The N₂ ligand in this system could be silylated at the β-nitrogen atom. At -95 °C, the [(CAAC)₂Fe] species was able to catalyze the reduction of N₂ to NH₃ with KC₅ and HBAR with a TON of 3.4. Recently, they improved the yield of the catalytic N₂ reduction reaction with P₃Fe (64 eq. of NH₃) and P₃Fe (47 eq. of NH₃) by an order of magnitude. They also hypothesized a reaction eliminating H₂ might help the catalyst return to the catalytic cycle from its resting state (iron-hydride complex).

![Figure 1.2 A series of Fe-N₂ complexes from Peters’ group.](image_url)

Holland and co-workers also made remarkable contributions to N₂ activation with iron complexes. Early in 2001, they reported a low-coordinate iron complex binding N₂ with an
intense band at 1778 cm\(^{-1}\) in the Raman spectrum (Scheme 1.4).\(^9a\) They later synthesized a series of \(\text{N}_2\) complexes with an FeNNFe moiety and studied the N-N bond weakening.\(^9b\) The reduction of the FeNNFe module with KC\(_8\) created potassium bridges that cooperatively weaken the N-N bond with iron centers. Calculations displayed this activation of \(\text{N}_2\) triple bond aroused from back-bonding to the \(\text{N}_2\) \(\pi^*\) orbitals. In 2011, the \(\text{N}_2\) triple bond cleavage was achieved within their system.\(^9c\) The addition of KC\(_8\) to an iron-chloride precursor resulted in the formation of two nitrides coordinating to three iron centers and two potassium atoms. The nitride fragments could react with acid to produce ammonia. These results provided important information to understanding the Haber-Bosch process. The iron atoms in this system featured low oxidation states and low coordination number, which resembled the surface iron in the Haber-Bosch process. Furthermore, the dinitrogen could possibly react with several cooperative iron atoms in either this system or surface irons. Potassiums might also participate in the Haber-Bosch process to assist N-N bond cleavage as a promoter just like the role in this work. In 2014, they demonstrated the addition of Lewis bases could reverse the splitting of N-N triple bond to regenerate \(\text{N}_2\) at r. t.\(^9d\) This evidenced the potential of multi-iron system to lower the energy barriers related to \(\text{N}_2\) activation. Another study showed variation of the alkali metals from K to Na, Rb and Cs resulted in new styles of \(\text{N}_2\) activation.\(^9e\) The addition of 1 eq. of Na or Rb as reductant to the \([(\text{NacNac})\text{FeCl}]_2\) dimer still split the triple bond and led to the formation of tri-iron bis-nitride cores. However, reactions between 4 eq. of K, Rb or Cs and \([(\text{NacNac})\text{FeCl}]_2\) gave rise to \(\text{Fe}_3(\text{N}_2)_3\) cores without breakage of \(\text{N}_2\) triple bond.
1.1.3 Polynuclear systems for multi-electron process

Model complexes with mutimetallic sites mimicking metalloenzyme cofactors and heterogeneous catalysts have been widely explored. The redox chemistry occurring on the polynuclear centers usually incorporates the cooperation among different metal atoms. For example, the oxygen-evolving center (OEC) consists of a Mn₃CaO₄ core plus a dangling Mn
bridged by an oxide. As water is oxidized on the OEC, the oxidation states of the core would change accordingly. This process involved multi-electron transfer between adjacent metal centers. In the Haber-Bosch process, it is proposed the splitting of N₂ took place at multi-iron sites on the surface. The biological N₂ reduction on the FeMo-cofactor might also occur on one or several iron sites. The hydrogenases found in some bacteria can manipulate the H₂ oxidation/reduction under mild conditions. Several models have been reported to mimic the core structure of [NiFe], [FeFe] and [Fe]-only hydrogenases. The reactivity of [NiFe] and [FeFe] hydrogenases might involve the cooperation between two metal centers.

Agapie and co-workers reported a synthetic model 1.1 to mimic the subunit of OEC (Figure 1.3). The complex featured a Mn₃CaO₄ cubane, which resembled the core in OEC. In 2015, Zhang and co-workers described another model complex 1.2 with a Mn₄-Ca cluster. This system was the first to successfully incorporate the fourth Mn to the dangling position of Mn₃CaO₄ fragment.

![Figure 1.3 Multimetallic complexes for OEC mimic. The first one only shows the core structure for clarity.](image)

In 2011, Zhao and Betley investigated the reactivity of a hexadentate amine ligand (Figure 1.4). The reaction between [Fe₂(HMDS)₄] and this ligand with the addition of phosphines assembled the trimetallic architecture. The short Fe-Fe distances in the 1.3 suggested strong interactions between the metal centers. Later, they reported another hexadentate ligand with silyl groups supporting multi-iron atoms. The tri-iron complex quickly reacted with tetrabutylammonium azide to produce a μ³-nitride species. This evidence demonstrated the
cooperation between three iron atoms to bind a small molecule substrate. In 2013, they reported 1.4 could react with hydrazine and phenylhydrazine to generate $\mu^3$-imido species with the release of ammonia and aniline. Breakage of azobenzene N=N bond by the tri-iron complex led to the formation of a bis-imido species. These results meant the multi-iron system was able to mediate processes with the cooperation between metal centers.

Figure 1.4 Multi-iron complexes from Betley’s group.

In 2014, Murray’s group synthesized a tricopper complex 1.5 based on the tris(β-diketimine) cyclophane ligand(Figure 1.5). Experiments showed an N$_2$ coordinating to the copper centers with a Raman peak at 1952 cm$^{-1}$. They also demonstrated the addition of KC$_8$ to a triiron complex led to the cleavage of N-N triple bond and the formation of a N-containing product 1.6.

Figure 1.5 Cu/Fe cyclophane complexes for N$_2$ activation.

Recently, Camara and Rauchfuss studied the reactivity of a ferrocenyl bis-iron frame 1.7 that modeled the function of ferredoxin of the [FeFe]-hydrogenase (Figure 1.6). The tethered ferrocenyl module acted as a one-electron mediator and replicated the function of Fe$_4$S$_4$ clusters in the [FeFe]hydrogenase. The diiron center was redox-active and facilitated H$_2$ oxidation with
help from the amine arm as the proton relay. In 2013, the Ogo group reported a [NiFe]H2ase mimic 1.8 that could catalyze the oxidation of H2. Based on their original [NiRu] model, another improved [NiFe] version was synthesized and this made a huge stride in the field. The addition of H2 and MeONa resulted in the formation of a hydride complex. Analogous to the natural [NiFe]H2ase, this hydride species could carry out hydride transfer to reproduce its oxidized form.

![Figure 1.6](image)

**Figure 1.6** [FeFe]-hydrogenase and [NiFe]-hydrogenase mimics.

### 1.2 CO2 activation and conversion

The combustion of fossil fuels has led to the significant amount of CO2 in the atmosphere and contributes greatly to the global warming. Cutting down the huge emissions of CO2 into the environment is critical in alleviating its adverse effects. Even though CO2 is well-known as a thermodynamic stable molecule, efforts are continuously made towards this challenging topic. In nature, organisms convert CO2 into biomass through the photosynthesis with enzymes. An enzyme, named ribulose bisphosphate carboxylase oxygenase (RubisCO), plays an important part in the carboxylation of ribulose 1,5-bisphosphate to two 3-phosphoglycerate, a critical step in the CO2 fixation. The CO2 fixation by RuBisCO involves MgII ion (Scheme 1.5). The catalysis starts with the activation of RuBisCO involving the binding of CO2 and Mg2+ to form the lysyl carbamate. The coordination of the ribulose 1,5-bisphosphate (RuBP) causes the release of two waters. The dehydration of the bound RuBP produces the enediol form of RuBP, which then reacts with CO2 through C-C bond formation. The C-C bond of the CO2 adduct breaks to produce two molecules of 3-phosphoglycerate.

The abundance of CO2 also makes it a cheap C1 building block for the construction of important complex chemicals. Examples have been reported for the incorporation of CO2 to produce epoxides, cyclic carbonates/carbamates, and polycarbonates/polycarbamates. The
conversion of CO₂ to new materials and fuels, such as methanol, has attracted wide attention in recent years as this route has the potential to generate renewable and sustainable energy. The introduction mainly covers the recent development of CO₂ activation and reduction from 2015 to 2017.

1.2.1 Activation of CO₂ in a stoichiometric manner

Many compounds have been described to react with CO₂. One of the common strategies is the insertion of CO₂ into a M-H bond to form a formate. Holland’s group synthesized the first iron sulfide formate complex through the reaction between an iron complex and 2.5 eq. of CO₂. This suggested a similar CO₂ reduction process catalyzed by nitrogenases could occur via a metal hydride intermediate (Scheme 1.5). Interestingly, Creutz and Peters also reported the formation of a diiron formate species with a thiolate bridge (Scheme 1.6).

![Scheme 1.5 First iron sulfide formate complex.](image1)

![Scheme 1.6 A diiron formate complex with sulfur bridge.](image2)

Li and co-workers prepared a series of arylimine iron-hydride complexes that allowed CO₂ to insert into the Fe-H bond. Based on these results, the iron complexes were also applied in the dehydrogenation of formic acid.

In 2015, the Murray group reported a Zn hydride cyclophane complex, which was air-stable and inert to water and methanol (Figure 1.7). Surprisingly, it reacted with 1 eq. of CO₂ to form the Zn-formate compound. On the other hand, the hydroxide version of this Zn complex
could not react with CO$_2$ at high temperature over several days. Later, they applied this ligand to Fe and Co and discovered different reactivity.\textsuperscript{17b} The Fe hydride complex could react with 1 eq. of CO$_2$ at r. t. but 3 eq. of CO$_2$ at 60 °C. In contrast, the Co version could only react with 1 eq. of CO$_2$ to insert into Co-H bond from r.t. to 80 °C.

![Figure 1.7 CO$_2$ adducts of some cyclophan complexes.](image)

Recently, Erker and co-workers investigated the reactivity of a zirconocene hydride species.\textsuperscript{18a} CO$_2$ could be reduced by inserting into Zr-H bond. The reaction between CO$_2$ and Zr-formylhydridoborate led to the formation of a cycloaddition product (Scheme 1.7).

![Scheme 1.7 Reaction between CO$_2$ and ZrCp* complexes](image)

The insertion of CO$_2$ into a M-H bond could occur with transition metal and main group metal hydrides. Knopf and Cummins reported that simple and cheap NaBH$_4$ was also able to react with CO$_2$ and the reaction produced [(HCOO)$_3$BH].\textsuperscript{18b} Upon quenching by aqueous acid, formic acid was obtained (1.5 eq. per B).
In addition to the insertion of CO\(_2\) into a M-H bond, the insertion into a M-C bond was also investigated. Recently, the O’Hare group synthesized a novel 14-electron pentalene Ti species (Scheme 1.8).\(^{19}\) Because the compound featured electron deficiency and vacant coordination sites, CO\(_2\) could insert into the two Ti-C bonds at r. t.. This work also represented an excellent example of CO\(_2\) insertion into a M-CH\(_2\)Ph bond.

![Scheme 1.8 CO\(_2\) insertion into Ti-C bonds.](image)

In fact, the insertion type reaction was not limited to M-H or M-C bonds. The insertion of CO\(_2\) into other bonds attracted significant attention as well. In 2015, Zn compounds bearing a 2-(phosphino(trimethylsilyl)methyl)pyridine framework were synthesized. These compounds could react with CO\(_2\) as the formal insertion of CO\(_2\) took place at the benzylic positions of C-Si bonds on the ligands (Scheme 1.9).\(^{20a}\)

![Scheme 1.9 CO\(_2\) insertion into a C-Si bond of Zn complexes.](image)

Recently, the first dimetalloxycarbene was isolated and its reaction with CO\(_2\) was investigated (Scheme 1.10).\(^{20b}\) The authors started from a Ti tris(anilide) complex. And the installation of a formato ligand rendered a bimetallic structure for stabilization. The combination of the formato species and [TiX\(_3\)][B(C\(_6\)F\(_5\))\(_4\)] resulted in the formation of a dimetalloxycarbene complex and its nucleophilic attack on CO\(_2\) finally produced an oxalate-bridged Ti species. Similarly, other complexes with scandium\(^{20c}\) or thorium\(^{20d}\) centers were also able to reduce CO\(_2\) to the oxalate level.
Scheme 1.10 The synthesis of the first dimetalloxycarbene involving CO$_2$.

Several examples provided a metal-free method for the activation of CO$_2$. This type of reaction usually involved the formation of heteroatom-CO$_2$ bonds. Weicker and Stephan demonstrated electronically saturated Lewis acids could accomplish CO$_2$ activation in the FLP style (Scheme 1.11).$^{21a}$ The combination of silyltriflates and phosphines could activate either 1 or 2 eq. of CO$_2$ depending on the conditions.

\[
\begin{align*}
\text{Ph}_{2}\text{Si(OTf)}_2 + PR_3 & \rightleftharpoons \text{CO}_2 \quad [\begin{array}{c}
\text{O} \\
\text{PR}_3
\end{array}] \\
R = \text{Et}, \text{t-Bu} & \quad [\begin{array}{c}
\text{O} \\
\text{SiPh}_2
\end{array}]_{\text{OTf}}
\end{align*}
\]

Scheme 1.11 CO$_2$ binding by by silyltriflates and phosphines.

Piers and co-workers discovered that when the potassium salts of the dianions of diborole were treated with CO$_2$, insertion products were obtained through ring-expansion to six-membered rings rather than seven-membered rings (Scheme 1.12).$^{21b}$
Scheme 1.12 CO₂ insertion into a C-B bond through ring-expansion.

A series of imidazolylidenes with phosphine oxide groups were synthesized and treated with CO₂ (Scheme 1.13). These compounds firstly bound CO₂ through the carbene carbon, and then the phosphorous part migrated to the oxide atom with the formation of carboxylic-phosphinic mixed anhydride.

Scheme 1.13 CO₂ insertion into an N-P bond after binding to carbene carbon.

Direct binding of CO₂ provided a useful avenue for the activation. Dielmann’s group designed a series of novel imidazolin-2-ylidenamino substituted phosphines (IAPs) with more electron richness than ordinary alkylphosphines (Scheme 1.14). These IAPs were tested and the first phosphine-CO₂ adduct was successfully synthesized under mild conditions. The CO₂ adduct of the most basic IAP was air-stable and offered a convenient route for the transfer of this IAP to transition metal centres.

Scheme 1.14 Reversible CO₂ binding by electron-rich phosphines.
Other approaches reducing CO\textsubscript{2} were also extensively explored and the reduction usually created formate or CO as a product. For instance, a Ru NADH model complex had been employed for the conversion of CO\textsubscript{2} to formate through an organic hydride transfer (Scheme 1.15).\textsuperscript{23}

![Scheme 1.15 CO\textsubscript{2} reduction by a Ru(NADH) model.]

Francisco and Kumar employed substituted amines or organic and inorganic acids for the hydrogen sulfide(H\textsubscript{2}S)-induced activation of CO\textsubscript{2}.\textsuperscript{24a} The reaction led to the formation of carbonyl sulfide(OCS) and water. The phosphorus biradical compound [P(\mu-NTer)]\textsubscript{2} [Ter=2,6-bis(2,4,6-trimethylphenyl)phenyl] could activate CO\textsubscript{2} at r.t. with release of CO (Scheme 1.16).\textsuperscript{24b}

![Scheme 1.16 CO\textsubscript{2} reduction by a phosphorus biradical compound.]

Cossairt and co-workers explored the reaction between a Ru(NH-NHC) complex and CO\textsubscript{2} (Scheme 1.17).\textsuperscript{24c} Initially, the reaction produced a carbamate species and subsequently deoxygenation gave rise to a Ru-formate complex with H\textsubscript{2} release.
Scheme 1.17 CO₂ reduction to generate a Ru-formate complex. The oxidized product E=O has not been identified.

Milstein and co-workers have developed a PNP pincer ligand and used it to coordinate to Rh or Ir (Scheme 1.18).²⁵ᵃᵇ This system featured the reductive cleavage of CO₂ to create CO. For the Rh complex, metal-ligand cooperation promoted the elimination of H₂O from the complex and CO₂ to form the CO species (Scheme 1.19). The CO complex could further activate the C-H bond of benzene by photocarbonylation. After the release of benzaldehyde, this stoichiometric cycle could be completed within steps. In the Ir counterpart, a reversible 1,3-addition of CO₂ to the side-arm occurred to give the kinetic product. Also, a di-CO₂ metallacycle compound was detected. Similarly, metal-ligand cooperation resulted in the formation of a CO complex with the release of H₂O.

Scheme 1.18 Metal-ligand cooperation for CO₂ reduction to CO.
The absorption of CO\(_2\) by organic compounds provided another route for CO\(_2\) capture. A hydrogen bonding network usually played an important role in these processes. Custelcean’s group reported the use of a guanidine sorbent to trap CO\(_2\) from the air as carbonate crystals.\(^{26a}\) Inagaki and co-workers introduced hydrophobic phenyl groups to the alkylamine absorbents.\(^{26b}\) This method significantly improved the efficiency of CO\(_2\) capture.

### 1.2.2 Catalytic reduction of CO\(_2\) by metal-free molecules

The catalytic conversion of CO\(_2\) by metal-free catalysts, including carbenes, FLPs (Frustrated Lewis Pairs), phosphines, and their derivatives, has been extensively studied. Current efforts focused on the hydroboration and hydrosilylation for the reduction of CO\(_2\).

![Scheme 1.19 Stoichiometric cycle for the conversion of CO\(_2\) to carbonyl group.](image)

![Figure 1.8 Metal-free catalysts with carbene-like structure for CO\(_2\) reduction.](image)
Some catalysts have a carbene-like structure with a lone pair of electrons on the carbon-center, which is critical for their catalytic reactivity (Figure 1.8). In 2015, Ong’s group described a variety of carbodicarbene (CDC) frameworks with unsymmetrical units, such as 1.9. They successfully applied these CDCs as organocatalysts in the methylation of amine with CO₂ as the C₁ source. The system could reach up to 90% yields for aniline substrates at 100 °C in toluene within 1.5 h. Later, they isolated a borane adduct of CDC as the product from the stoichiometric reaction between CDC and 9-BBN and demonstrated its role in the catalytic cycle (Scheme 1.20).

![Scheme 1.20 Mechanism for methylation of amine with CO₂ as C₁ source.](image)

Dyson and co-workers developed thiazolium carbenes, such as 1.10, as catalysts for the N-formylation and N-methylation of amine with CO₂ as the carbon source and polymethylhydrosiloxane (PMHS) as the reductant. The reactions with aromatic, alicyclic, and aliphatic amines as the substrates produced the product with up to 90% yields. Saptal and Bhanage prepared a series of N-Heterocyclic Olefins (NHOs) 1.11 that could activate CO₂ to generate the zwitterionic NHO-CO₂ adduct. This system could also perform the catalytic N-formylation of amines with polymethylsiloxane (PMHS) and 9-BBN as the hydrogen source and CO₂ as C₁ source, providing good-to-excellent yields. He’s group reported that simple salts such as cesium formate and tetrabutylammonium acetate are capable of N-methylation of a variety of secondary anilines using Ph₂SiH₂ as the reductant. Good yields were obtained at 50 °C under 5 mol% catalyst loading. Under certain conditions, the formation of N-formyl products was observed; the control experiments revealed that these were not the intermediates on the way to the N-methyl products. In 2016, an abnormal NHC (N-heterocyclic carbene) 1.12 was described to catalyze the hydroboration of CO₂. The reaction with 9-BBN as the hydride source reached a high TON of 6000. In addition, a borondiformate intermediate was isolated and revealed the
mechanism of the catalytic cycle. So far this system remains the most active catalyst when 9-BBN is used as the reducing agent.

![Phosphorus derivatives](image)

Figure 1.9 Phosphorus derivatives as catalyst for CO₂ conversion.

Various phosphorus derivatives were found to be active in the hydroboration, hydrosilylation and other transformations (Figure 1.9). Kinjo and Chong probed the first hydrophosphination of CO₂ with 1,3,2-diazaphospholene 1.13 to create phosphorus formate in 93% yield.²⁸ᵃ The hydrosilylation of CO₂ was also carried out with Ph₂SiH₂ as the reducing agent, using 5 mol% of this diazaphospholene. This reaction was extended to achieve 64-94% yields for the catalytic N-formylation of amines with CO₂. Fontaine and co-workers reported the phosphazene superbases 1.14 as the organocatalysts for the catalytic hydrosilylation of CO₂.²⁸ᵇ They discovered the phosphazene was converted to the corresponding phosphine oxide releasing isocyanate upon reacting with CO₂. In order to compare the efficiency of phosphazene with NHCs, they performed catalytic hydrosilylation of CO₂ with Ph₂SiH₂ as the reductant. The reaction could reach a high TOF of 32 h⁻¹ and a TON of 759 with silyl formate as the major product. By the addition of another load of silane, the silyl formate could be converted to methoxysilane derivatives. Recently, the Lu group reported the synthesis of a series of phosphorus ylides (P-ylides) 1.15, which could form stable CO₂ adducts.²⁸ᶜ These P-ylide CO₂ adducts were employed to catalyze the cycloaddition of CO₂ with various epoxide substrates to generate cyclic carbonates in 46-99% yields. The authors investigated the catalytic N-formylation and N-methylation of amines with P-ylide CO₂ adducts as catalysts and 9-BBN or PhSiH₃ as the hydrogen sources.
Figure 1.10 Some FLP examples for CO\(_2\) reduction.

FLP compound (Frustrated Lewis Pair) is another type of catalysts widely used in the conversion of CO\(_2\) and some examples are exhibited in Figure 1.10. Besides the stoichiometric reactions between FLPs and CO\(_2\) that were extensively explored, the catalytic results from hydrogenation, hydroboration and hydrosilylation of CO\(_2\) with FLPs as the catalysts were also shown in the literature. In 2015, the FLP species 1-BR\(_2\)-2-NMe\(_2\)-C\(_6\)H\(_4\) was reported to activate H\(_2\) in a protodeborylation fashion.\(^{29a}\) The reactions of these compounds with H\(_2\)/CO\(_2\) gave rise to boron bound formate, acetal and methoxy products under mild conditions. This method provided a potential route for the metal-free hydrogenation of CO\(_2\). Fontaine and co-workers investigated ambiphilic phosphine-borane derivatives as the catalysts for the hydroboration of CO\(_2\) to produce methoxyboranes. Their initial results suggested 1-Bcat-2-PPh\(_2\)-C\(_6\)H\(_4\) as the metal-free catalyst for the hydroboration of CO\(_2\).\(^{29b}\) But later studies revealed the catalysts were firstly transformed to the formaldehyde intermediates, and then participated in the catalysis to reduce CO\(_2\) to CH\(_3\)OBR\(_2\) products.\(^{29c}\) The system reached a TOF of 228 h\(^{-1}\) and a TON of 1005 at r.t. Cantat and co-workers synthesized a couple of base-stabilized silylium compounds and studied their reactivity towards CO\(_2\), the formation of a N/\(\text{Si}^+\) CO\(_2\) adduct in the FLP style (Scheme 1.2).

\[ \text{Scheme 1.21 CO}_2\text{ binding on a silylium compound.} \]

The catalytic performance of these silylium species was tested for the hydroboration of CO\(_2\) with 9-BBN, HBCat and HBpin as the reducing reagents. Their study revealed the reduction of CO\(_2\) to the methoxy level proceeded through two mechanisms depending on the boranes. Scheme 1.22 exhibits the mechanism for the conversion from CO\(_2\) to HCOOBcat.
Scheme 1.22 Mechanism for catalytic hydroboration of CO$_2$ with a silylium catalyst.

The FLP-activated pathway also existed in the cyclization of $o$-phenylene-diamines with CO$_2$ as the C$_1$ source and hydrosilanes as the hydride sources (Scheme 1.23).$^{29e}$

Scheme 1.23 Cyclization of $o$-phenylenediamines with CO$_2$ as C$_1$ source.

In addition to the above methods, some other compounds were also reported for the CO$_2$ conversion to valuable derivatives. Cantat and co-workers developed a metal-free system to catalyze the hydrosilylation of CO$_2$ with amines to form symmetrical and unsymmetrical aminals. The catalysts they used included NHCs, phosphorus bases, and N-containing bases (Figure 1.11).$^{30a}$

Figure 1.11 TBD, NHC, and phosphorus bases for CO$_2$ reduction.
In 2017, they successfully isolated a zwitterionic TBD-CO$_2$ adduct, which was proposed as an intermediate in the previous catalytic reactions (Scheme 1.24).\textsuperscript{30b}

\[
\text{Scheme 1.24 CO}_2 \text{ binding on TBD.}
\]

Triphenylborane was shown to promote the catalytic hydrosilylation of CO$_2$ to produce silyl formates with up to 95% yield.\textsuperscript{30c} γ-valerolactone was also capable of promoting CO$_2$ conversion to formamides with phenylsilane as the reductant.\textsuperscript{30d} Skrydstrup and co-workers reported the trapping of CO$_2$ by alkynyl indoles (Scheme 1.25).\textsuperscript{30e} With catalytic amounts of base, CO$_2$ could be converted to tricyclic indole species.

\[
\text{Scheme 1.25 Base-catalyzed CO}_2 \text{ trapping with alkynyl indole.}
\]

### 1.3 4,5-Diazafluorenide ligand chemistry

The 4,5-Diazafluorene ligand has been utilized in different areas of inorganic and organic chemistry. Its application in different areas is summarized by a recent review.\textsuperscript{31} It combines two pyridine rings with a central Cp ring. One proton on a CH$_2$ group is acidic and can be removed to form the anionic diazafluorenide ligand. The two nitrogen atoms can be used as a bidentate site to coordinate with various metal centers to serve distinct functions. Our group has done a variety of research on this ligand scaffold. In 2012, our group discovered the reversible formal insertion of CO$_2$ into the C-H bond of a Ru-diazafluorenyl complex under mild conditions (Figure 1.12).\textsuperscript{32a} The Ru-H bond remained intact during the reaction and the metal’s role was to mediate the acidity of the backbone C-H bond. Later, Rh(III), Rh(I) and Cu(I) also came into play as spectator metal centers in the reaction with CO$_2$.\textsuperscript{32b} The Rh(III) diazafluorenyl complex with two phosphines and two hydrides was shown to react with CO$_2$ in the same style with the Ru analog
as CO$_2$ inserted into the remote C-H bond reversibly. Interestingly, switching to Rh(I) and Cu(I) changed the pattern of this CO$_2$ reaction. In Rh(I) reaction, CO$_2$ insertion to C-H bond left the proton on carboxylic acid, and this proton was further deprotonated by another Rh(I)-diazafluorenide species. The loss of neutral 4,5-diazafluorene ligand resulted in the formation of a new bimetallic carboxylate compound (Scheme 1.26). The Cu(I) complex could react with CO$_2$ to form the CO$_2$ adduct as intermediate and it produced a bimetallic carboxylate species similar to Rh(I) fashion. The replacement of the metal moiety in the molecule by a methyl group led to the metal-free system with reversible CO$_2$ reactivity. The methyl group served a similar function as the metal centers to provide a positive charge for balancing the negative charge on the Cp ring of this molecule.

![Figure 1.12 CO$_2$ adducts of metal-diazafluorenide complexes.](image)

![Scheme 1.26 The reaction of a Rh(I) complex and CO$_2$ to the formation of a bimetallic carboxylate compound.](image)
1.4 Scope and objectives

The content in this thesis includes the synthesis and reactivity of a triaryl benzene ligand; application of 4,5-diazafluorenide species in the catalytic hydroboration of CO$_2$; syntheses of another two metal-free zwitterionic compounds and their reactivity with CO$_2$. The major topic in this thesis is small molecule activation and conversion.

Chapter 2 will discuss the polynuclear chemistry based on a tripodal ligand framework towards dinitrogen activation. Three nacac modules have been grafted on the triaryl base as three side arms to accommodate three metal centres. The three Nacac arms could rotate to the same plane and bring the metals close to cooperate in N$_2$ activation, similar to the multimetallic NacNac system in Holland’s report. Efforts to obtain multi-iron complexes will be shown. The synthesis and characterization of a trinuclear Ru complex will be discussed in detail.

Chapters 3-5 cover the second part of the thesis about CO$_2$ chemistry. Chapter 3 will continue the research on the N-methyl-4,5-diazafluorenide compound 3.1. The catalytic reduction of CO$_2$ with this compound as catalyst and various boranes as reducing agent has been surveyed. A possible intermediate in the catalytic cycle is observed and synthesized. And this may shed light upon the mechanism for this catalytic system.

Chapter 4 will comprise the synthesis of a new metal-free compound 4.1 with charge-separation feature. In comparison to 3.1, the new species has a smaller molecular weight and therefore higher CO$_2$ storage efficiency. The reaction between this compound and CO$_2$ produces an adduct in a similar fashion with 3.1 as expected. The catalytic hydroboration with this new compound as the catalyst is also presented here and it exhibits different efficiency compared to N-methyl-4,5-diazafluorenide.

Chapter 5 will cover the reactivity of another zwitterionic compound 5.1 with CO$_2$. This compound is different with previous ones as the uncharged resonance form is eliminated. This change makes the charge less delocalized across the aromatic ring and thus new compound is more reactive with CO$_2$. It can react with CO$_2$ reversibly the same way as before. In addition, 5.1 shows comparable performance to compounds 3.1 and 4.1 in the catalytic hydroboration of CO$_2$ with 9-BBN and BH$_3$·SMe$_2$ as reductants.
Chapter 6 will be the summary of the work in this thesis and offer some advice for future directions.

The experimental work was carried out by the author. Collection of X-ray crystallographic data was performed by Vince Annibale, Trevor Janes and Qiuming Liang. X-ray structures were solved by Vince Annibale, Trevor Janes, Charlie Kivi, Qiuming Liang and Prof. Datong Song. In Chapter 3, the N-methyl-4,5-diazafluorenide compound was first synthesized by undergraduate student Daniel Dalessandro under the guidance of Dr. Vince Annibale. The catalytic reactions involving $^{13}\text{CO}_2$ reactions received help from Stephan group. The protocol for the catalytic hydroboration of $\text{CO}_2$ was developed by the author. In Chapter 4, compound 4.1 was synthesized by an undergraduate student Maotong Xu under the author’s supervision. The DFT calculations were performed with Gaussian 09 program at the wB97X-D method with 6-31G* basis set by our collaborators from Prof. Ming Lei’s group.

Parts of chapters 3-5 of this thesis have been published:

Chapters 3 and 4:


Chapter 5:


1.5 References


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2 Chapter 2

Multimetallic systems towards N$_2$ activation

2.1 Abstract

In this chapter, the reactivity of a tripodal ligand is investigated. A new Ru complex 2.7 has been synthesized to show the coordination environment of the ligand. Other iron complexes were also obtained even though they were not the desired product. However, all this evidence demonstrated the ligand could support multimetallic centers as designed. The preliminary results displayed the potential for the three coordination sites to cooperate and carry out interesting reactions. This can be the focus of future study on this ligand.

2.2 Introduction

Polynuclear sites exist in various enzymes and they help perform the specific function, including N$_2$ reduction, CO$_2$ activation, and CH$_4$ oxidation. For example, the oxygen-evolving center (OEC) in photosystem II has a Mn$_4$Ca core and this structure undertakes reactions during the water-oxidation cycle.$^1$ The cofactors of nitrogenase (FeMo, FeFe and FeV) contain multi-iron sites, which might be responsible for the reduction of N$_2$.$^2$ Similarly, in the Haber-Bosch process, multiple iron atoms might participate in the N-N bond cleavage. Multimetallic model complexes mimicking the function of enzymes are of great interest and provide insight into the reactivity pattern and structural information. Several difficulties make the synthesis of multimetallic clusters challenging, such as nonselective coordination, instability in redox process, and flexibility of ligand side arm.

Agapie and co-workers described a [Mn$_3$CaO$_4$] system to mimic the role of OEC of photosystem II.$^3$ They used a trinucleating ligand with 6 pyridines and 3 OH groups to bridge 3 Manganeses through self-assembly. Ca$^{2+}$ ion was added to the architecture with help from KO$_2$. Characterization of this [Mn$_3$CaO$_4$] cubane by single crystal XRD and cyclic voltammetry indicated its resemblance to the tri-Mn-Ca subsite of OEC. Holland and co-workers investigated the reaction between N$_2$ and an iron complex with potassium as reductant. It produced a Fe$_3$N$_2$ cluster with two nitrides bound to Fe and K, indicating the importance of the cooperation between multi-iron atoms to cleave the N-N triple bond.$^4$ Recently, they found changing the alkali metals had significant impact in the way of N$_2$ activation (Scheme 2.1).$^4$ The addition of 2
eq. of Na to [(NacNac)FeCl]₂ dimer still enabled the cleavage of N-N triple bond. In contrast, reaction between 2 eq. of Rb and the iron complex led to a product with similar fashion to K. However, addition of 2 eq. of Cs or 4 eq. of K, Rb, or Cs to [(NacNac)FeCl]₂ resulted in multi-N₂ bridge species. In sum, these types of reactions all involved interaction between several iron centers.

![Chemical structures and reactions](image)

**Scheme 2.1** Binding and reduction of N₂ by a multi-iron system.

Recently, our group explored the reactivity of Pd-NacNac complexes with transmetallation reagents. The conventional transmetallation with MeLi replaced a Cl atom and put a Me- group onto Pd. In contrast, the unique transmetallation with phenylboronic acid resulted in the formation of a tetrapallada-macrocycle. Alternatively, we proposed to graft the similar Nacac moiety onto a triaryl benzene ligand framework. The design of this ligand originates from the performance of similar NacNac compounds in N₂ activation and the potential of the base-triaryl benzene-to support polynuclear structure. DFT calculations showed the three side arms could coordinate to three metals and the metal centers would possibly cooperate to
react with N\(_2\). A Ru complex 2.7 has been successfully synthesized and characterized by single crystal XRD. This species indicates the ligand coordination to three metals and the probable rotation of three side arms to one side in solution. This evidence suggested the possibility of cooperation between multimetallic centers.

### 2.3 Results and Discussion

The synthesis of this triarylbenzene ligand 2.4 is shown in Scheme 2.2. The first step is the trimerization of o-bromoacetophenone catalyzed by trifluoromethanesulfonic acid. Then, the bromo- groups on compound 2.1 are replaced by acetyl through Heck coupling. Later, ester condensation of 2.2 with EtONa/EtOAc leads to the formation of acac 2.3. Finally, the condensation of 2.3 and aniline catalyzed by p-toluenesulfonic acid produces Nacac ligand 2.4.

![Scheme 2.2 Synthesis of ligand 2.4.](image)
Figure 2.1 $^1$H NMR spectrum of 2.4 in CDCl$_3$.

The $^1$H NMR spectrum of 2.4 is shown in Figure 2.1. The major isomer is the enol version. The peak in the green circle at 1.87 ppm represents the methyl groups on side arm. The peak in the red circle at 5.23 ppm corresponds to the vinyl protons on side arm. The enol hydroxyl groups show up at 12.67 ppm in the black circle.

The ligand 2.4 could be deprotonated by KHMDS, NaOBu$^t$, KOBu$^t$ or KBn. The reaction between K$_3$L and FeBr$_2$(THF)$_2$ or FeCl$_2$(THF)$_{1.5}$ resulted in the formation of paramagnetic species [$L^3$ = 1,3,5-C$_6$H$_3$-(C$_6$H$_4$-o-3'- (phenylimino)buten-1'-olate)$_3$]. Only some broad peaks could be found on the $^1$H NMR spectrum (Figure 2.2). Another reaction between 2.4 and Fe(HMDS)$_2$ also produced a similar $^1$H NMR spectrum (Figure 2.3). Attempts to get crystals from these reactions were unsuccessful due to the moisture in the glovebox. A crystal of L$_2$Fe$_6$(OH)$_6$ (2.5) was obtained from the reaction between 2.4 and Fe$_2$(Mes)$_4$ with some H$_2$O from the glovebox (Figure 2.4). 2.5 has two ligands coordinating to 6 iron atoms bridged by hydroxide-group. Another reaction between Na$_3$L and 3eq. of Fe(OAc)$_2$ resulted in the formation of FeL(2.6) with three side arms coordinating to one iron center (Figure 2.5). In contrast to the paramagnetic compounds of first-row transition metals, the reaction of $\frac{3}{4}$ eq. of
(RuCp*Cl)$_4$ and 2.4 provided an easy entry for understanding the coordination modes of this multinucleating ligand. The Ru complexes were not very air-sensitive and therefore it would be easier to handle them for study with NMR spectroscopy. The $^1$H NMR spectrum of the Ru complex 2.7 is shown in Figure 2.6. A singlet is integrated to 45 representing the Cp*. The proton at vinyl position on the ligand side arm is integrated to 3 at 5.29 ppm. All the evidence implied 2.4 coordinated to 3 RuCp* groups and three side arms could position themselves above the same side of the central benzene ring in the solution.

The crystal structure of 2.7 is shown in Figure 2.7. In the solid state, two of the arms are situated in one plane while another arm is in another plane. When 2.7 was placed under 1 atm of H$_2$, no reaction was observed.

![Figure 2.2 $^1$H NMR spectrum of the reaction between K$_3$L and FeBr$_2$(THF)$_2$.](image-url)
Figure 2.3 $^1$H NMR spectrum of the reaction between 2.4 and Fe(HMDS)$_2$.

Figure 2.4 X-ray crystal structure of 2.5 with 50% probability ellipsoids. Hydrogen atoms and phenyl atoms on the nitrogen atoms of the side arms around the core are omitted for clarity. The
core structure is shown with atoms labelled. Selected bond lengths (Å) and angles (°) for 2.5:
Fe1-O4, 1.952(6); Fe1-O5, 2.361(6); Fe1-O6, 2.083(5); Fe2-Fe3, 3.115(2); Fe2-O4, 2.144(6);
Fe2-O5, 1.927(5); Fe2-O6, 2.040(6); Fe3-O4, 2.071(6); Fe3-O7, 2.029(6); Fe3-O6, 2.035(6);
Fe1-O4-Fe2, 101.1(2); Fe1-O4-Fe3, 134.0(3); Fe2-O4-Fe3, 95.3(2); Fe1-Fe5-Fe2, 94.6(3); Fe2-
O6-Fe3, 99.7(2).

Figure 2.5 X-ray crystal structure of 2.6 with 50% probability ellipsoids. Hydrogen atoms are
omitted for clarity. Selected bond lengths (Å) and angles (°) for 2.6: Fe1-N1, 2.172; Fe1-N2,
2.129(4); Fe1-N3, 2.169; Fe1-O1, 1.930(3); Fe1-O2, 1.980(6); Fe1-O3, 1.998.
Figure 2.6 $^1$H NMR spectrum of 2.7 in C$_6$D$_6$.

Figure 2.7 X-ray crystal structure of 2.7 with 50% probability ellipsoids. Hydrogen atoms and methyl groups on Cp* are omitted for clarity. Selected bond lengths (Å) and angles (°) for 2.7: Ru1-O1, 2.044(6); Ru1-N1, 2.037(8); Ru2-O2, 2.037(7); Ru2-N2, 2.069(7); Ru3-O3, 2.008(6); Ru3-N3, 2.053(8); N1-Ru1-O1, 88.6(3); N2-Ru2-O2, 89.1(3); N3-Ru3-O3, 88.3(3).

2.4 Conclusion

In summary, a hexadentate ligand platform has been constructed to support a multimetallic core. Even though the L$_2$Fe$_6$(OH)$_6$ complex 2.5 contains OH group, it provides an
understanding to the coordination environment of the ligand. The formation of a Ru complex 2.7 demonstrates the rotation of three side arms in solution to one side in contrast to that in the solid state. This evidence implies the potential for the metal centers to cooperate in small-molecule binding and activation. Future study can explore the use of other precursors to place metals onto the ligand framework and investigate the redox reactivity of the trinuclear core.

2.5 Experimental

2.5.1 General procedures.

The syntheses of 2.1, and 2.4 were done in air. All manipulations involving metals were carried out under a dinitrogen atmosphere using a glovebox or Schlenk techniques. Compound 2.1\(^6\) was prepared using modified literature methods. Compounds 2.2, 2.3, 2.4, 2.5, 2.6, and 2.7 are new compounds. All other chemicals were purchased from commercial source. All glassware was dried overnight in a 150 °C oven or by flame before use. THF was dried over Na/benzophenone and distilled under dinitrogen before use. CH\(_2\)Cl\(_2\), Et\(_2\)O, toluene, pentane, and hexanes were dried by passing through a Pure Solv Innovative Technology Grubbs-type solvent purification system and degassed through three freeze–pump–thaw cycles. CDCl\(_3\) was dried with P\(_2\)O\(_5\) at 60°C overnight, distilled under dinitrogen and stored over molecular sieves. C\(_6\)D\(_6\) was degassed through three freeze–pump–thaw cycles and dried over molecular sieves. \(^1\)H and \(^13\)C NMR data were collected on a Varian 400 MHz, Bruker Avance III 400 MHz, Agilent DD2–500 MHz or Agilent DD2–600 MHz NMR spectrometer. The chemical shifts were reported in ppm and referenced with the residual solvent signals. gHSQC, gCOSY and gHMBC NMR experiments were performed to assign signals properly. Elemental analyses were performed by ANALEST in our department at the University of Toronto.

2.5.2 Synthesis of 2.1

\(O\)-Bromoacetophenone (4.0 g, 0.02 mol) and trifluoromethanesulfonic acid (0.24 mL, 2.67 mmol) were combined in a round bottom flask and kept at 130 °C for 48 hours. The mixture was cooled down to r. t.. The organic components were extracted by 200 mL of CH\(_2\)Cl\(_2\) and washed with water (100 mL x 3). The CH\(_2\)Cl\(_2\) layer was dried over MgSO\(_4\). Volatiles in CH\(_2\)Cl\(_2\) layer were removed on a rotary evaporator. The remaining dark brown solids were dissolved in 50 mL of EtOAc and recrystallized at -10°C over 12h. Grey solids crashed out during this process. The
pure product 2.1 was washed with hexanes (20 mL x 3) and collected on a Buchner funnel as grey solids. (2.59 g, 70% yield). $^1$H NMR (CDCl$_3$, 400 MHz, Figure 2.8) $\delta$: 7.69 (dd, 3H), 7.50 (s, 3H), 7.45 (dd, 3H), 7.38 (dt, 3H), 7.21 (dt, 3H). $^{13}$C NMR (CDCl$_3$, 100 MHz, Figure 2.9) $\delta$: 142.15, 140.57, 133.36, 131.68, 129.78, 129.06, 127.58, 122.82.

![Image](https://via.placeholder.com/150)

Figure 2.8 $^1$H NMR spectrum of 2.1 in CDCl$_3$
2.5.3 Synthesis of 2.2

2.1 (10.0 g, 0.0185 mol), Pd(OAc)$_2$ (1.04 g, 4.63 mmol), and 1,3-bis(diphenylphosphino)propane (3.7 g, 8.97 mmol) were combined in a 1 L round bottom flask sealed with a rubber septum. The flask was pumped under vacuum through a needle over 10 min. Then butyl vinyl ether (22.28 mL, 0.172 mol), Et$_3$N (37.13 mL, 0.267 mol), and ethylene glycol (50 mL) were added to the flask. The reaction was kept at 160 °C for 48 hours. When the reaction was cooled down to r. t., 100 mL of concentrated HCl was added to neutralize the mixture. The organic components were extracted by 800 mL of CH$_2$Cl$_2$ and washed with water (400 mL x 3) and brine (300 mL). The CH$_2$Cl$_2$ layer was dried over MgSO$_4$. Volatiles in CH$_2$Cl$_2$ layer were removed on a rotary evaporator. The residue was purified by column chromatography (silica gel, EtOAc/hexanes = 1:4) to afford pure 2.2 as light yellow solids. (6.1 g, 78% yield). $^1$H NMR (CDCl$_3$, 400 MHz, Figure 2.10) $\delta$: 7.60 (dd, J = 7.6, 1.1 Hz, 3H, H7), 7.52 (dt, J = 7.5, 1.5 Hz, 3H, H5), 7.44 (dt, J = 7.5, 1.3 Hz, 3H, H6), 7.41 (dd, J = 7.5, 0.9 Hz, 3H, H4), 7.31 (s, 3H, H1), 2.26 (s, 9H, H10). $^{13}$C NMR (CDCl$_3$, 100 MHz, Figure 2.11) $\delta$: 204.11(C9), 141.96(C2), 140.76(C8), 139.80(C3), 131.06(C5), 130.71(C4), 128.67(C1), 128.23(C7), 128.03(C6), 30.63(C10). Anal. calcd for (C$_{30}$H$_{24}$O$_3$): C 83.31, H 5.59; Found: C 83.13, H 5.52.
Figure 2.10 $^1$H NMR spectrum of 2.2 in CDCl$_3$
2.5.4 Synthesis of 2.3

2.2 (5.0 g, 0.0116 mol), EtONa (5.51 g, 0.081 mol) were combined in a 250 mL Schlenk flask. The mixture was degassed by two cycles. Then 100 mL of anhydrous EtOAc was added to the flask and heated to reflux at 95 °C for 16 hours under N₂. When the reaction was cooled down to r. t., 60 mL of concentrated HCl was added to neutralize the mixture. The organic content was extracted by 200 mL of CH₂Cl₂ and washed with water (100 mL x 3) and brine (150 mL). The CH₂Cl₂ layer was dried over MgSO₄. Volatiles in CH₂Cl₂ layer were removed on a rotary evaporator. The residue was purified by column chromatography (silica gel, EtOAc/hexanes = 1: 4) to afford pure 2.3 as light yellow solids. (4.78 g, 74% yield). ¹H NMR (CDCl₃, 400 MHz, Figure 2.12) δ: 7.65 (dd, J = 7.7, 1.2 Hz, 3H, H7), 7.50 (dt, J = 7.5, 1.5 Hz, 3H, H5), 7.42 (dt, J = 7.5, 1.3 Hz, 3H, H6), 7.33 (dd, J = 7.6, 1.0 Hz, 3H, H4), 7.31 (s, 3H, H1), 5.57 (s, 3H, H10), 2.02 (s, 9H, H12), the peak for -OH might overlap with other peaks from 7.40-7.55 ppm. ¹³C NMR (CDCl₃, 100 MHz, Figure 2.13) δ: 191.65(C11), 188.40(C9), 141.02(C2), 140.65(C3), 136.10(C8), 130.94(C5), 130.91(C4), 128.99(C7), 128.67(C1), 127.72(C6), 102.34(C10), 25.24(C12). Anal. Calcd. for (C₃₆H₃₀O₆): C 77.40, H 5.41; Found: C 77.19, H 5.64.
Figure 2.12 $^1$H NMR spectrum of $2.3$ in CDCl$_3$. 
2.3 (1.57 g, 2.81 mmol), aniline (1.18 g, 0.0127 mol) and p-toluenesulfonic acid (0.05 g, 0.29 mmol) were combined in a 100 mL round bottom flask. Then 50 mL of toluene was added to the flask and heated to reflux at 142 °C for 16 hours with water separator. When the reaction was cooled down to r. t., NaOH solution (0.6 mL, 1 mol/L) was added to neutralize the mixture. The organic content was extracted by 150 mL of EtOAc and washed with water (50 mL x 2) and brine (100 mL). The EtOAc layer was dried over MgSO₄. Volatiles in EtOAc layer were removed on a rotary evaporator. The residue was purified by column chromatography (silica gel, EtOAc/hexanes = 1: 4) to afford pure 2.4 as light yellow solids (1.65 g, 75% yield). ¹H NMR (CDCl₃, 400 MHz, Figure 2.14) δ: 12.67 (s, 3H, OH), 7.62 (dd, J = 7.4, 1.2 Hz, 3H, H7), 7.49 (s, 3H, H1), 7.39 (d, 3H, H4), 7.37 (d, 3H, H5), 7.34 (dt, 3H, H6), 7.30 (t, 6H, H15), 7.18 (t, 3H, H16), 6.98 (d, 6H, H14), 5.23 (s, 3H, H10), 1.87 (s, 9H, H12). ¹³C NMR (CDCl₃, 100 MHz, Figure 2.15) δ: 193.27(C9), 161.00(C11), 141.97(C8), 140.82(C2), 140.07(C3), 138.72(C13), 130.29(C5), 129.45(C4), 129.23(C15), 128.98(C1), 128.28(C7), 127.24(C6), 125.79(C16), 124.91(C14), 100.33(C10), 20.04(C12). Anal. calcd for (C₅₄H₄₂N₃O₃): C 82.73, H 5.79, N 5.36; Found: C 82.43, H 5.90, N 4.93.
Figure 2.14 $^1$H NMR spectrum of 2.4 in CDCl$_3$
Figure 2.15 $^{13}$C NMR spectrum of 2.4 in CDCl$_3$

2.5.6 Formation of 2.5

In a glovebox, 2.4 (0.05 g, 0.064 mmol) and Fe$_2$(Mes)$_4$ (Mes = 2,4,6-Me$_3$C$_6$H$_2$) (0.056 g, 0.096 mmol) were combined in a 20 mL scintillation vial with 5 ml of toluene. The dark red solution was stirred at r. t. for 16 hours and then filtered. Volatiles were removed under vacuum resulting in dark red solids. The red solids were washed with hexanes and the hexane layer was decanted. The solids were dried under vacuum. 5 mL of toluene was used to re-dissolve the solids. X-ray crystals of 2.5 were obtained by diffusing hexanes to the toluene solution at r. t. (Table 2.1).

Table 2.1 Selected crystallographic data of 2.5:

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<tr>
<td>$c$ (Å)</td>
<td>27.105(3)</td>
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</table>
2.5.7 Formation of 2.6

In a glovebox, 2.4 (0.05 g, 0.064 mmol) and NaOBU\textsuperscript{t} (0.022 g, 0.229 mmol) were combined in a 20 mL scintillation vial with 5 ml of THF. The light yellow solution was stirred at r. t. for 2 hours and then added to solid Fe(OAc)\textsubscript{2} (0.033 g, 0.19 mmol). The reaction was stirred at r. t. for 16 hours and then filtered to give a red solution. Volatiles were removed under vacuum resulting in dark red solids. The red solids were washed with hexanes and the hexane layer was decanted. The solids were dried under vacuum and re-dissolved in 3.5 mL of toluene. X-ray crystals of 2.6 were obtained by diffusing hexanes to the toluene solution at r. t. Because the quality of the crystal was too bad, no enough data could be collected and only the structure of 2.6 was shown.

2.5.8 Synthesis of 2.7

In the glovebox, 2.4 (0.0268 g, 0.034 mmol) and NaOBU\textsuperscript{t} (0.0102 g, 0.106 mmol) were combined in a 20 mL scintillation vial with 5 ml of THF. The light yellow solution was stirred at r. t. for 12 hours and then added to solid (RuCp*Cl)\textsubscript{4} (0.0281 g, 0.0257 mmol). The reaction was stirred at r. t. for 16 hours and then filtered to give a red solution. Volatiles were removed under vacuum resulting in dark red solids. The red solids were re-dissolved with 7 mL of toluene and
filtered. Volatiles were removed under vacuum. The residue was purified by rapid passage through a short pad of alumina in the glovebox with hexanes and then Et₂O as eluent. Pure 2.7 was afforded as red solid (0.0332 g, 65%). X-ray crystals of 2.7 were obtained by evaporation of the toluene solution at r. t. (Table 2.2). ¹H NMR (C₆D₆, 500 MHz, Figure 2.16) δ: 7.85 (dd, J = 7.6, 1.1 Hz, 3H, H7), 7.60 (s, 3H, H1), 7.52 (dt, J = 7.5, 1.3 Hz, 3H, H5), 7.31 (d, 3H, H4), 7.29 (dt, 3H, H6), 7.23 (d, 6H, H14), 7.20 (t, 3H, H15), 6.96 (t, 6H, H16), 5.29 (s, 3H, H10), 1.50 (s, 9H, H12), 1.34 (s, 45H, H18). ¹³C NMR (C₆D₆, 125 MHz, Figure 2.17) δ: 178.31(C9), 162.10(C11), 158.21(C13), 143.39(C8), 141.44(C2), 140.67(C3), 130.97(C4), 129.78(C7), 129.19(C1), 128.73(C14), 128.35(C5), 127.12(C6), 124.44(C15), 123.98(C16), 100.34(C10), 76.15(C17), 24.53(C12), 10.42(C18).

Figure 2.16 ¹H NMR spectrum of 2.7 in C₆D₆. Note, two humps at 1.36 and 0.92 ppm are from grease.
Figure 2.17 $^{13}$C NMR spectrum of 2.7 in C$_6$D$_6$. Note, peaks at 137.90, 129.34, 128.57, 125.70 and 21.44 ppm are from trace amount of toluene. A peak at 30.24 ppm is from grease.

Table 2.2 Selected crystallographic data of 2.7:

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<td>no. of indept refln</td>
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$wR_2 = 0.2180$
2.6 References


3 Chapter 3
Catalytic hydroboration of CO$_2$ with a carbon-centered organocatalyst

3.1 Abstract

The charge separation compound 3.1 can not only reversibly bind CO$_2$, but also act as catalyst for hydroboration of CO$_2$. The catalytic performance of 3.1 with carbon-centered reactivity is among the best for organocatalysts. A possible intermediate 3.2 in the catalytic cycle was isolated as the mechanism for catalytic reaction was partly revealed.

3.2 Introduction

The use of fossil fuels has caused a drastic increase of CO$_2$ emissions over the past few decades. While the increase in CO$_2$ level in the atmosphere raises serious environmental concerns, it also presents an opportunity for using CO$_2$ as a sustainable C$_1$ feedstock for chemical syntheses. Many promising methods have been developed for the conversion of CO$_2$ to value-added chemicals, such as carbonates and derivatives, carboxylic acids and derivatives, formaldehyde, CO, alkanes, methylamines, and methanol. The catalytic reduction of CO$_2$ to methanol is particularly interesting as it converts the combustion product back to a liquid fuel. Three general routes have been reported for the catalytic conversion of CO$_2$ to methanol: hydrogenation, and hydroboration. A few transition metal and main group metal catalysts have been reported for the hydroboration of CO$_2$ into methylborylether, which upon hydrolysis produces methanol. The metal-free phosphine–borane frustrated Lewis pairs (FLPs) and a few borohydride species have also shown catalytic activity towards the same transformation. Most of the above catalysts are plagued with intrinsic air- and moisture-sensitivity. In 2014, Cantat and co-workers reported the air- and moisture-stable N-heterocycle-based catalysts that only contain carbon, hydrogen, and nitrogen. These catalysts feature nitrogen-centered activity for catalysis. Unfortunately, these catalysts have limited borane scope, i.e., 9-borabicyclo[3.3.1]nonane (9-BBN) only. Despite these recent advances in CO$_2$ reduction into methanol via catalytic hydroboration with heteroatom-centered reactivity, a catalyst with carbon-centered reactivity is unknown for this transformation. It is worth pointing out that although N-heterocyclic carbenes (NHCs) are known to catalyze the hydrosilylation of...
CO₂ to methylsilyl ethers⁶ᵃ,⁶ᵇ and the methylation of amines using CO₂ as the carbon source,¹² the hydroboration of CO₂ into methylborylethers catalyzed by NHCs remains unknown.

Previously our group discovered the reversible CO₂ insertion into the C–H bond of the actor 4,5-diazafluorenyl ligand supported by spectator-metal centers.¹³ To confirm the spectator role of the metal centers, we further demonstrated this new reactivity with a metal-free compound, N-methyl-4,5-diazafluorenide, 3.1(Scheme 3.1) by replacing spectator metal centers with a methyl group.¹³ᵇ Since the reversible binding of CO₂ can be achieved with these compounds, it is reasonable to extend the stoichiometric reactivity into the catalytic reduction.

3.3 Results and discussion

Our initial tests showed that 3.1 could catalyze the hydroboration of CO₂ with 9-BBN and catecholborane (HBcat). For example, when a C₆D₅Br solution of 3.1 and 10 eq. of 9-BBN was heated at 70 °C overnight under 1 atm of ¹³CO₂, the major product ¹³CH₃OBBN was observed along with a small amount of ¹³CH₂(OBBN)₂ in the ¹H and ¹³C NMR spectra (see Figure 3.1, 3.2). Similarly, when a C₆D₅Br solution of 3.1 and 30 eq. of HBcat was heated at 70 °C under 1 atm of ¹³CO₂ for 2 h, NMR experiments showed that ¹³CH₃OBcat was the only ¹³CO₂ reduction product (see Figure 3.3, 3.4). These preliminary results encouraged us to test the catalytic performance of 3.1 further. A C₆D₅Br solution of 3.1 and 100 eq. of HBcat was exposed to 1.5 atm of CO₂ at 25 °C and the reaction was monitored with ¹H and ¹¹B NMR spectroscopy.
The plot of TON vs time for this reaction is shown in Figure 3.5. The reaction started with a short induction period followed by fast catalysis. As HBcat was getting depleted toward the end of the reaction, the reaction rate was approaching 0. No induction period was observed at 70 °C and the reaction profile consisted of two stages: fast catalysis and plateau. The TOFs at the fast catalysis stage of the reactions were extracted from the plot: 41 and 231 h\(^{-1}\) for 25 °C and 70 °C reactions, respectively. Such TOFs put 3.1 amongst the most active organocatalysts for this transformation.

Figure 3.1 \(^1\)H NMR spectrum of the final mixture of the reaction between 3.1, 10 eq. of 9-BBN and CO\(_2\) at 70 °C.
Figure 3.2 $^{13}$C NMR spectrum of the final mixture of the reaction between 3.1, 10 eq. of 9-BBN and CO$_2$ at 70 °C.

Figure 3.3 $^1$H NMR spectrum of the final mixture of the reaction between 3.1, 30 eq. of HBcat and CO$_2$ at 70 °C.
Figure 3.4 $^{13}$C NMR spectrum of the final mixture of the reaction between 3.1, 30 eq. of HBcat and CO$_2$ at 70 °C.

Figure 3.5 TON vs time plot for the formation of CH$_3$OBcat catalyzed by 3.1. A C$_6$D$_5$Br solution of 3.1 and 100 eq. of HBcat was exposed to 1.5 atm CO$_2$ at 70 °C (■) and 25 °C (●).
When a C₆D₅Br solution of 3.1 and 100 eq. of HBcat was exposed to 1.5 atm of CO₂ at 25 °C, CH₃OBcat was produced with a TON of 97 within 6 h (Table 3.1, entry 1). When the same reaction was carried out at 70 °C, the reaction reached completion within 2 h (Table 3.1, entry 2); to test whether the catalyst was still active after 100 turnovers, 21.5 h after the complete consumption of the first 100 eq. of HBcat, another 100 eq. of HBcat was added to the reaction mixture, which was then re-charged with 1.5 atm of CO₂ and reheated at 70 °C. The second batch of HBcat was consumed within 3 h to give an overall TON of 196 (Table 3.1, entry 3), indicating that catalyst 3.1 was still highly active.¹⁴

When 9-BBN was used as the reductant under the same conditions, the formation of CH₂(OBBN)₂ and CH₃OBBN was observed at 25 °C within 8 h with a total TON of 58 (Table 3.1, entry 4); if the same reaction was carried out at 70 °C, the TON reached 66 within 2 h (Table 3.1, entry 5) and again CH₂(OBBN)₂ and CH₃OBBN were both produced. The lower reaction rates in entries 4 and 5 compared to those in entries 1 and 2, respectively, could be attributed to the low solubility of 9-BBN. When a less reactive reductant pinacolborane (HBpin) was used, the catalytic reaction only gave 14 total turnovers in 48 h at 100 °C, yielding three reduction products HCOOBpin, CH₂(OBpin)₂ and CH₃OBpin (Table 3.1, entry 6). Using 100 eq. of BH₃·SMe₂ (with respect to catalyst 3.1) as the reductant under 1.5 atm of CO₂ the reaction achieved a TON of 294 with BH₃ within 44 h at 25 °C to yield (CH₃OBO)₃ (Table 3.1, entry 7). Increasing the reaction temperature from 25 °C to 70 °C only improved the reaction rate by a factor of ~2 (Table 3.1, entry 8).

The formal insertion of CO₂ into 3.1 has been reported before.¹³b In that case, we proposed the mechanism likely involved the nucleophilic attack on CO₂ by the backbone carbanion of diazafluorenide followed by proton transferred to the carboxylate. We propose the similar insertion of CO₂ into a C-B bond within our system is possible since DFT calculations showed this step is feasible energetically and the insertion of CO₂ into the C-B bond has been realized within our system.¹³c The first step is the reaction between the pre-catalyst and a borane to release H₂ and generate 3.2 (Scheme 3.2). When 3.1 and 7 eq. of HBcat were combined in a J-Young tube, the solution was immediately analyzed by ¹H NMR. The ¹H NMR spectrum showed the formation of 3.2 within 5 min. After CO₂ insertion, the additional boranes could add to the boryl ester to produce the formate borane (HCOOBR₂), acetal borane(CH₂(OBR₂)₂), and methoxy borane(CH₃OBR₂) with R₂BOBR₂.
Table 3.1 Hydroboration of CO$_2$ by a variety of boranes$^a$ with 3.1 as catalyst

<table>
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<th>Entry</th>
<th>Borane</th>
<th>Equiv.</th>
<th>Solvent</th>
<th>T ($^\circ$C)</th>
<th>Time</th>
<th>TON$^b$ from the formation of each product</th>
<th>Total TON$^a$</th>
<th>Avg. TOF$^c$</th>
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<tr>
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<td>HBcat</td>
<td>100</td>
<td>C$_6$D$_5$Br</td>
<td>25</td>
<td>6h</td>
<td>97</td>
<td>97</td>
<td>16 (41)$^f$</td>
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<tr>
<td>2</td>
<td>HBcat</td>
<td>100</td>
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<td>70</td>
<td>2h</td>
<td>100</td>
<td>100</td>
<td>50 (231)$^f$</td>
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<tr>
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<td>2+3h$^c$</td>
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<td>C$_6$D$_5$Br</td>
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<td>44h</td>
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<td>8</td>
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<td>14.0</td>
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</table>

$^a$ Reaction conditions: a Schlenk bomb was charged with 1.0 mg 3.1 and 100 eq. of borane, ~0.6 mL of a deuterated solvent, and 1.5 atm$^{15}$ of CO$_2$. The internal standard, hexamethylbenzene was added to the reaction mixture upon completion. $^b$ TON is based on the number of C–H bonds formed in the reduced products per molecule of the catalyst, determined by $^1$H NMR integration against the internal standard. $^c$ The number in parentheses is the TOF at the fast catalysis stage of the reaction. $^d$ The second 100 eq. of HBcat was added 21.5 h after the complete consumption of the first 100 eq. $^e$ The two numbers are the time required to consume the two batches of HBcat, respectively. $^f$ Control experiment (i.e., same conditions except for the absence of the catalyst) for entry 8 showed 4.5% conversion of BH$_3$:SMe$_2$ to (CH$_3$:OBO)$_3$, while all other entries have no background reactions.

Scheme 3.2 Possible mechanism for the hydroboration of CO$_2$ with 3.1 as catalyst.

To probe the details of the mechanism for the conversion from 3.2 to HCOOBcat, DFT calculations have been performed to obtain key information (Figure 3.6).
 Figure 3.6 DFT calculations showing the mechanism for the formation of HCOOBCat. Note, the mechanism discussed above is not general, as different boranes and catalysts could give different energetics according to DFT.

After CO₂ insertion into a C-B bond, a bimolecular process takes place to form the adduct B1 and another HBcat can coordinate to the oxygen atom to form B2. Then the turnover-limiting intramolecular hydride transfer occurs to generate B3, from which a molecule of A1 could dissociate to form B4. Again, another bimolecular process happens to cleave the C-C bond and release the HCOOBCat product, the insertion intermediate A1, and the borane adduct 3.2.

To explore the feasibility of this mechanism, the intermediate 3.2 was synthesized by another method. When 2 eq. of 3.1 was used to react with ClBcat, 1 eq. of 3.2 was obtained as the other eq. of 3.1 could act as the base to deprotonate the 3.1-ClBcat adduct (Scheme 3.3). 3.2 is soluble in CH₂Cl₂, THF, CH₃CN, C₆D₃Br, benzene, but insoluble in Et₂O and hexanes, and gradually decomposes in DMSO-d₆. The reaction between 3.2 and CO₂ was carried out in a variety of solvents. However, due to its moisture-sensitivity, all the attempts have not been successful yet. Most of the reactions with CO₂ generated a side product 3.3, which was characterized by single crystal XRD (Figure 3.8 and Scheme 3.4). It was possible that trace moisture got involved in this disproportionation process.
Scheme 3.3 Synthesis of 3.2.

Figure 3.7 X-ray crystal structure of 3.2 with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) for 3.2: O1-B1, 1.410(8); O1-C13, 1.379(4); O2-B1, 1.409(9); O2-C14, 1.384(3); N1-C12, 1.471(4); B1-C8, 1.493(6); C4-C8, 1.434(8); C7-C8, 1.435(2); O1-B1-O2, 109.6(2); O1-B1-C8, 125.3(2); O2-B1-C8, 124.9(9); C4-C8-C7, 104.9(1).
Figure 3.8 X-ray crystal structure of 3.3 with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) for 3.3: N1-C47, 1.488(3); C7-C37, 1.480(6); C18-C37, 1.499(8); B2-O5, 1.505(5); B2-O6, 1.469(8); B2-O7, 1.493(6); B2-O8, 1.480(7); C7-C37-C18, 102.3(2); O6-B2-O5, 106.8(1); O6-B2-O8, 113.7(7); O5-B2-O7, 108.3(9); O7-B2-O8, 102.6(9).

Scheme 3.4 The reaction between 3.2 and CO₂.

The catalytic hydroboration of CO₂ with 3.2 as catalyst has been investigated. A C₆D₅Br solution of 3.2 and 100 eq. of HBcat was exposed to 1.5 atm of CO₂ at 25 °C. The reaction produced CH₃OBcat with a TON of 92 within 7 h. This result was comparable to that with 3.1 as catalyst and demonstrated the role of 3.2 in the catalytic cycle.

3.4 Conclusion

In conclusion, the stoichiometric binding of CO₂ with charge separation compound 3.1 has been extended to the catalytic hydroboration. Upon hydrolysis, the reaction can produce methanol from methylborylethers. 3.1 features carbon-centered reactivity and its catalytic
efficiency is comparable to the best organocatalysts with heteroatom-based activity. In addition, the mechanism for the catalytic cycle has been studied and a possible intermediate 3.2 has been synthesized. 3.2 is tested as the catalyst for hydroboration of CO\textsubscript{2} and it shows similar efficiency compared to 3.1, demonstrating its role in the catalytic cycle. However, the reaction between 3.2 and CO\textsubscript{2} has not been successful yet, due to the formation of a side product 3.3.

3.5 Experimental

3.5.1 General procedures

All manipulations involving boranes were carried out under a dinitrogen atmosphere using a glovebox or Schlenk techniques. Compound 3.2 is a new compound. All other chemicals were purchased from commercial source. All glassware was dried overnight in a 150°C oven or by flame before use. The J. Young NMR tubes were dried in a 60°C oven overnight. Catalytic reactions under 1.5 atm of CO\textsubscript{2} were conducted in sealed Schlenk bombs. CO\textsubscript{2} was purchased from Linde (Grade 4.0) and used as received. THF was dried over Na/benzophenone and distilled under dinitrogen before use. CH\textsubscript{2}Cl\textsubscript{2}, Et\textsubscript{2}O, toluene, pentane, and hexanes were dried by passing through a Pure Solv InnovativeTechnology Grubbs-type solvent purification system and degassed through three freeze–pump–thaw cycles. DMSO-d\textsubscript{6} was dried with CaH\textsubscript{2} at 60°C overnight, vacuum distilled and stored over molecular sieves. CDCl\textsubscript{3} was dried with P\textsubscript{2}O\textsubscript{5} at 60°C overnight, distilled under dinitrogen and stored over molecular sieves. C\textsubscript{6}D\textsubscript{6} and C\textsubscript{6}D\textsubscript{5}Br were degassed through three freeze–pump–thaw cycles and dried over molecular sieves. \textsuperscript{1}H, \textsuperscript{11}B, and \textsuperscript{13}C NMR data were collected on a Varian 400 MHz, Bruker Avance III 400 MHz, Agilent DD2–500 MHz or Agilent DD2–600 MHz NMR spectrometer. The chemical shifts were reported in ppm and referenced with the residual solvent signals. gHSQC, gCOSY and gHMBC NMR experiments were performed to assign signals properly. Elemental analyses were performed by ANALEST in our department at the University of Toronto. The commercial HBcat was vacuum-distilled at 50°C. The purity of the redistilled HBcat was determined by \textsuperscript{1}H NMR with hexamethylbenzene as the internal standard to be ranging from 65% to 70% between batches. The measured purity of HBcat is specified in each individual experiment below.
3.5.2 Reaction between 9-BBN and $^{13}$CO$_2$ in the presence of catalyst 3.1 at 70 °C

In a N$_2$-filled glovebox 9-BBN dimer (69 mg, 0.282 mmol) was added into a J. Young NMR tube containing a solution of 3.1 (10.0 mg, 0.0549 mmol in 0.6 mL of C$_6$D$_5$Br). The tube was treated by the “freeze pump” process once in liquid nitrogen and then immediately transferred to a -70 °C dry ice/iPrOH bath and opened to 1 atm of $^{13}$CO$_2$ for 10 min to allow heat exchange, during which only the frozen solution-containing portion of the tube was immersed in the cold bath. The tube was then sealed and warmed up to r. t. and heated at 70 °C for 17 h. The conversion of 9-BBN to $^{13}$CH$_2$(OBBN)$_2$ and $^{13}$CH$_3$OBBN was monitored by $^1$H and $^{11}$B NMR.

\[ 3.1 + 5 \xrightarrow{^{13}\text{CO}_2, \text{C}_6\text{D}_5\text{Br}, 70^\circ \text{C}, 17\text{h}} \text{^{13}CH}_2(\text{OBBN})_2 + \text{^{13}CH}_3\text{OBBN} + \text{O(BBN)$_2$} \]

$^{13}$CH$_2$(OBBN)$_2$: $^1$H NMR (C$_6$D$_5$Br, 400 MHz) δ: 5.46 (d, $^1J_{\text{C-H}} = 164.6$ Hz, $^{13}$CH$_2$(OBBN)$_2$). $^{13}$C NMR (C$_6$D$_5$Br, 100 MHz) δ: 85.56 (t, $^1J_{\text{C-H}} = 164$ Hz, $^{13}$CH$_2$(OBBN)$_2$).

$^{13}$CH$_3$OBBN: $^1$H NMR (C$_6$D$_5$Br, 400 MHz) δ: 3.56 (d, $^1J_{\text{C-H}} = 142.7$ Hz, $^{13}$CH$_3$OBBN). $^{13}$C NMR (C$_6$D$_5$Br, 100 MHz) δ: 52.80 (q, $^1J_{\text{C-H}} = 142$ Hz, $^{13}$CH$_3$OBBN).

The $^{11}$B NMR spectrum showed a broad singlet at 58.6 ppm.

3.5.3 Reaction between HBcat and $^{13}$CO$_2$ in the presence of catalyst 3.1 at 70 °C

In a N$_2$-filled glovebox, HBcat (28.3 mg, 70% purity, 0.165 mmol) was added into a J. Young NMR tube containing a solution of 3.1 (1.0 mg, 0.00549 mmol in 0.6 mL of C$_6$D$_5$Br). The tube was treated by the “freeze pump” process once in liquid nitrogen and then immediately transferred to a -70 °C dry ice/iPrOH bath and opened to 1 atm of $^{13}$CO$_2$ for 10 min to allow heat exchange, during which only the frozen solution-containing portion of the tube was immersed in the cold bath. The tube was then sealed and warmed up to r. t. and heated at 70 °C for 2 h. The conversion of HBcat to $^{13}$CH$_3$OBcat was monitored by $^1$H and $^{11}$B NMR.
3.1 + 30 HBcat $\xrightarrow{^{13}\text{CO}_2/C_6\text{D}_5\text{Br}}$ $^{13}\text{CH}_3\text{OBcat} + \text{catBOBcat}$

$^{13}\text{CH}_3\text{OBcat}$: $^1\text{H}$ NMR (C$_6$D$_5$Br, 400 MHz) $\delta$: 3.60 (d, $^1J_{\text{C}-\text{H}} = 145.3$ Hz, $^{13}\text{CH}_3\text{OBcat}$); $^{13}$C NMR (C$_6$D$_5$Br, 100 MHz) $\delta$: 52.80 (q, $^1J_{\text{C}-\text{H}} = 145$ Hz, $^{13}\text{CH}_3\text{OBcat}$).

The $^{11}$B NMR spectrum showed a broad signal at 23.1 ppm.

3.5.4 Reaction between 9-BBN and CO$_2$ in the presence of catalyst 3.1 at 25°C

In a N$_2$-filled glovebox, 9-BBN dimer (67 mg, 0.274 mmol) was added into a 50 mL Schlenk bomb containing a solution of 3.1 (1.0 mg, 0.00549 mmol in 0.6 mL of C$_6$D$_5$Br). The bomb was immersed in liquid N$_2$ to freeze the solution; the headspace was then evacuated. The entire bomb was then immersed in a −70°C dry ice-isopropanol bath to keep the solution frozen and cool the headspace. The bomb was then opened to 1 atm of CO$_2$ for 10 minutes to allow the temperature to equilibrate. Subsequently the bomb was sealed and allowed to warm to 25°C quickly to achieve ~1.5 atm pressure. The reaction mixture was stirred 25°C for 8 h. It gradually changed from a dark blue solution to an orange suspension and finally to a light yellow suspension with white precipitates. The bomb was shipped into a N$_2$-filled glovebox. After the release of CO$_2$ gas from the system, hexamethylbenzene (9.6 mg, 0.0593 mmol) was added to the mixture. The TON was calculated based on the integration of the products with respect to that of hexamethylbenzene in the $^1$H NMR spectrum (Figure 3.9 and Figure 3.10).

3.1 + 50 $\xrightarrow{\text{CO}_2/C_6\text{D}_5\text{Br}}$ CH$_2$(OBBN)$_2$ + CH$_3$OBBN + O(BBN)$_2$

CH$_2$(OBBN)$_2$: $^1$H NMR (C$_6$D$_5$Br, 400 MHz) $\delta$: 5.46 (s, CH$_2$(OBBN)$_2$); $^{13}$C NMR (C$_6$D$_5$Br, 100 MHz) $\delta$: 85.56 (CH$_2$(OBBN)$_2$).

CH$_3$OBBN: $^1$H NMR (C$_6$D$_5$Br, 400 MHz) $\delta$: 3.58 (s, CH$_3$OBBN), $^{13}$C NMR (C$_6$D$_5$Br, 100 MHz) $\delta$: 52.80 (CH$_3$OBBN).
Figure 3.9 $^1$H NMR spectrum of the reaction between 9-BBN and CO$_2$ in the presence of catalyst 3.1 at 25 °C. A peak at 2.11 ppm refers to hexamethylbenzene as the internal standard.

Figure 3.10 $^{11}$B NMR spectrum of the reaction between 9-BBN and CO$_2$ in the presence of catalyst 3.1 at 25 °C.
3.5.5 Reaction between 9-BBN and CO$_2$ in the presence of catalyst 3.1 at 70 °C

In a N$_2$-filled glovebox, 9-BBN dimer (67 mg, 0.274 mmol) was added into a 50 mL Schlenk bomb containing a solution of 3.1 (1.0 mg, 0.00549 mmol in 0.6 mL of C$_6$D$_5$Br). CO$_2$ was introduced using the same protocol as above. The reaction mixture was stirred at 70 °C for 2h. The bomb was shipped into a N$_2$-filled glovebox. After cooling and the release of CO$_2$ gas from the system, hexamethylbenzene (11.8 mg, 0.0728 mmol) was added to the mixture. The TON was calculated based on the integration of the products with respect to that of hexamethylbenzene in the $^1$H NMR spectrum (Figure 3.11 and Figure 3.12).

![Chemical reaction diagram](image)

Figure 3.11 $^1$H NMR spectrum of the reaction between 9-BBN and CO$_2$ in the presence of catalyst 3.1 at 70 °C. A peak at 2.09 ppm refers to hexamethylbenzene as the internal standard.
Figure 3.12 $^{11}$B NMR spectrum of the the reaction between 9-BBN and CO$_2$ in the presence of catalyst 3.1 at 70 °C.

3.5.6 Reaction between HBcat and CO$_2$ in the presence of catalyst 3.1 at 25 °C

In a N$_2$-filled glovebox, HBcat (94.7 mg, 69.6% purity, 0.549 mmol) was added into a 50 mL Schlenk bomb containing a solution of 3.1 (1.0 mg, 0.00549 mmol in 0.6 mL of C$_6$D$_3$Br). CO$_2$ was introduced using the same protocol as above. The reaction mixture was stirred at 25 °C for 6 h. It gradually changed from a dark brown solution to a light yellow suspension with white precipitates. After the release of CO$_2$ gas from the system, hexamethylbenzene (11.1 mg, 0.0685 mmol) was added to the mixture. The TON was calculated based on the integration of the product with respect to that of hexamethylbenzene in the $^1$H NMR spectrum (Figure 3.13 and Figure 3.14).

$$3.1 + 100 \text{HBcat} \xrightarrow{\text{CO}_2} \text{CH}_3\text{OBcat + catBOBcat}$$

TON = 97

25°C, 6h

CH$_3$OBcat: $^1$H NMR (C$_6$D$_3$Br, 400 MHz) $\delta$: 3.60 (s, CH$_3$OBcat); $^{13}$C NMR (C$_6$D$_3$Br, 100 MHz) $\delta$: 52.80 (CH$_3$OBcat).

The $^{11}$B NMR spectrum showed two broad signals at 23.3 and 22.5 ppm.
Figure 3.13 $^1$H NMR spectra of the reaction between HBcat and CO$_2$ in the presence of catalyst 3.1 at 25 °C from 5 min (bottom) to 6 h (top).

Figure 3.14 $^{11}$B NMR spectrum of the reaction between HBcat and CO$_2$ in the presence of catalyst 3.1 at 25 °C from 5 min (bottom) to 6 h (top)
3.5.7 Reaction between HBcat and CO\(_2\) in the presence of catalyst 3.1 at 70 °C

In a N\(_2\)-filled glovebox, HBcat (101.2 mg, 65.2% purity, 0.549 mmol) was added into a 50 mL Schlenk bomb containing a solution of 3.1 (1.0 mg, 0.00549 mmol in 0.6 mL of C\(_6\)D\(_5\)Br). CO\(_2\) was introduced using the same protocol as above. The reaction mixture was stirred at 70 °C for 2 h. The solution rapidly changed color from dark brown to light yellow. When the reaction mixture was cooled down to ambient temperature, a lot of white precipitate appeared. After the release of CO\(_2\) gas from the system, hexamethylbenzene (0.1 mg, 0.0623 mmol) was added to the mixture. The conversion of HBcat to CH\(_3\)OBcat was monitored by \(^1\)H NMR and \(^{11}\)B NMR. The TON was calculated based on the integration of the product with respect to that of hexamethylbenzene in the \(^1\)H NMR spectrum (Figure 3.15 and Figure 3.16).

\[
3.1 + 100 \text{ HBcat} \xrightarrow{\text{CO}_2, \text{C}_6\text{D}_5\text{Br}, 70^\circ\text{C}, 2\text{h}} \text{CH}_3\text{OBcat} + \text{catBOBcat}
\]

TON = 100

Figure 3.15 \(^1\)H NMR spectrum of the reaction between HBcat and CO\(_2\) in the presence of catalyst 3.1 at 70 °C from 15 min (bottom) to 2 h (top).
3.5.8 Reaction between HBcat and CO$_2$ in the presence of catalyst 3.1 at 70 °C

In a N$_2$-filled glovebox, HBcat (99.9 mg, 65.9% purity, 0.549 mmol) was added into a 50 mL Schlenk bomb containing a solution of 3.1 (1.0 mg, 0.00549 mmol in 0.6 mL of C$_6$D$_5$Br). CO$_2$ was introduced using the same protocol as above. The reaction mixture was stirred at 70 °C for 2 h. The solution rapidly changed color from dark brown to light yellow. When the reaction mixture was cooled to ambient temperature, a lot of white precipitates appeared. After 21.5 h, another batch of HBcat (100.0 mg, 65.9% purity, 0.549 mmol) was added into the reaction mixture. CO$_2$ was introduced using the same protocol as above. The reaction mixture was again stirred at 70 °C for 3 h. After cooling and the release of CO$_2$ gas from the system, hexamethylbenzene (11.4 mg, 0.0704 mmol) was added. The TON was calculated based on the integration of the product with respect to that of hexamethylbenzene in the $^1$H NMR spectrum (Figure 3.17 and Figure 3.18).

$$\text{3.1} + 100 \text{ HBcat} \xrightarrow{\text{CO}_2} 100 \text{ HBcat} \xrightarrow{\text{C}_6\text{D}_5\text{Br}} \text{CH}_3\text{OBcat} + \text{catBOBcat}$$

Figure 3.16 $^{11}$B NMR spectrum of the reaction between HBcat and CO$_2$ in the presence of catalyst 3.1 at 70 °C from 15 min (bottom) to 2 h (top).
Figure 3.17 $^1$H NMR spectrum of the reaction between HBcat and CO$_2$ in the presence of catalyst 3.1 at 70 °C. A peak at 2.10 ppm refers to hexamethylbenzene as the internal standard.

Figure 3.18 $^{11}$B NMR spectrum of the reaction between HBcat and CO$_2$ in the presence of catalyst 3.1 at 70 °C.
3.5.9 Reaction between HBpin and CO\textsubscript{2} in the presence of catalyst \textbf{3.1} at 100 °C

In a N\textsubscript{2}-filled glovebox, HBpin (70.3 mg, 0.549 mmol) was added into a 50 mL Schlenk bomb containing a solution of \textbf{3.1} (1.0 mg, 0.00549 mmol in 0.6 mL of CDCl\textsubscript{3}). CO\textsubscript{2} was introduced using the same protocol as above. The reaction mixture was stirred at 100 °C for 48 h. The solution gradually changed color from dark blue to red and finally brown. After cooling and the release of CO\textsubscript{2} gas from the system, hexamethylbenzene (11.9 mg, 0.0734 mmol) was added to the mixture. The TON was calculated based on the integration of the product with respect to that of hexamethylbenzene in the \textsuperscript{1}H NMR spectrum (Figure 3.19 and Figure 3.20).

\[ \textbf{3.1} + 100 \text{ HBpin} \xrightarrow{\text{CO}_2, \text{CDCl}_3, 100\degree C, 2 \text{ days}} \text{HCO}_2\text{Bpin} + \text{CH}_2(\text{OBpin})_2 \]

\[ \text{TON} = 6.82 \]

\[ \text{CH}_3\text{OBpin} + \text{pinBOBpin} \]

\[ \text{TON} = 6.28 \]

HCO\textsubscript{2}Bpin: \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz) \(\delta\): 8.42 (s, HCO\textsubscript{2}Bpin)

CH\textsubscript{2}(OBpin)\textsubscript{2}: \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz) \(\delta\): 5.24 (s, CH\textsubscript{2}(OBpin)\textsubscript{2})

CH\textsubscript{3}OBpin: \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz) \(\delta\): 3.60 (s, CH\textsubscript{3}OBpin)

Figure 3.19 \textsuperscript{1}H NMR spectrum of the reaction between HBpin and CO\textsubscript{2} in the presence of catalyst \textbf{3.1} at 100 °C. A peak at 2.23 ppm refers to hexamethylbenzene as the internal standard.
3.5.10 Reaction between BH$_3$·SMe$_2$ and CO$_2$ in the presence of catalyst 3.1 at 25 °C

In a N$_2$-filled glovebox, a solution of BH$_3$·SMe$_2$ (2.0 M in THF, 0.33 mL, 0.66 mmol) was added into a 50 mL Schlenk bomb containing a solution of 3.1 (1.2 mg, 0.00659 mmol in 0.6 mL of C$_6$D$_6$). CO$_2$ was introduced using the same protocol as above. The reaction mixture was stirred at 25 °C for 44 h. After the release of CO$_2$ gas from the system, hexamethylbenzene (0.9 mg, 0.0056 mmol) was added to the mixture. The TON was calculated based on the integration of the product with respect to that of hexamethylbenzene in the $^1$H NMR spectrum (Figure 3.21 and Figure 3.22).

$$3.1 + 100 \text{BH}_3\cdot\text{SMe}_2 \xrightarrow{\text{C}_6\text{D}_6, \text{25°C, 44 h}} \text{(CH}_3\text{OBO)}_3 \quad \text{TON} = 294$$

(CH$_3$OBO)$_3$: $^1$H NMR (C$_6$D$_6$, 400 MHz) δ: 3.39 (s, (CH$_3$OBO)$_3$); $^{13}$C NMR (C$_6$D$_6$, 100 MHz) δ: 51.34 ((CH$_3$OBO)$_3$).
Figure 3.21 $^1$H NMR spectrum of the reaction between BH$_3$·SMe$_2$ and CO$_2$ in the presence of catalyst 3.1 at 25 °C. A peak at 2.10 ppm refers to hexamethylbenzene as the internal standard.

Figure 3.22 $^{11}$B NMR spectrum of the reaction between BH$_3$·SMe$_2$ and CO$_2$ in the presence of catalyst 3.1 at 25 °C.
3.5.11 Reaction between BH$_3$·SMe$_2$ and CO$_2$ in the presence of catalyst 3.1 at 70 °C

In a N$_2$-filled glovebox, a solution of BH$_3$·SMe$_2$ (2.0 M in THF, 0.275 mL, 0.549 mmol) was added into a 50 mL Schlenk bomb containing a solution of 3.1 (1.0 mg, 0.00549 mmol in 0.6 mL of CDCl$_3$). CO$_2$ was introduced using the same protocol as above. The reaction mixture was stirred at 70 °C for 20.5 h. After cooling and the release of CO$_2$ gas from the system, hexamethylbenzene (1.0 mg, 0.0062 mmol) was added to the mixture. The TON was calculated based on the integration of the product with respect to that of hexamethylbenzene in the $^1H$ NMR spectrum (Figure 3.23 and Figure 3.24).

\[
3.1 + 100 \text{BH}_3\cdot\text{SMe}_2 \xrightarrow{\text{CO}_2, \text{CDCl}_3, 70^\circ\text{C}, 20.5\text{h}} (\text{CH}_3\text{OBO})_3 \\
\text{TON} = 286
\]

(CH$_3$OBO)$_3$: $^1H$ NMR (CDCl$_3$, 400 MHz) δ: 3.51 (s, (CH$_3$OBO)$_3$)

Figure 3.23 $^1H$ NMR spectrum of the reaction between BH$_3$·SMe$_2$ and CO$_2$ in the presence of catalyst 3.1 at 70 °C. A peak at 2.06 ppm refers to hexamethylbenzene as the internal standard.
Figure 3.24 $^{11}$B NMR spectrum of the reaction between BH$_3$·SMe$_2$ and CO$_2$ in the presence of catalyst 3.1 at 70 °C.

### 3.5.12 Synthesis of 3.2

**Method A:** In the glovebox, 3.1 (0.039 g, 0.214 mmol) and ClBcat (0.018 g, 0.117 mmol) were combined in a 20 mL scintillation vial with 10 ml of CH$_2$Cl$_2$. The dark pink solution was stirred at r. t. for 16 hours and then filtered to give a dark pink solution. Volatiles were removed under vacuum resulting in dark pink solids as pure 3.2 (0.030 g, 85%).

**Method B:** In the glovebox, 3.1 (3.2 mg, 0.0176 mmol) and HBcat (21.1 mg, 70% purity, 0.123 mmol) were combined in a 20 mL scintillation vial with 5 ml of CH$_2$Cl$_2$. The solution was stirred at r.t. for 2 hours and the volatiles were removed under vacuum. Dark pink solids were obtained as pure 3.2 (4.3 mg, 82%).

X-ray crystals of 3.2 were obtained by evaporation of the benzene solution at r. t. or slow diffusion of pentane into CH$_3$CN at -35 °C (Table 3.2). $^1$H NMR (C$_6$D$_6$, 400 MHz, Figure 3.25) δ: 9.17(dd, J = 8.4, 1.6 Hz, 1H, H10), 9.12(d, J = 8.1 Hz, 1H, H4), 8.68(dd, J = 4.1, 1.6 Hz, 1H, H8), 7.34(dd, J = 5.7, 3.3 Hz, 2H, H14), 7.24(dd, J = 8.24, 4.1 Hz, 1H, H9), 6.95(dd, J = 5.8, 3.3 Hz, 2H, H15), 6.55(dd, J = 8.2, 5.7 Hz, 1H, H3), 6.26(d, J = 5.7 Hz, 1H, H2), 4.07(s, 3H, H1). $^{13}$C NMR (C$_6$D$_6$, 100 MHz, Figure 3.26) δ: 149.82(C13), 141.27(C8), 141.15(C11), 139.21(C5), 136.66(C7), 133.09(C4), 131.06(C6), 129.72(C10), 129.10(C2), 122.19(C15), 121.08(C9), 114.77(C3), 112.20(C14), 105.41(C12), 44.22(C1). The $^{11}$B NMR spectrum showed a broad signal at 32.6 ppm (Figure 3.27).
Figure 3.25 $^1$H NMR spectrum of 3.2 in C$_6$D$_6$. Note, a peak at 4.27 ppm refers to CH$_2$Cl$_2$. Two humps at 1.36 and 0.92 ppm are from grease.
Figure 3.26 $^{13}$C NMR spectrum of 3.2 in C$_6$D$_6$.

Figure 3.27 $^{11}$B NMR spectrum of 3.2 in C$_6$D$_6$. 
Table 3.2 Selected crystallographic data of 3.2:

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3.5.13 Reaction between HBcat and CO₂ in the presence of catalyst 3.2 at 25 °C

In a N₂-filled glovebox, HBcat (113.5 mg, 70.5% purity, 0.667 mmol) was added into a 50 mL Schlenk bomb containing a solution of 3.2 (2.0 mg, 0.0067 mmol in 0.6 mL of C₆D₅Br). CO₂ was introduced using the same protocol as above. The reaction mixture was stirred at 25 °C for 7 h. It gradually changed from a dark pink solution to a light yellow suspension with white precipitates. After the release of CO₂ gas from the system, hexamethylbenzene (2.14 mg, 0.013 mmol) was added to the mixture. The TON was calculated based on the integration of the product with respect to that of hexamethylbenzene in the ¹H NMR spectrum (Figure 3.28).

\[
\begin{align*}
3.2 + 100\text{HBcat} & \xrightarrow{\text{CO}_2, C_6D_5Br} \text{CH}_3\text{OBcat} + \text{catBOBcat} \\
& \text{TON = 92} \\
& 25°C, 7h
\end{align*}
\]

CH₃OBcat: ¹H NMR (C₆D₅Br, 400 MHz) δ: 3.61 (s, CH₃OBcat).

The ¹¹B NMR spectrum showed two broad signals at 23.3 and 22.4 ppm (Figure 3.29).
Figure 3.28 $^1$H NMR spectrum of the reaction between HBcat and CO$_2$ in the presence of catalyst 3.2 at 25 °C. A peak at 2.22 ppm refers to hexamethylbenzene as the internal standard.

Figure 3.29 $^{11}$B NMR spectrum of the reaction between HBcat and CO$_2$ in the presence of catalyst 3.2 at 25 °C.
3.5.14 Formation of 3.3

In a glovebox, 3.2 (4.5 mg, 0.015 mmol) was dissolved in 0.7 mL of CDCl₃ and transferred to a J-Young NMR tube. After two cycles of “freeze-pump-thaw” process, CO₂ was introduced to the J-Young tube. Then, the solution immediately changed colour from dark pink to light orange with some yellow crystals crashing out. The crystals were characterized by ¹H NMR and X-ray crystallography and were determined as 3.3 (5.3 mg, 86%) (Table 3.3).

¹H NMR (CDCl₃, 300 MHz, Figure 3.30) δ: 9.29(d, J = 6.1 Hz, 1H), 8.81(dd, J = 4.8, 1.4 Hz, 1H), 8.49(d, J = 7.7 Hz, 1H), 8.07(dd, J = 4.3, 3.6 Hz, 1H), 7.81(dd, J = 7.7, 6.2 Hz, 1H), 7.53(dd, J = 7.9, 4.8 Hz, 1H), 6.4(m, 4H), 4.99(s, 3H), 4.14(s, 2H).

Figure 3.30 ¹H NMR spectrum of 3.3 in CDCl₃. Note, the integration of H at 6.4 ppm from B(cat)₂ is smaller than expected. A peak at 5.30 ppm refers to CH₂Cl₂.

Table 3.3 Selected crystallographic data of 3.3:

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<tr>
<td>space group</td>
<td>P 2₁/c</td>
</tr>
<tr>
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<td>Value</td>
</tr>
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<td>-----------</td>
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</tr>
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</tr>
<tr>
<td>$b$ (Å)</td>
<td>6.9333(15)</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>25.353(6)</td>
</tr>
<tr>
<td>$\alpha$ (deg)</td>
<td>90</td>
</tr>
<tr>
<td>$\beta$ (deg)</td>
<td>118.142(10)</td>
</tr>
<tr>
<td>$\gamma$ (deg)</td>
<td>90</td>
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<tr>
<td>$V$ (Å³)</td>
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<tr>
<td>$Z$</td>
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</tr>
<tr>
<td>$D_c$ (g·cm⁻³)</td>
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<tr>
<td>$\mu$ (mm⁻¹)</td>
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<tr>
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<td>29369</td>
</tr>
<tr>
<td>no. of indept refln</td>
<td>8478</td>
</tr>
<tr>
<td>GOF on $F^2$</td>
<td>1.008</td>
</tr>
</tbody>
</table>
| $R [I > 2\sigma(I)]$ | $R_1 = 0.0736$  
| w$R_2$ | 0.1728 |
| $R$ (all data) | $R_1 = 0.1707$  
| w$R_2$ | 0.2135 |

### 3.6 References


14. The slightly slower conversion of the second batch of HBcat was likely due to the inefficient mixing of the reactants caused by the large amount of solid produced in the reaction.

15. The Schlenk bomb charged with all other reagents and solvents was immersed in liquid N\textsubscript{2} to freeze the solution; the headspace was then evacuated. The entire bomb was then immersed in a −70 °C dry ice-isopropanol bath to keep the solution frozen and cool the headspace. The bomb was then opened to 1 atm of CO\textsubscript{2} for 10 minutes to allow the temperature to equilibrate. The bomb was then sealed and allowed to warm to 25 °C to achieve ~1.5 atm pressure. Safety Warning: if CO\textsubscript{2} gas was introduced below -78 °C, dry ice would condense in the reaction vessel and the final pressure becomes time-dependent and can no longer be calculated easily. Using our protocol with a low-melting solvent (i.e., the solvent is not frozen at -70 °C), the final pressure is again time-dependent, because of the dramatically increased solubility of CO\textsubscript{2} at -70 °C. In both scenarios prolonged CO\textsubscript{2} exposure could cause serious explosions due to uncontrolled high pressures and make the results incomparable to others due to unknown CO\textsubscript{2} pressure.
4 Chapter 4
Catalytic hydroboration of CO$_2$ with a pyridine derivative

4.1 Abstract

The characteristic of positive and negative charge separation within our system is critical for the reversible CO$_2$ binding. Based on previous research, we design a new metal free compound 4.1 with charge separation attribute. 4.1 could bind CO$_2$ in a similar fashion while it features a smaller molecular weight, compared to 3.1. We also extend this stoichiometric binding fashion into catalytic style reducing CO$_2$ into methoxy boryl derivatives followed by hydrolysis to generate methanol.

4.2 Introduction

The abundant emission of CO$_2$ from fossil fuels causes serious environmental concerns around the world since CO$_2$ is a major source of greenhouse gas and contributes to global warming. Many preliminary approaches have shown bright potential for the conversion of CO$_2$ to other valuable chemicals.\textsuperscript{1} Transforming CO$_2$ to hydrocarbon molecules, such as methanol, is a main interest of many researchers.\textsuperscript{2} Hydrocarbon products such as methanol, have exhibited promise as the candidate for renewable energy in the future. Towards this goal, many metal-containing and metal-free systems have been developed for the conversion of CO$_2$ to other desirable products. A nickel pincer catalyst could catalyze the transformation of CO$_2$ to MeOBcat, subsequently hydrolyzed to MeOH, with a TON of 495. The insertion of CO$_2$ into M-Hydride bond is a key step in this system.\textsuperscript{3a} Later, a series of POCOP-pincer ligated Pd thiolate complexes were synthesized and tested for catalytic hydroboration of CO$_2$. The new system could produce MeOBcat with high TOFs up to 1780 h$^{-1}$.\textsuperscript{3b} In 2015, Murray group reported a series of metal-hydride cyclophane complexes that could react with CO$_2$ from one to three times.\textsuperscript{4} The Zn version could be stable towards H$_2$O and MeOH but react with CO$_2$ only once.\textsuperscript{4a} Similarly, the Co counterpart reacted with CO$_2$ only once, no matter what temperature was used.\textsuperscript{4b} In contrast, the Fe version allowed CO$_2$ to insert into Fe-H bond one time at low temperature but three times at high temperature. Recently, Milstein and co-workers employed PNP pincer complexes for the CO$_2$ reduction.\textsuperscript{5} The metal-ligand cooperation feature in this system facilitated the elimination of H$_2$O to help reduce CO$_2$ to CO. In addition to transition
metal systems, main group metals are also involved in the reduction of \( \text{CO}_2 \). A gallium hydride species supported by NacNac ligand was found to be active in the catalytic reduction of \( \text{CO}_2 \) with HBpin as reductant. In 2015, a Li-bidentate catalyst displayed high efficiency in the catalytic conversion of \( \text{CO}_2 \) to methane or methanol with hydrosilane or hydroborane as reducing agent. Besides homogeneous organometallic systems, the metal free catalysts also attracted great attention in recent years. Catalytic hydrosilylation of \( \text{CO}_2 \) to produce methoxy silane and methane have also been successfully realized utilizing N-heterocyclic carbene (NHC) or Frustrated Lewis Pair (FLP) catalysts. Recently, the reduction of \( \text{CO}_2 \) by using a variety of boranes as reductant provides another intriguing revenue. An ambiphilic phosphine-borane FLP catalyst has shown high reactivity in the hydroboration of \( \text{CO}_2 \). This system achieves a TON of 2950 and a TOF of 973 h\(^{-1}\), for the reduction of \( \text{CO}_2 \) with BH\(_3\)-SMe\(_2\) at 70 °C. In 2014, another FLP catalysts have been reported with high efficiency for the transformation of \( \text{CO}_2 \) to corresponding methoxy boryl species with different boranes. It is noteworthy that none of these systems exhibit the binding of \( \text{CO}_2 \) to the catalyst itself. The weak Lewis acidity is proposed to play an important role in accelerating the catalytic rate. Last year, Mandal and co-authors investigated the reactivity of an aNHC (abnormal N-heterocyclic carbene). This compound could not only bind \( \text{CO}_2 \) but also catalyze the hydroboration of \( \text{CO}_2 \) with 9-BBN to a TON of 6000.

Our group has reported the reversible insertion of \( \text{CO}_2 \) into a C–H bond of diazafluorenide ligand on a Ru(II) complex. This system was further evolving into a metal free style as N-methylated diazafluorenide derivative, which could also reversibly let \( \text{CO}_2 \) insert into its C–H bond. To probe what structural features are essential for this new type of \( \text{CO}_2 \) reactivity, we simplified the molecule from the three-ring system in 3.1 to a two-ring system in 4.1 (Scheme 4.1), because one of the pyridine moieties (color coated in gray) has no obvious role in \( \text{CO}_2 \) binding. Gratifyingly, 4.1 can indeed react with \( \text{CO}_2 \) reversibly by inserting \( \text{CO}_2 \) into the C–H bond (Scheme 4.1) on the C\(_5\) ring. Both 3.1 and 4.1 bind with \( \text{CO}_2 \) at the reactive carbon center, which is reminiscent of \( \text{CO}_2 \)-binding activity of NHCs. To the best of our knowledge, the air- and moisture-stable and C/H/N-only compounds 3.1 and 4.1 are the first examples of carbon-centered catalysts for the hydroboration of \( \text{CO}_2 \) into methylborylethers.
Scheme 4.1 Reversible CO₂ binding by 3.1 (R = Me, with the gray portion) and 4.1 (R = n-Pr, without the gray portion).

4.3 Results and discussion

Scheme 4.2 Synthesis of 4.1.

Compound 4.1 is an orange oil and can be synthesized using a modified literature procedure. The synthesis of 4.1 is shown in Scheme 4.2. The oxidation of 2,3-cyclopentenopyridine by H₂O₂ results in 4.3, which can react with acetic anhydride to produce 4.4. Hydrolysis of 4.4 will generate 4.5 that is propylated to form 4.6. The elimination of H₂O from 4.6 gives rise to 4.1.

Compared to 3.1, whose solution is stable in air for several hours, the solution of 4.1 can be stored at −15 °C in air for weeks without significant change. Compound 4.1 is soluble in all common organic solvents. When CO₂ was introduced into a DMSO-d₆ solution of 4.1 within a J.
Young NMR tube, the colour changed from orange to dark brown as the temperature rose from 0 °C to r. t. over ~17 h. A peak at 11.02 ppm in the $^1$H NMR spectrum appears after the reaction, which corresponds to the peak of a carboxylic acid (Figure 4.1). The $^{13}$C NMR spectrum confirms the formation of a carboxylic acid species 4.2 with a new peak at 166.37 ppm (Figure 4.2). IR spectrum reveals a C=O resonance at 1629 cm$^{-1}$ (Figure 4.3).

Figure 4.1 $^1$H NMR spectrum of 4.2 in DMSO-d$_6$. The peak at 11.02 ppm in the $^1$H NMR spectrum corresponds to a carboxylic acid.
Figure 4.2 $^{13}$C NMR spectrum of 4.2 in DMSO-$d_6$. The $^{13}$C NMR spectrum confirms the formation of a carboxylic acid species with a new peak at 166.37 ppm.

Figure 4.3 IR spectrum of 4.2 in CDCl$_3$
CO₂ adduct formation was unequivocally proven via X-ray crystallography. (Scheme 4.3)

Stability of the CO₂ adduct has been tested under several conditions. Under an N₂ atmosphere within 3 weeks, 15% of 4.2 reverted to 4.1 at r. t. In a J. Young NMR tube, a CDCl₃ solution of 4.2 was heated under 1 atm of N₂ at 40 °C for 3.5 h. The ¹H NMR spectrum showed over 90% of 4.2 decomposed back to 4.1. TGA-DSC indicates that 4.2 loses CO₂ completely at 110 °C (Figure 4.4). 4.2 may be stable under vacuum as no 4.1 is observed after 2 hours of applied vacuum.

Scheme 4.3 Reversible CO₂ reaction with 4.1. The X-ray crystal structure of 4.2. Thermal ellipsoids at 50% probability level. Key bond length[Å] and angles[°]: C7-C11, 1.427(2); C7-C8, 1.409(2); C7-C12, 1.424(2); O1-C12, 1.250(2); O2-C12, 1.338(2); N1-C4, 1.360(2); N1-C3, 1.477(2); N1-C10, 1.362(2); C11-C7-C8, 106.9(1); C11-C7-C12, 125.5(1); C8-C7-C12, 127.5(1).
Figure 4.4 TGA trace of compound 4.2. The 20.88% mass loss between 40 °C and 110 °C matches with the expected weight loss of 21.67%. TGA methods: 1. Ramp 5 °C/min to 40 °C; 2. Isothermal at 40 °C for 5 min; 3. Ramp 5 °C/min to 200 °C.

We propose that the carbanion is acting as the nucleophile to attack CO$_2$. The resulting carboxylate would then deprotonate the proton on the C7 to form carboxylic acid (Scheme 4.4)$^{11}$.

Scheme 4.4 Possible mechanism for insertion of CO$_2$ to C-H bond of 4.1.
Table 4.1 Hydroboration of CO$_2$ by a variety of boranes$^d$ with 4.1 as catalyst

<table>
<thead>
<tr>
<th>Entry</th>
<th>Borane</th>
<th>Equiv.</th>
<th>Solvent</th>
<th>T (°C)</th>
<th>Time</th>
<th>TON from the formation of each product</th>
<th>total TON$^b$</th>
<th>avg. TOF (h$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9-BBN</td>
<td>100</td>
<td>CDCl$_3$</td>
<td>25</td>
<td>19h</td>
<td>12.5</td>
<td>48.6</td>
<td>61</td>
</tr>
<tr>
<td>2</td>
<td>9-BBN</td>
<td>100</td>
<td>CDCl$_3$</td>
<td>70</td>
<td>2h</td>
<td>7.2</td>
<td>59</td>
<td>66.2</td>
</tr>
<tr>
<td>3</td>
<td>HBpin</td>
<td>100</td>
<td>CDCl$_3$</td>
<td>90</td>
<td>46h</td>
<td>1.6</td>
<td>73</td>
<td>74.6</td>
</tr>
<tr>
<td>4</td>
<td>HBcat</td>
<td>100</td>
<td>CDCl$_3$</td>
<td>25</td>
<td>19h</td>
<td>97</td>
<td>97</td>
<td>97</td>
</tr>
<tr>
<td>5</td>
<td>BH$_3$·SMe$_2$</td>
<td>100</td>
<td>CDCl$_3$</td>
<td>25</td>
<td>7h</td>
<td>298$^d$</td>
<td>298$^d$</td>
<td>42.6 (55.6)$^d$</td>
</tr>
</tbody>
</table>

$^a$ Reaction conditions: a Schlenk bomb was charged with 1.0 mg 4.1 and 100 eq. of borane, ~0.6 mL of a deuterated solvent, and 1.5 atm$^{10\text{atm}}$ of CO$_2$. The internal standard, hexamethylbenzene was added to the reaction mixture upon completion. $^b$ TON is based on the number of C–H bonds formed in the reduced products per molecule of the catalyst, determined by $^1$H NMR integration against the internal standard. $^c$ The number in parentheses is the TOF at the fast catalysis stage of the reaction. $d$ Control experiment (i.e., same conditions except for the absence of the catalyst) for entry 5 showed 4.5% conversion of BH$_3$·SMe$_2$ to (CH$_3$OBO)$_3$, while all other entries have no background reactions.

Figure 4.5 TON vs time plot for the formation of (CH$_3$OBO)$_3$ catalyzed by 4.1. A CDCl$_3$ solution of 4.1 and 100 eq. of BH$_3$·SMe$_2$ was exposed to 1.5 atm of CO$_2$ at 25 °C.

Next, we tested the catalytic activity of 4.1. When a CDCl$_3$ solution of 4.1 and 100 eq. of 9-BBN was exposed to 1.5 atm of CO$_2$ at 25 °C, CH$_2$(OBR)$_2$ and CH$_3$OBpin were produced with an overall TON of 61 within 19 h (Table 4.1, entry 1); the reaction is much slower than that catalyzed by 3.1. When the same reaction was carried out at 70 °C, however, the reaction rate is comparable to that catalyzed by 3.1 at 70 °C, i.e., the reaction reached 66 TON within 2 h (Table 4.1, entry 2). Compared to 3.1, 4.1 showed a higher activity when HBpin was used as the reductant, i.e., the reaction catalyzed by 4.1 gave CH$_3$OBpin as the dominant CO$_2$ reduction product with a TON of 75 in 46 h at 90 °C (Table 4.1, entry 3). In contrast, when HBcat was
used as the reductant, catalyst 4.1 showed lower activity than 3.1 (Table 4.1, entry 4). We speculate that the difference in catalytic activity between 3.1 and 4.1 may originate partly from the preferred interactions between the catalyst and borane: the larger system in 3.1 interacts with the aromatic backbone of HBcat more strongly, while the longer aliphatic propyl chain and smaller system in 4.1 favor the aliphatic backbone of HBpin. Interestingly, 4.1 showed much higher catalytic activity than 3.1 when BH$_3$·SMe$_2$ was used as the reductant, i.e., complete conversion to (CH$_3$OBO)$_3$ was observed in 7 h at 25 °C with a TON of 298 and average TOF of 42.6 h$^{-1}$ (Table 4.1, entry 5). This reaction also has a short induction period at 25°C (Figure 4.5). A TOF of 56 h$^{-1}$ at the fast catalysis stage was extracted from the plot of TON vs time. Such TOFs make 4.1 one of the best organocatalysts for this transformation.

4.4 Conclusion

In summary, we have demonstrated compound 4.1 not only binds CO$_2$ reversibly via the formal insertion of CO$_2$ into a C–H bond of the C$_5$ ring, but also catalyzes the hydroboration of CO$_2$ to methylborylethers which upon hydrolysis can produce methanol. This air- and moisture-stable catalyst features broad borane scope and its catalytic activities are comparable to the best organocatalysts with heteroatom-based activity.

4.5 Experimental

4.5.1 General procedures

The syntheses of 4.3–4.6, 4.1, and 4.2 were done in air. All manipulations involving boranes were carried out under a dinitrogen atmosphere using a glovebox or Schlenk techniques. Intermediates 4.3–4.5$^{13}$ were prepared using modified literature methods. Compounds 4.1, 4.2 and intermediate 4.6 are new compounds. All other chemicals were purchased from commercial source. All glassware was dried overnight in a 150 °C oven or by flame before use. The J. Young NMR tubes were dried in a 60 °C oven overnight. Catalytic reactions under 1.5 atm of CO$_2$ were conducted in sealed Schlenk bombs. CO$_2$ was purchased from Linde (Grade 4.0) and used as received. THF was dried over Na/benzophenone and distilled under dinitrogen before use. CH$_2$Cl$_2$, Et$_2$O, toluene, pentane, and hexanes were dried by passing through a Pure Solv InnovativeTechnology Grubbs-type solvent purification system and degassed through three freeze–pump–thaw cycles. DMSO-d$_6$ was dried with CaH$_2$ at 60 °C overnight, vacuum distilled
and stored over molecular sieves. CDCl₃ was dried with P₂O₅ at 60 °C overnight, distilled under dinitrogen and stored over molecular sieves. C₆D₆ was degassed through three freeze–pump–thaw cycles and dried over molecular sieves. ¹H, ¹¹B, and ¹³C NMR data were collected on a Varian 400 MHz, Bruker Avance III 400 MHz, Agilent DD2–500 MHz or Agilent DD2–600 MHz NMR spectrometer. The chemical shifts were reported in ppm and referenced with the residual solvent signals. gHSQC, gCOSY and gHMBC NMR experiments were performed to assign signals properly. Elemental analyses were performed by ANALEST in our department at the University of Toronto. The commercial HBcat was vacuum-distilled at 50 °C. The purity of the redistilled HBcat was determined by ¹H NMR with hexamethylbenzene as the internal standard to be ranging from 65% to 70% between batches. The measured purity of HBcat is specified in each individual experiment below.

4.5.2 Synthesis of 4.3

2,3-Cyclopentenopyridine (5.0 g, 0.037 mol), acetic acid (25 mL, 0.437 mol), and 30% H₂O₂ (4.15 mL, 0.0411 mol) were combined in a round bottom flask and heated at 75 °C for 18 h, during which 30% H₂O₂ (3.35 mL, 0.0332 mol) was added at 3 h. The solution gradually changed color from pale brown to pale yellow. Volatiles were removed on a rotary evaporator. The remaining dark brown liquid was transferred into a K₂CO₃ aqueous solution (12 g of K₂CO₃ in 90 mL of H₂O), which was then extracted with CH₂Cl₂ (400 mL x 3). The combined CH₂Cl₂ layer was washed with brine and dried over MgSO₄. The removal of CH₂Cl₂ gave 4.3 as a white solid (4.6 g, 82% yield). ¹H NMR (CDCl₃, 500 MHz, Figure 4.6) δ: 7.83 (dd, J = 6.3, 1.0 Hz, 1H, H1), 6.94 (dd, J = 7.6, 1.3 Hz, 1H, H3), 6.89 (dd, J = 7.6, 6.4 Hz, 1H, H2), 2.95 (t, J = 7.7 Hz, 2H, H6), 2.83 (t, J = 7.7 Hz, 2H, H4), 2.0 (quintet, J = 8.75 Hz, 2H, H5). ¹³C NMR (CDCl₃, 125 MHz, Figure 4.7) δ: 152.73(C7), 141.99(C8), 136.9(C1), 123.62(C2), 122.38(C3), 31.29(C4), 29.23(C6), 21.72(C5).
Figure 4.6 $^1$H NMR spectrum of 4.3 in CDCl$_3$

Figure 4.7 $^{13}$C NMR spectrum of 4.3 in CDCl$_3$
4.5.3 Synthesis of 4.4

4.3 (4.6 g, 0.034 mol), H₂O (0.3 mL, 5.4 mmol), and acetic anhydride (34 mL, 0.36 mol) were mixed in 100 mL round bottom flask. The pink solution was stirred at r. t. for 30 min and then heated at 70 °C for 30 min. The colour of the solution gradually turned to dark purple. The solution was then heated at 100 °C for 2.5 h. Volatiles were removed on a rotary evaporator. The remaining black oil was added to a K₂CO₃ aqueous solution (10 g of K₂CO₃ in 70 mL of H₂O), which was then extracted with CH₂Cl₂ (500 mL x 3). The combined CH₂Cl₂ layer was washed with brine and dried over MgSO₄. The removal of CH₂Cl₂ gave 4.4 as a brown oil (80.4% yield).

¹H NMR (CDCl₃, 500 MHz, Figure 4.8) δ: 8.51 (d, J = 4.2 Hz, 1H, H1), 7.60 (dd, J = 7.7, 0.6 Hz, 1H, H3), 7.19 (dd, J = 7.7, 4.9 Hz, 1H, H2), 6.13 (dd, J = 7.5, 5.0 Hz, 1H, H6), 3.07 (m, 1H, H4), 2.89 (m, 1H, H4'), 2.65 (m, 1H, H5), 2.12 (s, 3H, H10), 2.05 (m, 1H, H5'). ¹³C NMR (CDCl₃, 125 MHz, Figure 4.9) δ: 170.88(C9), 160.53(C7), 148.95(C1), 137.46(C8), 133.17(C3), 123.41(C2), 77.32(C6), 30.85(C5), 27.87(C4), 21.31(C10).

Figure 4.8 ¹H NMR spectrum of 4.4 in CDCl₃
4.4 (7.05 g, 0.0398 mol) and NaOH (2.15 g, 0.0538 mol) were mixed with 19.4 mL of H₂O in a 50 mL round bottom flask. The solution was stirred at r. t. for 30 min and then heated at 100 °C for 15 min. The dark solution was cooled down and added to a K₂CO₃ aqueous solution (20 g of K₂CO₃ in 300 mL of H₂O), which was then extracted with CH₂Cl₂ (830 mL x 3). The combined CH₂Cl₂ layer was washed with brine and dried over MgSO₄. The removal of CH₂Cl₂ on a rotary evaporator gave the crude product as a brown solid. Recrystallization from cyclohexane gave pure 4.5 as a pale-yellow solid (4.61 g, 86.3% yield).

1H NMR (CDCl₃, 500 MHz, Figure 4.10) δ: 8.42 (d, J = 4.8 Hz, 1H, H1), 7.58 (dd, J = 7.6, 1.3 Hz, 1H, H3), 7.15 (dd, J = 7.6, 4.9 Hz, 1H, H2), 5.26 (dd, J = 7.4, 6.1 Hz, 1H, H6), 4.98 (s, 1H, OH), 3.06 (ddd, J = 16.2, 8.9, 4.1 Hz, 1H, H4), 2.83 (m, 1H, H4'), 2.56 (m, 1H, H5), 2.07 (dddd, J = 13.3, 8.9, 7.2, 6.1 Hz, 1H, H5').

13C NMR (CDCl₃, 125 MHz, Figure 4.11) δ: 164.99(C7), 147.78(C1), 136.72(C3), 122.90(C2), 74.42(C6), 32.95(C5), 27.65(C4).
Figure 4.10 $^1$H NMR spectrum of 4.5 in CDCl$_3$

Figure 4.11 $^{13}$C NMR spectrum of 4.5 in CDCl$_3$
4.5.5 Synthesis of 4.6

4.5 (0.56 g, 4.1 mmol) and 1-iodopropane (3 mL, 0.0274 mol) were mixed in a 25 mL round bottom flask, and heated at 70°C for 18 hours. When the reaction was complete, the colorless liquid phase turned yellow, which was decanted. The residual black-brown solid in the flask was ground and washed with 20 mL of cyclohexane. The solid was then dissolved in 300 mL of CH₂Cl₂. The resulting solution was dried over MgSO₄. The removal of CH₂Cl₂ gave 4.6 as a brown solid (1.13 g, 83.9% yield). ¹H NMR (CD₃CN, 500 MHz, Figure 4.12) δ: 8.60 (dd, J = 6.1, 0.6 Hz, 1H, H₄), 8.31 (dd, J = 7.8, 1.0 Hz, 1H, H₆), 7.84 (dd, J = 7.6, 6.3 Hz, 1H, H₅), 5.62 (d, J = 4.7 Hz, 1H, H₉), 4.96 (d, J = 6.9Hz, 1H, OH), 4.76 (ddd, J = 13.0, 8.8, 6.7 Hz, 1H, H₃), 4.55 (ddd, J = 13.0, 8.9, 6.8 Hz, 1H, H₃’), 3.26 (ddd, J = 9.0, 5.7Hz, 1H, H₇), 3.01 (ddd, J = 9.0, 5.6 Hz, 1H, H₇’), 2.58 (m, 1H, H₈), 2.19 (m, 1H, H₈’), 2.0 (m, 2H, H₂), 0.99 (t, J = 7.4 Hz, 3H). ¹³C NMR (CD₃CN, 125 MHz, Figure 4.13) δ: 159.55(C₁₀), 146.27(C₁₁), 143.75(C₄), 143.10(C₆), 127.99(C₅), 72.86(C₉), 59.49(C₃), 33.81(C₈), 28.92(C₇), 25.09(C₂), 10.91(C₁).

Anal. calcd for (C₁₁H₁₆NOI): C 43.29, H 5.25, N 4.59; Found: C 43.40, H 5.05, N 4.46.
Figure 4.12 $^1$H NMR spectrum of 4.6 in CD$_3$CN

Figure 4.13 $^{13}$C NMR spectrum of 4.6 in CD$_3$CN
4.5.6 Synthesis of 4.1

4.6 (0.33 g, 1.08 mmol) and 98% H₂SO₄ (0.356 mL, 6.5 mmol) were mixed in a 25 mL round bottom flask and heated at 60 °C for 2 h. The solution was cooled down followed by the addition of 10 mL of water. The solid iodine was removed through vacuum filtration. To the filtrate was added a solution of BaCl₂·2H₂O (1.69 g in 10 mL of H₂O). The white precipitate was filtered off. The resulting pale-brown aqueous filtrate was washed with 80 mL of CH₂Cl₂ and added dropwise to a solution of Na₂CO₃ (2.2 g in 10 mL of H₂O). The colorless transparent Na₂CO₃ solution turned into bright orange suspension immediately. The product was extracted with CH₂Cl₂ (200 mL x 3). The CH₂Cl₂ layer was dried over MgSO₄. The removal of CH₂Cl₂ gave pure 4.1 as an orange oil (0.17 g, 94.3% yield). ¹H NMR (CDCl₃, 500 MHz, Figure 4.14) δ: 8.01 (d, J = 7.4 Hz, 1H, H6), 7.43 (d, J = 6.1 Hz, 1H, H4), 7.39 (dd, J = 4.3,4.3 Hz, 1H, H8), 6.62 (dd, J = 7.4, 6.1 Hz, 1H, H5), 6.54 (dd, J = 4.3, 1.5Hz, 1H, H7), 6.18 (m, 1H, H9), 4.33 (t, J = 7.4 Hz, 2H, H3), 2.11 (qt, J = 7.4, 5.5Hz, 2H, H2), 1.02 (t, J = 7.4 Hz, 3H, H1). ¹³C NMR (CDCl₃, 125 MHz, Figure 4.15) δ: 133.59(C10), 130.4(C11), 129.24(C8), 129.13(C6), 128.97(C4), 105.29(C5), 99.58(C7), 88.54(C9), 57.77(C3), 21.90(C2), 11.58(C1). ESI-MS: 159.83 [M+1].
Figure 4.14 $^1$H NMR spectrum of 4.1 in CDCl$_3$

Figure 4.15 $^{13}$C NMR spectrum of 4.1 in CDCl$_3$
4.5.7 Synthesis of 4.2

A solution of 4.1 (11.6 mg in 0.1 mL of Et₂O) was stirred under 10 atm of CO₂ at 22.6 °C in a Parr high pressure reactor for 15 h. Unreacted 2 was washed away with 5 mL of Et₂O, yielding 4.2 as a yellow solid (11.0 mg, 74% yield). X-ray quality crystals of 4.2 were grown via slow evaporation of an Et₂O solution of 4.2 (Table 4.2). ¹H NMR (DMSO-d₆, 500 MHz) δ: 11.02 (s, 1H, OH), 8.59 (d, J = 7.6 Hz, 1H, H6), 8.08 (d, J = 6.0 Hz, 1H, H4), 7.67 (d, J = 4.1 Hz, 1H, H8), 7.01 (dd, J = 7.6, 6.1 Hz, 1H, H5), 6.29 (d, J = 4.1 Hz, 1H, H9), 4.47 (t, J = 7.2 Hz, 2H, H3), 1.94 (qt, J = 7.4, 7.3 Hz, 2H, H2), 0.89 (t, J = 7.4 Hz, 3H, H1). ¹³C NMR (DMSO-d₆, 125 MHz) δ: 166.37(C12), 137.54(C10), 133.89(C8), 131.55(C4), 130.66(C6), 129.17(C11), 109.69(C5), 102.48(C7), 92.60(C9), 56.64(C3), 22.01(C2), 10.73(C1). Anal. calcd for C₁₂H₁₃NO₂: C 70.93, H 6.40, N 6.89; found: C 70.45, H 6.31, N 6.65. IR(CDCl₃ solution): ν(C=O) 1629 cm⁻¹.

![Diagram of 4.2]

Table 4.2 Selected crystallographic data of 4.2:

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4.5.8 Reaction between 9-BBN and CO$_2$ in the presence of catalyst 4.1 at 25 °C

In a N$_2$-filled glovebox, 9-BBN dimer (76.8 mg, 0.315 mmol) was added into a 50 mL Schlenk bomb containing a solution of 4.1 (1.0 mg, 0.00629 mmol in 0.3 mL of CDCl$_3$). CO$_2$ was introduced using the same protocol as above in Chapter 3. The reaction mixture was stirred at 25 °C for 19 h. The bomb was shipped into a N$_2$-filled glovebox. After releasing CO$_2$ gas from the system, hexamethylbenzene (13.0 mg, 0.0802 mmol) was then added to the reaction mixture. The TON was calculated based on the integration of the product with respect to that of hexamethylbenzene in the $^1$H NMR spectrum (Figure 4.16 and Figure 4.17).

CH$_2$(OBBN)$_2$: $^1$H NMR (CDCl$_3$, 600 MHz) δ: 5.57 (s, CH$_2$(OBBN)$_2$); $^{13}$C NMR (CDCl$_3$, 150 MHz) δ: 86.39 (CH$_2$(OBBN)$_2$).

CH$_3$OBBN: $^1$H NMR (CDCl$_3$, 600 MHz) δ: 3.77 (s, CH$_3$OBBN); $^{13}$C NMR (CDCl$_3$, 150 MHz) δ: 53.73 (CH$_3$OBBN).
Figure 4.16 $^1$H NMR spectrum of the reaction between 9-BBN and CO$_2$ in the presence of catalyst 4.1 at 25 °C. A peak at 2.24 ppm refers to hexamethylbenzene as the internal standard.

Figure 4.17 $^{11}$B NMR spectrum of the reaction between 9-BBN and CO$_2$ in the presence of catalyst 4.1 at 25 °C.
4.5.9 Reaction between 9-BBN and CO$_2$ in the presence of catalyst 4.1 at 70 °C

In a N$_2$-filled glovebox, 9-BBN dimer (76.8 mg, 0.315 mmol) was added into a 50 mL Schlenk bomb containing a solution of 4.1 (1.0 mg, 0.00629 mmol in 0.3 mL of CDCl$_3$). CO$_2$ was introduced using the same protocol as above. The reaction mixture was stirred at 70 °C for 2 h. The bomb was shipped into a N$_2$-filled glovebox. After cooling and releasing CO$_2$ gas from the system, hexamethylbenzene (14.2 mg, 0.00876 mmol) was added to the mixture. The TON was calculated based on the integration of the product with respect to that of hexamethylbenzene in the $^1$H NMR spectrum (Figure 4.18 and Figure 4.19).

![Reaction diagram](image)

**Figure 4.18** $^1$H NMR spectrum of the reaction between 9-BBN and CO$_2$ in the presence of catalyst 4.1 at 70 °C. A peak at 2.25 ppm refers to hexamethylbenzene as the internal standard.
Figure 4.19 $^{11}$B NMR spectrum of the reaction between 9-BBN and CO$_2$ in the presence of catalyst 4.1 at 70 °C.

4.5.10 Reaction between HBcat and CO$_2$ in the presence of catalyst 4.1 at 25 °C

In a N$_2$-filled glovebox, HBcat (107.0 mg, 70.5% purity, 0.629 mmol) was added into a 50 mL Schlenk bomb containing a solution of 4.1 (1.0 mg, 0.00629 mmol in 0.3 mL of CDCl$_3$). CO$_2$ was introduced using the same protocol as above. The reaction mixture was stirred at 25 °C for 19 h. After the release of CO$_2$ gas from the system, hexamethylbenzene (16.3 mg, 0.100 mmol) was added to the mixture. The TON was calculated based on the integration of the product with respect to that of hexamethylbenzene in the $^1$H NMR spectrum (Figure 4.20 and Figure 4.21).

\[
4.1 + 100 \text{ HBcat} \xrightarrow{\text{CO}_2, \text{CDCl}_3, 25 \degree C, 19 \text{ h}} \text{CH}_3\text{OBcat} + \text{catBOBcat}
\]

TON = 97

CH$_3$OBcat: $^1$H NMR (CDCl$_3$, 600 MHz) $\delta$: 3.90 (s, CH$_3$OBcat); $^{13}$C NMR (CDCl$_3$, 150 MHz) $\delta$: 53.67 (CH$_3$OBcat).
Figure 4.20 $^1$H NMR spectrum of the reaction between HBcat and CO$_2$ in the presence of catalyst 4.1 at 25 °C. A peak at 2.24 ppm refers to hexamethylbenzene as the internal standard.

Figure 4.21 $^{11}$B NMR spectrum of the reaction between HBcat and CO$_2$ in the presence of catalyst 4.1 at 25 °C.
4.5.11 Reaction between HBpin and CO$_2$ in the presence of catalyst 4.1 at 90 °C

In a N$_2$-filled glovebox, HBpin (81.1 mg, 0.629 mmol) was added into a 50 mL Schlenk bomb containing a solution of 4.1 (1.0 mg, 0.00629 mmol in 0.3 mL of CDCl$_3$). CO$_2$ was introduced using the same protocol as above. The reaction mixture was stirred at 90 °C for 46 h. After cooling and the release of CO$_2$ gas from the system, hexamethylbenzene (13.8 mg, 0.0852 mmol) was added to the mixture. The TON was calculated based on the integration of the product with respect to that of hexamethylbenzene in the $^1$H NMR spectrum (Figure 4.22 and Figure 4.23).

$$\text{4.1} + 100 \text{HBpin} \xrightarrow{\text{CO}_2, \text{CDCl}_3, 90 \degree \text{C}, 46 \text{h}} \text{HCO}_2\text{Bpin} + \text{CH}_3\text{OBpin} + \text{pinBOBpin}$$

$\text{HCO}_2\text{Bpin}: \text{$^1$H NMR (CDCl}_3, 600 \text{MHz}) \delta: 8.42 (s, HCO}_2\text{Bpin); \text{^{13}$C NMR (CDCl}_3, 150 \text{MHz}) \delta: 158.04 (HCO}_2\text{Bpin).}$

$\text{CH}_3\text{OBpin}: \text{$^1$H NMR (CDCl}_3, 600 \text{MHz}) \delta: 3.59 (s, CH}_3\text{OBpin); \text{^{13}$C NMR (CDCl}_3, 150 \text{MHz}) \delta: 52.71 (CH}_3\text{OBpin).}$

Figure 4.22 $^1$H NMR spectrum of the reaction between HBpin and CO$_2$ in the presence of catalyst 4.1 at 90 °C. A peak at 2.22 ppm refers to hexamethylbenzene as the internal standard.
Figure 4.23 $^{11}$B NMR spectrum of the reaction between HBpin and CO$_2$ in the presence of catalyst 4.1 at 90 °C.

### 4.5.12 Reaction between BH$_3$·SMe$_2$ and CO$_2$ in the presence of catalyst 4.1 at 25 °C

In a N$_2$-filled glovebox, a solution of BH$_3$·SMe$_2$ (2.0 M in THF, 0.31 mL, 0.629 mmol) was added into a 50 mL Schlenk bomb containing a solution of 4.1 (1.0 mg, 0.00629 mmol in 0.4 mL of CDCl$_3$). CO$_2$ was introduced using the same protocol as above. The reaction mixture was stirred at 25 °C for 7 h. After the release of CO$_2$ gas from the system, hexamethylbenzene (17.4 mg, 0.107 mmol) was added to the mixture. The TON was calculated based on the integration of the product with respect to that of hexamethylbenzene in the $^1$H NMR spectrum (Figure 4.24 and Figure 4.25).

$$\text{4.1} + 100 \text{BH}_3\cdot\text{SMe}_2 \xrightarrow{\text{CO}_2, \text{CDCl}_3} \text{(CH}_3\text{OBO)}_3, \text{TON} = 2.98$$

(CH$_3$OBO)$_3$: $^1$H NMR (CDCl$_3$, 600 MHz) δ: 3.27 (s, (CH$_3$OBO)$_3$); $^{13}$C NMR (CDCl$_3$, 150 MHz) δ: 50.57 ((CH$_3$OBO)$_3$).
Figure 4.24 $^1$H NMR spectra of the reaction between BH$_3$·SMe$_2$ and CO$_2$ in the presence of catalyst 4.1 at 25 °C from 1 h (bottom) to 7 h (top).

Figure 4.25 $^{11}$B NMR spectrum of the reaction between BH$_3$·SMe$_2$ and CO$_2$ in the presence of catalyst 4.1 at 25 °C above from 1 h (bottom) to 7 h (top).

4.6 References


13. The Schlenk bomb charged with all other reagents and solvents was immersed in liquid N$_2$ to freeze the solution; the headspace was then evacuated. The entire bomb was then immersed in a −70 °C dry ice-isopropanol bath to keep the solution frozen and cool the headspace. The bomb was then opened to 1 atm of CO$_2$ for 10 minutes to allow the temperature to equilibrate. Subsequently the bomb was sealed and allowed to warm to 25 °C to achieve ~1.5 atm pressure. Safety Warning: if CO$_2$ gas was introduced below -78 °C, dry ice would condense in the reaction vessel and the final pressure becomes time-dependent and can no longer be calculated easily. Using our protocol with a low-melting solvent (i.e., the solvent is not frozen at -70 °C), the final pressure is again time-dependent, because of the dramatically increased solubility of CO$_2$ at -70 °C. In both scenarios prolonged CO$_2$ exposure could cause serious explosions due to uncontrolled high pressures and make the results incomparable to others due to unknown CO$_2$ pressure.
5 Chapter 5
Catalytic hydroboration of CO$_2$ with an indenylammonium compound

5.1 Abstract

We report the synthesis of a zwitterionic indenylammonium compound and its carbon-centred reactivity toward reversible CO$_2$ binding through the formal insertion into a C−H bond as well as catalytic hydroboration of CO$_2$ to methanol derivatives.

5.2 Introduction

The increasing level of CO$_2$ in the atmosphere is the root of many environmental concerns. This overabundance also provides an incentive to utilize CO$_2$ as C$_1$ feedstock to synthesize valuable chemicals.\textsuperscript{1} However, due to the thermodynamic stability of CO$_2$, it remains a challenge to transform CO$_2$ into fuels such as methanol.\textsuperscript{2} Several review articles have summarized past research work on CO$_2$ activation.\textsuperscript{3} Recently, Cummins and coworkers have reported the reaction of the first dimetalloxycarbene with CO$_2$, which gives an oxalate complex.\textsuperscript{4a} Weicker and Stephan have employed silyltriflates to react with CO$_2$ in the presence of tetramethylpiperidine or phosphines.\textsuperscript{4b} Formal insertion of CO$_2$ into the C−Si bonds of a zinc compound or C−B bond of a boronic ester ligand have also been described.\textsuperscript{4c,4d} Dielmann and co-workers have demonstrated the reversible binding of CO$_2$ under mild conditions with novel electron-rich phosphines.\textsuperscript{4e} In addition to the above mentioned stoichiometric reactivity of CO$_2$, catalytic conversions of CO$_2$ to carbonate, carboxylate, methylamine, methanol and other derivatives have also been widely explored, using both metal-containing and metal-free catalysts.\textsuperscript{5} One of the commonly used reductants in catalytic CO$_2$ reduction is borane.\textsuperscript{6,7} Ong and coworkers have investigated the carbodiicarbene-mediated catalytic N-methylation of amines with CO$_2$ as C$_1$ source and boranes as hydride source.\textsuperscript{8} Mandal and coworkers have reported the abnormal NHC-based catalysts for the reduction of CO$_2$ into methoxyborane with the impressive TONs under ambient conditions.\textsuperscript{9} Although NHCs have been known for their catalytic activity toward hydrosilylation and hydroboration of CO$_2$, in general, examples of carbon-centred catalysts for CO$_2$ binding and conversion are still scarce with limited structural diversity.
Recently, our group has reported reversible insertion of CO$_2$ into the C-H bond of compounds 3.1 and 4.1 (Scheme 5.1),$^{11}$ as well as the catalytic activity of these compounds toward the hydroboration of CO$_2$. The zwitterionic resonance forms of 3.1 and 4.1 play a key role in these processes, which involves the nucleophilic attack of CO$_2$ by the carbanion followed by proton migration. It is conceivable that the overall structures of 3.1 and 4.1 still have contributions from the uncharged resonance forms (Scheme 5.1). To eliminate the possible uncharged resonance form and generalize the CO$_2$ insertion reactivity, we designed a new zwitterionic compound 5.1 (Scheme 5.1), where the positive charge is localized on an exocyclic quaternary nitrogen centre at the 1-position of the indenyl and the negative charge is mostly localized on an endocyclic carbon atom at 3-position. Herein we report the synthesis and reactivity of 5.1 toward CO$_2$.

![Scheme 5.1](image)

Scheme 5.1 Previous charge separation compounds 3.1 and 4.1.

5.3 Results and discussion

The synthesis of compound is 5.1 shown in Scheme 5.2. The reaction between $N,N$-diethylhydroxylamine and $p$-toluenesulfonyl chloride can afford 5.3, which can react with indenyl lithium to yield 5.4.$^{12}$ The amine nitrogen of 5.4 can be methylated with Me$_3$OBF$_4$ to give compound 5.5, which can then be deprotonated with KO'Bu to form compound 5.1. The air-sensitive compound 5.1 can be stored in the $-35^\circ$C freezer under N$_2$, but decomposes slowly to Et$_2$NMe and unidentified species standing at ambient temperature under N$_2$. Compound 5.1 is soluble in THF, CH$_2$Cl$_2$, CHCl$_3$ and DMSO but not in Et$_2$O, hexanes or toluene. In the $^1$H NMR
spectrum of 5.1 in DMSO-d₆, the two protons on C₅ ring resonate as two doublets at 6.49 and 5.75 ppm, respectively.

![Scheme 5.2 Synthesis of compound 5.1.](image)

Gratifyingly, compared to 3.1 and 4.1, which require low temperature/high CO₂ pressure for complete conversion to the corresponding carboxylic acids, 5.1 is much more reactive toward CO₂. When a DMSO-d₆ solution of 5.1 was exposed to 1 atm of CO₂ at ambient temperature, the solution changed colour immediately from dark brown to dark pink, accompanied by the disappearance of the doublet at 5.75 ppm and the appearance of a new singlet at 9.98 ppm in the ¹H NMR spectrum (Figure 5.1). This new ¹H signal along with the new peak at 166.6 ppm in the ¹³C NMR spectrum indicates the formation of a carboxylic acid product 5.2 (Figure 5.2). The IR spectrum of 5.2 has a C=O stretching frequency at 1608 cm⁻¹ (Figure 5.3), similar to those of the CO₂ insertion products of 3.1 (1602 cm⁻¹) and 4.1 (1629 cm⁻¹).
Figure 5.1 $^1$H NMR spectrum of 5.2 in DMSO-$d_6$. The peak at 9.98 ppm in the $^1$H NMR spectrum corresponds to a carboxylic acid. Note, the peak at 5.75 ppm refers to CH$_2$Cl$_2$.

Figure 5.2 $^{13}$C NMR spectrum of 5.2 in DMSO-$d_6$. The $^{13}$C NMR spectrum confirms the formation of a carboxylic acid species with a new peak a 166.63 ppm.
X-ray quality crystals of 5.2 were obtained by slow diffusion of CO₂ into a CH₂Cl₂ solution of 5.1, which allows for unambiguous structural determination by X-ray crystallography (Figure 5.4). The sum of the bond angles around C2 is 359.9(3), consistent with \(sp^2\) hybridization. The C3–C4 bond length is 1.369(4) Å, while other C–C bond lengths of the five-membered ring are in the range of 1.425(4)–1.440(4) Å. This C–C bond length pattern around the five-membered ring is consistent with the resonance structure of 5.2 drawn in Figure 5.4.

Compared to 5.1, compound 5.2 is air-stable and thermally stable in both the solid state and in solution at ambient temperature. The reversibility of the CO₂ insertion was also tested. When a DMSO-d₆ solution of 5.2 was placed under vacuum at ambient temperature for 10 h, decarboxylation occurred to give a mixture of 5.1 and 5.2 in a 2.5:1 molar ratio along with a small amount of the decomposition products of 5.1 according to the \(^1\)H NMR spectrum. Upon a refill of CO₂, 5.1 in the mixture can be converted back to 5.2, while the decomposition products remain unchanged. The reaction of 5.1 with CO₂ likely involves the nucleophilic attack of CO₂ by the carbanion at the 3-position of the indenyl ring followed by proton transfer to the newly formed carboxylate group.
Scheme 5.3 Reversible binding of CO\(_2\) (left) and the molecular structure of 5.2 (right). Thermal ellipsoids are shown at 50% probability. All C–H protons are omitted for clarity. Selected bond lengths [Å] and angles [°]: O1–C1 1.248(4), O2–C1 1.331(4), C1–C2 1.420(4), C2–C3 1.425(4), C3–C4 1.369(4), C4–C5 1.440(4), C2–C10 1.435(4), C5–C10 1.437(4), N1–C4 1.486(4), O1–C1–O2 120.5(3), O1–C1–C2 124.4(3), O2–C1–C2 115.1(3), C1–C2–C3 126.1(3), C1–C2–C10 127.2(3), C3–C2–C10 106.6(3).

As compound 5.1 showed reactivity towards CO\(_2\), its performance for the catalytic hydroboration of CO\(_2\) was also investigated. Our preliminary results revealed that 5.1 could catalyze the hydroboration of CO\(_2\) using 9-BBN and BH\(_3\)·SMe\(_2\) as the reductants. For example, when a CDCl\(_3\) solution of 5.1 (1 eq.) and 100 eq. of 9-BBN was combined at ambient temperature under 1 atm of CO\(_2\), the reaction produced CH\(_3\)OBBN and CH\(_2\)(OBBN)\(_2\) with a total TON of 71.5 over 10 h according to the \(^1\)H NMR spectroscopic data (Table 5.1, entry 1). If the temperature was raised to 70 °C, the reaction produced the product with a total TON of 55.4 over 10 h (entry 2). The decrease in TON could be attributed to the thermal instability of 4. Similarly, when BH\(_3\)·SMe\(_2\) was used, higher temperature resulted in lower TON (entries 3 and 4). When higher CO\(_2\) pressures were used, much higher TONs could be achieved at ambient temperature (entries 5–7). These catalytic results were comparable to those of 3.1 and 4.1 with 9-BBN and BH\(_3\)·SMe\(_2\) as hydride source.\(^{11}\)
Table 5.1 Hydroboration of CO$_2$ by 9-BBN and BH$_3$·SMe$_2$ with 5.1 as catalyst$^a$

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<th>TON$^b$ from CH$_3$OBR$_2$</th>
<th>TON$^b$ from (CH$_3$OBO)$_3$</th>
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$^a$ Reaction conditions: a Schlenk bomb was charged with 1.0 mg 5.1 (1 eq.) and 100 eq. of borane, ~0.6 mL of CDCl$_3$, and 1 atm of CO$_2$. The reactions with greater than 1 atm of CO$_2$ were carried out in stainless steel high-pressure reactors with glass liners. The internal standard, hexamethylbenzene, was added to the reaction mixture after the replacement of CO$_2$ with N$_2$ atmosphere at the specified time. $^b$ TON is based on the number of C–H bonds formed in the reduced products per molecule of the catalyst, determined by $^1$H NMR integration against the internal standard.

5.4 Conclusion

In summary, we have demonstrated that zwitterionic compound 5.1 can reversibly bind CO$_2$ through the formal insertion into a C–H bond at the 3-position of the indenyl group at ambient temperature and pressure. The lack of uncharged resonance structure of 5.1 might have contributed to the facile CO$_2$ binding under mild conditions. The catalytic activity of 5.1 toward hydroboration of CO$_2$ is comparable to that of 3.1 and 4.1 when 9-BBN and BH$_3$·SMe$_2$ are used as reductants.

5.5 Experimental

5.5.1 General procedures

The synthesis of 5.3 was done in air. All manipulations involving boranes were carried out under a dinitrogen atmosphere using a glovebox or Schlenk techniques. Intermediates 5.3-5.4$^{12}$ and indenyllithium$^{13}$ were prepared via modified literature methods. Compounds 5.1, 5.2 and intermediates 5.4-5.5 are new compounds. All other chemicals were from commercial sources. All glassware was dried overnight in a 150 °C oven or by flame before use. The J. Young NMR tubes were dried in a 60 °C oven overnight. Catalytic reactions under 1 atm of CO$_2$ were conducted in sealed Schlenk bombs. Catalytic reactions under 2.5, 5 or 10 atm of CO$_2$ were
carried out in a high-pressure reactor. CO₂ was purchased from Linde (Grade 4.0) and used as received. THF was dried over Na/benzophenone and distilled under dinitrogen before use. CH₂Cl₂, Et₂O, toluene, pentane, and hexanes were dried by passing through a Pure Solv InnovativeTechnology Grubbs-type solvent purification system and degassed through three freeze–pump–thaw cycles. DMSO-d₆ was dried with CaH₂ at 60 °C overnight, vacuum distilled and stored over molecular sieves. CDCl₃ was dried with P₂O₅ at 60 °C overnight, distilled under dinitrogen and stored over molecular sieves. ¹H, ¹¹B, ¹⁹F and ¹³C NMR data were collected on a Varian 300 MHz, Bruker Avance III 400 MHz, Agilent DD2–500 MHz or Agilent DD2–600 MHz NMR spectrometer. The chemical shifts were reported in ppm and referenced according to residual solvent signals. gHSQC, gCOSY and gHMBC NMR experiments were performed to assign the signals. Elemental analyses were performed by ANALEST in the chemistry department at the University of Toronto.

5.5.2 Synthesis of 5.3

N,N-Diethylhydroxylamine (0.46 mL, 4.50 mmol) and triethylamine (0.8 mL, 5.78 mmol) were combined with 25 mL of CH₂Cl₂ in a round bottom flask and kept at -18 °C. p-Toluenesulfonyl chloride (0.75 g, 3.93 mmol) was dissolved in 25 mL of CH₂Cl₂ and added slowly to the mixture over 1 h. The solution was left to stir for another 2 h after the addition of p-toluenesulfonyl chloride was complete. The mixture was washed with 50 mL of ice-water. Volatiles in CH₂Cl₂ layer were removed on a rotary evaporator. The remaining colourless oil was combined with 15 mL of H₂O and this mixture was sonicated for 10 min. White solids crashed out during this process. These white solids were washed with H₂O (20 mL x 3) and then dissolved in 50 mL of Et₂O. The Et₂O layer was dried over Na₂SO₄. The removal of Et₂O gave 5.3 as a white solid (0.64 g, 67% yield). ¹H NMR (CDCl₃, 400 MHz, Figure 5.4) δ: 7.86 (d, J = 8.3 Hz, 2H, H4), 7.32 (d, J = 8.0 Hz, 2H, H3), 2.92 (q, J = 7.2 Hz, 4H, H6), 2.45 (s, 3H, H1), 0.89 (t, J = 7.2 Hz, 6H, H7). ¹³C NMR (CDCl₃, 100 MHz, Figure 5.5) δ: 144.93(C2), 132.96(C5), 129.47(C4), 129.44(C3), 52.27(C6), 21.85(C1), 10.86(C7). Anal. calcd for (C₁₁H₁₇NO₃S): C 54.30, H 7.04, N 5.76; Found: C 54.30, H 6.93, N 5.57.
Indene (0.507 g, 4.37 mmol) was mixed with 8 mL of Et₂O and cooled to -35 °C in a glovebox. nBuLi (3.2 mL, 1.6 M in hexane, 5.12 mmol) was mixed with 3 mL of Et₂O and cooled to -35 °C in the glovebox. The indene solution was transferred to a 100 mL round bottom flask. The nBuLi solution was slowly added to it dropwise. When the addition was complete, the mixture was
stirred at r. t. for 2 h. Volatiles were removed under reduced vacuum. Then 12 mL of hexane was added to the remaining yellow solids and the suspension was stirred at r. t. over 1 h. The suspension was filtered and light yellow solid indenyllithium was collected on a frit (0.519 g, 97% yield).

5.5.4 Synthesis of 5.4

5.3 (0.281 g, 1.16 mmol) was mixed with 5 mL of THF and cooled to -35 °C in a glovebox. Indenyllithium (0.141 g, 1.16 mmol) was mixed with 5 mL of THF and cooled to -35°C in the glovebox. The solution of indenyllithium was slowly added to the solution of 5.3 dropwise over 30 min. When the addition was complete, the mixture was stirred at r. t. for 9.5 h. Volatiles were removed under reduced vacuum. Then 10 mL of hexanes was added to the remaining dark brown solids and the suspension was stirred at r. t. over 2 h. The suspension was filtered and the isolated brown solids were discarded. The removal of hexanes gave the product 5.4 as a brown oil (0.123 g, 57% yield). $^1$H NMR (CDCl$_3$, 400 MHz, Figure 5.6) δ: 7.48 (d, $J = 7.6$ Hz, 1H, H9), 7.44 (d, $J = 7.4$ Hz, 1H, H7), 7.31 (t, $J = 7.5$ Hz, 2H, H8), 7.22 (t, $J = 7.4$ Hz, 1H, H6), 5.49 (t, $J = 2.5$ Hz, 1H, H4), 3.36 (d, $J = 2.5$ Hz, 2H, H5), 3.25 (q, $J = 7.1$ Hz, 4H, H2), 1.17 (t, $J = 7.1$ Hz, 6H, H1). $^{13}$C NMR (CDCl$_3$, 100 MHz, Figure 5.7) δ: 150.94(C3), 144.74(C10), 142.62(C11), 125.82(C8), 124.59(C6), 124.07(C7), 119.98(C9), 109.14(C4), 44.92(C2), 35.76(C5), 12.17(C1). ESI-MS: 188.16 [M+1]
5.5.5 Synthesis of 5.5

5.4 (0.248 g, 1.33 mmol) and trimethyloxonium tetrafluoroborate (0.186 g, 1.26 mmol) were mixed with 15 mL of CH$_2$Cl$_2$ and stirred at r. t. for 48 h. Then the solution was filtered to remove
unreacted Me₃OBF₄. Volatiles were removed under reduced vacuum. Then 15 mL of Et₂O was added to the remaining yellow solids and the suspension was stirred at r. t. over 2 h. The suspension was filtered and yellow solids were collected on a frit. The yellow solids were further washed with THF (5 mL x 2) on the frit. THF was removed through vacuum filtration to give pure 5.5 as yellow solid (0.254 g, 70% yield). ¹H NMR (CDCl₃, 500 MHz, Figure 5.8) δ: 7.63 (d, J = 7.7 Hz, 1H, H10), 7.59 (d, J = 7.3 Hz, 1H, H7), 7.46 (t, J = 7.1 Hz, 1H, H8), 7.41 (t, J = 7.0 Hz, 1H, H9), 6.94 (t, J = 2.1 Hz, 1H, H5), 4.21 (dq, J = 14.4, 7.3 Hz, 2H, H2), 4.05 (dq, J = 14.1, 7.1 Hz, 2H, H2’), 3.63 (d, J = 1.7Hz, 2H, H6), 3.54 (s, 3H, H1), 1.24 (t, J = 7.2 Hz, 6H, H3). ¹³C NMR (CDCl₃, 125 MHz, Figure 5.9) δ: 144.05(C11), 141.72(C4), 134.10(C12), 131.78(C5), 127.86(C9), 127.66(C8), 125.80(C7), 120.34(C10), 61.09(C2), 47.50(C1), 36.47(C6), 8.89(C3). The ¹¹B NMR spectrum showed a broad signal at -0.9 ppm. The ¹⁹F NMR spectrum showed a singlet at -151.85 ppm. Anal. calcd for (C₁₄H₂₀NBF₄)·0.045(CH₂Cl₂): C 57.37, H 6.83, N 4.78; Found: C 57.53, H 6.80, N 4.60.
Figure 5.8 $^1$H NMR spectrum of 5.5 in CDCl$_3$

Figure 5.9 $^{13}$C NMR spectrum of 5.5 in CDCl$_3$
5.5.6 Synthesis of 5.1

5.5 (0.0795 g, 0.275 mmol) and KO\textsuperscript{t}Bu (0.0308 g, 0.275 mmol) were mixed with 10 mL of THF in a glovebox. The solution was stirred at -35 °C over 10 h. The suspension was filtered and the volatiles were removed under reduced vacuum. To the remaining grey solids was added a 10 mL of pentane. The pentane suspension was stirred at -35 °C over 1 h. The suspension was filtered and grey solids were collected on a frit. The grey solids were further dissolved in 5 mL of CH\textsubscript{2}Cl\textsubscript{2} and this CH\textsubscript{2}Cl\textsubscript{2} solution was filtered. The removal of CH\textsubscript{2}Cl\textsubscript{2} gave pure 5.1 as a grey solid (0.0529 g, 96% yield). \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 500 MHz, Figure 5.10) δ: 7.63 (d, J = 7.7 Hz, 1H, H7), 7.30 (d, J = 8.1 Hz, 1H, H10), 6.80 (ddd, J = 8.1, 6.6, 1.2 Hz, 1H, H9), 6.76 (ddd, J = 7.7, 6.6, 1.2 Hz, 1H, H8), 6.64 (d, J = 4.2 Hz, 1H, H5), 6.18 (dd, J = 4.2, 0.8 Hz, 1H, H6), 4.17 (dq, J = 12.7, 7.3 Hz, 2H, H2), 3.65 (dq, J = 12.5, 7.0 Hz, 2H, H2’), 3.37 (s, 3H, H1), 1.17 (t, J = 7.1 Hz, 6H, H3). \textsuperscript{1}H NMR (DMSO-d\textsubscript{6}, 400 MHz, Figure 5.11) δ: 7.31 (d, J = 7.8 Hz, 1H, H7), 7.21 (d, J = 7.1 Hz, 1H, H10), 6.49 (d, J = 4.3 Hz, 1H, H5), 6.46 (m, 2H, H8, H9), 5.75 (d, J = 4.1 Hz, 1H, H6), 4.02 (dq, J = 14.3, 7.2 Hz, 2H, H2), 3.68 (dq, J = 14.1, 7.1 Hz, 2H, H2’), 3.32 (s, 3H, H1), 0.96 (t, J = 7.0 Hz, 6H, H3). \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 125 MHz, Figure 5.12) δ: 130.33(C12), 120.96(C7), 117.90(C11), 115.03(C9), 114.29(C10), 113.77(C8), 111.38(C5), 106.06(C4), 92.68(C6), 61.73(C2), 48.38(C1), 9.05(C3). Anal. calcd for (C\textsubscript{14}H\textsubscript{19}N)·0.037(n-pentane): C 82.50, H 9.33, N 6.87; Found: C 82.60, H 9.41, N 6.89.

![Diagram of 5.1]
Figure 5.10 $^1$H NMR spectrum of 5.1 in CDCl$_3$

Figure 5.11 $^1$H NMR spectrum of 5.1 in DMSO-d$_6$. Note, the peaks from 3.38 and 1.09 ppm are from Et$_2$O.
5.5.7 Synthesis of 5.2

A solution of 5.1 (20.5 mg in 2 mL of CH$_2$Cl$_2$) was stirred under 10 atm of CO$_2$ at 20.5 °C in a Parr high pressure reactor for 15 h. The mixture was filtered through a frit, yielding 5.2 as a pink solid (20.3 mg, 81% yield). X-ray quality crystals of 5.2 were grown via slow diffusion of CO$_2$ into a CH$_2$Cl$_2$ solution of 5.1 at -10 °C (Figure 5.13 and Table 5.2). $^1$H NMR (DMSO-d$_6$, 500 MHz) $\delta$: 9.98 (s, 1H, OH), 8.02 (d, J = 7.9 Hz, 1H, H), 7.46 (d, J = 8.1 Hz, 1H, H), 7.04 (s, 1H, H5), 6.79 (t, J = 7.4 Hz, 1H, H), 6.72 (t, J = 7.4 Hz, 1H, H), 4.07 (m, 2H, H2), 3.72 (m, 2H, H2'), 3.35 (s, 3H, H1), 0.96 (t, J = 7.0 Hz, 6H, H3). $^{13}$C NMR (DMSO-d$_6$, 125 MHz) $\delta$: 166.37(C13), 131.86(C12), 121.85(C11), 120.24(C7), 118.64(C5), 117.15(C8), 116.30(C9), 115.96(C10), 112.84(C4), 95.57(C6), 60.55(C2), 47.16(C1), 8.34(C3). IR(nujol): v(C=O) 1608 cm$^{-1}$. Anal. calcd for (C$_{15}$H$_{19}$NO$_2$)$\cdot$0.37(CH$_2$Cl$_2$): C 65.11, H 6.87, N 5.06; Found: C 65.12, H 6.94, N 4.71.
Figure 5.13 The hydrogen bonded pair in the crystal lattice of 5.2. The intermolecular O1–O2 distance is ~2.6 Å.

Table 5.2 Selected crystallographic data of 5.2:

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5.5.8 Reaction between 9-BBN and CO_2 in the presence of catalyst 5.1 at 25 °C

In a N_2-filled glovebox, 9-BBN dimer (60.7 mg, 0.249 mmol) was added into a 50 mL Schlenk bomb containing a solution of 5.1 (1.0 mg, 0.00498 mmol in 0.6 mL of CDCl_3). The bomb was immersed in liquid N_2 to freeze the solution; the headspace was then evacuated. The entire bomb
was then immersed in a r. t. water bath for 3 minutes to let the temperature equilibrate. The bomb was then opened to 1 atm of CO$_2$ and quickly sealed. The reaction mixture was stirred 25 °C for 10 h. It gradually changed from a pink solution to a light yellow suspension with white precipitates. The bomb was shipped into a N$_2$-filled glovebox. After the release of CO$_2$ gas from the system, hexamethylbenzene (10.4 mg, 0.0642 mmol) was added to the mixture. The TON was calculated based on the integration of the products with respect to that of hexamethylbenzene in the $^1$H NMR spectrum (Figure 5.14 and Figure 5.15). CH$_2$(OBBN)$_2$: $^1$H NMR (CDCl$_3$, 400 MHz) δ: 5.56 (s, CH$_2$(OBBN)$_2$). CH$_3$OBBN: $^1$H NMR (CDCl$_3$, 400 MHz) δ: 3.77 (s, CH$_3$OBBN).

Figure 5.14 $^1$H NMR spectrum of the reaction between 9-BBN and CO$_2$ in the presence of catalyst 5.1 at 25 °C. A peak at 2.24 ppm refers to hexamethylbenzene as the internal standard.
5.5.9 Reaction between 9-BBN and CO₂ in the presence of catalyst 5.1 at 70 °C

In a N₂-filled glovebox, 9-BBN dimer (60.7 mg, 0.249 mmol) was added into a 50 mL Schlenk bomb containing a solution of 5.1 (1.0 mg, 0.00498 mmol in 0.6 mL of CDCl₃). CO₂ was introduced using the same protocol as above. The reaction mixture was stirred at 70 °C for 10 h. The bomb was shipped into a N₂-filled glovebox. After cooling and the release of CO₂ gas from the system, hexamethylbenzene (10.5 mg, 0.0648 mmol) was added to the mixture. The TON was calculated based on the integration of the products with respect to that of hexamethylbenzene in the ¹H NMR spectrum (Figure 5.16 and Figure 5.17).

Figure 5.15 ¹¹B NMR spectrum of the reaction between 9-BBN and CO₂ in the presence of catalyst 5.1 at 25 °C.
Figure 5.16 $^1$H NMR spectrum of the reaction between 9-BBN and CO$_2$ in the presence of catalyst 5.1 at 70 °C. A peak at 2.25 ppm refers to hexamethylbenzene as the internal standard.

Figure 5.17 $^{11}$B NMR spectrum of the reaction between 9-BBN and CO$_2$ in the presence of catalyst 5.1 at 70 °C.
5.5.10 Reaction between BH$_3$·SMe$_2$ and CO$_2$ in the presence of catalyst 5.1 at 25 °C

In a N$_2$-filled glovebox, a solution of BH$_3$·SMe$_2$ (2.0 M in THF, 0.25 mL, 0.5 mmol) was added into a 50 mL Schlenk bomb containing a solution of 5.1 (1.0 mg, 0.00497 mmol in 0.6 mL of CDCl$_3$). CO$_2$ was introduced using the same protocol as above. The reaction mixture was stirred at 25°C for 12 h. After the release of CO$_2$ gas from the system, hexamethylbenzene (13.4 mg, 0.0827 mmol) was added to the mixture. The TON was calculated based on the integration of the product with respect to that of hexamethylbenzene in the $^1$H NMR spectrum (Figure 5.18 and Figure 5.19). (CH$_3$OBO)$_3$: $^1$H NMR (CDCl$_3$, 400 MHz) δ: 3.60 (s, (CH$_3$OBO)$_3$).

$$5.1 + 100\text{BH}_3\cdot\text{SMe}_2 \xrightarrow{\text{CO}_2, \text{CDCl}_3} \text{(CH}_3\text{OBO)}_3 \quad \text{TON} = 109$$

Figure 5.18 $^1$H NMR spectrum of the reaction between BH$_3$·SMe$_2$ and CO$_2$ in the presence of catalyst 5.1 at 25 °C. A peak at 2.15 ppm refers to hexamethylbenzene as the internal standard.
Figure 5.19 $^{11}$B NMR spectrum of the reaction between BH$_3$·SMe$_2$ and CO$_2$ in the presence of catalyst 5.1 at 25 °C.

5.5.11 Reaction between BH$_3$·SMe$_2$ and CO$_2$ in the presence of catalyst 5.1 at 70 °C

In a N$_2$-filled glovebox, a solution of BH$_3$·SMe$_2$ (2.0 M in THF, 0.25 mL, 0.5 mmol) was added into a 50 mL Schlenk bomb containing a solution of 5.1 (1.0 mg, 0.00497 mmol in 0.6 mL of CDCl$_3$). CO$_2$ was introduced using the same protocol as above. The reaction mixture was stirred at 70 °C for 12 h. After cooling and the release of CO$_2$ gas from the system, hexamethylbenzene (9.7 mg, 0.0599 mmol) was added to the mixture. The TON was calculated based on the integration of the product with respect to that of hexamethylbenzene in the $^1$H NMR spectrum (Figure 5.20 and Figure 5.21). (CH$_3$OBO)$_3$: $^1$H NMR (CDCl$_3$, 400 MHz) δ: 3.59 (s, (CH$_3$OBO)$_3$).

$5.1 + 100$BH$_3$·SMe$_2$ $\xrightarrow{CO_2}$ CDCl$_3$ $\xrightarrow{70 \text{ °C, 12 h}}$ (CH$_3$OBO)$_3$ TON = 72.7
Figure 5.20 $^1$H NMR spectrum of the reaction between BH$_3$·SMe$_2$ and CO$_2$ in the presence of catalyst 5.1 at 70 °C. A peak at 2.14 ppm refers to hexamethylbenzene as the internal standard.

Figure 5.21 $^{11}$B NMR spectrum of the reaction between BH$_3$·SMe$_2$ and CO$_2$ in the presence of catalyst 5.1 at 70 °C.
5.5.12 Reaction between BH$_3$·SMe$_2$ and 2.5 atm of CO$_2$ in the presence of catalyst 5.1 at 25 °C

In a N$_2$-filled glovebox, a solution of BH$_3$·SMe$_2$ (2.0 M in THF, 0.25 mL, 0.5 mmol) was added into a high pressure reactor containing a solution of 5.1 (1.0 mg, 0.00497 mmol in 0.6 mL of CDCl$_3$). Then the mixture was stirred under 2.5 atm of CO$_2$ at 25 °C for 10 h. After the release of CO$_2$ gas from the system, hexamethylbenzene (10.3 mg, 0.0636 mmol) was added to the mixture. The TON was calculated based on the integration of the product with respect to that of hexamethylbenzene in the $^1$H NMR spectrum (Figure 5.22 and Figure 5.23). (CH$_3$OBO)$_3$: $^1$H NMR (CDCl$_3$, 300 MHz) δ: 3.62 (s, (CH$_3$OBO)$_3$).

$$5.1 + 100\text{BH}_3\cdot\text{SMe}_2 \xrightarrow{2.5\text{ atm CO}_2} \text{25 °C, 10 h} \xrightarrow{\text{CDCl}_3} \text{(CH}_3\text{OBO)}_3 \quad \text{TON} = 104$$

Figure 5.22 $^1$H NMR spectrum of the reaction between BH$_3$·SMe$_2$ and 2.5 atm of CO$_2$ in the presence of catalyst 5.1 at 25 °C. A peak at 2.17 ppm refers to hexamethylbenzene as the internal standard.
5.5.13 Reaction between BH$_3$·SMe$_2$ and 5 atm of CO$_2$ in the presence of catalyst 5.1 at 25 °C

In a N$_2$-filled glovebox, a solution of BH$_3$·SMe$_2$ (2.0 M in THF, 0.25 mL, 0.5 mmol) was added into a high pressure reactor containing a solution of 5.1 (1.0 mg, 0.00497 mmol in 0.6 mL of CDCl$_3$). Then the mixture was stirred under 5 atm of CO$_2$ at 25 °C for 10 h. After the release of CO$_2$ gas from the system, hexamethylbenzene (11.1 mg, 0.0685 mmol) was added to the mixture. The TON was calculated based on the integration of the product with respect to that of hexamethylbenzene in the $^1$H NMR spectrum (Figure 5.24 and Figure 5.25).

(CH$_3$OBO)$_3$: $^1$H NMR (CDCl$_3$, 300 MHz) δ: 3.62 (s, (CH$_3$OBO)$_3$).

$$\text{5.1} + 100 \text{BH}_3\cdot\text{SMe}_2 \xrightarrow{\text{5 atm CO}_2} \text{CDCl}_3 \xrightarrow{25 \degree\text{C, 10 h}} (\text{CH}_3\text{OBO})_3 \quad \text{TON} = 269$$
Figure 5.24 $^1$H NMR spectrum of the reaction between BH$_3$·SMe$_2$ and 5 atm of CO$_2$ in the presence of catalyst 5.1 at 25 °C. A peak at 2.17 ppm refers to hexamethylbenzene as the internal standard.

Figure 5.25 $^{11}$B NMR spectrum of the reaction between BH$_3$·SMe$_2$ and 5 atm of CO$_2$ in the presence of catalyst 5.1 at 25 °C.
5.5.14 Reaction between BH₃·SMe₂ and 10 atm of CO₂ in the presence of catalyst 5.1 at 25 °C

In a N₂-filled glovebox, a solution of BH₃·SMe₂ (2.0 M in THF, 0.25 mL, 0.5 mmol) was added into a high pressure reactor containing a solution of 5.1 (1.0 mg, 0.00497 mmol in 0.6 mL of CDCl₃). Then the mixture was stirred under 10 atm of CO₂ at 25 °C for 10 h. After the release of CO₂ gas from the system, hexamethylbenzene (12.2 mg, 0.0753 mmol) was added to the mixture. The TON was calculated based on the integration of the product with respect to that of hexamethylbenzene in the ¹H NMR spectrum (Figure 5.26 and Figure 5.27).

(CH₃OBO)₃: ¹H NMR (CDCl₃, 300 MHz) δ: 3.62 (s, (CH₃OBO)₃).

\[
\text{5.1} + 100\text{BH₃·SMe₂ → } 10 \text{ atm CO₂} \begin{array}{c} \text{CDCl₃} \\ 25 \text{ °C, 10 h} \end{array} \begin{array}{c} \text{(CH₃OBO)₃} \\ \text{TON = 281} \end{array}
\]

Figure 5.26 ¹H NMR spectrum of the reaction between BH₃·SMe₂ and 10 atm of CO₂ in the presence of catalyst 5.1 at 25 °C. A peak at 2.17 ppm refers to hexamethylbenzene as the internal standard.
Figure 5.27 $^{11}$B NMR spectrum of the reaction between BH$_3$·SMe$_2$ and 10 atm of CO$_2$ in the presence of catalyst 5.1 at 25 °C.

5.5.15 X-ray crystallography

The X-ray diffraction data were collected using a Bruker Kappa Apex II diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 150 K controlled by an Oxford Cryostream 700 series low-temperature system and processed with the Bruker Apex 2 software package. The structures were solved by direct methods and refined using SHELXL-2016/6. All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were located directly from the difference Fourier map. The disordered methylene chloride solvent molecule was modelled successfully over two orientations. Selected crystallographic data are listed in Table 5.2.

5.6 References


6 Chapter 6
Summary

6.1 Abstract

This thesis reported the synthesis of a tripodal ligand and the reactivity of a series of zwitterionic compounds with CO$_2$. This chapter will give a brief summary for each chapter and potential directions for future work.

6.2 Chapter 2

The original design of the triaryl benzene ligand is based on the fascinating reactions from Holland’s NacNac ligand system to cleave the N-N triple bond. Bringing three Nacac substituents closer to the top of a benzene base could possible promote the cooperation between the three metal centers to facilitate a multiple electron process and cleave the strong N-N triple bond. The experiments demonstrated the plausibility of this idea as the $^1$H NMR spectrum of the Ru complex 2.7 exhibited only one peak for the three side arm alkenyl proton. Even though three side arms could rotate to different sides in the solid state, they stayed on the same side of the central benzene ring in the solution. And this shows that the ligand might enable the cooperation between the metal ions in reactions with small molecules. Unfortunately, as the results showed, the moisture in the glovebox prevented the isolation of any desired tri-iron halide complex. In fact, the X-ray crystal structure of 2.5 evidenced the ligand able to support multi-iron centers to form a cluster. The drawback is the hydroxide groups occupy the possible positions for halides. The elucidation of this structure provides guidance for future routes to the binding or even reduction of the N$_2$ molecule.

Future research should focus on the removal of the moisture in the atmosphere of the glovebox and dry any reagents or solvents used in the reactions. Furthermore, the formation of the potential tri-iron complexes could be temperature sensitive. Future students may consider this factor and carry out the reactions at low temperatures. The addition of PMe$_3$ or other small phosphines may convert the paramagnetic iron complex to diamagnetic species. Therefore, NMR could be used in characterizing the product. The addition of other small molecule building blocks, such as organic azides or thiols, may also help assemble the iron atoms with bridging nitrides or thiolates instead of hydroxyl groups. In addition, some modifications have been made
with the ligand scaffold. The future investigation may also include the other versions of this ligand family (Figure 6.1). 6.1 and 6.4 have a bigger steric hindrance to prevent dimerization. 6.2 may have a different solubility compared to 2.4 and 6.1 to let the complexes crystallize out. The addition of methyl and t-butyl groups in 6.1, 6.2 and 6.4 could make the compounds hydrophobic and avoid the moisture problem. The fluorine version 6.3 can be monitored by $^{19}$F NMR. The sulfur mesityl version 6.5 has sulfur atoms that resemble the sulfur bridges in the FeMo cofactor.

![Figure 6.1 Other available versions of the tripodal ligand family. Two of the three side arms are omitted for clarity.](Image)

### 6.3 Chapter 3–5

Due to the similarity of these three chapters, the discussion for these chapters can be combined here.

In Chapter 3, the $N$-methyl-4,5-diazafluorenide compound 3.1 was synthesized before. In this chapter, its efficiency in the catalytic hydroboration of CO$_2$ was discussed. A possible intermediate 3.2 from the catalytic cycle was also synthesized. Interestingly, compared to 3.1, 3.2 exhibited similar performance in the catalytic reactions when HBcat was used as the hydride source. However, all the trials between 3.2 and CO$_2$ have not been successful, because of the decomposition path to form 3.3 as a side product. In Chapter 4, a new charge-separation compound 4.1 was synthesized and characterized. Compared to 3.1, one of the pyridine rings was removed but the reactivity with CO$_2$ still remained. In Chapter 5, another zwitterionic
species 5.1 was reported and the uncharged resonance structure was totally eliminated. 5.1 could also react with CO₂ reversibly, allowing the insertion of CO₂ to the C-H bond. Both 4.1 and 5.1 can be used as the catalysts for the hydroboration of CO₂ with different performance. The mechanism for the catalytic reactions with 4.1 and 5.1 is still elusive as no possible intermediate was isolated, in contrast with that in Chapter 3. So future students could try to install borane fragment onto the carbanion in the five-member ring of 4.1 or 5.1, and explore the reactivity of borane-adduct with CO₂.

Since the mechanism for the catalytic reactions is not clear yet, future students could attempt to shed light upon this. Possible plans include altering the methyl group and/or adding other boranes to the back bone carbanion. The boranes could be any other one rather than the moisture-sensitive HBcat. Another direction is the methylation or formylation of amines with CO₂ as the C₁ source and boranes as the hydrogen source (Scheme 6.1 and 6.2). In fact, the methylation of amines with 3.1 and 4.1 as the catalyst has already produced some preliminary results. Future work could concentrate on screening the best conditions and testing a broader amine substrate scope. Also, the catalytic hydrosilylation of CO₂ with 3.1, 4.1, and 5.1 as catalyst is worth trying.

\[ \text{CO}_2 + 4\text{HBR}_2 + \text{R}_2\text{NH} \xrightarrow{3\text{.1, 4 mof\%}} \text{R}_2\text{NMe} + \text{R}_2\text{N} \xrightarrow{\text{H}} \]

Scheme 6.1 Methylation or formylation of amine with 3.1 as catalyst.

\[ \text{CO}_2 + 4\text{BH}_3\text{SMe}_2 + \text{PhNHMe} \xrightarrow{4\text{.1, 4 mof\% THF}} \xrightarrow{22^\circ\text{C, 12 h}} \text{PhNMe}_2 + \text{PhN\{CHO\}Me} \]

Scheme 6.2 Methylation or formylation of amine with 4.1 as the catalyst.

As this thesis witnesses the success of compounds with a charge separation feature in the reversible CO₂ binding and catalytic reduction, other candidates also have the potential to be a better catalyst and worth a trial (Figure 6.2). If the indenyl ring is replaced by a Cp ring, the negative charge will be less delocalized and the compounds could be more reactive towards CO₂. The two separate negative rings could react with CO₂ respectively and thus achieve a higher CO₂ storage efficiency. Scheme 6.3 shows the possible routes for the synthesis of these compounds.
Figure 6.2 Other candidates with the charge-separation feature.

Scheme 6.3 Possible routes for the synthesis of other charge separation compounds.

6.4 Final remark

This thesis spans metal-containing system towards N₂ activation to metal-free systems for CO₂ conversion. The consistent theme of the thesis is small molecule activation. The work presented here is still the preliminary exploration into the interesting field. A lot of work remains to be complete and there is a long road to go forward. I hope that this thesis provides an inspiration and directions for the future students.