Transition Metal Complexes of Modified Azaphosphatranes

DISSERTATION

submitted in partial satisfaction of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

in Chemistry

by

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2019
DEDICATION

For my mother, Kor, and my father, Vinai, who sacrificed their lives for me to live out mine.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIST OF FIGURES</td>
<td>vii</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>xv</td>
</tr>
<tr>
<td>LIST OF SCHEMES</td>
<td>xvi</td>
</tr>
<tr>
<td>LIST OF CHARTS</td>
<td>xvii</td>
</tr>
<tr>
<td>ACKNOWLEDGMENTS</td>
<td>xviii</td>
</tr>
<tr>
<td>CURRICULUM VITAE</td>
<td>xix</td>
</tr>
<tr>
<td>ABSTRACT OF THE DISSERTATION</td>
<td>xxv</td>
</tr>
<tr>
<td>INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>CHAPTER 1: The Electronic and Steric Tolman Parameters of Proazaphosphatranes: Synthesis, Characterization, and Measurements</td>
<td>12</td>
</tr>
<tr>
<td>1.1. Motivation and Specific Aims</td>
<td>13</td>
</tr>
<tr>
<td>1.2. Background</td>
<td>13</td>
</tr>
<tr>
<td>1.3. Results and Discussion</td>
<td>15</td>
</tr>
<tr>
<td>1.3.1. Synthesis and Structure of Ni(L^R)(CO)_3 Complexes (1-4)</td>
<td>15</td>
</tr>
<tr>
<td>1.3.2. Synthesis and Structure of Ni(L^{Me})_2(CO)_2 Complex (5)</td>
<td>18</td>
</tr>
<tr>
<td>1.3.3. Tolman Electronic Parameters and Cone Angles of Ni(L^R)(CO)_3 Complexes (1-4)</td>
<td>21</td>
</tr>
<tr>
<td>1.4. Conclusion</td>
<td>23</td>
</tr>
<tr>
<td>1.5. Experimental Details</td>
<td>24</td>
</tr>
<tr>
<td>1.6. References</td>
<td>38</td>
</tr>
<tr>
<td>CHAPTER 2: Expanding the Denticity of Proazaphosphatrane: Ligand Synthesis</td>
<td>41</td>
</tr>
<tr>
<td>2.1. Motivation and Specific Aims</td>
<td>42</td>
</tr>
<tr>
<td>2.2. Background</td>
<td>43</td>
</tr>
<tr>
<td>2.3. Results and Discussion</td>
<td>43</td>
</tr>
<tr>
<td>2.3.1. Synthesis of Tri-Substituted Tris(2-aminoethyl)amines</td>
<td>43</td>
</tr>
<tr>
<td>2.3.2. Synthesis of Protonated Tri-Substituted Azaphosphatranes</td>
<td>44</td>
</tr>
<tr>
<td>2.3.3. Synthesis of Tri-Substituted Proazaphosphatranes</td>
<td>46</td>
</tr>
<tr>
<td>2.4. Conclusion</td>
<td>49</td>
</tr>
<tr>
<td>2.5. Experimental Details</td>
<td>49</td>
</tr>
<tr>
<td>2.6. References</td>
<td>70</td>
</tr>
</tbody>
</table>
CHAPTER 3: Tracking the Transannular Bond Interaction in Tris(2-pyridylmethyl)-azaphosphatrane (TPAP) with Various Transition Metal ions

3.1. Motivation and Specific Aims
3.2. Background
3.3. Results and Discussion
  3.3.1. Synthesis and Structure of CoTPAP Complexes (1 & 2)
  3.3.2. Attempted Synthesis and Characterization of Co(III)TPAP Complexes (2a-e)
  3.3.3. Synthesis and Structure of NiTPAP (3, 4 & 3a), PdTPAP (5) and PtTPAP (6) Complexes
  3.3.4. Comparison of the Transannular Distance of Co(I)TPAP and Co(II)TPAP
  3.3.5. Comparison of the Transannular Distance between Group 10 TPAP Complexes
  3.3.6. Metal Ion Oxidation State Effects on TPAP
  3.3.7. Quantum Mechanical Calculations
3.4. Conclusion
3.5. Experimental Details
3.6. References

CHAPTER 4: Small Molecule Activation with Transition Metal Tris(2-pyridylmethyl)azaphosphatrane Complexes

4.1. Motivation and Specific Aims
  4.1.1. CO₂ Reduction
  4.1.2. O₂ Reactivity
  4.1.3. Hydrogenation (H₂)
4.2. Background
  4.2.1. Ni-CO₂ Complexes
  4.2.2. Cu₂O₂ Complexes
  4.2.3. Ir-H₂ Complexes
4.3. Results and Discussion
  4.3.1. Reaction of Ni(TPAP)(COD) with CO₂
  4.3.2. Synthesis and Structure of CuTPAP Complex
  4.3.3. Reaction of CuTPAP with O₂
  4.3.4. Synthesis of IrH(TPAP)Cl
  4.3.5. Synthesis of IrH₂(TPAP)
  4.3.6. Reaction of IrH(TPAP)Cl with H₂
4.4. Conclusion
  4.4.1. Ni(TPAP)(COD) + CO₂
  4.4.2. Cu(TPAP) + O₂
  4.4.3. IrH(TPAP)Cl + H₂
4.5. Experimental Details
4.6. References
APPENDIX A: Crystal Structure of NiFe(CO)$_5$(Tris(2-pyridylmethyl)azaphosphatrane); A Synthetic Mimic of the NiFe Hydrogenase Active Site Incorporating a Pendant Pyridine Base 148
A.1. Motivation and Specific Aims 149
A.2. Background 150
A.3. Results and Discussion 151
   A.3.1. Structural Commentary 151
   A.3.2. Database Survey 153
A.4. Conclusion 154
A.5. Experimental Details 154
A.6. References 158

APPENDIX B: Attempted Protonation and pK$_a$ Measurement of Tris(2-pyridylmethyl)azaphosphatraneoxide 160
B.1. Motivation and Specific Aims 161
B.2. Background 161
B.3. Results and Discussion 162
   B.3.1. Synthesis and Characterization of Tris(2-pyridylmethyl)azaphosphatraneoxide (TPAPO) 162
   B.3.2. Protonation study of Tris(2-pyridylmethyl)azaphosphatraneoxide (TPAPO) 163
   B.3.3. Protonation study of Tris(benzyl)azaphosphatraneoxide (TBAPO) 166
B.4. Conclusion 168
B.5. Experimental Details 169
B.6. References 173

APPENDIX C: Coordination Complexes of Phosphine Ligands without Transannular Interactions 174
C.1. Motivation and Specific Aims 175
C.2. Background 175
C.3. Results and Discussion 176
   C.3.1. Synthesis of Co(II)(Tris(2-pyridylmethyl)aminophosphine) Complex 176
   C.3.2. Synthesis of Tris(2-pyridylethyl)aminophosphine (TPEAP) 177
   C.3.3. Synthesis of Co(II)TPEAP Complex 178
C.4. Conclusion 180
C.5. Experimental Details 180
C.6. References 184

APPENDIX D: Attempted Synthesis of an Fe-Sulfur-Carbide Cluster 185
D.1. Motivation and Specific Aims 186
D.2. Background 186
D.3. Results and Discussion 187
D.4. Conclusion 190
D.5. Experimental Details 191
D.6. References 202
APPENDIX E: CH₄ Activation Study with Fe(depe)₂ Derivatives 203
E.1. Motivation and Specific Aims 204
E.2. Background 204
   E.2.1. Oxidative Addition 205
   E.2.2. Sigma-Bond Metathesis 206
   E.2.3. 1,2-Addition 206
   E.2.4. Metalloradicals 206
   E.2.5. Electrophilic Activation 207
   E.2.6. Base Assisted Activation for C-H Activation 207
E.3. Results and Discussion 207
   E.3.1. Synthesis of [FeCl(CO)(depe)₂]Cl 207
   E.3.2. Reactivity with CH₄ 208
   E.3.3. Reactivity with CH₄ and DBU 209
E.4. Conclusion 210
E.5. Experimental Details 210
E.6. References 215
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>Chemical Structures of the work done by (left) Stephan’s group, (middle) Krempner’s group and (right) Martinez’s group on expanding the use of azaphosphatranes.</td>
<td>2</td>
</tr>
<tr>
<td>0.2</td>
<td>Chemical Structures of transition metal complexes of isobutyl-azaphosphatrane by (left) Martinez’s group and (right) Johnson’s group.</td>
<td>4</td>
</tr>
<tr>
<td>1.1</td>
<td>Chemdraw depicting the Tolman Electronic (TEP) and Steric Parameter (cone angle $\Theta$) of a generic Ni(phosphine)(CO)$_3$.</td>
<td>14</td>
</tr>
<tr>
<td>1.2</td>
<td>IR spectra of (purple) Ni(L$^{Me}$)(CO)$_3$ (1), (green) Ni(L$^{Pr}$)(CO)$_3$ (2), (red) Ni(L$^{Bu}$)(CO)$_3$ (3) and (brown) Ni(L$^{Bz}$)(CO)$_3$ (4) in CH$_2$Cl$_2$.</td>
<td>16</td>
</tr>
<tr>
<td>1.3</td>
<td>Crystal structure of Ni(L$^{Pr}$)(CO)$_3$ (2), Ni(L$^{Bu}$)(CO)$_3$ (3), Ni(L$^{Bz}$)(CO)$_3$ (4) and Ni(L$^{Me}$)$_2$(CO)$_2$ (5). Thermal ellipsoids are drawn at 80% probability; hydrogen atoms are omitted for clarity. Carbon atoms from the minor part of a disorder in 3 are also omitted.</td>
<td>19</td>
</tr>
<tr>
<td>1.4</td>
<td>Comparison of Tolman electronic parameter (TEP) and cone angles. Red dots (●) represent proazaphosphatranes measured herein and black dots (●) represent phosphines measured by Tolman.</td>
<td>21</td>
</tr>
<tr>
<td>1.5</td>
<td>Proposed electronic properties of generic tri(dialkylamino)phosphine and the metrical parameters observed from crystal structures.</td>
<td>23</td>
</tr>
<tr>
<td>1.6</td>
<td>$^1$H NMR spectrum of Ni(L$^{Me}$)(CO)$_3$ (1) in C$_6$D$_6$.</td>
<td>27</td>
</tr>
<tr>
<td>1.7</td>
<td>$^{13}$C NMR spectrum of Ni(L$^{Me}$)(CO)$_3$ (1) in C$_6$D$_6$.</td>
<td>28</td>
</tr>
<tr>
<td>1.8</td>
<td>$^{31}$P NMR spectrum of Ni(L$^{Me}$)(CO)$_3$ (1) in C$_6$D$_6$.</td>
<td>28</td>
</tr>
<tr>
<td>1.9</td>
<td>$^1$H NMR spectrum of Ni(L$^{Pr}$)(CO)$_3$ (2) in C$_6$D$_6$.</td>
<td>29</td>
</tr>
<tr>
<td>1.10</td>
<td>$^{13}$C NMR spectrum of Ni(L$^{Pr}$)(CO)$_3$ (2) in C$_6$D$_6$.</td>
<td>30</td>
</tr>
<tr>
<td>1.11</td>
<td>$^{31}$P NMR spectrum of Ni(L$^{Pr}$)(CO)$_3$ (2) in C$_6$D$_6$.</td>
<td>30</td>
</tr>
<tr>
<td>1.12</td>
<td>$^1$H NMR spectrum of Ni(L$^{Bu}$)(CO)$_3$ (3) in C$_6$D$_6$.</td>
<td>31</td>
</tr>
<tr>
<td>1.13</td>
<td>$^{13}$C NMR spectrum of Ni(L$^{Bu}$)(CO)$_3$ (3) in C$_6$D$_6$.</td>
<td>32</td>
</tr>
</tbody>
</table>
Figure 1.1. $^{31}$P NMR spectrum of Ni(L\textsuperscript{Bu})(CO)\textsubscript{3} (3) in C\textsubscript{6}D\textsubscript{6}. Resonances around 20 ppm are due to oxidized L\textsuperscript{Bu}.

Figure 1.5. $^1$H NMR spectrum of Ni(L\textsuperscript{Bz})(CO)\textsubscript{3} (4) in C\textsubscript{6}D\textsubscript{6}.

Figure 1.6. $^{13}$C NMR spectrum of Ni(L\textsuperscript{Bz})(CO)\textsubscript{3} (4) in C\textsubscript{6}D\textsubscript{6}.

Figure 1.7. $^{31}$P NMR spectrum of Ni(L\textsuperscript{Bz})(CO)\textsubscript{3} (4) in C\textsubscript{6}D\textsubscript{6}.

Figure 1.8. $^1$H NMR spectrum of Ni(L\textsuperscript{Me})\textsubscript{2}(CO)\textsubscript{2} (5) in C\textsubscript{6}D\textsubscript{6}.

Figure 1.9. $^{13}$C NMR spectrum of Ni(L\textsuperscript{Me})\textsubscript{2}(CO)\textsubscript{2} (5) in C\textsubscript{6}D\textsubscript{6}.

Figure 1.10. $^{31}$P NMR spectrum of Ni(L\textsuperscript{Me})\textsubscript{2}(CO)\textsubscript{2} (5) in C\textsubscript{6}D\textsubscript{6}.

Figure 1.11. IR spectrum Ni(L\textsuperscript{Me})\textsubscript{2}(CO)\textsubscript{2} (5) in CH\textsubscript{2}Cl\textsubscript{2}.

Figure 2.1. Crystal structure of [HP((2-PyrCH\textsubscript{2})-NCH\textsubscript{2}CH\textsubscript{2})\textsubscript{3}N][Cl] (1b). Thermal ellipsoids are drawn at 50% probability; hydrogen atoms except for H1, which is located in the difference map and refined freely, and Cl\textsuperscript{−} anion were omitted for clarity.

Figure 2.2. Crystal structure of [P((3-PyrCH\textsubscript{2})-NCH\textsubscript{2}CH\textsubscript{2})\textsubscript{3}N] (2c). Thermal ellipsoids are drawn at 50% probability; hydrogen atoms were omitted for clarity.

Figure 2.3. $^1$H NMR spectrum of tris[((4-(2-pyridyl)benzyl)amino)ethyl]amine (4a) in CDCl\textsubscript{3}.

Figure 2.4. $^{13}$C $^1$H NMR spectrum of tris[((4-(2-pyridyl)benzyl)amino)ethyl]amine (4a) in CDCl\textsubscript{3}.

Figure 2.5. $^1$H NMR spectrum of [HP((2-PyrCH\textsubscript{2})-NCH\textsubscript{2}CH\textsubscript{2})\textsubscript{3}N][Cl] (1b) in CD\textsubscript{3}CN.

Figure 2.6. $^{31}$P $^1$H NMR spectrum of [HP((2-PyrCH\textsubscript{2})-NCH\textsubscript{2}CH\textsubscript{2})\textsubscript{3}N][Cl] (1b) in CD\textsubscript{3}CN.

Figure 2.7. $^{31}$P NMR spectrum of [HP((2-PyrCH\textsubscript{2})-NCH\textsubscript{2}CH\textsubscript{2})\textsubscript{3}N][Cl] (1b) in CD\textsubscript{3}CN.

Figure 2.8. $^{13}$C $^1$H NMR spectrum of [HP((2-PyrCH\textsubscript{2})-NCH\textsubscript{2}CH\textsubscript{2})\textsubscript{3}N][Cl] (1b) in CD\textsubscript{3}CN.

Figure 2.9. $^1$H NMR spectrum of [P((2-PyrCH\textsubscript{2})-NCH\textsubscript{2}CH\textsubscript{2})\textsubscript{3}N] (1c) in CD\textsubscript{3}CN.
Figure 2.10. $^{31}$P NMR spectrum of [P((2-PyrCH$_2$)-NCH$_2$CH$_2$)$_3$N] (1c) in CD$_3$CN.

Figure 2.11. $^{31}$P{$^1$H} NMR spectrum of [P((2-PyrCH$_2$)-NCH$_2$CH$_2$)$_3$N] (1c) in C$_6$D$_6$.

Figure 2.12. $^{13}$C{$^1$H} NMR spectrum of [P((2-PyrCH$_2$)-NCH$_2$CH$_2$)$_3$N] (1c) in CD$_3$CN.

Figure 2.13. $^1$H NMR spectrum of [P((3-PyrCH$_2$)-NCH$_2$CH$_2$)$_3$N] (2c) in CD$_3$CN.

Figure 2.14. $^{31}$P{$^1$H} NMR spectrum of [P((3-PyrCH$_2$)-NCH$_2$CH$_2$)$_3$N] (2c) in C$_6$D$_6$.

Figure 2.15. $^{13}$C{$^1$H} NMR spectrum of [P((3-PyrCH$_2$)-NCH$_2$CH$_2$)$_3$N] (2c) in CD$_3$CN.

Figure 2.16. $^1$H NMR spectrum of [P((Furan-CH$_2$)-NCH$_2$CH$_2$)$_3$N] (3c) in CD$_3$CN.

Figure 2.17. $^{31}$P{$^1$H} NMR spectrum of [P((Furan-CH$_2$)-NCH$_2$CH$_2$)$_3$N] (3c) in C$_6$D$_6$.

Figure 2.18. $^{13}$C{$^1$H} NMR spectrum of [P((Furan-CH$_2$)-NCH$_2$CH$_2$)$_3$N] (3c) in CD$_3$CN.

Figure 2.19. $^1$H NMR spectrum of [P((2-Pyr-Ph-CH$_2$)-NCH$_2$CH$_2$)$_3$N] (4c) in CD$_3$CN.

Figure 2.20. $^{13}$C{$^1$H} NMR spectrum of [P((2-Pyr-Ph-CH$_2$)-NCH$_2$CH$_2$)$_3$N] (4c) in CD$_3$CN.

Figure 2.21. $^{31}$P{$^1$H} NMR spectrum of [P((2-Pyr-Ph-CH$_2$)-NCH$_2$CH$_2$)$_3$N] (4c) in C$_6$D$_6$.

Figure 2.22. $^1$H NMR spectrum of [P((2-CH$_3$-Thiophene-CH$_2$)-NCH$_2$CH$_2$)$_3$N] (5c) in CD$_3$CN.

Figure 2.23. $^{31}$P{$^1$H} NMR spectrum of [P((2-CH$_3$-Thiophene-CH$_2$)-NCH$_2$CH$_2$)$_3$N] (5c) in C$_6$D$_6$.

Figure 2.24. $^{13}$C{$^1$H} NMR spectrum of [P((2-CH$_3$-Thiophene-CH$_2$)-NCH$_2$CH$_2$)$_3$N] (5c) in CD$_3$CN.

Figure 3.1. Chemdraw structures of azaphosphatrane in three different forms based on the transannular distance of P–N$_{ax}$.

Figure 3.2. Chemdraw structures of (a) Peters’, (b) Parkin’s, (c) Lu’s and (d) Agapie’s transition metal complexes, featuring an adaptable ligand platform.
Figure 3.3. (Left) Plot of the transannular distance versus the θ puckering of the axial nitrogen above the plane of the three adjacent carbon atoms for Verkade’s Superbase with various main groups (denoted in black circles ●) and TPAP with various transition metals (denoted in red diamonds ◆). (Right) Depiction of the angle, θ, as the degree of puckering of the axial nitrogen (N_{ax}) out of the C_1–C_3–C_5 plane. Values used in this figure are from structural data.

Figure 3.4. Crystal structure of CoTPAP(Cl) (1). Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms and counteranions are omitted for clarity.

Figure 3.5. Crystal structure of [Co(TPAP)(CH_3CN)][BF_4]_2 (2). Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms and counteranions are omitted for clarity.

Figure 3.6. Crystal structure of [Co(II)(acac)][TPAPH] (2a). Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms are omitted for clarity.

Figure 3.7. Crystal structure of [TPAP][BF_4]_2 (2b). Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms and BF_4 counteranions are omitted for clarity.

Figure 3.8. Crystal structure of [CoCl_3(TPAPH)] (2c). Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms are omitted for clarity.

Figure 3.9. Crystal structure of NiTPAP(COD) (3). Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms are omitted for clarity.

Figure 3.10. Crystal structure of NiTPAP(CO_2) (3a). Thermal ellipsoids are drawn at 80% probability. Hydrogen atoms and counteranions are omitted for clarity.

Figure 3.11. Crystal structure of (a) [NiTPAP(CH_3CN)][BF_4]_2 (4), (b) [PdTPAP-(CH_3CN)][BF_4]_2 (5) and (c) [PtTPAP(Cl)][PF_6] (6). Structures 5 and 6 display one of two molecules in the asymmetric unit. Thermal ellipsoids drawn are at 50% probability. Hydrogen atoms and counteranions are omitted for clarity. Electron density from the minor disorder of the Pt atom in 6 is also omitted.

Figure 3.12. (Left) HOMOs of Ni(0)TPAP(CO)_2 (3a) and (Right) [Ni(II)TPAP(CH_3CN)]^{2+} (4). All surfaces are at an isovalue of 0.035.
Figure 3.13. Crystal structure of CoTPAP(Cl) (1b) Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms are omitted for clarity. Grown from a pentane diffusion into a concentrated THF solution by Reed J. Eisenhart from the University of Minnesota.

Figure 3.14. EPR spectrum of [CoTPAP(CH$_3$CN)][BF$_4$]$_2$ (2) in a frozen solution of acetonitrile at 77 K.

Figure 3.15. UV-vis spectrum of [CoTPAP(CH$_3$CN)][BF$_4$]$_2$ (2) in acetonitrile at 22°C. An inset display a close up of the bands between 500 and 1000 nm.

Figure 3.16. Variable scan rate cyclic voltammograms of [CoTPAP(CH$_3$CN)][BF$_4$]$_2$ (2) with 1.0 mM analyte in acetonitrile with 0.02 M Bu$_4$NPF$_6$.

Figure 3.17. Solution magnetic susceptibility. $^1$H NMR spectra of [CoTPAP(CH$_3$CN)][BF$_4$]$_2$ (2) at 237, 268 and 298 K in in CD$_3$CN.

Figure 3.18. $^1$H NMR spectrum of NiTPAP(COD) (3) in C$_6$D$_6$.

Figure 3.19. $^{31}$P{$^1$H} spectrum of NiTPAP(COD) (3) in C$_6$D$_6$.

Figure 3.20. IR spectrum of NiTPAP(CO)$_2$ (3a) in CH$_2$Cl$_2$.

Figure 3.21. $^1$H NMR spectrum of NiTPAP(CO)$_2$ (3a) in C$_6$D$_6$.

Figure 3.22. $^{13}$C NMR spectrum of NiTPAP(CO)$_2$ (3a) in C$_6$D$_6$.

Figure 3.23. $^{31}$P{$^1$H} NMR spectrum of NiTPAP(CO)$_2$ (3a) in C$_6$D$_6$.

Figure 3.24. $^1$H NMR of spectrum of [NiTPAP(CH$_3$CN)][BF$_4$]$_2$ (4) in CD$_3$CN.

Figure 3.25. $^1$H NMR spectrum of [PdTPAP(CH$_3$CN)][BF$_4$]$_2$ (5) in CD$_3$CN.

Figure 3.26. $^{31}$P{$^1$H} NMR spectrum of [PdTPAP(CH$_3$CN)][BF$_4$]$_2$ (5) in CD$_3$CN.

Figure 3.27. $^1$H NMR spectrum of [PtTPAPCl][PF$_6$]$_2$ (6) in CD$_3$CN.

Figure 3.28. $^{31}$P{$^1$H} NMR spectrum of [PtTPAPCl][PF$_6$]$_2$ (6) in CD$_3$CN.

Figure 4.1. Structurally characterized Ni-CO$_2$ mononuclear complexes.

Figure 4.2. Structurally characterized Cu$_2$O$_2$ complexes with di- and tri-dentate N ligands.

Figure 4.3. Ir(III) complexes bearing strong sigma donor ligands.
Figure 4.4. IR spectrum of brown solid from the reactivity of Ni(TPAP)(COD) with CO₂.

Figure 4.5. IR spectra of (blue) NiTPAP(CO)₂ and (red) Ni(TPAP)(COD) + CO₂ after 3 days of sitting at room temperature.

Figure 4.6. Crystal structure of [Cu(TPAP)]₂[BF₄]₂. Thermal ellipsoids are drawn at 50% probability; hydrogen atoms and counter anions omitted for clarity.

Figure 4.7. UV-vis spectra of (red) CuTPAP and (green) CuTPAP + O₂ in CH₃CN.

Figure 4.8. EPR spectrum of green product from the reaction of CuTPAP with O₂ in CH₃CN at 77K.

Figure 4.9. Crystal structure of IrH(TPAP)Cl. Solvents molecules (dichloromethane and diethyl ether) and hydrogens are omitted for clarity except for H1, which was located in the difference map and refined freely.

Figure 4.10. Crystal structure of IrH₂(TPAP). Solvents molecule (tetrahydrofuran), LiCl, and hydrogens are omitted for clarity except for H1 and H2, which were located in the difference map and refined freely.

Figure 4.11. ¹H NMR spectrum of IrH(TPAP)Cl + AgBF₄ + H₂ in CD₂Cl₂. Inset displays a close up view of the hydride region.

Figure 4.12. ¹H NMR spectrum of Cu(TPAP) complex in CD₃CN.

Figure 4.13. ³¹P{¹H} NMR spectrum of Cu(TPAP) complex in CD₃CN.

Figure 4.14. ¹H NMR spectrum of IrH(TPAP)Cl in CD₂Cl₂. Inset displays a close up view of the hydride region.

Figure 4.15. ³¹P{¹H} NMR spectrum of IrH(TPAP)Cl in CD₂Cl₂. Inset displays a close up view of the resonance.

Figure 4.16. ¹H NMR spectrum of IrH₂(TPAP) in CD₂Cl₂.

Figure 4.17. ³¹P{¹H} NMR spectrum of IrH₂(TPAP) in CD₂Cl₂.

Figure 4.18. ³¹P{¹H} NMR spectrum of [IrH(TPAP)Cl] + AgBF₄ + H₂ in CD₂Cl₂.
Figure A.1. The molecular structure of complex NiFe(TPAP)(CO)$_5$. The displacement ellipsoids are drawn at the 50% probability level. For clarity, the hydrogen atoms have been omitted.

Figure A.2. $^1$H NMR spectrum of NiFe(TPAP)(CO)$_5$ in C$_6$D$_6$.

Figure A.3. $^{31}$P{$^1$H} NMR spectrum of NiFe(TPAP)(CO)$_5$ in C$_6$D$_6$.

Figure B.1. $^{31}$P{$^1$H} NMR spectrum of tris(2-pyridylmethyl)azaphosphatraneoxide (TPAPO) + HBF$_4$ in CD$_3$CN.

Figure B.2. $^{31}$P{$^1$H} NMR spectrum of tris(2-pyridylmethyl)azaphosphatraneoxide (TPAPO) + TsOH in CD$_3$CN.

Figure B.3. $^{31}$P{$^1$H} NMR spectrum of tris(benzy)azaphosphatraneoxide (TBAPO) + HBF$_4$ in CD$_3$CN.

Figure B.4. $^{31}$P{$^1$H} NMR spectrum of tris(benzy)azaphosphatraneoxide (TBAPO) + TsOH in CD$_3$CN.

Figure B.5. $^1$H NMR spectrum of tris(2-pyridylmethyl)azaphosphatraneoxide (TPAPO) in CD$_3$CN.

Figure B.6. $^{31}$P{$^1$H} NMR spectrum of tris(2-pyridylmethyl)azaphosphatraneoxide (TPAPO) in CD$_3$CN.

Figure C.1. Crystal structure of [Co(TPMAP)$_2$][BF$_4$]$_2$. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms and counter anions are omitted for clarity.

Figure C.2. Crystal structure of [Co(TPEAP)(CH$_3$CN)][BF$_4$]$_2$. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms and counter anions are omitted for clarity.

Figure C.3. $^1$H NMR spectrum of tris(2-pyridylethyl)aminophosphine (TPEAP) in CD$_3$CN.

Figure C.4. $^{31}$P{$^1$H} NMR spectrum of tris(2-pyridylethyl)aminophosphine (TPEAP) in CD$_3$CN.

Figure D.1. Structurally characterized Fe complexes containing either sulfur or carbide-like components as partial FeMoco synthetic mimics.

Figure D.2. Crystal structure of Fe$_5$(CO)$_{15}$C. Thermal ellipsoids are drawn at 50% probability.
Figure D.3. IR spectra of (red, top) [Me₄N]₂[Fe₆(CO)₁₆C²⁻] and the product of (blue, bottom) [Me₄N]₂[Fe₆(CO)₁₆C²⁻] + S₈. 192

Figure D.4. IR spectra of (red, top) [Me₄N]₂[Fe₆(CO)₁₆C²⁻] and the product of (blue, bottom) [Me₄N]₂[Fe₆(CO)₁₆C²⁻] + S₈ under UV light. 193

Figure D.5. IR spectra of (red, top) [Me₄N]₂[Fe₆(CO)₁₆C²⁻] and the product of (blue, bottom) [Me₄N]₂[Fe₆(CO)₁₆C²⁻] + PhCH₂SH. 194

Figure D.6. IR spectra of (red, top) [Me₄N]₂[Fe₆(CO)₁₆C²⁻] and the product of (blue, bottom) [Me₄N]₂[Fe₆(CO)₁₆C²⁻] + PhCH₂SH under UV light. 195

Figure D.7. IR spectra of (red, top) [Me₄N]₂[Fe₆(CO)₁₆C²⁻] and the product of (blue, bottom) [Me₄N]₂[Fe₆(CO)₁₆C²⁻] + ⁴PrSH. 196

Figure D.8. IR spectra of (red, top) [Me₄N]₂[Fe₆(CO)₁₆C²⁻] and the product of (blue, bottom) [Me₄N]₂[Fe₆(CO)₁₆C²⁻] + ⁴PrSH under UV light. 197

Figure D.9. IR spectra of (red, top) [Me₄N]₂[Fe₆(CO)₁₆C²⁻] and the product of (blue, bottom) [Me₄N]₂[Fe₆(CO)₁₆C²⁻] + p-FC₆H₄SH. 198

Figure D.10. IR spectra of (red, top) [Me₄N]₂[Fe₆(CO)₁₆C²⁻] and the product of (blue, bottom) [Me₄N]₂[Fe₆(CO)₁₆C²⁻] + p-FC₆H₄SH under UV light. 199

Figure D.11. IR spectra of (red, top) [Me₄N]₂[Fe₆(CO)₁₆C²⁻] and the product of (blue, bottom) [Me₄N]₂[Fe₆(CO)₁₆C²⁻] + Me₂S₂. 200

Figure D.12. IR spectra of (red, top) [Me₄N]₂[Fe₆(CO)₁₆C²⁻] and the product of (blue, bottom) [Me₄N]₂[Fe₆(CO)₁₆C²⁻] + Me₂S₂ under UV light. 201

Figure E.1. ¹H NMR spectrum of [Fe(CO)(depe)₂]Cl + AgSbF₆ + CH₄ in CD₂Cl₂. 212

Figure E.2. ³¹P{¹H} NMR spectrum of [Fe(CO)(depe)₂]Cl + AgSbF₆ + CH₄ in CD₂Cl₂. 212

Figure E.3. ¹H NMR spectrum of [Fe(CO)(depe)₂]Cl + AgSbF₆ + CH₄ + DBU in CD₂Cl₂. 213

Figure E.4. ³¹P{¹H} NMR spectrum of [Fe(CO)(depe)₂]Cl + AgSbF₆ + CH₄ + DBU in CD₂Cl₂. 214
## LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Table 1.1.</td>
<td>CO vibrational frequencies (in CH₂Cl₂) and cone angle of complexes 1-4 and selected Ni(CO)₃(PR₃) complexes.</td>
<td>17</td>
</tr>
<tr>
<td>Table 1.2.</td>
<td>Crystallographic data and refinement parameters for complexes 2-5.</td>
<td>20</td>
</tr>
<tr>
<td>Table 1.3.</td>
<td>Selected distances and angles of 2-5.</td>
<td>20</td>
</tr>
<tr>
<td>Table 2.1.</td>
<td>³¹P NMR values of 1c-5c and various alkyl- and benzyl-substituted proazaphosphatranes in C₆D₆ reported by Verkade et al. Grey out rows represents asymmetric proazaphosphatranes.</td>
<td>48</td>
</tr>
<tr>
<td>Table 3.1.</td>
<td>Bond lengths and angles of complexes 1-6. Metrics 5 and 6 were taken from one of two molecules in the asymmetric unit. Metal ion is denoted as M. Non-italicized values are from the X-ray structural analysis and italicized values are from the geometry optimized structures calculated using quantum mechanical methods.</td>
<td>91</td>
</tr>
<tr>
<td>Table 3.2.</td>
<td>Results of NBO analysis of donor-acceptor interactions in compound adducts, estimated by second-order perturbation theory, E⁽²⁾ᵢ→ⱼ (kcal mol⁻¹).</td>
<td>94</td>
</tr>
<tr>
<td>Table 3.3.</td>
<td>Calculated geometrical parameters for selected mono-Cationic and dicationic comparison.</td>
<td>96</td>
</tr>
<tr>
<td>Table A.1.</td>
<td>Selected geometric parameters of NiFe(TPAP)(CO)₅ (Å, °).</td>
<td>153</td>
</tr>
<tr>
<td>Table D.1.</td>
<td>Attempted substitution of carbonyl with sulfur reagents in [Me₄N]₂[Fe₆(CO)₁₆C²⁻].</td>
<td>188</td>
</tr>
</tbody>
</table>
LIST OF SCHEMES

<table>
<thead>
<tr>
<th>Scheme</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Synthesis of tri-substituted tris(2-aminoethyl)amine.</td>
<td>44</td>
</tr>
<tr>
<td>2.2</td>
<td>Synthesis of protonated tri-substituted azaphosphatranes</td>
<td>45</td>
</tr>
<tr>
<td>2.3</td>
<td>Synthesis of tri-substituted proazaphosphatranes</td>
<td>47</td>
</tr>
<tr>
<td>4.1</td>
<td>Proposed reactivity of CO₂ with NiTPAP(COD).</td>
<td>128</td>
</tr>
<tr>
<td>4.2</td>
<td>Synthesis of [Cu(TPAP)]₂[BF₄]₂ complex.</td>
<td>130</td>
</tr>
<tr>
<td>4.3</td>
<td>Synthesis of [IrH(TPAP)Cl] and [IrH₂(TPAP)].</td>
<td>133</td>
</tr>
<tr>
<td>A.1</td>
<td>Synthesis of NiFe(TPAP)(CO)₅.</td>
<td>151</td>
</tr>
<tr>
<td>B.1</td>
<td>Proposed Reduction-Coupled Oxo Activation (ROA) mechanism in VPO system.</td>
<td>161</td>
</tr>
<tr>
<td>B.2</td>
<td>Synthesis of tris(2-pyridylmethyl)azaphosphatraneoxide (TPAPO).</td>
<td>162</td>
</tr>
<tr>
<td>B.3</td>
<td>Proposed reactivity of tris(2-pyridylmethyl)azaphosphatraneoxide (TPAPO) with HBF₄.</td>
<td>163</td>
</tr>
<tr>
<td>B.4</td>
<td>Proposed reactivity of tris(2-pyridylmethyl)azaphosphatraneoxide (TPAPO) with TsOH.</td>
<td>165</td>
</tr>
<tr>
<td>B.5</td>
<td>Reactivity of tris(benzyl)azaphosphatraneoxide (TBAPO) with HBF₄ or TsOH.</td>
<td>166</td>
</tr>
<tr>
<td>C.1</td>
<td>Coordination of TPMAP with [Co(CH₃CN)₆][BF₄]₂.</td>
<td>176</td>
</tr>
<tr>
<td>C.2</td>
<td>Synthesis of tris(2-pyridylethyl)aminophosphine (TPEAP).</td>
<td>178</td>
</tr>
<tr>
<td>C.3</td>
<td>Coordination of TPEAP with [Co(CH₃CN)₆][BF₄]₂.</td>
<td>178</td>
</tr>
<tr>
<td>E.1</td>
<td>Categories of C-H activation of methane. a) oxidative addition, b) σ-bond metathesis, c) electrophilic activation, d) 1,2 addition and e) metalloradical.</td>
<td>205</td>
</tr>
<tr>
<td>E.2</td>
<td>Synthesis of FeCl₂(depe)₂ and [FeCl(CO)(depe)₂]Cl.</td>
<td>208</td>
</tr>
<tr>
<td>E.3</td>
<td>Reactivity of [FeCl(CO)(depe)₂]Cl with CH₄.</td>
<td>209</td>
</tr>
<tr>
<td>E.4</td>
<td>Reactivity of [FeCl(CO)(depe)₂]Cl with CH₄ and DBU.</td>
<td>210</td>
</tr>
</tbody>
</table>
**LIST OF CHARTS**

| Chart 0.1. | Protonation of proazaphosphatranes (Verkade’s Superbases) with a generic proton. The $pK_a$ values of the conjugate acid shown in the table to the right, with various R groups. | 1 |
| Chart 1.1. | Series of Ni(CO)$_x$ ($x = 2$ or $3$) complexes of Verkade’s Superbases. | 15 |
| Chart 2.1. | Series of Proazaphosphatrane Compounds with Various Functional Groups. | 42 |
| Chart 3.1. | Transition Metal Complexes of TPAP. | 81 |
| Chart C.1. | Ligand with Bicyclic Caged Framed (TPAP) and without (TPMAP & TPEAP). | 175 |
ACKNOWLEDGMENTS

I want to thank my professor for encouraging me every step of the way.
(Professor Jenny Y. Yang)

I want to thank my committee members for pushing me to become the best chemist I can be.
(Professor A.S. Borovik & Professor Bill Evans)

I want to thank everyone in the Yang lab for making my time in graduate school feel like home.
(Brian, Bianca, Juliet, Charlene, Annie, Steve, Jake, Alex, Caitlin, Jeff, Drew, Ivy, Wyeth, Rebecca, Sam, Nehal, Natty, Kevin, Hazel, Reyna, Jessica and Andrew)

I want to thank every graduate student at UCI that shared a meal with me.
(Austin, Dan, Casey, Rommy, Miles, Mike x2, Sarah, Luke, Stan, Kevin, Kellen, Lin, Raph, Yilin, Kate, Gerald, Tyler, Claudia, Chad, David, Dalen, Millie, and Adam)

I want to thank my family and friends who came to visit me.
(Som, Sarah, Eric, Pranee, Ular, Lincy, Nalong, Thongsai, Aunt Phet, Ali, Russ, Andrea, Ryan, Andrew x2, Dennis, Will, Tien, Randy, Val, Daniel and Eddie)

I want to thank the Irvine friends that made Southern California feel like home.
(Frank, Shauna, John, Jina, Khang, Lawrence, Robert, Pranee and Sensei)

I want to thank my parents for inspiring me to work hard.
(Kor and Vinai)

I want to thank my grandparents for their love and care.
(Mong and Thongdam)

I want to thank my wife for everything. I love her with every atom in my body. I would not have made it through graduate school without her. I am happy to have completed this journey with her and I look forward to the rest of our journey together on this planet.
(Kim V. Le)
CURRICULUM VITAE

Zachary Thammavongsy

Education

University of California, Irvine, Irvine, CA
Ph.D. in Chemistry: Spring 2019

Western Washington University, Bellingham, WA
M.S. in Chemistry: June 2013
B.S. in Chemistry: June 2011
Minor in German

Research Experience

University of California, Irvine, Graduate Research, Irvine, CA
Advisor: Professor Jenny Y. Yang
Research Project Title: “Transition Metal Complexes of Modified Azaphosphatranes”

Western Washington University, Graduate Research, Bellingham, WA
Advisor: Professor John D. Gilbertson
Research Project Title: “Ligand Based Reduction of Carbon Dioxide and Release of Carbon Monoxide on Iron (II)”

Western Washington University, Undergraduate Research, Bellingham, WA
Advisor: Professor John D. Gilbertson
Research Project Title: “Metalloenzyme Mimics with Hydrogen Bond Directors Located in the Secondary Coordination Sphere”

Peer-Reviewed Research Publications *corresponding author


3. Thammavongsy, Z.; Kha, I. M.; Ziller, J. W.; Yang, J. Y.* "Electronic and Steric Tolman Parameters for Proazaphosphatranes, the Superbase Core of the Tri(pyridylmethyl)azaphosphatran (TPAP) Ligand." Dalton Trans. 2016, 45, 9853-9859


Presentations (Oral and Poster – Primary Presenter Only)

1. Oral Presentation: “Playing a cooperative 1H NMR board game during office hour: Lessons Learned.” ACS Biennial Conference on Chemical Education 2018, South Bend, IN, July 29th – August 2nd, 2018

2. Poster Presentation: “Utilizing Proazaphosphatrane Ligands in Metal Complexes.” UC Chemical Symposium 2018, Los Angeles, CA, March 26th–28th, 2018


# Teaching Experience

*University of California, Irvine, Graduate Teaching Assistant, Irvine, CA* 2013 - 2019

**Lecture Course Teaching Assistant, Inorganic Chemistry I, Chem 107** Fall 2017  
*Discussion enrollment: 90 students (3 sections)*  
- Integrated active learning activities such as Kahoot to address prior knowledge  
- Prepared weekly problem sets and mini lectures  
- Led weekly discussions on inorganic topics  
- Set up iClicker quizzes for instructor  
- Worked with a diverse population of students including international and EAL students

**Lecture Course Teaching Assistant, Inorganic Chemistry I, Chem 127** Winter 2014  
*Discussion enrollment: ~29 students (3 sections)*  
- Prepared weekly problem sets and mini lectures  
- Assisted in the preparation of exams and homework  
- Encouraged a friendly learning environment by learning names  
- Held reviews for students and graded exams to provide students with helpful feedback

**Lecture Course Teaching Assistant, Organic Chemistry I, II & III, Chem 51A, B & C** Spring 2019, Summer 2018  
*Discussion enrollment: ~179 students (5 sections)*  
- Led discussions on organic chemistry worksheets via think-pair-share  
- Assisted in the preparation of teaching materials such as problem sets and exams  
- Held review sessions and graded exams to provide students with helpful feedback  
- Worked with a diverse population of students including international and EAL students

**Laboratory Course Teaching Assistant, Inorganic Chemistry, Chem 107** Winter 2016  
*Laboratory enrollment: 11*  
- Supervised and instructed students in inorganic chemistry lab techniques  
- Graded and provided feedback on student’s lab report  
- Began each lab section with an overview of laboratory technique and set-up, objectives, and safety

**Laboratory Course Teaching Assistant, Organic Chemistry, Chem 51LB & 51LC** Winter 2017  
*Laboratory enrollment: 40 (2 sections)*  
- Supervised and instructed students in organic chemistry lab techniques  
- Graded and provided feedback on student’s electronic laboratory notebook and lab reports  
- Began each lab section with an overview of laboratory technique and set-up, objectives, and safety

**Laboratory Course Teaching Assistant, General Chemistry, Chem 1LC** Summer 2016  
*Laboratory enrollment: 50 (2 sections)*  
- Supervised and instructed students in general chemistry lab techniques  
- Taught students to keep complete and accurate scientific records  
- Graded and provided feedback on student’s electronic laboratory notebook and post labs  
*Western Washington University, Graduate Teaching Assistant, Bellingham, WA* 2011-2013

**Laboratory Course Teaching Assistant, General Chemistry, Chem 121 - 123** Winter 2013  
*Laboratory enrollment: 40 (2 sections)*  
- Supervised and instructed students in general chemistry lab techniques  
- Taught students to keep complete and accurate scientific records  
- Graded and provided feedback on student’s post lab  
- Began each lab section with a demo of laboratory techniques and safety  
*Western Washington University, Undergraduate Teaching Assistant, Bellingham, WA* 2010-2011
Laboratory Course Teaching Assistant, General Chemistry, Chem 123  
- Helped supervise students in general chemistry lab techniques  
- Stocked chemicals and make solutions  
- Collected post lab and entered in grades  
- Assisted in students understanding of the experiment through the Socratic method

Professional Development

*University of California, Irvine, Division of Teaching Excellence & Innovation (DTEI)*  
**University Studies 395, Teaching as Research**  
- Winter 2018  
- Be familiarized with the primary aspects of doing educational research (IRB)  
- Planned and carry out a small study to measure the effectiveness of teaching

**University Studies 390A, Advanced Pedagogy and Academic Job Preparation**  
- Winter 2017  
- Introduced to principles of course design and instructional development  
- This course covers topics on active learning, inclusive learning, and educational research

**University Studies 390B, Advanced Pedagogy and Academic Job Preparation**  
- Spring 2017  
- Application of US 390A material in the design and implementation of the Teaching Assistant Professional Development Program (TAPDP)  
- Design a workshop meant to model best teaching practices as well as introduce new TAs to their roles and responsibilities

**University Studies 390C, Advanced Pedagogy and Academic Job Preparation**  
- Fall 2017  
- Recruited and interviewed potential pedagogical fellows  
- Designed a course to assist pedagogical fellows to develop long-term teaching plans and prepared for the academic job market

**Center for Integration of Research, Teaching and Learning (CIRTL) Associate**  
- Winter 2017  
- Designed a potential research project around teaching with definable goals and outcomes  
- This program teaches graduate students and faculty to effectively implement research-based practices in different learning environments

*University of California, Irvine Graduate Resource Center Workshop*  
**Public Speaking: Activate to Captivate**  
- Winter 2018  
- Learned techniques to turn passive presentations into active ones  
- Practice our research presentation in front of a general audience

**Improv for Teaching**  
- Spring 2018  
- Learned to think on our feet and engaged in active listening techniques  
- Expanding our imagination to lead a dynamic classroom

**Southern California PKAL Regional Network Annual Meeting**  
**Building More Transparent Assignments and Evaluation in STEM Courses**  
- Winter 2019  
- Apply the principles of a transparent design, evaluation, and assessment to our own class work  
- Look at common assignments in STEM classrooms in light of transparent pedagogy

**Inclusive Pedagogy: Finding the Right Approach for You and Your Context**  
- Winter 2018  
- Shared inclusive practices between professors and graduate students in their respective field  
- Listed inclusive activities that could be effortlessly implemented in chemistry and physics
Active Learning in Chemistry: Using Toys, Simulations, and Data Analysis to Enhance Learning  
Winter 2018

- A workshop aimed to introduce cheap and effective science demonstration to enhance student’s chemistry concepts.

Discipline-Based Education Research 101  
Spring 2017

- Designed a study to conduct at an institution
- A workshop that introduced educators on effective educational research studies in their college science classroom

A Conversation Forum Between Two and Four-Year Faculty about Transfer Students  
Spring 2017

- Listened to the discussion between instructors in two and four year institutions about the challenges and success stories of transfer students
- A workshop aimed towards sharing ideas between instructors on how to improve the transition of transfer students to four year institutions

Mentorship (Undergraduate Researcher)

Jessica Mendoza
Current Location: Undergraduate at UC Berkeley  
Summer Undergraduate Researcher from UC Berkeley  
Summer 2018

Natwara Sutthirat
Current Location: Undergraduate Researcher at UCI  
DAAD RISE Germany Summer Internship ($3,000)  
Undergraduate Research Opportunities Program (UROP) Grant ($1,500)  
Poster Presentation at 255th ACS National Meeting, New Orleans, LA  
2017 - 2018

Ivy Kha
Current Location: Western University – Optometry Program  
Undergraduate Research Opportunities Program (UROP) Grant ($2,000)  
Poster Presentation at 251st ACS National Meeting, San Diego, CA  
2015 - 2017

Hannah Bui
Current Location: George Washington University – Master in Public Health  
Poster Presentation at 251st ACS National Meeting, San Diego, CA  
2015 - 2017

Service

University of California Chemical Symposium, Social Media Manager  
University of California  
2018 - 2019

- Advertise the UC Chemical Symposium to UC graduate and postdoctoral members
- Engage with the scientific community on the scientific breakthroughs from UC schools
- Manage UC Chemical Symposium social media accounts (Twitter and Instagram)

Teaching Assistant Professional Development Program, Workshop Instructor  
University of California, Irvine, Irvine, CA  
Fall 2018

- Led a day and a half long workshop for incoming graduate student TAs on their roles and responsibilities
- Introduced TA duties such as grading, holding office hours and teaching via active learning
- Provided feedback to new TAs on their microteaching lessons
Chemistry Outreach, *Volunteer*  
*University of California, Irvine*, Irvine, CA  
2017 - 2019
- Travel to elementary and middle schools to perform chemistry demonstrations
- Engaged with elementary and middle school students on the topic of chemistry once every month
- Expose students to the world of chemistry and explain the life of a chemist

Laboratory Experiments and Activities in Physical Sciences (LEAPS), *Volunteer*  
*University of California, Irvine*, Irvine, CA  
2014 - 2019
- Students and teachers take a tour around the Yang Lab
- Engaged with middle and high school students on the topic of chemistry once every quarter
- Demonstrate chemistry experiments and explain their applicability in the world around them

Research Saturday, *Volunteer*  
*University of California, Irvine*, Irvine, CA  
2014 - 2019
- Tour undergraduate students around the chemistry laboratory
- Advise undergraduate students in picking research groups
- Assist undergraduate students in drafting admission emails to research professors

SoCal Undergraduate Research Symposium, *Poster Judge*  
*University of California, Irvine*, Irvine, CA  
2014 - 2019
- Judge posters presented by undergraduate researchers
- Ask scientific questions on undergraduate research projects
- Encourage undergraduate researchers to keep pursuing their scientific goals

Awards
- UCI Dissertation Fellowship  
- UCI Chemistry Most Promising Future Chemistry Teacher  
- UCI Most Promising Future Faculty Member Award  
- UC Chemical Symposium Social Media Award  
- UCI Chemistry Outstanding Contributions to the Department Award  
- CIRTL Certification, Associate Level  
- UCI Pedagogical Fellow Award  
- UCI Chemistry Gebel Award  
- UCI Graduate Student Travel Grant

Affiliations
- American Chemical Society, Member  
- UC Chemical Symposium Organizing Member  
- Association of American Colleges & University, Member

Related Affiliations
- Founder and Designer of *d-Orbital Games* – *Science Table Top Game Company*  
Game Titles Produced:
  1. Selenium Argon Carbon Hydrogen [SeArCH] – Periodic Table Game
  2. Slap Count – *d*-Electron Count Game
  3. Sym Slam – Point Group Game
  4. LINK – Amino Acid Game
  5. 1H NMR Spectrum – Proton NMR Game
  6. 18 Electron Rule
  7. Rare Earth Elements
- Website: [www.dorbitalgames.org](http://www.dorbitalgames.org)
ABSTRACT OF THE DISSERTATION

Transition Metal Complexes of Modified Azaphosphatranes

by

Zachary Thammavongsy

Doctor of Philosophy in Chemistry

University of California, Irvine, 2019

Professor Jenny Y. Yang, Chair

The non-ionic, super-basic phosphorus of proazaphosphatranes has been extensively studied as organic catalysts and stoichiometric bases. They are commercially available and have been used as ligands for palladium cross-coupling reactions. Despite this utility, a fundamental understanding of proazaphosphatranes as ligands in coordination chemistry and transition metal catalysis has not been thoroughly investigated. Herein, modification of proazaphosphatrane compounds with pyridine, thiophene, and furan groups expand its chelating ability beyond its monodentate frame. The coordination chemistry of modified and unmodified proazaphosphatranes with various transition metal ions is explored, specifically investigating their electron donating properties and transannular interactions. Additionally, the reactivity of these transition metal azaphosphatrane complexes with small molecules (CO$_2$, H$_2$, and O$_2$) is examined. A multidisciplinary approach is employed to study these transition metal azaphosphatrane complexes, founded on the design and synthesis of organic ligands and the development of metal complexes. Reactivity studies and inorganic, organic, and analytical characterization methods are carried out.
Chapter 1 describes the electronic and steric parameters of azaphosphatranes using the Tolman electronic parameters and cone angle.

Chapter 2 describes the modification of azaphosphatranes incorporating pyridine, thiophene and furan substituents.

Chapter 3 describes the experimental and computational investigation of the varying degree of transannular interaction in tris(2-pyridylmethyl)azaphosphatrane (TPAP) when coordinated to transition metals ions in different oxidation states.

Chapter 4 describes the attempted reactivity of transition metal complexes of TPAP with small molecules such as H₂, O₂, and CO₂.
INTRODUCTION

0.1. Proazaphosphatranes (Verkade’s Superbases)

Proazaphosphatranes are powerful non-ionic organic bases. Proazaphosphatranes have demonstrated great utility and versatility in synthetic chemistry, and have been used as stochiometric bases,\textsuperscript{1-17} organic catalysts\textsuperscript{18-46} and ligands in organometallic reactions.\textsuperscript{47-60} Pioneered by the late John G. Verkade, the “molecular football” shaped compound is commonly known as Verkade’s Superbase.\textsuperscript{61-63} The term “Superbase” is given to organic compounds whose basicity is greater than that of 1,8-bis(dimethylamino)naphthalene (proton sponge), which have a pK\textsubscript{a} of 18.6 (conjugate acid form) in acetonitrile.\textsuperscript{64} The pK\textsubscript{a} of the protonated form of proazaphosphatranes ranges from 31.6 to 33.6 in acetonitrile depending on the substituents attached to the equatorial nitrogen atoms (R) (Chart 0.1). The most basic site on proazaphosphatrane is the phosphorus center,\textsuperscript{65} which owes its extreme basicity to the electron donation from its three neighboring equatorial nitrogen atoms, and the potential formation of a stable three-centered four-electron transannular interaction between P and N\textsubscript{ax}.\textsuperscript{66, 67}

Chart 0.1. Protonation of proazaphosphatranes (Verkade’s Superbases) with a generic proton. The pK\textsubscript{a} values of the conjugate acid shown in the table to the right, with various R groups.

<table>
<thead>
<tr>
<th>R</th>
<th>pK\textsubscript{a} (CH\textsubscript{3}CN)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me</td>
<td>32.90</td>
</tr>
<tr>
<td>\textsuperscript{i}Pr</td>
<td>33.63</td>
</tr>
<tr>
<td>\textsuperscript{i}Bu</td>
<td>33.53</td>
</tr>
<tr>
<td>Bz</td>
<td>31.60</td>
</tr>
</tbody>
</table>
0.2. Expanding the Use of Proazaphosphatranes

Outside of Verkade’s work on proazaphosphatranes in the 1990s and early 2000s, most groups have been using proazaphosphatranes as stochiometric bases, particularly in inorganic chemistry. The recent development of proazaphosphatranes outside of their use as stochiometric bases started in the 2010s, with effort from Martinez and coworkers. The design of a molecular cage that incorporated the azaphosphatrane system is established (Figure 0.1) for the catalytic conversation of CO$_2$ into cyclic carbonates. The “Cage Effect” found by Martinez and coworkers described an increase in stability of the organocatalyst by protecting the azaphosphatrane framework from potential deactivation pathways. In addition, Martinez and coworkers expanded the use of their azaphosphatrane caged systems to encapsulate anions from water.

![Figure 0.1](image-url)

**Figure 0.1.** Chemical structures of the work done by (left) Stephan’s group, (middle) Krempner’s group and (right) Martinez’s group on expanding the use of azaphosphatranes.
Krempner et al., along with work by Stephan et al. have been investigating proazaphosphatranes as strong Lewis bases in frustrated Lewis acid-base pair systems. They noted the ability of proazaphosphatranes to activate Si-H and Si-C bonds in Verkade’s previous work, and subsequently examined the activation of H-H bond of H₂ and C=O bond of CO₂ (Figure 0.1). Krempner et al. demonstrated the frustrated Lewis acid-base pair, with isopropyl-proazaphosphatrane as the Lewis base could not only activate H₂, but could also catalyze the hydrogenation of imines. Stephan et al. demonstrated the smaller sterically constrained methyl-proazaphosphatrane cooperatively activated CO₂ with B(C₆F₅)₃. Furthermore, the classical Lewis adduct of the methyl-proazaphosphatrane/B(C₆F₅)₃ activated other small molecules in the same way as fully frustrated Lewis acid-base pair systems.

More recently, the successful use of proazaphosphatranes as ligands in organometallic cross-coupling reactions have prompted the laboratory of Martinez and Johnson to explore the coordination chemistry of proazaphosphatranes (Figure 0.2). Martinez’s group structurally characterized a gold-azaphosphatrane complex by applying a synthetic approach similar to that for gold-N-heterocyclic carbene (NHC) complexes. Martinez concluded by stating that proazaphosphatrane should make interesting alternatives to NHC, due to their shared properties, such as high basicity, efficiency as organic catalysts, strong electron donating ability and the similarities between the azaphosphatrane salts and imidazolium salts as pre-ligands (precursors). Johnson’s group structurally characterized several palladium-azaphosphatrane complexes, and investigated the effects of the transannular interaction in azaphosphatranes during palladium
catalyzed cross-coupling reactions. From these two studies, proazaphosphatranes are found to display unique properties as ligands. Yet, complexation studies with various transition metals have been lacking. In addition, the ligand design of proazaphosphatranes have been limited to alkyl substituents, thereby restricting its growth as ligands in organometallic catalysis. A modular synthetic pathway can help expand the proazaphosphatrane beyond its mono-dentate framework and increase its stability as a ligand through the chelate effect.

![Figure 0.2. Chemical structures of transition metal complexes of isobutyl-azaphosphatrane by (left) Martinez’s group and (right) Johnson’s group.](image)

### 0.3. Research Goals

The research presented in this dissertation is a synthetic inorganic approach to advancing the design of proazaphosphatranes as ligands in inorganic and organometallic chemistry. The facile modification of proazaphosphatranes will be utilized to increase the denticity and flexibility of the framework. Structural characterization of inorganic complexes with modified proazaphosphatranes will reveal the unique coordination environment and properties of the proazaphosphatrane ligands. Small molecule activation, such as CO₂, H₂ and O₂ will be explored, along with attempted stabilization of high valent transition metal ions.
The chapters of this dissertation follows the schematic outline in Chart 0.2, where Chapter 1 reveals the strong donor-ability of proazaphosphatranes (outlined in purple in Chart 0.2), Chapter 2 presents the facile modification of proazaphosphatranes incorporating pyridine and other functional donors (outlined in blue in Chart 0.2), Chapter 3 displays the coordination mode and unique transannular interaction of the modified azaphosphatranes (outlined in red and green in Chart 0.2), Chapter 4 demonstrates the reactivity of transition metal azaphosphatranes complexes with small molecules (outlined in orange in Chart 0.2).

**Chart 0.2.** Proazaphosphatranes Framework with Various Donor Groups and Transition Metal Ions Employed in this Research.

Data found in this dissertation were collected using nuclear magnetic resonance (NMR), ultraviolet-visible (UV-vis), infrared (IR) and electron paramagnetic resonance (EPR) spectroscopies, mass spectrometry, elemental analysis, X-ray crystallography and cyclic voltammetry.
0.4. References


CHAPTER 1

The Electronic and Steric Tolman Parameters of Proazaphosphatrane: Synthesis, Characterization, and Measurements

Portions of this chapter have been published:

1.1. Motivation and Specific Aims

Proazaphosphatranes are widely utilized as ligands in organometallic catalysis, but a fundamental understanding of why these proazaphosphatranes are good ligands is lacking. Insights into the properties of the proazaphosphatranes can be obtained by measuring their steric and electron parameters. Key elemental steps in organometallic catalysis, such as oxidative addition and reductive elimination are highly dependent on the electronic and steric parameters of the ligand. This chapter describes the experimental determination of the Tolman electronic parameters (TEP) and cone angles for a series of substituted proazaphosphatranne ligands. Tolman parameters of phosphine ligands are classically determined by the synthesis of their respective Ni(L^R)(CO)_3 complexes and evaluating their steric parameters and CO vibrational frequencies. The complexes Ni(L^{Me})(CO)_3 (1), Ni(L^{iPr})(CO)_3 (2), Ni(L^{iBu})(CO)_3 (3) and Ni(L^{Bz})(CO)_3 (4) are synthesized and their properties are compared to previously described Ni(phosphine)(CO)_3 complexes.

1.2. Background

Phosphines are ubiquitous ligands in transition metal synthesis\textsuperscript{1} and catalysis,\textsuperscript{2,3} as their steric and electronic properties can be easily tuned \textit{via} substituent modification.\textsuperscript{4} The relative stereoelectronic effects between phosphine ligands are most commonly evaluated by the Tolman electronic parameter (TEP) and cone angle (Figure 1.1).\textsuperscript{5}
Figure 1.1. Chemdraw depicting the Tolman Electronic (TEP) and Steric Parameter (cone angle Θ) of a generic Ni(phosphine)(CO)₃.⁵

Proazaphosphatranes are monodentate phosphines that serve as ligands in organometallic catalysis. Recently, mechanistic insights were provided with Pd catalyzed C-C cross-coupling reactions utilizing the isobutyl version of proazaphosphatrane.⁷ Although prior studies suggested that proazaphosphatranes (colloquially known as Verkade’s Superbases) are strong electron donor ligands,⁸⁻¹⁰ the Tolman parameters had never been measured. In this chapter, experimental measurements of the TEP and cone angle for a series of proazaphosphatranes (L) with various functionalities (Lᵣ, R = Me, iPr, iBu, and Bz) are presented. The corresponding Ni(Lᵣ)(CO)₃ complexes were synthesized, shown in Chart 1.1 as complexes 1-4. The TEP was evaluated by the infrared vibrational stretching frequencies of the CO bonds,¹¹ and the cone angle was measured using X-ray crystallographic analysis of complexes 2-5.¹² The Tolman electronic parameters for the proazaphosphatranes place them among the most electron donating phosphine ligands. The TEPs are comparable to P(iBu)₃, the most donating phosphine measured by Tolman, and only recently exceeded by a series of imidazolin-2-ylideaminophosphines.¹³ The cone angles are also
larger compared to the equivalently substituted trialkyl phosphines. The combined electron donor strength and large steric size of proazaphosphatranes is likely an important factor in their successful use as ligands in Pd and Pt catalyzed C–C,14-17 C–N,9,18-23 and C–Si24 bond coupling reactions.

Chart 1.1. Series of Ni(CO)x (x = 2 or 3) complexes of Verkade’s Superbases. Reproduced by permission of The Royal Society of Chemistry.

1.3. Results and Discussion

1.3.1. Synthesis and Structure of Ni(L^R)(CO)_3 Complexes (1-4)

Bis(1,5-cyclooctadiene)nickel(0) was added to a solution of L^R (L = P(RNCH_2CH_2)_3N, R = Me, iBu, iPr and Bz) in THF. After stirring for 1 hour, CO gas (1 atm) was added and the respective products were isolated by recrystallization to furnish Ni(L^Me)(CO)_3 (1), Ni(L^iPr)(CO)_3 (2), Ni(L^iBu)(CO)_3 (3), and Ni(L^Bz)(CO)_3 (4) in 84, 87, 74 and 93% yield, respectively. Complexes 1-4 were analyzed by ^1H, ^13C, and ^31P NMR spectroscopies (shown in Experimental Details), and their purity was confirmed by elemental analysis.
Solution infrared spectra of 1-4 in CH$_2$Cl$_2$ displayed two CO vibrational stretches assigned to the A$_1$ and E vibrational modes (Figure 1.2). The A$_1$ resonances for 1-4 are at 2057.0, 2054.6, 2054.9, and 2059.1 cm$^{-1}$, and the E resonances are at 1977.7, 1974.7, 1975.3, and 1981.1 cm$^{-1}$, respectively. The values are also listed in Table 1.1.

![IR spectra of complexes 1-4](image)

**Figure 1.2.** IR spectra of (purple) Ni(L$^{Me}$)(CO)$_3$ (1), (green) Ni(L$^{Pr}$)(CO)$_3$ (2), (red) Ni(L$^{Bu}$)(CO)$_3$ (3) and (brown) Ni(L$^{Bz}$)(CO)$_3$ (4) in CH$_2$Cl$_2$. Reproduced by permission of The Royal Society of Chemistry.

Single crystals suitable for X-ray analysis were grown from slow evaporation of pentane solutions of 2-4. Crystallographic data and selected bond distances and angles are given in Tables 1.2 and 1.3, respectively. The structures are shown in Figure 1.3 and are used to determine the cone angles for L$^R$. 
Table 1.1. CO vibrational frequencies (in CH₂Cl₂) and cone angle of complexes 1-4 and selected Ni(CO)₃(PR₃) complexes. Reproduced by permission of The Royal Society of Chemistry.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\tilde{\nu}_{co}$ A₁ (cm⁻¹)</th>
<th>$\tilde{\nu}_{co}$ E (cm⁻¹)</th>
<th>Cone Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(CO)₃(LMe) (1)</td>
<td>2057.0</td>
<td>1977.7</td>
<td>152⁺</td>
</tr>
<tr>
<td>Ni(CO)₃(LiPr) (2)</td>
<td>2054.6</td>
<td>1974.7</td>
<td>179</td>
</tr>
<tr>
<td>Ni(CO)₃(LiBu) (3)</td>
<td>2054.9</td>
<td>1975.3</td>
<td>200</td>
</tr>
<tr>
<td>Ni(CO)₃(LBz) (4)</td>
<td>2059.1</td>
<td>1981.1</td>
<td>207</td>
</tr>
<tr>
<td>Ni(CO)₃(P(tBu))b</td>
<td>2056.1</td>
<td>1971</td>
<td>182</td>
</tr>
<tr>
<td>Ni(CO)₃(P(Me))b</td>
<td>2064.1</td>
<td>1982</td>
<td>118</td>
</tr>
<tr>
<td>Ni(CO)₃(P(iPr)₃)b</td>
<td>2059.2</td>
<td>1977</td>
<td>160</td>
</tr>
<tr>
<td>Ni(CO)₃(P(iBu)₃)b</td>
<td>2059.7</td>
<td>-------</td>
<td>143</td>
</tr>
<tr>
<td>Ni(CO)₃(P(Bz)₃)b</td>
<td>2066.2</td>
<td>1986</td>
<td>165</td>
</tr>
</tbody>
</table>

a. Cone angle is measured from crystal structure of 5.  
b. TEP values taken from Tolman et al.⁵

Most Ni(phosphine)(CO)₃ complexes prepared by Tolman were not structurally characterized. Instead, cone angles were determined by a space-filling CPK (Corey–Pauling–Koltun) model based on a tetrahedral coordination geometry and a P–Ni bond length of 2.28 Å.²⁵ Consistent with this model, the structures of 2-4 display near ideal tetrahedral geometries with $\tau_4$ values of 0.977, 0.955, and 0.968, respectively, where $\tau_4 = 1$ represents a tetrahedral geometry and $\tau_4 = 0$ represents a square planar geometry.²⁶ The P–Ni distances of 2-4 are 2.2680(5), 2.2519(3) and 2.2424(5) Å, respectively. Although the P–Ni distances are slightly shorter, Tolman remarked that variations of up to 0.1 Å “seldom change the cone angle by more than 3 or 4°”.⁵ Therefore, the structurally determined cone angles are consistent with the parameters originally reported by Tolman using the CPK model. The values for the P–Ni bond lengths in 2-4 display an inverse relationship with Tolman’s cone angle parameters. Additionally, more electronegative substituents on the proazaphosphatranes (R = Bz > iBu > iPr)²⁷ results in shorter P–Ni bond lengths. The
observed trend is consistent with Tolman’s observation that more electronegative substituents increase the phosphorus s orbital character, which shortens the bond.\textsuperscript{5}

1.3.2. Synthesis and Structure of Ni(L\textsuperscript{Me})\textsubscript{2}(CO)\textsubscript{2} Complex (5)

Complex 5 was synthesized and crystallized in a similar fashion as complexes 2-4, in order to experimentally measure the cone angle of L\textsuperscript{Me}. Ni(L\textsuperscript{Me})\textsubscript{2}(CO)\textsubscript{2} (5) was synthesized from a 2:1 ratio of L\textsuperscript{Me} and bis(1,5-cyclooctadiene)nickel(0) in THF under an atmosphere of CO gas. Upon exposure to CO the color changed from dark orange to colorless. The crude product was recrystallized from CH\textsubscript{2}Cl\textsubscript{2} to give the product in 62\% yield. Complex 5 was characterized by \textsuperscript{1}H, \textsuperscript{13}C, and \textsuperscript{31}P NMR and IR spectroscopies (shown in Experimental Details), and the purity was confirmed by elemental analysis. Single crystals suitable for X-ray analysis were grown from slow evaporation of a diethyl ether solution. The structure of 5 shown in Figure 1.3, displays a tetrahedral geometry around Ni with $\tau_4$ values of 0.971.\textsuperscript{26} Crystallographic data and selected bond distances and angles are given in Tables 1.2 and 1.3, respectively.
Figure 1.3. Crystal structure of Ni(L^{Pr})(CO)_3 (2), Ni(L^{Bu})(CO)_3 (3), Ni(L^{Bz})(CO)_3 (4) and Ni(L^{Me})_2(CO)_2 (5). Thermal ellipsoids are drawn at 80% probability; hydrogen atoms are omitted for clarity. Carbon atoms from the minor part of a disorder in 3 are also omitted. Reproduced by permission of The Royal Society of Chemistry.
Table 1.2. Crystallographic data and refinement parameters for complexes 2-5. Reproduced by permission of The Royal Society of Chemistry.

<table>
<thead>
<tr>
<th>Complex</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C₁₈H₃₃N₄O₃PNi</td>
<td>C₂₁H₃₉N₄O₃PNi</td>
<td>C₃₀H₃₃N₄O₃PNi</td>
<td>C₂₉H₂₄N₄O₃P₂Ni</td>
</tr>
<tr>
<td>Molar Mass</td>
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<td>485.24</td>
<td>587.28</td>
<td>547.27</td>
</tr>
<tr>
<td>Crystal System</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space Group</td>
<td>P2(1)/n</td>
<td>P2(1)/n</td>
<td>P2(1)/n</td>
<td>P2(1)/n</td>
</tr>
<tr>
<td>T[K]</td>
<td>133(2)</td>
<td>88(2)</td>
<td>133(2)</td>
<td>133(2)</td>
</tr>
<tr>
<td>a[Å]</td>
<td>9.4521(6)</td>
<td>10.4524(5)</td>
<td>9.7263(8)</td>
<td>8.5551(5)</td>
</tr>
<tr>
<td>b[Å]</td>
<td>16.0515(11)</td>
<td>17.9047(8)</td>
<td>23.412(2)</td>
<td>19.4034(12)</td>
</tr>
<tr>
<td>c[Å]</td>
<td>14.5677(10)</td>
<td>13.5993(6)</td>
<td>12.5881(11)</td>
<td>15.9663(1)</td>
</tr>
<tr>
<td>α[°]</td>
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<td>90.00</td>
<td>90.00</td>
<td>90.00</td>
</tr>
<tr>
<td>β[°]</td>
<td>93.8772(8)</td>
<td>97.2348(6)</td>
<td>99.3160(10)</td>
<td>104.7970(10)</td>
</tr>
<tr>
<td>γ[°]</td>
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<td>90.00</td>
<td>90.00</td>
<td>90.00</td>
</tr>
<tr>
<td>V[Å³]</td>
<td>2205.2(3)</td>
<td>2524.8(2)</td>
<td>2828.6(4)</td>
<td>2562.5(3)</td>
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<tr>
<td>Z</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
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<tr>
<td>D(calcld) [Mgm⁻³]</td>
<td>1.335</td>
<td>1.277</td>
<td>1.379</td>
<td>1.419</td>
</tr>
<tr>
<td>μ(Mo-Kα) [mm⁻¹]</td>
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<td>0.859</td>
<td>0.781</td>
<td>0.916</td>
</tr>
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<td>-11 ≤ h ≤ 11</td>
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<td>-25 ≤ k ≤ 25</td>
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<td></td>
<td>-19 ≤ l ≤ 19</td>
<td>-18 ≤ l ≤ 18</td>
<td>-16 ≤ l ≤ 17</td>
<td>-21 ≤ l ≤ 21</td>
</tr>
<tr>
<td>Reflection Collected</td>
<td>24569</td>
<td>31264</td>
<td>70276</td>
<td>62910</td>
</tr>
<tr>
<td>Independent Reflections</td>
<td>5360</td>
<td>6479</td>
<td>7270</td>
<td>6562</td>
</tr>
<tr>
<td>Data/Restrains/Parameters</td>
<td>5360 / 0 / 250</td>
<td>6479 / 0 / 431</td>
<td>7270 / 0 / 352</td>
<td>6562 / 0 / 304</td>
</tr>
<tr>
<td>R₁, wR₂ [I &gt; 2σ(I)]</td>
<td>0.0359, 0.0749</td>
<td>0.0272, 0.0665</td>
<td>0.0400, 0.1283</td>
<td>0.0232, 0.1097</td>
</tr>
<tr>
<td>R₁, wR₂ [all data]</td>
<td>0.0544, 0.0810</td>
<td>0.0341, 0.0701</td>
<td>0.0470, 0.1393</td>
<td>0.0242, 0.1122</td>
</tr>
<tr>
<td>GOF</td>
<td>1.220</td>
<td>1.029</td>
<td>1.168</td>
<td>1.056</td>
</tr>
</tbody>
</table>

Table 1.3. Selected distances and angles of 2-5. Reproduced by permission of The Royal Society of Chemistry.

<table>
<thead>
<tr>
<th>Complex</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5⁵</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-Ni (Å)</td>
<td>2.2680(5)</td>
<td>2.2519(3)</td>
<td>2.2424(5)</td>
<td>2.2320(3)</td>
</tr>
<tr>
<td>P-N2 (Å)</td>
<td>1.6927(14)</td>
<td>1.6899(11)</td>
<td>1.6879(13)</td>
<td>1.6892(9)</td>
</tr>
<tr>
<td>P-N3 (Å)</td>
<td>1.6900(14)</td>
<td>1.6885(11)</td>
<td>1.6824(13)</td>
<td>1.6902(9)</td>
</tr>
<tr>
<td>P-N4 (Å)</td>
<td>1.6894(14)</td>
<td>1.6876(11)</td>
<td>1.6890(13)</td>
<td>1.6939(9)</td>
</tr>
<tr>
<td>C-O1 (Å)</td>
<td>1.140(2)</td>
<td>1.1385(17)</td>
<td>1.146(2)</td>
<td>1.1500(15)</td>
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<td>C-O2 (Å)</td>
<td>1.143(2)</td>
<td>1.1447(18)</td>
<td>1.140(2)</td>
<td>1.1506(14)</td>
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<tr>
<td>C-O3 (Å)</td>
<td>1.133(2)</td>
<td>1.1404(18)</td>
<td>1.142(2)</td>
<td></td>
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<tr>
<td>N2-P-Ni (°)</td>
<td>114.59(5)</td>
<td>113.93(4)</td>
<td>112.74(5)</td>
<td>112.92(3)</td>
</tr>
<tr>
<td>N3-P-Ni (°)</td>
<td>113.96(5)</td>
<td>113.77(4)</td>
<td>114.01(5)</td>
<td>120.25(3)</td>
</tr>
<tr>
<td>N4-P-Ni (°)</td>
<td>115.05(5)</td>
<td>115.12(4)</td>
<td>115.49(5)</td>
<td>113.12(3)</td>
</tr>
<tr>
<td>N4-P-N3 (°)</td>
<td>103.34(7)</td>
<td>104.00(5)</td>
<td>105.32(6)</td>
<td>102.74(5)</td>
</tr>
<tr>
<td>N3-P-N2 (°)</td>
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<td>104.18(5)</td>
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</tr>
<tr>
<td>N2-P-N4 (°)</td>
<td>104.46(7)</td>
<td>104.64(5)</td>
<td>104.32(6)</td>
<td>102.71(4)</td>
</tr>
</tbody>
</table>

⁵one of the two LMe measurements in complex 5
1.3.3. Tolman Electronic Parameters and Cone Angles of Ni(L^3)(CO)₃ Complexes (1-4)

The electronic and steric properties of the strongest electron donating trialkyl substituted phosphines measured by Tolman⁵ are used as a comparison to the proazaphosphatranes summarized in Table 1.1 and shown in Figure 1.4. Complexes of 1-3 display CO vibrational frequencies similar to those reported for the most donating alkyl-phosphine ligand, P(tBu)₃ (Ni(P(tBu)₃)(CO)₃, \( \tilde{v}_{\text{co}} = 2056.1 \text{ cm}^{-1} \)), while the CO vibrational frequency of complex 4 is closer to those observed for the acyclic triaminophosphine ligand (Ni(P(NMe₂)₃)(CO)₃, \( \tilde{v}_{\text{co}} = 2061.9 \text{ cm}^{-1} \)).⁵ The trend in electron donor properties of the trisubstituted proazaphosphatrane follows the same trend as the trialkyl substituted phosphines originally measured by Tolman (stronger donor > weaker donor: iPr ≥ iBu > Me > Bz). However, the overall strength of electronic donation for the proazaphosphatranes is greater than that of the equivalently substituted tertiary phosphine.

![Figure 1.4](image.png)

**Figure 1.4.** Comparison of Tolman electronic parameter (TEP) and cone angles. Red dots (●) represent proazaphosphatranes measured herein and black dots (●) represent phosphines measured by Tolman.⁵ Reproduced by permission of The Royal Society of Chemistry.
The greater overall donor strengths of the proazaphosphatranes are primarily due to the replacement of the alkyl functionalities on the phosphine with alkyl-substituted amine donors. Amine substituents are known to increase the strength of electron donation when bound to phosphorus ligands. A prior study by Woollins et al. systematically investigated this effect on acyclic phosphines and determined that the strength of phosphorus electron donation increases after the first and second P–C bonds are replaced by P–N bonds. However, the replacement of the third P–C bond with a P–N bond results in a decrease in the electron donor strength because the effect of a stronger σ donor is outweighed by the electron-withdrawing character of the more electronegative nitrogen atoms due to steric constraints. This phenomenon is observable in the X-ray crystal structure of acyclic tris(dialkylamino)phosphine ligands, where two of the nitrogen atoms are nearly planar (sum of angles at nitrogen ~ 360°) and one of the nitrogens is not (sum of the angles at nitrogen < 350°) (Figure 1.5). As a result, the two planar nitrogen atoms can donate electron density to the phosphorus through their lone pairs, which are nearly orthogonal to the phosphorus lone pair. However, the third nitrogen only contributes electron-withdrawing character due to its orientation (anti) to the lone pair on phosphorus (Figure 1.5). In contrast, structural characterizations of the cyclic proazaphosphatrane ligands in this chapter (Figure 1.3) demonstrate that all three nitrogens bound to the phosphorus are nearly planar (sum of angles at nitrogen = 358 to 360°). Verkade et al. hypothesized that the rigid bicyclic framework of the proazaphosphatrane molecule constrains all three nitrogens to adopt this geometry, resulting in stronger overall electron-donating character compared to the previously studied acyclic tris(dialkylamino)phosphines.
Figure 1.5. Proposed electronic properties of a generic tri(dialkylamino)phosphine and the metrical parameters observed from crystal structures.

Overall, the proazaphosphatranes exhibit greater cone angles compared to the equivalent trialkyl substituted phosphines. In fact, L^{Bz} displayed a cone angle close to the highest cone angle (P(mesityl)_3 = 212°) measured by Tolman.\(^5\) The TEP vs. cone angle for L^R in 1-4 (using Tolman cone angle measured from the structure of 5 for 1) are graphed along with comparable phosphines in Figure 1.4, which demonstrates that while the cone angle of proazaphosphatranes are highly substituent dependent, they all maintain their strong electron donating character.

1.4. Conclusion

The first experimentally measured Tolman electronic parameters and cone angles for a series of proazaphosphatranes are presented. The proazaphosphatranes in this study display lower TEPs and greater cone angles compared to equivalently substituted trialkyl phosphines. The unique cyclic structure of the proazaphosphatranes contributes to its high donor strength, which is also greater than comparable acyclic triaminophosphines. Another interesting feature of the
proazaphosphatranes is the large effect that alkyl substitution plays on the cone angle while having a negligible effect on the electron donor strength. This property allows the steric bulk to be independently tuned. The quantification of Tolman parameters for proazaphosphatranes permits the rational modification of steric and electronic properties for this synthetically modular class of ligands.

1.5. Experimental Details

General Considerations

The complexes described below are air- and moisture-sensitive, and must be handled under an inert atmosphere of nitrogen using standard glovebox and Schlenk techniques. Unless otherwise noted, all procedures were performed at ambient temperature (21-24 °C). All solvents were sparged with argon and dried using a solvent purification system. Tetrahydrofuran, pentane, diethyl ether, and dichloromethane were passed through two columns of neutral alumina. Compounds 2,8,9-tribenzyl-2,3,8,9-tetraaza-1-phosphabicyclo[3,3,3]undecane (L_{Bz}^{3}), and 2,8,9-triisopropyl-2,3,8,9-tetraaza-1-phosphabicyclo[3,3,3]undecane (L_{Pr}^{3}) \textsuperscript{34} were synthesized according to established procedures. C_{6}D_{6} was freeze-pump-thawed three times and dried over molecular sieves. 2,8,9-trimethyl-2,3,8,9-tetraaza-1-phosphabicyclo[3,3,3]undecane (L_{Me}^{3}) was purchased from Sigma-Aldrich with unspecified purity; therefore further extraction with pentane was necessary to obtain the product in high purity. 2,8,9-triisobutyl-2,3,8,9-tetraaza-1-phosphabicyclo[3,3,3]undecane (L_{Bu}^{3}), bis(1,5-cyclooctadiene) nickel(0) (98%), and carbon monoxide (100%) were purchased from commercial sources and used without further purification.
Physical Methods

Nuclear Magnetic Resonance (NMR) Spectroscopy: Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker DRX500 spectrometer fitted with a TCI cryoprobe ($^{13}$C) or a DRX400 with a switchable QNP probe ($^1$H and $^{31}$P) in dry, degassed solvents. $^1$H NMR spectra were referenced to (tetramethylsilane) TMS using the residual proteo impurities of the solvent; $^{13}$C NMR spectra were referenced to TMS using the natural abundance $^{13}$C of the solvent; $^{31}$P NMR spectra were referenced to H$_3$PO$_4$ using the Ξ scale with the corresponding $^1$H spectra. All chemical shifts are reported in the standard δ notation in parts per million; positive chemical shifts are to a higher frequency from the given reference.

Infrared (IR) Spectroscopy: Infrared (IR) absorption measurements of the solution of 1-5 in CH$_2$Cl$_2$ was taken in a OMNI-Cell CaF$_2$ sealed cell (1.00 mm) on a Thermo Scientific Nicolet iS5 spectrophotometer with an iD1 transmission attachment.

Elemental Analysis (EA): Elemental analyses were performed on a PerkinElmer 2400 Series II CHNS elemental analyzer or on an Exeter Analytical, Inc. CE-440 Elemental Analyzer.

X-ray Crystallography (XRC): X-ray diffraction studies were carried out at the UCI Department of Chemistry X-ray Crystallography Facility on a Bruker SMART APEX II diffractometer. Data was collected at 88K for 3 and 133K for 2, 4, and 5 using Mo Kα radiation ($\lambda = 0.71073$ Å). A full sphere of data was collected for each crystal structure. The APEX2 program suite was used to determine unit-cell parameters and for collection. (30 sec/frame scan time for a sphere of diffraction data). The raw frame data were processed
and absorption corrected using the SAINT and SADABS programs, respectively, to yield the reflection data files. Structures were solved by direct methods using SHELXS and refined against $F^2$ on all data by full-matrix least squares with SHELXL-97. The analytical scattering factors for neutral atoms were used throughout the analysis. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at geometrically calculated positions and refined using a riding model, and their isotropic displacement parameters were fixed at 1.2 (1.5 for methyl groups) times the Ueq of the atoms to which they are bonded. For structure 3, carbon atoms C(16), C(17) and C(18) were disordered and modeled using multiple components with partial site-occupancy-factors.

**General Synthesis of Ni(L\textsuperscript{R})(CO)\textsubscript{3} Complexes**

In the glove box, a solution of bis(1,5-cyclooctadiene)nickel(0) (1 equiv.) in 5 mL of tetrahydrofuran was added to a solution of L\textsuperscript{R} (1 equiv.) in 5 mL of tetrahydrofuran. The solution was stirred for 1 hour at room temperature. The solution was then transferred to a 100 mL Schlenk flask and brought out of the glove box and filled with CO gas (1 atm). The solution was stirred overnight under a CO atmosphere, after which the solution became colorless. The solvent was removed under reduced pressure and the resulting light yellow solid was brought back into the glove box and dissolved in diethyl ether or pentane. Colorless crystals were grown from slow evaporation of diethyl ether (1) or pentane (2-4).
Ni(LMe)(CO)₃ (1): LMe (74.5 mg, 0.345 mmol) and bis(1,5-cyclooctadiene)nickel(0) (94.8 mg, 0.345 mmol). 84% Yield. ¹H NMR (C₆D₆, 400 MHz) δ = 2.39 (br, 9H, CH₃NP), 2.47 (s, 6H, NCH₂CH₂NP), 2.50 (s, 6H, NCH₂CH₂NP). ¹³C{¹H} NMR (C₆D₆, 126 MHz) δ = 35.8 (CH₃NP), 50.4 (NCH₂CH₂NP), 50.6 (NCH₂CH₂NP), 199 (CO). ³¹P NMR (C₆D₆, 162 MHz) δ = 136. FTIR (CH₂Cl₂): ν = 2057.0 (CO-A₁), 1977.7 (CO-E). Analytical Calculation for C₁₂H₂₁N₄NiO₃P: C, 40.15; H, 5.90; N, 15.61 Found: C, 39.67; H, 5.99; N, 15.15.

**Figure 1.6.** ¹H NMR spectrum of Ni(LMe)(CO)₃ (1) in C₆D₆.
Figure 1.7. $^{13}$C NMR spectrum of Ni($L_{	ext{Me}}$(CO)$_3$ (1) in C$_6$D$_6$.

Figure 1.8. $^{31}$P NMR spectrum of Ni($L_{	ext{Me}}$(CO)$_3$ (1) in C$_6$D$_6$. 

28
Ni(L^{Pr})(CO)_3 (2): L^{Pr} (194 mg, 0.647 mmol) and bis(1,5-cyclooctadiene)nickel(0) (178 mg, 0.647 mmol). 87% Yield. $^1$H NMR (C_6D_6, 400 MHz) δ = 1.04 (d, $J = 6.6$ Hz, 18H, NCH(CH_3)_2), 2.55-2.69 (A_2B_2, 12H, CH_2CH_2NP), 3.90 (septet, $J = 6.7$ Hz, 3H, NCH(CH_3)_2). $^{13}$C {$^1$H} NMR (C_6D_6, 126 MHz) δ = 22.7 (NCH(CH_3)_2), 39.9 (CH_2CH_2NP), 49.7 (NCH(CH_3)_2), 54.8 (CH_2CH_2NP), 199 (CO). $^{31}$P NMR (C_6D_6, 162 MHz) δ = 137. FTIR (CH_2Cl_2): $\tilde{\nu} = 2054.6$ (CO-A_1), 1974.7 (CO-E). Analytical Calculation for C_{18}H_{33}N_{4}NiO_{3}P: C, 48.79; H, 7.51; N, 12.64 Found: C, 48.75; H, 7.39; N, 12.58.

Figure 1.9. $^1$H NMR spectrum of Ni(L^{Pr})(CO)_3 (2) in C_6D_6.
Figure 1.10. $^{13}$C NMR spectrum of Ni($^{1}$Pr)(CO)$_{3}$ (2) in C$_{6}$D$_{6}$.

Figure 1.11. $^{31}$P NMR spectrum of Ni($^{1}$Pr)(CO)$_{3}$ (2) in C$_{6}$D$_{6}$.
Ni(L^{Bu})(CO)_3 (3): L^{Bu} (195 mg, 0.569 mmol) and bis(1,5-cyclooctadiene)nickel(0) (157 mg, 0.569 mmol). 74% Yield. $^1$H NMR (C$_6$D$_6$, 400 MHz) $\delta = 0.94$ (d, $J = 6.7$ Hz, 18H, NCH$_2$CH(CH$_3$)$_2$), 2.06 (septet, $J = 6.9$ Hz, 3H, NCH$_2$CH(CH$_3$)$_2$), 2.55 (t, $J = 4.8$ Hz, 6H, CH$_2$CH$_2$NP), 2.82-2.67 (br, 12H, NCH$_2$CH$_2$NP, NCH$_2$CH(CH$_3$)$_2$). $^{13}$C\{$^1$H\} NMR (C$_6$D$_6$, 126 MHz) $\delta = 21.1$ (NCH$_2$CH(CH$_3$)$_2$), 28.8 (NCH$_2$CH(CH$_3$)$_2$), 48.2 (NCH$_2$CH$_2$NP), 50.3 (NCH$_2$CH$_2$NP), 55.4 (NCH$_2$CH(CH$_3$)$_2$), 199 (CO). $^{31}$P NMR (C$_6$D$_6$, 162 MHz) $\delta = 141$. FTIR (CH$_2$Cl$_2$): $\tilde{\nu} = 2054.9$ (CO-A$_1$), 1975.3 (CO-E). Analytical Calculation for C$_{21}$H$_{39}$N$_4$NiO$_3$P: C, 51.98; H, 8.10; N, 11.55 Found: C, 51.56; H, 7.94; N, 11.86.

![Figure 1.12](image)

Figure 1.12. $^1$H NMR spectrum of Ni(L^{Bu})(CO)$_3$ (3) in C$_6$D$_6$.  

31
Figure 1.13. $^{13}$C NMR spectrum of Ni($^{i}$Bu)(CO)$_3$ (3) in C$_6$D$_6$.

Figure 1.14. $^{31}$P NMR spectrum of Ni($^{i}$Bu)(CO)$_3$ (3) in C$_6$D$_6$. Resonances around 20 ppm are due to oxidized $^{i}$Bu.$^{35}$
**Ni(L^Bz)(CO)\textsubscript{3} (4):** L^Bz (146 mg, 0.328 mmol) and bis(1,5-cyclooctadiene)nickel(0) (90.0 mg, 0.328 mmol). 93% Yield. \textsuperscript{1}H NMR (C\textsubscript{6}D\textsubscript{6}, 400 MHz) δ = 2.45 (t, J = 4.8 Hz, 6H, NCH\textsubscript{2}CH\textsubscript{2}NP), 2.68 (br, 6H, NCH\textsubscript{2}CH\textsubscript{2}NP), 4.31 (br, 6H, PhCH\textsubscript{2}NP), 7.14 (m, 3H, p-Ph), 7.30 (t, J = 7.7 Hz, 6H, m-Ph), 7.40 (d, J = 7.3 Hz, 6H, o-Ph). \textsuperscript{13}C {\textsuperscript{1}H} NMR (C\textsubscript{6}D\textsubscript{6}, 126 MHz) δ = 46.7 (NCH\textsubscript{2}CH\textsubscript{2}NP), 49.9 (NCH\textsubscript{2}Ph), 50.7 (NCH\textsubscript{2}CH\textsubscript{2}NP), 128 (Ph), 128 (Ph), 129 (Ph), 139 (Ph), 198 (CO). \textsuperscript{31}P NMR (C\textsubscript{6}D\textsubscript{6}, 162 MHz) δ = 143. FTIR (CH\textsubscript{2}Cl\textsubscript{2}): ν = 2059.1 (CO-A\textsubscript{1}), 1981.1 (CO-E). Analytical Calculation for C\textsubscript{30}H\textsubscript{33}N\textsubscript{4}NiO\textsubscript{3}P: C, 61.36; H, 5.66; N, 9.54 Found: C, 61.02; H, 5.64; N, 9.48.

**Figure 1.15.** \textsuperscript{1}H NMR spectrum of Ni(L^Bz)(CO)\textsubscript{3} (4) in C\textsubscript{6}D\textsubscript{6}.
Figure 1.16. $^{13}$C NMR spectrum of Ni(L$_{Bz}$)(CO)$_3$ (4) in C$_6$D$_6$.

Figure 1.17. $^{31}$P NMR spectrum of Ni(L$_{Bz}$)(CO)$_3$ (4) in C$_6$D$_6$. 
**Ni(L^Me)_2(CO)_2 (5):** In the glove box, a solution of bis(1,5-cyclooctadiene)nickel(0) (26.2 mg, 0.093 mmol) in 5 mL of tetrahydrofuran was added to a solution of L^Me (41.2 mg, 0.191 mmol) in 5 mL of tetrahydrofuran. The solution was stirred for 1 hour at room temperature. The solution was transferred to a 100 mL Schlenk flask, brought out of the glove box, and filled with CO gas (1 atm). The solution was stirred overnight under a CO atmosphere, during which time the color changed from dark orange to colorless. The solvent was removed under reduced pressure and the resulting light yellow solid was brought back into the glove box and washed with pentane. Colorless crystals of 5 were grown from slow evaporation of dichloromethane to give the product in 62% yield. ¹H NMR (C₆D₆, 400 MHz) δ = 2.61 (s, 18H, CH₃NP), 2.74 (d, J = 8.7 Hz, 24H, NCH₂CH₂NP). ¹³C {¹H} NMR (C₆D₆, 126 MHz) δ = 36.2 (CH₃NP), 50.6 (NCH₂CH₂NP), 51.1 (NCH₂CH₂NP), 204 (CO). ³¹P NMR (C₆D₆, 162 MHz) δ = 144. FTIR (CH₂Cl₂): ʋ = 1976.8 (CO), 1909.3 (CO). Analytical Calculation for C₂₀H₄₂N₈NiO₂P₂: C, 43.90; H, 7.74; N, 20.48 Found: C, 43.51; H, 7.79; N, 20.49.
Figure 1.18. $^1$H NMR spectrum of Ni($^{Me}$)2(CO)$_2$ (5) in C$_6$D$_6$.

Figure 1.19. $^{13}$C NMR spectrum of Ni($^{Me}$)$_2$(CO)$_2$ (5) in C$_6$D$_6$.
Figure 1.20. $^{31}$P NMR spectrum of Ni(L$_{Me}$)$_2$(CO)$_2$ (5) in C$_6$D$_6$.

Figure 1.21. IR spectrum Ni(L$_{Me}$)$_2$(CO)$_2$ (5) in CH$_2$Cl$_2$. 
1.6. References


CHAPTER 2

Expanding the Denticity of Proazaphosphatrane:

Ligand Synthesis

Portions of this chapter have been published:

2.1. Motivation and Specific Aims

Proazaphosphatranes are strong, non-ionic bases that are easily modifiable. However, the functionalization of proazaphosphatranes outside of simple alkyl groups is lacking in the literature. Current interest in proazaphosphatranes has expanded their use outside of simple acid/base chemistry, highlighting the multilateral utility of this electron rich molecule. In this chapter, the facile synthesis of proazaphosphatrane that incorporates heteroatom donors, (2-pyridine, 3-pyridine, 4-(2-pyridinyl-benzene), furan and 2-methylthiophene) for use as ligands in inorganic complexes with primary and secondary coordination effects is reported (Chart 2.1).

**Chart 2.1.** Series of Proazaphosphatrane Compounds with Various Functional Groups.

\[ R = \text{Me, Et, iPr, iBu and Bz} \]

Verkade et al.

This Chapter

\[ R = \text{ } \]

\[ \text{1H, 13C, and 31P NMR spectra, along with high resolution mass spectra of these compounds are presented. A solid state structure from X-ray crystallographic analysis of protonated ([tris(2-pyridylmethyl)proazaphosphatrane-H]chloride) and the unprotonated form (tris(3-pyridylmethyl)-proazaphosphatrane) are also included.} \]
2.2. Background

There are numerous publications highlighting the properties\textsuperscript{6-10} and utility\textsuperscript{11, 12} of proazaphosphatranes. The majority of proazaphosphatranes used in these studies have alkyl substituents, due to their commercial availability (Chart 2.1).\textsuperscript{2, 40, 42, 43, 45} However, there have been recent efforts to expand and develop the design of proazaphosphatranes, for use in anion binding,\textsuperscript{46} enhanced organic\textsuperscript{47} and organometallic\textsuperscript{39} catalysis, and immobilization on solid silica support (See Introduction).\textsuperscript{48, 49} In addition, proazaphosphatranes are highly modular, with facile synthetic approaches to incorporate various functional groups. This chapter seeks to advance the proazaphosphatrane framework, by incorporate multi-donor atom sites, for the purpose of increasing chelating stability and/or potential secondary coordination effects in inorganic complexes.

In this chapter, the facile synthesis of symmetric proazaphosphatranes bearing heteroatoms donors, (2-pyridine, 3-pyridine, 4-(2-pyridinyl-benzene), furan and 2-methylthiophene) is reported (Chart 2.1).

2.3. Results and Discussion

2.3.1. Synthesis of Tri-Substituted Tris(2-aminoethyl)amines

The compounds, tris[((2-pyridyl)methyl)-amino]ethyl]-amine (1a), tris[((3-pyridyl)methyl)-amino]ethyl]-amine (2a), tris[[(furan)methyl]-amino]ethyl]-amine (3a) and tris[[(2-methylthiophene)methyl]-amino]ethyl]-amine (5a) were synthesized with slight modifications from previously published procedures.\textsuperscript{54-56} The new compound tris[[(4-(2-pyridyl)benzyl)-amino]ethyl]-amine (4a) is synthesized via the Schiff-base condensation of a 3:1
ratio of 4-(2-pyridyl)benzaldehyde to tris(2-aminoethyl)-amine in methanol, followed by hydrogenation with H\textsubscript{2} gas and a Pd/C catalyst (Scheme 2.1). After work-up, a waxy white solid (4a) was isolated in a 79.1 percent yield. Spectroscopic and ESI-MS data confirmed the identity of 4a. This general synthesis works well with aldehydes, providing easy access to various donor groups (R in Scheme 2.1), albeit, only neutral donors have so far been incorporated.

**Scheme 2.1.** Synthesis of tri-substituted tris(2-aminoethyl)amine.

\[
\text{N(CH}_2\text{CH}_2\text{NH}_2)_3 + 3 \text{ RCH}=\text{O} \xrightarrow{1 \text{ atm H}_2 / 10\% \text{ Pd/C MeOH}} \text{N(CH}_2\text{CH}_2\text{NHCH}_2\text{R})_3
\]

\[
\begin{array}{c}
\text{R} = \begin{array}{c}
(1) \\
(2) \\
(3) \\
(4) \\
(5)
\end{array}
\end{array}
\]

2.3.2. Synthesis of Protonated Tri-Substituted Azaphosphatranes

The addition of excess bis(dimethylamino)chlorophosphine to 1a-5a yielded the protonated azaphosphatranne compounds 1b-5b along with the by-product, dimethylamine (Scheme 2.2). The latter can be removed by excessive washing with tetrahydrofuran. Drying the resulting solid under reduced pressure overnight furnishes [HP((2-PyrCH\textsubscript{2})-NCH\textsubscript{2}CH\textsubscript{2})\textsubscript{3}N][Cl] (1b) as a white solid in 61.9 percent yield. The compounds 2b-5b were not fully characterized due to high levels of impurities of the by-product, dimethylamine. However, the $^{31}$P\textsuperscript{1H} NMR spectra of 2b-5b confirmed the presence of one phosphorus atom around -10.0 ppm, corresponding to the product. The $^{31}$P\textsuperscript{1H} NMR spectrum of 1b features a singlet at -10.0 ppm, which appears as a
doublet in the $^{31}\text{P}$ NMR spectrum with a $J$-coupling of 506 Hz, consistent with previously published protonated azaphosphatranes (see Experimental Details).\(^6\)

**Scheme 2.2.** Synthesis of protonated tri-substituted azaphosphatranes.

Single crystals suitable for X-ray analysis were grown by layering diethyl ether over a solution of 1b in acetonitrile. The solid-state structure of compound 1b displayed a P–N1 distance of 1.971(16) Å and a P–H distance of 1.24(2) Å (Figure 2.1). These bond distances are similar to previously reported protonated forms of Verkade’s Superbases.\(^2\), \(^18\) The significant Brönsted basicity of Verkade’s superbase ($\text{pK}_a$ of protonated superbase = 32.9 in CH$_3$CN)\(^4\) is attributed to electron donation from the trans nitrogen atom (N$_{\text{ax}}$, or N1 in structure of 1b) to the phosphorus, which stabilizes the protonated form. This strong interaction between the P and N$_{\text{ax}}$ has been observed in prior structural characterization of protonated versus non-protonated bases.\(^5\) When protonated, the P–N$_{\text{ax}}$ distances are typically 2.0 Å or less, while the corresponding free bases have P–N$_{\text{ax}}$ distances of over 3.0 Å.
2.3.3. Synthesis of Tri-Substituted Proazaphosphatrane

After the isolation of the protonated azaphosphatrane compounds 1b-5b, excess KO'Bu is added to deprotonate the protonated azaphosphatranes, providing the symmetric tri-substituted proazaphosphatrane compounds 1c-5c, in 85.4, 55.7, 79.1, 59.1 and 59.1 percent yield (Scheme 2.3). The presence of the dimethylamine by-product in 2b-5b does not hinder the deprotonation step. Compounds 1c-5c were characterized by 1H, 13C{1H}, and 31P{1H} NMR spectroscopies. The composition of 1c-5c was confirmed through electrospray ionization mass spectrometry.
Scheme 2.3. Synthesis of Tri-Substituted Proazaphosphatranes

The $^{31}\text{P}$ NMR spectra of $1\text{c-5c}$ displayed shifts at 126.4, 127.1, 126.9, 127.3 and 125.7 ppm, respectively. Compound $1\text{c-5c}$ were performed in $C_6D_6$ in order to compare the $^{31}\text{P}$ NMR shifts to the alkyl-substituted proazaphosphatranes (Table 2.1), measured by Verkade co-workers.\textsuperscript{2, 34, 41-43} The $^{31}\text{P}\{^1\text{H}\}$ NMR shifts of $1\text{c-5c}$ in $C_6D_6$ are in the range of the symmetric benzyl substituted proazaphosphatranes (127.9 ppm in Table 2.1), likely due to the aromatic ring system. Compound $1\text{c-5c}$ are downfield shifted relative to the symmetric methyl (120.8 ppm), ethyl (119.4 ppm) and isopropyl-substituted (118.7 ppm) proazaphosphatranes, except for the symmetric isobutyl-substituted (130.9 ppm) proazaphosphatane (Table 2.1). Interestingly, the upfield trend observed in the $^{31}\text{P}$ NMR shift from methyl to isopropyl-substitution of Verkade’s Superbases does not continue with the isobutyl group. Instead, a downfield shift ($\Delta$12.2 ppm going from isopropyl to isobutyl-substituted proazaphosphatane) is observed. This trend is opposite to what is seen with alkyl phosphines.\textsuperscript{57} However, the trend observed for Verkade’s asymmetric proazaphosphatranes (where isobutyl groups are replaced with benzyl groups) does fall in line with the expected observation of an upfield $^{31}\text{P}$ NMR shift, due to a less electron donating group.
Table 2.1. $^{31}$P NMR values of 1c-5c and various alkyl- and benzyl-substituted proazaphosphatranes in C$_6$D$_6$ reported by Verkade et al. Greyed out rows represent asymmetric proazaphosphatranes.

![Diagram of proazaphosphatranes]

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In addition, an X-ray quality crystal of compound 2c was grown from a concentrated sample of 2c in tetrahydrofuran/pentane mixture at -35°C. The crystal structure of 2c displayed a P1-N6 distance of 3.322 Å, similar to other previously published proazaphosphatranes (Figure 2.2).$^{18, 20, 24, 58-60}$ All three P-N$_{eq}$ distances are close, measuring 1.696, 1.697 and 1.702 Å for P1-N1, P1-N2, and P1-N4, respectively. In addition, the sum of angles at nitrogen (N1, N2, and N4) is $\sim$360°, due to the rigid cage frame of proazaphosphatranes.$^{34}$ The combination of these two metrics indicate all three equatorial nitrogen atoms donate their electron density to the phosphorus contributing to its donor strength.
Figure 2.2. Crystal structure of \([P((3-PyrCH_2)\text{NCH}_2\text{CH}_2)_3\text{N}] (2c)\). Thermal ellipsoids are drawn at 50% probability; hydrogen atoms were omitted for clarity.

2.4. Conclusion

The design of proazaphosphatranes expanded to incorporate heteroatom donors for use as ligands in inorganic complexes. Incorporation of the N, O, and S donors involved a facile synthesis of amine precursors, which goes through a well-known Schiff-based reaction, followed by hydrogenation. Coordination studies of the tris(2-pyridylmethyl)-azaphosphatrane (1c) ligand with transition metal ions will be focused on in Chapter 3.

2.5. Experimental Details

General Considerations

Compounds 1c-5c described below are moisture-sensitive, and must be handled under an inert atmosphere of nitrogen using standard glovebox and Schlenk techniques. Unless otherwise noted, all procedures were performed at ambient temperature (21-24 °C). All solvents were sparged with argon and dried using a solvent purification system.
Tetrahydrofuran, pentane, diethyl ether, and dichloromethane were passed through two columns of neutral alumina. Compounds tris[((2-pyridyl)methyl)-amino]ethyl]amine, tris[((3-pyridyl)methyl)-amino]ethyl]amine, tris[((furan)methyl)-amino]ethyl]amine and tris[((2-methylthiophene)methyl)-amino]ethyl]amine were synthesized according to established procedures.\textsuperscript{54-56} \textsuperscript{13}C\textsubscript{6}D\textsubscript{6} and CD\textsubscript{3}N were freeze-pump-thawed three times and dried over molecular sieves. Furfural, 3-methyl-2-thiophenecarboxyaldehyde, 3-pyridinecarboxyaldehyde, 2-pyridinecarboxyaldehyde, 4-(2-pyridyl)benzaldehyde, bis(dimethylamino)chlorophosphine, Pd/C (10%) and potassium tert-butoxide were purchased from commercial sources and used without further purification.

**Physical Methods**

**Nuclear Magnetic Resonance (NMR) Spectroscopy:** Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker DRX500 spectrometer fitted with a TCI cryoprobe (\textsuperscript{1}H and \textsuperscript{13}C), a Bruker AVANCE 600 MHz (\textsuperscript{1}H, \textsuperscript{13}C, and \textsuperscript{31}P) or a DRX400 with a switchable QNP probe (\textsuperscript{1}H and \textsuperscript{31}P). \textsuperscript{1}H NMR spectra were referenced to (tetramethylsilane) TMS using the residual proton signal of the solvent; \textsuperscript{13}C NMR spectra were referenced to TMS using the natural abundance \textsuperscript{13}C of the solvent; \textsuperscript{31}P NMR spectra were referenced to an internal H\textsubscript{3}PO\textsubscript{4} sample in D\textsubscript{2}O or to H\textsubscript{3}PO\textsubscript{4} using the Ξ scale with the corresponding \textsuperscript{1}H spectra. All chemical shifts are reported in the standard δ notation in parts per million.

**Mass Spectrometry (MS):** High resolution mass spectra (HR-MS) and electrospray ionization mass spectra (ESI-MS) were obtained on a Micromass LCT and collected at the University of California-Irvine Mass Spectrometry Facility.
**X-ray Crystallography (XRC):** X-ray Crystallography. X-ray diffraction studies were carried out at the UCI Department of Chemistry X-ray Crystallography Facility on a Bruker SMART APEX II diffractometer. Data were collected at 296 K for 1b and 88 K for 2c using Mo Kα radiation (λ = 0.710 73 Å). A full sphere of data was collected for each crystal structure. The APEX2 program suite was used to determine unit-cell parameters and to collect data. The raw frame data were processed and absorption corrected using the SAINT and SADABS programs, respectively, to yield the reflection data files. Structures were solved by direct methods using SHELXS and refined against F2 on all data by full-matrix least-squares with SHELXL-97. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms other than H1 in 1b were placed at geometrically calculated positions and refined using a riding model, and their isotropic displacement parameters were fixed at 1.2 (1.5 for methyl groups) times the Ueq of the atoms to which they are bonded. H1 in 1b was located in the difference map and refined freely. For the structure of 1b, checkCIF reports three level B alerts (PLAT230_ALERT_2_B) due to unequal anisotropic displacement parameters (ADPs) along chemical bonds, which can signify an incorrect atom type assignment. However, we are confident in our assignments, as all three alerts involve bonds within a pyridine ring of the TPAP ligand whose identity has been confirmed through other spectroscopic techniques. An additional level B alert (PLAT411_ALERT_2_B) was reported for this structure due to a short nonbonding intermolecular H···H distance between two ligand hydrogen atoms (H21 and H23); this is likely a result of crystal packing. For the structure of 2c, a finalized structure is yet to be collected. All values are reported using preliminary data.
Tris[[4-(2-pyridyl)benzyl]-amino][ethyl]amine (4a): 4-(dimethylamino)benzaldehyde (1.00 g, 5.46 mmol) was added to a stirred solution of tris(2-aminoethyl)-amine (266 mg, 1.82 mmol) in 60 mL of dry methanol. A 10% palladium on activated carbon (500 mg) was added and the reaction was brought outside the glovebox and put under one atmosphere of H₂ for 12 h at room temperature. The reaction mixture was filtered off using a Büchner funnel and washed with 15 mL of dry methanol. The filtrate was dried under reduced pressure at 50 °C, producing a waxy solid in 79.1% yield. 

\[ \text{1H NMR (CDCl}_3, 500 MHz) \delta = 1.75 (b, 3H, NH), 2.62 (t, 6H, CH}_2CH}_2N), 2.72 (t, 6H, NCH}_2CH}_2), 3.81 (s, 6H, PhCH}_2N), 7.17 (t, 3H, Py), 7.35 (d, 6H, Ph), 7.62 (m, 6H, Py), 7.88 (d, 6H, Ph), 8.65 (d, 3, Py). \] 

\[ \text{13C\(_\{1H\}\) NMR (CDCl}_3, 126 MHz) \delta = 47.39, 53.98, 54.44, 120.6, 122.1, 127.1, 128.6, 136.8, 138.1, 141.6, 149.8, 157.4. \]

Figure 2.3. $^1$H NMR spectrum of tris[(4-(2-pyridyl)benzyl)-amino]ethyl]amine (4a) in CDCl$_3$.

Figure 2.4. $^{13}$C{$^1$H} NMR spectrum of tris[(4-(2-pyridyl)benzyl)-amino]ethyl]amine (4a) in CDCl$_3$. 

53
[HP((2-PyrCH₂)-NCH₂CH₂)₃N][Cl] (1b): In the glovebox, a solution of 1a (200 mg, 0.476 mmol) in 5 mL of tetrahydrofuran was added to a solution of bis(dimethylamino)-chlorophosphine (111 mg, 0.715 mmol) in 10 mL of tetrahydrofuran. The mixture was stirred overnight, at which time a white solid precipitated out of solution. The solution was filtered through a medium fritted funnel, the precipitate was washed with tetrahydrofuran, and the solvent was removed on the high vacuum line to afford a white solid in 61.9% yield. Single crystals suitable for X-ray analysis were grown by layering diethyl ether over a solution of 1b in acetonitrile. $^1$H NMR (CD₃CN, 400 MHz) δ = 3.16 (m, 6H, PNC₂H₂N), 3.25 (m, 6H, PNC₂H₂N), 4.25 (d, $J = 19.1$ Hz, 6H, PyrCH₂N), 5.84 (d, $J = 506$ Hz, 1H, P-H), 7.23 (m, 3H, Pyr), 7.28 (d, $J = 7.8$ Hz, 3H, Pyr), 7.70 (td, $J = 7.7$, 1.9 Hz, 3H, Pyr), 8.51 (d, $J = 5.5$ Hz, 3H, Pyr). $^{13}$C{$^1$H} NMR (CD₃CN, 126 MHz) δ = 40.25, 47.91, 53.39, 122.6, 123.4, 137.87, 150.5, 159.2. $^{31}$P{$^1$H} NMR (CD₃CN, 162 MHz) δ = −10.00. $^{31}$P NMR (CD₃CN, 162 MHz) δ = −10.00 (d, $^{1}J_{P-H} = 506$ Hz). ESI-MS (m/z): [M − Cl]$^+$ calcd for C₂₄H₃₁N₇P, 448.27; Found, 448.23.
Figure 2.5. $^1$H NMR spectrum of $[\text{HP((2-PyrCH}_2\text{-NCH}_2\text{CH}_2)_3\text{N}}]\text{[Cl]}$ (1b) in CD$_3$CN.

Figure 2.6. $^{31}$P{$^1$H} NMR spectrum of $[\text{HP((2-PyrCH}_2\text{-NCH}_2\text{CH}_2)_3\text{N}}]\text{[Cl]}$ (1b) in CD$_3$CN.
Figure 2.7. $^{31}$P NMR spectrum of [HP((2-PyrCH$_2$)-NCH$_2$CH$_2$)$_3$N][Cl] (1b) in CD$_3$CN.

Figure 2.8. $^{13}$C-$^1$H NMR spectrum of [HP((2-PyrCH$_2$)-NCH$_2$CH$_2$)$_3$N][Cl] (1b) in CD$_3$CN.
General Synthesis of 1c-5c: In the glove box, ~1.5 equivalents of bis(dimethylamino)chlorophosphine was added to a solution of 1a-5d in 10 mL of dichloromethane. The mixture was stirred for 1 day. Diethyl ether was added to this solution, producing a white precipitate. The mixture was filtered through a medium fritted funnel to afford a white solid. The white solid was taken to the next step without further purification. In the glove box, ~2 equivalents of potassium tert-butoxide were added to a suspension of the white solid in 10 mL of tetrahydrofuran. The mixture was stirred for 1 day, during which time a white solid (KCl) precipitated out of solution. The solution was filtered through a medium fritted funnel. The filtrate was collected and the solvent was removed under reduced pressure. The solid was re-dissolved in acetonitrile and once again filtered through a medium fritted funnel in order to separate out excess potassium tert-butoxide and KCl. Acetonitrile was removed under reduced pressure and the solid was re-dissolved in dry tetrahydrofuran and layered with dry pentane. After 1 day of standing, the solution was filtered from crystalline KCl and the solvents from the filtrate were removed under reduced pressure to obtain products (1c-5c).
[P((2-PyrCH2)-NCH2CH2)3N] (1c): Potassium tert-butoxide (148 mg, 0.132 mmol) was added in this step of the reaction producing a white solid in 85.4% yield. 1H NMR (CD3CN, 400 MHz) \( \delta = 2.76 \) (m, 6H, PNCH2CH2N), 2.84 (m, 6H, PNCH2CH2N), 4.29 (d, \( J = 10.8 \) Hz, 6H, PyrCH2N), 7.19 (m, 3H, Pyr), 7.47 (m, 3H, Pyr), 7.71 (td, \( J = 7.6, 1.8 \) Hz, 3H, Pyr), 8.49 (m, 3H, Pyr). 13C{1H} NMR (CD3CN, 126 MHz) \( \delta = 47.2, 51.7, 55.8, 122.8, 122.9, 137.5, 150.0, 162.5 \). 31P{1H} NMR (CD3CN, 162 MHz) \( \delta = 126.6 \). 31P{1H} NMR (C6D6, 243 MHz) \( \delta = 126.6 \). ESI-MS (m/z): [M + H]+ calecd for C24H31N7P, 448.27; Found, 448.27.

Figure 2.9. 1H NMR spectrum of [P((2-PyrCH2)-NCH2CH2)3N] (1c) in CD3CN.
Figure 2.10. $^{31}$P NMR spectrum of $[\text{P}((2\text{-PyrCH}_2)\text{-NCH}_2\text{CH}_2)_3\text{N}]$ (1c) in CD$_3$CN.

Figure 2.11. $^{31}$P $^1$H NMR spectrum of $[\text{P}((2\text{-PyrCH}_2)\text{-NCH}_2\text{CH}_2)_3\text{N}]$ (1c) in C$_6$D$_6$. 
Figure 2.12. $^{13}\text{C}^{1}\text{H}$ NMR spectrum of [P((2-PyrCH$_2$)-NCH$_2$CH$_2$)$_3$N] (1c) in CD$_3$CN.
[P((3-PyrCH₂-NCH₂CH₂)₂N] (2c): Bis(dimethylamino)chlorophosphine (0.690 mg, 0.446 mmol) and 2a (122 mg, 0.290 mmol) were mixed in the first step. Potassium tert-butoxide (0.066 mg, 0.58 mmol) was added in the second step of the reaction producing a white solid in 55.7% yield. Colorless crystals were grown from a concentrated sample of tetrahydrofuran/pentane mixture at -35°C. ¹H NMR (CD₃CN, 500 MHz) δ = 2.75 (s, 12H, CH₂CH₂N), 4.19 (d, 6H, PyrCH₂N), 7.29 (m, 3H, Py), 7.71 (m, 3H, Py), 8.45 (m, 3H, Py), 8.53 (m, 3H, Py). ¹³C{¹H}NMR (CD₃CN, 126 MHz) δ = 46.08, 50.81, 51.37, 124.3, 136.5, 137.5, 149.2, 150.5. ³¹P{¹H}NMR (C₆D₆, 243 MHz) δ = 127.1. HR-ESI-MS (m/z): [M+H]⁺ calcd for C₂₄H₃₀N₇P 448.2; found 448.1.
Figure 2.13. $^1$H NMR spectrum of [P((3-PyrCH$_2$)-NCH$_2$CH$_2$)$_3$N] (2e) in CD$_3$CN.

Figure 2.14. $^{31}$P{$^1$H} NMR spectrum of [P((3-PyrCH$_2$)-NCH$_2$CH$_2$)$_3$N] (2e) in C$_6$D$_6$. 

62
Figure 2.15. $^{13}$C($^1$H) NMR spectrum of [P(3-PyrCH$_2$)-NCH$_2$CH$_2$)$_3$N] (2e) in CD$_3$CN.
[P((Furan-CH$_2$)-NCH$_2$CH$_2$)$_3$N] (3c): Bis(dimethylamino)chlorophosphine (0.51 mg, 0.33 mmol) and 3a (137 mg, 0.211 mmol) were mixed in the first step. Potassium tert-butoxide (.048 mg, 0.43 mmol) was added in the second step of the reaction producing a white solid in 59.1% yield. $^1$H NMR (CD$_3$CN, 600 MHz) $\delta = 2.82$ (m, 12H, CH$_2$CH$_2$N), 4.28 (d, 6H, PhCH$_2$N), 7.27 (m, 3H, Py), 7.48 (d, 6H, Py), 7.80 (m, 6H, Ph), 8.01 (m, 6H, Ph), 8.63 (m, 3H, Py). $^{13}$C{$^1$H}NMR (CD$_3$CN, 151 MHz) $\delta = 46.48$, 51.56, 53.24, 121.1, 123.2, 127.6, 129.4, 137.9, 138.8, 143.6, 150.6, 157.7. $^{31}$P{$^1$H}NMR (C$_6$D$_6$, 243 MHz) $\delta = 127.3$. HR-ESI-MS ($m/z$): [M+H]$^+$ calcd for C$_{42}$H$_{42}$N$_7$P 676.3; found 676.6.

Figure 2.16. $^1$H NMR spectrum of [P((Furan-CH$_2$)-NCH$_2$CH$_2$)$_3$N] (3c) in CD$_3$CN.
Figure 2.17. $^{31}P{^{1}H}$ NMR spectrum of [P((Furan-CH$_2$)-NCH$_2$CH$_2$)$_3$N] (3c) in C$_6$D$_6$.

Figure 2.18. $^{13}C{^{1}H}$ NMR spectrum of [P((Furan-CH$_2$)-NCH$_2$CH$_2$)$_3$N] (3c) in CD$_3$CN.
[P((2-Pyr-Ph-CH\textsubscript{2})-NCH\textsubscript{2}CH\textsubscript{2})\textsubscript{3}N] (4c): Bis(dimethylamino)chlorophosphine (138 mg, 0.893 mmol) and 4a (230 mg, 0.595 mmol) were mixed in the first step. Potassium tert-butoxide (148 mg, 1.32 mmol) was added in the second step of the reaction producing a yellow oil in 76.9% yield. \(^1\)H NMR (CD\textsubscript{3}CN, 600 MHz) \(\delta = 2.71\) (m, 12H, NCH\textsubscript{2}CH\textsubscript{2}), 4.05 (d, 6H, CH\textsubscript{2}N), 6.20 (m, 3H, C\textsubscript{4}H\textsubscript{2}O), 6.34 (m, 3H, C\textsubscript{4}H\textsubscript{2}O), 7.41 (m, 3H, C\textsubscript{4}H\textsubscript{2}O). \(^{13}\)C\(^{\{1\}H}\) NMR (CD\textsubscript{3}CN, 151 MHz) \(\delta = 46.20, 47.45, 51.88, 107.4, 110.9, 142.4, 155.9\). \(^{31}\)P\(^{\{1\}H}\) NMR (C\textsubscript{6}D\textsubscript{6}, 243 MHz) \(\delta = 126.9\). HR-ESI-MS (m/z): [M+H]\(^+\) calcd for C\textsubscript{21}H\textsubscript{27}N\textsubscript{4}PO\textsubscript{3} 415.2; found 415.0.

Figure 2.19. \(^1\)H NMR spectrum of [P((2-Pyr-Ph-CH\textsubscript{2})-NCH\textsubscript{2}CH\textsubscript{2})\textsubscript{3}N] (4c) in CD\textsubscript{3}CN.
Figure 2.20. $^{13}$C{$^{1}$H} NMR spectrum of [P((2-Pyr-Ph-CH$_2$)-NCH$_2$CH$_2$)$_3$N] (4c) in CD$_3$CN.

Figure 2.21. $^{31}$P{$^{1}$H} NMR spectrum of [P((2-Pyr-Ph-CH$_2$)-NCH$_2$CH$_2$)$_3$N] (4c) in C$_6$D$_6$. 
[P((2-CH3-Thiophene-CH2)-NCH2CH2)3N] (5c): Bis(dimethylamino)chlorophosphine (124 mg, 0.801 mmol) and 5a (253 mg, 0.531 mmol) were mixed in the first step. Potassium tert-butoxide (131 mg, 1.17 mmol) was added in the second step of the reaction producing a white oily solid in 59.1% yield. $^1$H NMR (CD$_3$CN, 600 MHz) $\delta = 2.18$ (s, 9H, CH$_3$), 2.80 (m, 12H, NCH$_2$CH$_2$), 4.23 (m, 6H, CH$_2$N), 6.80 (m, 3H, C$_4$H$_2$S), 7.13 (m, 3H, C$_4$H$_2$S). $^{13}$C $\{^1$H$\}$NMR (CD$_3$CN, 151 MHz) $\delta = 13.83, 45.99, 46.53, 51.69, 123.5, 131.0, 134.3, 140.2$. $^{31}$P $\{^1$H$\}$NMR (C$_6$D$_6$, 243 MHz) $\delta = 125.7$. HR-ESI-MS (m/z): [M+H]$^+$ calcd for C$_{24}$H$_{33}$N$_4$PS$_3$ 505.2; found 505.0.

Figure 2.22. $^1$H NMR spectrum of [P((2-CH$_3$-Thiophene-CH$_2$)-NCH$_2$CH$_2$)$_3$N] (5c) in CD$_3$CN.
Figure 2.23. $^{31}\text{P} \{^1\text{H}\}$ NMR spectrum of $[\text{P}(\text{2-CH}_3\text{-Thiophene-CH}_2)\text{-NCH}_2\text{CH}_2)_3\text{N}]$ (5c) in C$_6$D$_6$.

Figure 2.24. $^{13}\text{C} \{^1\text{H}\}$ NMR spectrum of $[\text{P}(\text{2-CH}_3\text{-Thiophene-CH}_2)\text{-NCH}_2\text{CH}_2)_3\text{N}]$ (5c) in CD$_3$CN.
2.6. References


CHAPTER 3

Tracking the Transannular Bond Interaction in Tris(2-pyridylmethyl)-azaphosphatrane (TPAP) with Various Transition Metal ions

Portions of this chapter have been published:


Computational analysis in this chapter was performed by graduate student Drew W. Cunningham.
3.1. Motivation and Specific Aims

Flexible ligands that can adapt their donor strength have enabled unique reactivity in a wide range of inorganic complexes. Most examples are composed of flexible multi-dentate ligands containing a donor that can vary its interaction through its distance to the metal center. This chapter describes an alternative type of adaptable ligand interaction in the neutral multi-dentate ligand tris(2-pyridylmethyl)-azaphosphatrane (TPAP) which contains a proazaphosphatrane unit. Proazaphosphatrane can accept additional electron density from a tertiary nitrogen to form a transannular bond upon coordination of the P to more Lewis acidic atoms (Figure 3.1).

Figure 3.1. Chemdraw structures of azaphosphatrane in three different forms based on the transannular distance of P–N_{ax}.

An experimental investigation of the varying degree of transannular interaction in TPAP coordinated to late transition metals in different oxidation states is reported. The synthesis and characterization of the complexes M(TPAP), where M = Co(I)Cl, [Co(II)(CH_{3}CN)](BF_{4})_{2}, Ni(0)(1,5-cyclooctadiene), [Ni(II)(CH_{3}CN)](BF_{4})_{2}, [Pd(II)(CH_{3}CN)](BF_{4})_{2}, or [Pt(II)Cl](PF_{6}) are described. Structural characterization and density functional theory of these complexes establish a significant increase in the degree of transannular interaction of the proazaphosphatrane unit when...
coordinated to more electron deficient metal ions. Additionally, an effort to synthesize a Co(III)TPAP complex is presented to investigate the transannular bond of CoTPAP in three different oxidation states.

3.2. Background

Ligands that can adapt their donor strength provide a versatile method for adjusting electronic structure in order to access reactive transition metal intermediates. For example, Peters et al. extensively explored first row transition metal complexes with tripodal phosphine ligands containing a B, C, or Si heteroatom, where the interaction between the metal and heteroatom adjusts depending on the metal oxidation state and identity of ligands trans to the interaction (Figure 3.2a).1-7 Parkin et al. demonstrated that the flexible interactions of an apical carbon in atrane-type ligands contributed to unique reactivity,8-10 and that the interaction can be modified through ligand design (Figure 3.2b).11,12 Lu et al. designed tripodal ligands that encapsulate a Lewis acidic cation that can tune the electronic structure and reactivity at the metal (Figure 3.2c).13-16 In addition, the Agapie17-31 and Meyer32-34 labs have utilized phenyl or mesitylene linkers strategically positioned near a metal to serve as electron reservoirs to support multi-electron reactivity (Figure 3.2d). In all of the above cases, the adaptable interaction was incorporated into flexible chelating ligands, and the degree of interaction can be evaluated by the metal-donor distance.
Figure 3.2. Chemdraw structures of (a) Peters’, (b) Parkin’s, (c) Lu’s and (d) Agapie’s transition metal complexes, featuring an adaptable ligand platform.

In this chapter, the description of an alternative type of adaptable interaction will be presented. The metal and donor maintain a fixed distance, but the latter can harness electron density through a transannular interaction when coordinated to more electron deficient metals. The ligand is based on proazaphosphatranes, a structurally unique class of neutral organic superbases more commonly known as Verkade’s Superbases (Figure 3.1).\(^{35-39}\) The \(pK_a\) of the protonated form, or azaphosphatranes, ranges from 32.8 to 34.5 in acetonitrile depending on the substituents attached to the equatorial nitrogens (R).\(^{40-43}\) The extreme basicity of proazaphosphatranes stem from the formation of a stable three-centered four-electron transannular bond\(^{44}\) between P and N\(_{ax}\) upon protonation.\(^{36,45,46}\)

Verkade et al. previously utilized the P⋯N\(_{ax}\) distance as a useful indicator for evaluating the extent of the transannular interaction. Proazaphosphatranes have P⋯N\(_{ax}\) distances measured by X-ray crystallography of >3.2 Å (3.35 Å is the sum of the van der Waals radii, which assumes no bonding interactions between P and N\(_{ax}\)).\(^{39,47-52}\) In contrast, azaphosphatranes have P⋯N\(_{ax}\) distances of under 2.0 Å (compared to the two electron covalent radius between P and N\(_{ax}\) of 1.72 Å), providing structural evidence for the transannular interaction. In addition to protons, Verkade
et al. also explored the interaction of azaphosphatranes with Lewis acidic main group acceptors. In these derivatives, the P⋯N\textsubscript{ax} distance varies between 2.55 (X = NHPh) and 3.28 (X = CH\textsubscript{2}) Å (black circles, Figure 3.3). These intermediate, or “quasi” structures represent distances between the sum of the van der Waals of P and N (3.35 Å) and covalent transannular bond distance in protonated Verkade’s Superbase (R = Me, 1.97 Å).\textsuperscript{37,53} Verkade noted a correlation with the degree of transannular interaction and the Lewis acidity of the substituent on P, with the strongest interaction with a proton.\textsuperscript{54}

![Figure 3.3](Image)

Figure 3.3. (Left) A plot of the transannular distance versus the θ puckering of the axial nitrogen above the plane of the three adjacent carbon atoms for Verkade’s Superbase with various main groups (denoted in black circles ●) and TPAP with various transition metals (denoted in red diamonds ◆). (Right) Depiction of the angle, θ, as the degree of puckering of the axial nitrogen (N\textsubscript{ax}) out of the C\textsubscript{1}–C\textsubscript{3}–C\textsubscript{5} plane. Values used in this figure are from structural data. Reproduced by permission of The Royal Society of Chemistry.
Although azaphosphatranes have been used as ligands in palladium-catalyzed C–C,\textsuperscript{55-57} and C–N,\textsuperscript{58-60} cross-coupling and platinum-catalyzed hydrosilylation,\textsuperscript{61} the transannular interaction upon coordination to transition metal complexes had not been systematically interrogated at the time of this study.\textsuperscript{47, 54, 62-64} The dynamic nature of azaphosphatranes motivated this investigation into whether the P⋯N\textsubscript{ax} distance would adjust to different metals and oxidation states according to their Lewis acidity. To provide greater coordinative stability, a proazaphosphatrane unit was incorporated in a tetradentate ligand to form tris(2-pyridylmethyl)-azaphosphatrane (TPAP), shown in Chart 3.1.\textsuperscript{62, 63} The proazaphosphatrane in TPAP retains its ability to form a transannular bond; structural characterization of the protonated TPAP has a P⋯N\textsubscript{ax} distance of 1.97(16) Å.\textsuperscript{63} All three pyridine arms in TPAP can potentially coordinate to the metal ion,\textsuperscript{63} but for some of the complexes reported only one or two pyridine arms are coordinated. In this study, discussion of the structural and computational investigation of TPAP coordinated to two different metals in two different oxidation states: Co(I), Co(II) and Ni(0), Ni(II), as well as the TPAP complexes of Pd(II) and Pt(II), shown in Chart 3.1 as complexes 1-6 (and 3a). The P⋯N\textsubscript{ax} transannular distance was determined through structural characterization by X-ray crystallography. The varying degree of transannular interactions evident in the solid-state was supported by computational studies on the orbital interactions between the P and N\textsubscript{ax} atoms in complexes 1, 2, 4, 5, and 6 and an analogue of complex 3, [NiTPAP(CO)\textsubscript{2}] (complex 3a).
3.3. Results and Discussion

3.3.1. Synthesis and Structure of CoTPAP Complexes (1 & 2)

The ligand TPAP was synthesized as described in chapter 2 and previously reported.\(^{63}\) The purple complex [CoTPAP(Cl)] (1) was prepared by adding stoichiometric amounts of TPAP to Co(1)Cl(PPh\(_3\))\(_3\) in tetrahydrofuran. Complex 1 is paramagnetic with a solution \(\mu_{\text{eff}}\) of 3.34 \(\mu\)B (C\(_6\)D\(_6\)) corresponding to an \(S = 1\) system. Elemental analysis was used to confirm the analytical purity of the complex. X-ray quality crystals were grown from diethyl ether at −35 °C. The solid-state structure of complex 1 is shown in Figure 3.2 and selected bond distances and angles are shown in Table 3.1. The pseudo-tetrahedral cobalt center has a \(\tau_4\) parameter of 0.77, where a value
of 1 represents an ideal tetrahedral geometry, and a value of 0 represents an ideal square planar geometry.\textsuperscript{65} The TPAP ligand chelates in a tridentate fashion through the phosphorus donor and two of the three pyridine N atoms. The fourth coordination site is occupied by a chloride ion. In 1, TPAP has a transannular P⋯N1 distance of 3.2647(14) Å and θ (puckering of the axial nitrogen above the plane of the three adjacent carbon atoms) of $-9.1349^\circ$ (Figure 3.4, Table 3.1).

![Figure 3.4](image)

**Figure 3.4.** Crystal structure of [CoTPAP(Cl)] \((1)\). Thermal ellipsoids are drawn at 50\% probability. Hydrogen atoms and counteranions are omitted for clarity. Reproduced by permission of The Royal Society of Chemistry.

[CoTPAP(CH\textsubscript{3}CN)][BF\textsubscript{4}]\textsubscript{2} \((2)\) was prepared by reacting stoichiometric quantities of TPAP with [Co(CH\textsubscript{3}CN)\textsubscript{6}][BF\textsubscript{4}]\textsubscript{2} in acetonitrile.\textsuperscript{63} The product was precipitated and washed with diethyl ether to give the analytically pure product in 56.2\% yield. A single crystal for X-ray analysis was grown by layering pentane on a solution of 2 in dichloromethane. The structure is shown in Figure 3.5, and selected bond distances and angles are shown in Table 3.1. The Co–N\textsubscript{py} distance is similar
for all three pyridines (1.997(2), 2.035(2), and 2.094(2) Å), and the Co–P distance is 2.1693(7) Å. The ligand chelates in a tetradentate fashion, with an acetonitrile solvent taking up a fifth coordination site. The pseudo-square pyramidal cobalt center has a $\tau_5$ parameter of 0.4176, where a value of 0 represents an ideal square pyramid, and a value of 1 represents an ideal trigonal bipyramid.66

Figure 3.5. Crystal structure of [CoTPAP(CH$_3$CN)][BF$_4$]$_2$ (2). Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms and counteranions are omitted for clarity. Adapted with permission from Thammavongsy, Z.; Khosrowabadi Kotyk, J. F.; Tsay, C.; Yang, J. Y. *Inorg. Chem.* **2015**, *54*, 11505-11510. Copyright 2015 American Chemical Society.
3.3.2. Attempted Synthesis and Characterization of Co(III)TPAP Complexes (2a-c)

The first attempt of a Co(III)TPAP complex was the metalation of TPAP with Co(III)(acac)$_3$ (where acac = acetylacetonate) in acetonitrile. The color changed from green to orange after 1 day of mixing. A brown solid was obtained after solvents were removed under reduced pressure. An X-ray quality crystal was grown from the slow evaporation of the brown solid in tetrahydrofuran/diethyl ether mixture. The crystal structure displayed a [Co(II)(acac)]$^-$ complex with an outer-sphere protonated TPAP ([TPAPH]$^+$) molecule (Figure 3.6). The P–N$_{ax}$ distance in [TPAPH]$^+$ is 1.934 Å, consistent with previously published [TPAPH]$^+$ structures. The [Co(II)(acac)]$^-$ is in an octahedral geometry and the Co ion has an assigned oxidation state of +2. The proton source to generate [TPAPH]$^+$ could be from adventitious water.

![Figure 3.6](image_url)

**Figure 3.6.** Crystal structure of [Co(II)(acac)][TPAPH] (2a). Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms are omitted for clarity.
Due to the limited diversity of Co(III) starting materials, attempts were made to oxidize the known [CoTPAP(CH$_3$CN)][BF$_4$]$_2$ with AgBF$_4$. The reaction of [CoTPAP(CH$_3$CN)][BF$_4$]$_2$ with AgBF$_4$ was performed in the dark due to light sensitivity of AgBF$_4$. The reaction was filtered and an orange solution was obtained. The solution was concentrated and the $^{31}$P{$^1$H} NMR spectrum had a resonance at -20 ppm, in the range of a fully transannulated P–N$_{ax}$ bond.\textsuperscript{67} Attempts to recrystallize the product failed, producing orange oils.

Another route was tried, where CoCl$_2$, TPAP and FcBF$_4$ (where Fc = Ferrocenium) were mixed in a 1:1:1 ratio. The mixture of the CoCl$_2$ and TPAP in acetonitrile were stirred for 1 day before adding FcBF$_4$. Once the FcBF$_4$ was added, the solution turned dark green. The solvent was removed under reduced pressure and the remaining green solid was washed with diethyl ether to remove ferrocene as a yellow solution. An X-ray quality crystal was grown from a slow vapor diffusion of diethyl ether into a solution of the green product in acetonitrile. The crystal structure revealed TPAP with two counter BF$_4$ anions and an oxidized phosphorus(V) center (Figure 3.7). The P–N$_{ax}$ distance is 1.90 Å, consistent with a full transannulation of the P and N$_{ax}$.\textsuperscript{40} This structure is unique, as it represents an elusive dicationic azaphosphatrane species proposed by Verkade.\textsuperscript{68}
Surprisingly, the crystal structure from the reaction of a 1:1 ratio of CoCl$_2$ and TPAP in acetonitrile produced a CoCl$_3$(TPAPH) complex (Figure 3.8). The crystal structure displayed a protonated TPAP ([TPAPH]$^+$) with a CoCl$_3$ bound to one of the pyridine donors of TPAP. The Co metal ion is in the +2 oxidation state, where the [CoCl$_3$]$^-$ balances the positively charged ligand [TPAPH]$^+$. The P–N$_{ax}$ distance is 1.941 Å, consistent with previously published protonated TPAP molecules.$^{63}$

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**Figure 3.7.** Crystal structure of $[\text{TPAP}]^{2+}$ (2b). Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms and BF$_4$ counteranions are omitted for clarity.
Figure 3.8. Crystal structure of CoCl$_3$(TPAPH) (2c). Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms are omitted for clarity.

Thus, the attempted synthesis of Co(III)TPAP resulted in a Co(II)TPAP complex with a protonated TPAP ligand or an oxidized TPAP molecule.

3.3.3. Synthesis and Structure of NiTPAP (3, 4 & 7), PdTPAP (5) and PtTPAP (6) Complexes

[NiTPAP(COD)] (COD = 1,5-cyclooctadiene) (3) was synthesized through the reaction of stoichiometric amounts of TPAP with Ni(COD)$_2$ in tetrahydrofuran; the crude product was recrystallized from diethyl ether. Complex 3 is diamagnetic and was characterized by $^1$H and $^{31}$P{$_1$H} NMR spectroscopies. X-ray quality crystals of 3 were grown from a concentrated solution in diethyl ether at $-35$ °C; the solid-state structure is shown in Figure 3.9. In 3, TPAP coordinates in a bidentate fashion through the phosphorus donor and one of the pyridines. The P⋯N1 distance is 3.3915(17) Å and $\theta$ is $-10.9882^\circ$ (Table 3.1). The analogue of complex 3, [NiTPAP(CO$_2$)] (complex 7) was also synthesized to compare with density functional studies.
Complex 3a was synthesized in a similar fashion as complexes 3. Bis(1,5-cyclooctadiene)nickel(0) was added to a solution of TPAP in tetrahydrofuran, which produced a green intermediate complex. Once CO gas (1 atm) was introduced, the color changed from dark green to colorless. The solvent was removed and recrystallization of the crude product by slow evaporation in diethyl ether resulted in a 77% yield for 3a. Complexes 3a was characterized by $^1$H, $^{13}$C, $^{31}$P{$^1$H} NMR and IR spectroscopies, and the purity was confirmed by elemental analysis. Single crystals suitable for X-ray analysis were grown from slow evaporation of a diethyl ether solution; the solid-state structure of 3a is shown in Figure 3.10. In this chapter, the structure of complex 3a is used to computationally model a Ni(0)TPAP complex, due to difficulties in modeling complex 3.
The divalent complexes [NiTPAP(CH$_3$CN)][BF$_4$]$_2$ (4) and [PdTPAP(CH$_3$CN)][BF$_4$]$_2$ (5) were synthesized by mixing TPAP with [Ni(CH$_3$CN)$_{6.5}$][BF$_4$]$_2$ and [Pd(CH$_3$CN)$_4$][BF$_4$]$_2$, respectively in acetonitrile. Complexes 4 and 5 are diamagnetic and were characterized by $^1$H NMR spectroscopy. X-ray quality crystals were obtained using the same method. The solid-state structures of 4 (Figure 3.11a) and 5 (Figure 3.11b) are displayed below, along with selected bond distances and angles (Table 3.1). Both 4 and 5 are four coordinate square planar complexes with $\tau_4$ values of 0.20 and 0.06, respectively. The P⋯N1 distances of 4 and 5 are 2.948(2) and 2.6747(18) Å (P2⋯N9 = 2.6613(18) Å), respectively.

[PtTPAP(Cl)][PF$_6$] (6) was synthesized in two steps. PtCl$_2$(COD) was first added to TPAP in acetonitrile. After one hour, two equivalents of AgPF$_6$ were added in the dark and the solution was stirred for 5 minutes. A colorless crystal was grown from diethyl ether and acetonitrile.
Complex 6 is diamagnetic and was characterized by $^1$H and $^{31}$P{$^1$H} NMR spectroscopies. The solid-state structure of 6 is shown in Figure 3.11c and selected bond distances and angles are shown in Table 3.1. The coordination environment of 6 is similar to that of 4 and 5, except an acetonitrile ligand is replaced by a chloride anion in the inner sphere. Complex 6 is closer to a square planar coordination geometry, with a $\tau_4$ values of 0.12. TPAP in 6 displayed a P⋯N1 distance of 2.927(4) Å (P2⋯N8 = 2.821(4) Å), with $\theta$ of 8.8644°.

![Figure 3.11](image)

**Figure 3.11.** Crystal structure of (a) [NiTPAP(CH$_3$CN)][BF$_4$]$_2$ (4), (b) [PdTPAP(CH$_3$CN)][BF$_4$]$_2$ (5) and (c) [PtTPAP(Cl)][PF$_6$] (6). Structures 5 and 6 display one of two molecules in the asymmetric unit. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms and counteranions are omitted for clarity. Electron density from the minor disorder of the Pt atom in 6 is also omitted. Reproduced by permission of The Royal Society of Chemistry.
Table 3.1. Bond lengths and angles of complexes 1-6. Metrics 5 and 6 were taken from one of two molecules in the asymmetric unit. The metal ion is denoted as M. Non-italicized values are from the X-ray structural analysis and italicized values are from the geometry optimized structures calculated using quantum mechanical methods. Reproduced by permission of The Royal Society of Chemistry.

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<td>2.877(2)</td>
<td>3.3915(17)</td>
<td>2.948(2)</td>
<td>2.6747(18)</td>
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<td>2.1670(7)</td>
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<td>2.354</td>
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<td>9.9140</td>
<td>-10.9882</td>
<td>13.0123</td>
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<tr>
<td>Calc. C1-C3-C5 θ (°)</td>
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<td>16.62</td>
<td>----</td>
<td>17.32</td>
<td>18.62</td>
<td>13.79</td>
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3.3.4. Comparison of the Transannular Distance between Co(I)TPAP and Co(II)TPAP

The P⋯N1 (or P⋯Nax) distance of TPAP when bound to a Co(I) ion in complex 1 (3.2647(14) Å) indicates a minimal transannular interaction with a value closer to the “pro” (or free base) rather than the “quasi” form. An additional crystal of 1, complex 1b was grown by pentane diffusion into a concentrated tetrahydrofuran solution and exhibited a P⋯N1 distance in TPAP of 3.339(2) Å, a difference of 0.0743 Å between structures. Verkade observed that differences in crystal packing could influence the transannular distance by up to 0.1 Å, providing an estimated boundary for error in the solid-state distances. The transannular distance observed in both Co(I) structures is comparable to those found when proazaphosphatrane is coordinated to main group elements such as sulfur and oxygen (Figure 3.3).

Upon coordination of TPAP to a more Lewis acidic Co(II) ion (complex 2), the P⋯N1 distance shortens to 2.877(2) Å, a significant shift of 0.39 Å. In Figure 3.3, complex 2 is in the middle of the plot (“quasi” form of azaphosphatrane).
3.3.5. Comparison of the Transannular Distance between Group 10 TPAP Complexes

Complex 3, with a Ni(0) ion, has a P⋯N1 distance of 3.3915(17) Å, outside of the van der Waals radii of P⋯N and signifying no transannular interaction. The P⋯N1 distance of 3 falls within the range of four other previously reported Ni(0)azaphosphatrane complexes that bind in a monodentate fashion. The consistent P⋯N axial across the series highlights the fact that denticity of TPAP has little influence on the P⋯N axial transannular interaction compared to monodentate azaphosphatranes when Ni(0) is bound. When TPAP is bound to a Ni(II) ion in complex 4, the P⋯N1 distance shortens to 2.948(2) Å, which lies within the “quasi” form of azaphosphatranes. As seen in the CoTPAP case, there is a significant decrease in the P⋯N1 transannular distance with an increase in the oxidation state of the Ni metal center.

The Pd(II) and Pt(II) TPAP complexes (5 and 6) were also investigated in order to determine if the transannular distance changes upon coordination to larger metal ions. The transannular distance decreases by 0.273 Å from Ni(II) to Pd(II), whereas the P⋯N1 distance in Pt(II) resembles that of Ni(II). The chloride ligand in 6 could increase the P⋯N1 distance due to the π donation of Cl⁻, which would decrease the Lewis acidity of the Pt metal center. Attempted isolation of the [Pt(II)TPAP(CH₃CN)]²⁺ was unsuccessful, even when an excess of AgPF₆ was added to complex 6. Therefore, the effect of the Cl⁻ anion on the Pt(II) center cannot be experimentally quantified.
3.3.6. Metal Ion Oxidation State Effects on TPAP

Verkade found that the P⋯N$_{ax}$ distance in azaphosphatranes is influenced by the Lewis acidity of the atom or group when bound to the phosphorus. When coordinated to Ni and Co, the P⋯N$_{ax}$ distance decreases with an increasing oxidation state of the metal (and concomitant increase in Lewis acidity of the metal ion). As the oxidation state increases from Co(I) to Co(II), $\theta$ increases by 19.05° and the P⋯N1 distance contracts by 0.39 Å (Table 3.1, Co(I) and Co(II)). A more prominent trend is observed with Ni(0) and Ni(II), where $\theta$ increases by 24° and the P⋯N1 distance shorten by 0.44 Å upon oxidation (Table 3.1, Ni(0) and Ni(II)).

3.3.7. Quantum Mechanical Calculations

DFT calculations were carried out by Drew W. Cunningham and performed using the Gaussian program suite with the incorporate NBO 3.1 package at the M06 level of theory with 6–311G++(3df,3pd) basis set for 3rd row main groups, 6-311G**++ basis set for 2nd row main groups, and LANL2DZ basis set for all metals. Geometry optimizations of the complexes from the X-ray coordinates, followed by harmonic frequency calculations indicated that all of the compounds are minima on the potential energy surface. A comparison of selected calculated and experimental geometrical parameters are tabulated in Table 3.1.

The shortening of the P⋯N$_{ax}$ distance with concurrent puckering of the axial nitrogen above the plane of the three adjacent carbon atoms ($\theta$ in Figure 3.3) is due to electron donation between the axial nitrogen (N$_{ax}$) and the phosphorus atom of the azaphosphatrane unit. To probe the nature of the P⋯N$_{ax}$ interaction and observe electron density in a chemically intuitive manner, an analysis utilizing natural bond orbital (NBO) perturbation theory was carried out with a focus
on the NBOs of the M–P–N\textsubscript{ax} fragment. All calculated values for each metal ion coordinated to TPAP utilized the complexes in Chart 3.1 except [NiTPAP(COD)] (3). The latter could not be modeled computationally because the structure failed to converge to a minimum on the potential energy surface. Therefore, [NiTPAP(CO)\textsubscript{2}] (3a)\textsuperscript{62} was used as an alternative model for the transannular interaction of a Ni(0) bound to TPAP. Table 3.2 summarizes the calculated stabilization energies for each compound.

**Table 3.2.** Results of NBO analysis of donor-acceptor interactions in compound adducts, estimated by second-order perturbation theory, \( E^{(2)}_{i\rightarrow j} \) (kcal mol\(^{-1}\)). Reproduced by permission of The Royal Society of Chemistry.

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<tr>
<td>LP(N\textsubscript{ax}) (\rightarrow) (\sigma^*(M\rightarrow P))</td>
<td>&lt;0.5</td>
<td>1.09</td>
<td>2.09</td>
<td>7.23</td>
<td>3.11</td>
<td>&lt;0.5</td>
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<td>LP(N\textsubscript{ax}) (\rightarrow) (\sigma^*(P\rightarrow N\textsubscript{eq}))\textsuperscript{a}</td>
<td>&lt;1.5</td>
<td>2.86</td>
<td>6.74</td>
<td>8.05</td>
<td>4.22</td>
<td>&lt;1.5</td>
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\(\textsuperscript{a}\)These values are the sum of the three LP(N\textsubscript{ax}) \(\rightarrow\) \(\sigma^*(P\rightarrow N\textsubscript{eq})\).

When the oxidation state of the metal is greater than +1, there is a significant donation from the lone pair (LP) of N\textsubscript{ax} into unfilled antibonding NBOs. The LP(N\textsubscript{ax}) \(\rightarrow\) \(\sigma^*(M\rightarrow P)\) stabilization is ca. 2 kcal mol\(^{-1}\) for the case of Ni(II) and Co(II). For Co(I) and Ni(0), where minimal or no transannular interaction is observed experimentally, the stabilization energy is negligible (<0.5 kcal mol\(^{-1}\)). For second- and third-row metals the LP(N\textsubscript{ax}) \(\rightarrow\) \(\sigma^*(M\rightarrow P)\) interaction provides 7.2 kcal mol\(^{-1}\) and 3.1 kcal mol\(^{-1}\) of stabilization energy for Pd(II) and Pt(II), respectively. In addition to the LP(N\textsubscript{ax}) \(\rightarrow\) \(\sigma^*(M\rightarrow P)\) donation, there is a significant interaction of the axial nitrogen with the three \(\sigma^*(P\rightarrow N\textsubscript{eq})\) NBOs (Table 3.2). These calculations suggest the interaction of the axial nitrogen with the phosphorus atom is the dominating factor that influences the puckering angle, \(\theta\), and P⋯N\textsubscript{ax} distance.
The proposed interaction between the phosphorus atom and axial nitrogen can be seen by visualizing the highest occupied molecular orbitals (HOMO) for Ni(0) and Ni(II) (Figure 3.12). In the case of Ni(0), which lacks any significant P⋯N_{ax} interactions, the axial nitrogen contributes only 7% to the HOMO and does not interact with any orbitals of phosphorus; however, for Ni(II) the axial nitrogen contributes 51% to the HOMO and results in a shortening on the P⋯N_{ax} as well as a positive value of $\theta$.

**Figure 3.12.** (Left) HOMOs of [Ni(0)TPAP(CO)₂] (3a) and (Right) [Ni(II)TPAP(CH₃CN)]²⁺ (4). All surfaces are at an isovalue of 0.035. Reproduced by permission of The Royal Society of Chemistry.

Additionally, a computational analysis of a Pd(II) analogue with a Cl⁻ anion and a Pt(II) analogue with an acetonitrile ligand was done to probe whether the overall complex charge significantly impacts the M–P and P⋯N_{ax} distances. The compounds [PdTPAPCl]⁻ and [PtTPAP(CH₃CN)]²⁺ were investigated computationally and compared to their di-cationic (5) and mono-cationic (6) analogues, respectively. Computational data indicate the P⋯N_{ax} distance is...
close for Pd(II) and Pt(II) when they have the same fourth ligand. However, the P⋯N\textsubscript{ax} distance is consistently larger when Pd(II) or Pt(II) is bound by a Cl\textsuperscript{−} anion compared to CH\textsubscript{3}CN (Table 3.3).

Table 3.3 shows that the M–P distances are not particularly sensitive to changes in the overall complex charges, as increasing the charge changes the M–P distances at most by ca. 0.01 Å. For both Pt and Pd compounds, the angles θ and P⋯N\textsubscript{ax} distances increase by 5.1° and 0.15 Å, respectively, when going from mono-cationic to di-cationic. Because the differences in changes of θ and P⋯N\textsubscript{ax} are identical for each compound, the complex charge does not account for any non-monotonic trends observed.

**Table 3.3.** Calculated geometrical parameters for selected mono-cationic and di-cationic comparison. Reproduced by permission of The Royal Society of Chemistry.

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<th>[PtTPAP(CH\textsubscript{3}CN)]\textsuperscript{2+}</th>
<th>[PtTPAPCl]\textsuperscript{+}</th>
<th>[PdTPAP(CH\textsubscript{3}CN)]\textsuperscript{2+}</th>
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### 3.4. Conclusion

The use of flexible ligands with adjustable coordinative interactions has shown great utility in accessing reactive metal sites. In this chapter, an azaphosphatrane core was incorporated into a chelating ligand to provide a new type of variable ligand interaction. The metal–ligand distance remains constant for first row transition metals while the non-coordinating nitrogen in the azaphosphatrane can donate additional electron density into the phosphorus ligand. The Tolman electronic parameter measured for azaphosphatranes, described in Chapter 1, establishes that even in the absence of a transannular interaction, they are among the most strongly donating phosphine ligands.\textsuperscript{62} Thus, the TPAP ligand represents an inherently strong ligand that can increase its donor
strength in contrast to prior systems that utilize weaker interactions. The higher donor strength available with TPAP may be valuable for stabilizing more electron deficient metal ions.

3.5. Experimental Details

General Considerations

The complexes described below are air- and moisture-sensitive and must be handled under an inert atmosphere of nitrogen using standard glovebox and Schlenk techniques. Unless otherwise noted, all procedures were performed at ambient temperature (21–24 °C). All solvents were sparged with argon and dried using a solvent purification system. Acetonitrile, diethyl ether, and halogenated solvents were passed through two columns of neutral alumina. Compounds tris(2-pyridylmethyl)proazaphosphatrane,\textsuperscript{63} CoCl(PPh\textsubscript{3})\textsubscript{3},\textsuperscript{72} [Co(CH\textsubscript{3}CN)\textsubscript{6}][BF\textsubscript{4}]\textsubscript{2}\textsuperscript{73} and [Ni(CH\textsubscript{3}CN)\textsubscript{6.5}]-[BF\textsubscript{4}]\textsubscript{2}\textsuperscript{73} were synthesized according to established procedures. CD\textsubscript{3}CN and C\textsubscript{6}D\textsubscript{6} were freeze–pump–thawed three times and dried over molecular sieves. CoCl\textsubscript{2}, [Pd(CH\textsubscript{3}CN)\textsubscript{4}][BF\textsubscript{4}]\textsubscript{2}, PtCl\textsubscript{2}(COD), Co(acac)\textsubscript{3}, AgPF\textsubscript{6}, AgBF\textsubscript{4}, FcBF\textsubscript{4} and carbon monoxide (100%) were purchased from commercial sources and used without further purification.

Physical Methods

Nuclear Magnetic Resonance (NMR) Spectroscopy: Nuclear magnetic resonance (NMR) spectra were recorded on a DRX400 with a switchable QNP probe (\textsuperscript{1}H and \textsuperscript{31}P) or a Bruker AVANCE 600 MHz (\textsuperscript{1}H and \textsuperscript{31}P). \textsuperscript{1}H NMR spectra were referenced to (tetramethylsilane) TMS using the residual proteo impurities of the solvent; \textsuperscript{13}C NMR spectra were referenced to TMS using the natural abundance \textsuperscript{13}C of the solvent; \textsuperscript{31}P \textsuperscript{\{\textsuperscript{1}H\}} NMR spectroscopy experiments are referenced to the absolute frequency of 0 ppm in the \textsuperscript{1}H dimension according to the Xi scale.\textsuperscript{74}
**Infrared (IR) Spectroscopy:** Infrared (IR) absorption measurements of the solution of 1-5 in CH₂Cl₂ was taken in a OMNI-Cell CaF₂ sealed cell (1.00 mm) on a Thermo Scientific Nicolet iS5 spectrophotometer with an iD1 transmission attachment.

**Electrospray ionization mass spectrometry (ESI-MS):** ESI-MS was performed with an ESI LC-TOF Micromass LCT 3 mass spectrometer in the Department of Chemistry at UC Irvine.

**Electrochemistry:** Electrochemical experiments were carried out on a Pine Wavedriver 10 potentiostat. Electrochemical experiments were carried out in acetonitrile solutions with 1.0 mM analyte and 0.20 M Bu₄NBF₄. The working electrode was a glassy carbon disc with a diameter of 2 mm, the counter electrode was a glassy carbon rod, and a Ag/AgCl pseudoreference electrode. Potentials were referenced to the ferrocene/ferrocenium couple at 0 V using ferrocene as an internal reference. UV–vis spectrum was collected in acetonitrile solution using an Agilent Technologies Cary 60 UV–vis.

**Electron Paramagnetic Resonance (EPR):** Perpendicular-mode X-band electron paramagnetic resonance (EPR) spectrum was collected using a Bruker EMX spectrometer.

**Elemental Analysis (EA):** Elemental analyses were performed on a PerkinElmer 2400 Series II CHNS elemental analyzer.

**X-ray Crystallography (XRC):** X-ray diffraction studies were carried out at the UCI Department of Chemistry X-ray Crystallography Facility on a Bruker SMART APEX II diffractometer. Data were collected at 133 K for 1, 3, 5 and 6, and 88 K for 2, 2a-c, 3a, and 4 using Mo Kα radiation (λ = 0.710 73 Å). The APEX2 program package was used to determine the unit cell parameters and for data collection. The raw frame data was processed using SAINT and SADABS to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL program.
For structure 2, Hydrogen atoms other than H1 in 2 were placed at geometrically calculated positions and refined using a riding model, and their isotropic displacement parameters were fixed at 1.2 (1.5 for methyl groups) times the Ueq of the atoms to which they are bonded. H1 in 2 was located in the difference map and refined freely. For the structure of 2, checkCIF reports three level B alerts (PLAT230_ALERT_2_B) due to unequal anisotropic displacement parameters (ADPs) along chemical bonds, which can signify an incorrect atom type assignment. However, all three alerts involve bonds within a pyridine ring of the TPAP ligand whose identity has been confirmed through other spectroscopic techniques. An additional level B alert (PLAT411_ALERT_2_B) was reported for this structure due to a short nonbonding intermolecular \( \text{H} \cdots \text{H} \) distance between two ligand hydrogen atoms (H21 and H23); this is likely a result of crystal packing.

For the structure of 4, checkCIF reports one level B alert (PLAT214_ALERT_2_B) due to a high ratio of maximum to minimum anisotropic displacement parameters (ADPs) for atom F2B, which can signify a substitutional or positional disorder. As this atom is in the minor part of a disordered BF\(_4\) anion, the identity of which is not in question, no further modeling was done. For structure 4, atoms F(7) and F(8) were disordered and included using multiple components with partial site-occupancy-factors.

For structure 5, atoms C(54), F(5), F(6), F(7) and F(8) were disordered and included using multiple components with partial site-occupancy-factors.

For structure 6, there were several high residuals present in the final difference-Fourier map. It was not possible to determine the nature of the residuals although it was probable that
diethyl ether solvent was present. The SQUEEZE routine in the PLATON program package was used to account for the electrons in the solvent accessible voids.

Structural analysis for complex 1b was carried out at the University of Minnesota, Minneapolis X-ray Crystallography Facility on a Bruker D8 Photon 100 CMOS diffractometer. Data were collected at 123 K. Crystals were grown by a graduate student at the University of Minnesota, Reed J. Eisenhart.
[**CoTPAP(Cl)**] **(1)**: In the glove box, a solution of TPAP (34.2 mg, 0.0764 mmol) in 5 mL tetrahydrofuran was added to a solution of CoCl(PPh$_3$)$_3$ (67.3 mg, 0.0764 mmol) in 2 mL tetrahydrofuran. The solution immediately turned dark purple and was stirred for 1 day at room temperature. The solvent was removed under reduced pressure. The resulting purple solid was redissolved in diethyl ether and filtered through a glass pipette packed with a glass microfiber filter (22 µm). X-ray quality crystals were grown from a concentrated solution of 1 in diethyl ether at −35 °C (28.7 mg, 0.053 mmol, 69.4% yield). Analytical calculation for C$_{24}$H$_{30}$ClCoN$_7$P: C, 53.19; H, 5.58; N, 18.09. Found: C, 53.67; H, 5.25; N, 17.45. $\mu_{\text{eff}}$ (solution) = 3.34µB. ESI-MS data could not be obtained due to the air sensitivity of complex 1 in solution.

**Figure 3.13.** Crystal structure of [CoTPAP(Cl)] **(1b)** Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms are omitted for clarity. Grown from a pentane diffusion into a concentrated THF solution by Reed J. Eisenhart from the University of Minnesota.
[CoTPAP(CH\textsubscript{3}CN)][BF\textsubscript{4}]\textsubscript{2} (2): In the glovebox, [Co(CH\textsubscript{3}CN)\textsubscript{6}][BF\textsubscript{4}]\textsubscript{2} (23.8 mg, 0.0496 mmol) was added to a solution of TPAP (22.2 mg, 0.0496 mmol) in 3 mL of acetonitrile. The solution immediately turned dark greenish brown and was stirred for 6 h at room temperature. The solvent was removed under reduced pressure, and the resulting green solid was washed with diethyl ether. The green solid was redissolved in dichloromethane and filtered through a glass pipet packed with a glass microfiber filter. To this solution, diethyl ether was layered to afford green crystals that were isolated in 56.2% yield. ESI-MS (m/z): [M − BF\textsubscript{4} − CH\textsubscript{3}CN]\textsuperscript{+} Calculation for C\textsubscript{24}H\textsubscript{30}BCoF\textsubscript{4}N\textsubscript{7}P, 593.17; Found, 593.17. UV−vis (CH\textsubscript{3}CN) \lambda_{\text{max}}, nm (\varepsilon): 255 (8064), 400 (3058), 595 (212) and 975 (50.3). Analytical Calculation for C\textsubscript{26}H\textsubscript{33}B\textsubscript{2}CoF\textsubscript{8}N\textsubscript{8}P: C, 43.31; H, 4.61; N, 15.54. Found: C, 42.64; H, 4.58; N, 15.01. \mu_{\text{eff}} (solution) = 2.67 \mu\text{B}. (⊥)-Mode EPR (CH\textsubscript{3}CN, 77K) g = 2.18.

Figure 3.14. EPR spectrum of [CoTPAP(CH\textsubscript{3}CN)][BF\textsubscript{4}]\textsubscript{2} (2) in a frozen solution of acetonitrile at 77 K. The spectrum display a g = 2.18, which corresponds to an S = ½ system with a Co(II) d\textsuperscript{7} low spin complex.
Figure 3.15. UV-vis spectrum of [CoTPAP(CH$_3$CN)][BF$_4$]$_2$ (2) in acetonitrile at 22° C. An inset display a close up of the bands between 500 and 1000 nm.

Figure 3.16. Variable scan rate cyclic voltammograms of [CoTPAP(CH$_3$CN)][BF$_4$]$_2$ (2) with 1.0 mM analyte in acetonitrile with 0.02 M Bu$_4$NPF$_6$. The voltammagrams display a reversible event at -1.47 V (vs Fe(C$_5$H$_5$)$_2$) and is assigned as the Co$^{3+}$/2$^-$ couple.
Figure 3.17. Solution magnetic susceptibility. $^1$H NMR spectra of [CoTPAP(CH$_3$CN)][BF$_4$]$_2$ (2) at 237, 268 and 298 K in CD$_3$CN.
[NiTPAP(COD)] (3): In the glove box, a solution of TPAP (100 mg, 0.223 mmol) in 3 mL tetrahydrofuran was added to a solution of Ni(COD)₂ (61.5 mg, 0.223 mmol) in 7 mL tetrahydrofuran. The solution immediately turned dark green and was stirred for 1 day at room temperature. The solvent was removed under reduced pressure. The resulting green solid was re-dissolved in diethyl ether and filtered through a glass pipette packed with a glass microfiber filter (22 µm). X-ray quality crystals were grown from a concentrated solution of 3 in diethyl ether at −35 °C. ¹H NMR (C₆D₆, 600 MHz) δ = 2.07 (s, 8H, COD), 2.64–2.84 (br, 12H, NCH₂CH₂N), 4.30 (s, 6H, PyCH₂), 4.43 (br, 4H, COD), 6.59 (t, 3H, Py), 7.08 (m, 3H, Py), 7.12 (t, 3H, Py), 8.68 (m, 3H, Py). ³¹P{¹H} NMR (C₆D₆, 243 MHz) δ = 150.7. Analytical calculation for C₂₄H₃₀N₇NiP·(C₈H₁₂)₀.₅: C, 64.68; H, 7.24; N, 14.67. Found: C, 64.04; H, 6.77; N, 14.29. ESI-MS data could not be obtained due to the air sensitivity of complex 3 in solution. The yield is not reported due to the presence of COD impurities in both the ¹H NMR and elemental analysis data.
Figure 3.18. $^1$H NMR spectrum of [NiTPAP(COD)] (3) in C$_6$D$_6$.

Figure 3.19. $^{31}$P{$^1$H} spectrum of [NiTPAP(COD)] (3) in C$_6$D$_6$. 
[NiTPAP(CO)₂] (3a): In the glove box, a solution of bis(1,5- cyclooctadiene)nickel(0) (13.8 mg, 0.0503 mmol) in 5 mL of tetrahydrofuran was added to a solution of TPAP (22.5 mg, 0.0503 mmol) in 5 mL of tetrahydrofuran. The solution was stirred for 1 hour at room temperature. The solution was then transferred to a 100 mL Schlenk flask and brought out of the glove box and filled with CO gas (1 atm). The solution was stirred overnight under a CO atmosphere, after which the color changed from dark green to colorless. The CO gas was removed under reduced pressure with four cycles of freeze–pump–thaw and the resulting light yellow solution was brought back into the glove box. The oil that remained after solvent evaporation was washed with cold pentane to yield a yellow solid. Yellow crystals of 3a were grown from a slow evaporation of diethyl ether to give the product in 77% yield. NMR studies of 3a were conducted in a J. Young tube, in 1 atm of CO gas. ¹H NMR (C₆D₆, 400 MHz) δ = 2.46 (t, J = 10.8 Hz, 6H, NCH₂CH₂NP), 2.76 (br, 6H, NCH₂CH₂NP), 4.58 (br, 6H, PyrCH₂N), 6.67 (dd, J = 7.1, 5.1 Hz, 3H, Pyr), 7.25 (td, J = 7.7, 1.7 Hz, 3H, Pyr), 7.38 (d, J = 7.8 Hz, 3H, Pyr), 8.53 (m, 3H, Pyr). ¹³C{¹H} NMR (C₆D₆, 126 MHz) δ = 47.7 (NCH₂CH₂NP), 50.2 (PyrCH₂N), 53.3 (NCH₂CH₂NP), 122 (Pyr), 122 (Pyr), 136 (Pyr), 150 (Pyr), 160 (Pyr), 198 (CO). ³¹P NMR (C₆D₆, 162 MHz) δ = 142. FTIR (CH₂Cl₂): ν = 1981.7 (CO), 1906.5 (CO). Analytical Calculation for C₂₆H₃₀N₇NiO₂P: C, 55.54; H, 5.38; N, 17.44 Found: C, 55.02; H, 5.19; N, 17.50.
Figure 3.20. IR spectrum of [NiTPAP(CO)₂] (3a) in CH₂Cl₂.

Figure 3.21. ¹H NMR spectrum of [NiTPAP(CO)₂] (3a) in C₆D₆.
Figure 3.22. $^{13}$C NMR spectrum of [NiTPAP(CO)$_2$] (3a) in C$_6$D$_6$.

Figure 3.23. $^{31}$P{$^1$H} NMR spectrum of [NiTPAP(CO)$_2$] (3a) in C$_6$D$_6$. 
[NiTPAP(CH$_3$CN)][BF$_4$]$_2$ (4): In the glove box, a solution of TPAP (109 mg, 0.250 mmol) in 7 mL of acetonitrile was added to a solution of [Ni(CH$_3$CN)$_{6.5}$][BF$_4$]$_2$ (122 mg, 0.250 mmol) in 2 mL of acetonitrile. The solution immediately turned dark orange and was stirred for 1 day at room temperature. The solvent was removed under reduced pressure. The resulting orange solid was redissolved in dichloromethane, filtered through a glass pipette packed with a glass microfiber filter (22 µm). X-ray quality crystals of 4 were grown from acetonitrile and diethyl ether (97.5 mg, 0.135 mmol, 55.1% yield). $^1$H NMR (CD$_3$CN, 400 MHz) δ = 2.82 (t, 6H, NCH$_2$CH$_2$N), 2.94 (t, 6H, NCH$_2$CH$_2$N), 4.50 (s, 6H, PyCH$_2$), 7.61 (m, 6H, Py), 7.97 (t, 3H, Py), 9.51 (s, 3H, Py). ESI-MS (m/z): [M − 2BF$_4$ − CH$_3$CN + Cl]$^+$. Calculation for C$_{24}$H$_{50}$N$_{7}$PNiCl, 540.13; found, 540.20. Analytical calculation for C$_{26}$H$_{33}$B$_2$F$_8$N$_8$NiP: C, 43.32; H, 4.61; N, 15.54. Found: C, 43.65; H, 5.02; N, 15.18. Although the sample is analytically pure and the $^1$H NMR is consistent with the proposed structure, a $^{31}$P{$^1$H} NMR resonance was unable to be resolved. The lack of resonance may be due to fluxional coordination in solution.
Figure 3.24. $^1$H NMR of spectrum of $[^\text{NiTPAP(CH}_3\text{CN)}][\text{BF}_4]^2(4)$ in CD$_3$CN.
[PdTPAP(CH$_3$CN)][BF$_4$]$_2$ (5): In the glove box, a solution of TPAP (81.0 mg, 0.181 mmol) in 6 mL of acetonitrile was added to a solution of [Pd(CH$_3$CN)$_4$][BF$_4$]$_2$ (80.1 mg, 0.181 mmol) in 2 mL of acetonitrile. The solution immediately turned orange and was stirred for 1 day at room temperature. The solvent was removed under reduced pressure. The resulting yellow solid was re-dissolved in acetonitrile, filtered through a glass pipette packed with a glass microfiber filter (22 µm). X-ray quality crystals of 5 were grown from acetonitrile and diethyl ether (121 mg, 157 mmol, 86.9% yield). $^1$H NMR (CD$_3$CN, 400 MHz) δ = 2.72 (t, 6H, NCH$_2$CH$_2$N), 2.94 (m, 6H, NCH$_2$CH$_2$N), 4.45 (d, 6H, PyCH$_2$), 7.46 (m, 6H, Py), 7.97 (dt, 3H, Py), 8.66 (d, 3H, Py). $^{31}$P{$^1$H}NMR (CD$_3$CN, 162 MHz) δ = 50.8. ESI-MS (m/z): [M − 2BF$_4$ − CH$_3$CN + Cl]$^+$ . Calculation for C$_{24}$H$_{30}$N$_7$PPdCl, 588.1; found, 588.0. Analytical calculation for C$_{26}$H$_{33}$B$_2$F$_8$N$_8$PdP: C, 40.63; H, 4.33; N, 14.58. Found: C, 40.35; H, 4.20; N, 14.37.
Figure 3.25. $^1$H NMR spectrum of [PdTPAP(\text{CH}_3\text{CN})][\text{BF}_4]_2 (5) in CD$_3$CN.

Figure 3.26. $^{31}$P\text{\{}$^1$H\text{\}} NMR spectrum of [PdTPAP(\text{CH}_3\text{CN})][\text{BF}_4]_2 (5) in CD$_3$CN.
[PtTPAP(Cl)][PF$_6$]$_2$ (6): In the glove box, a solution of TPAP (78.1 mg, 0.175 mmol) in 6 mL of acetonitrile was added to a solution of PtCl$_2$(COD) (65.3 mg, 0.175 mmol) in 6 mL acetonitrile. The solution immediately turned tan and was stirred for 1 h at room temperature. Then a solution of AgPF$_6$ (68.0 mg, 0.350 mmol) in 2 mL acetonitrile was added in the dark and stirred for 5 min. The solvent was removed under reduced pressure. The white solid was re-dissolved in dichloromethane and filtered through a medium fritted funnel. The solvent was removed under reduced pressure. The resulting white solid was re-dissolved in acetonitrile and filtered through a glass pipette packed with a glass microfiber filter (22 µm). The filtrate was recrystallized by addition of diethyl ether. Only single crystals of 6 were collected which contributed to the low yield of the pure sample. No attempts were made to further purify the crude product in order to increase the yield. X-ray quality crystals of 6 were grown from the same conditions as the recrystallization (17.3 mg, 0.021 mmol, 12.1% yield). $^1$H NMR (CD$_3$CN, 600 MHz) $\delta = 2.64$ (t, 2H, NCH$_2$CH$_2$N), 2.78 (m, 2H, NCH$_2$CH$_2$N), 2.89 (m, 6H, NCH$_2$CH$_2$N), 3.17 (m, 2H, NCH$_2$CH$_2$N), 3.97 (d, 2H, PyCH$_2$), 4.25 (dd, 2H, PyCH$_2$), 4.88 (dd, 2H, PyCH$_2$), 6.75 (d, 1H, Py), 7.27 (m, 1H, Py), 7.46 (t, 2H, Py), 7.61 (m, 3H, Py), 8.08 (t, 2H, Py), 8.42 (m, 1H, Py), 8.95 (m, 2H, Py). $^{31}$P{$^1$H} NMR (CD$_3$CN, 243 MHz) $\delta = 39.8$. ESI-MS (m/ z): [M – PF$_4$]$^+$. Calculation for C$_{24}$H$_{30}$N$_7$P$_2$PtCl, 677.2; found, 677.1. Analytical calculation for C$_{24}$H$_{30}$ClF$_6$N$_7$P$_2$Pt: C, 35.02; H, 3.67; N, 11.91. Found: C, 34.96; H, 3.51; N, 11.84.
Figure 3.27. $^1$H NMR spectrum of [PtTPAPCl][PF$_6$]$_2$ (6) in CD$_3$CN.

Figure 3.28. $^{31}$P($^1$H) NMR spectrum of [PtTPAPCl][PF$_6$]$_2$ (6) in CD$_3$CN.
3.6. References


116


CHAPTER 4

Small Molecule Activation with Transition Metal
Tris(2-pyridylmethyl)azaphosphatrane Complexes
4.1. Motivation and Specific Aims

This chapter is divided into three sections and concentrates on individual small molecule activation reactions with transition metal tris(2-pyridylmethyl)azaphosphatranes (TPAP) complexes. The first section will focus on CO$_2$ reduction to CO on a Ni(0)(TPAP) complex, followed by O$_2$ reactivity with a Cu(I)(TPAP) complex, and the last section will highlight hydride complexes of Ir(III)(TPAP) for H$_2$ activation.

4.1.1. CO$_2$ Reduction

The rapid burning of fossil fuels has led to increasing concentration of CO$_2$ in our atmosphere, causing adverse effects on our planet. Research on converting CO$_2$ to valued chemical commodities is the goal for a net carbon neutral cycle. A fundamental step to accomplish this task is to activate the CO$_2$ molecule by binding it to a transition metal center. In this chapter, efforts are made to bind and reduce CO$_2$ to CO with a Ni(0)(TPAP) complex.

4.1.2. O$_2$ Reactivity

Metalloenzymes serve as models for chemists who seek to mimic their functionality and understand their structures. One example is the tyrosinase enzyme, which controls the production of melanin by oxidation of phenolic precursors to form ortho-quinones. Chemists had synthesized model complexes of the dicopper active site of tyrosinase to investigate potential key intermediates in its reaction with O$_2$. This chapter aims to add to the rich bioinorganic reactivity of tyrosinase biomimics through studying the reaction of O$_2$ with a Cu(I)(TPAP) complex. Copper complexes with strong donor ligands have previously been hypothesized to trigger O-O bond cleavage to yield more reactive species.$^1$
4.1.3. Hydrogenation (H₂)

Hydrogenation is one of the most important reactions in chemistry. Nobel prizes have been issued to organometallic chemists in two separate years for their work in this area; Wilkinson’s Rh catalyst for the hydrogenation of olefins and the Noyori chiral Ru catalyst for the asymmetric hydrogenation of carbonyls. Homogenous hydrogenation catalysis is still an active research area, with chemists designing and synthesizing intricate ligands to push the efficiency and selectivity of hydrogenation reactions. This chapter aims to add to the rich chemistry of Ir hydrogenation catalysts by synthesizing Ir-hydride complexes with TPAP, a strong σ donating azaphosphatrane ligand.

4.2. Background

4.2.1. Ni-CO₂ Complexes

Aresta structurally characterized the first Ni-CO₂ complex in 1975, which demonstrated the importance of strong donor ligands to generate an electron rich Ni(0) center for CO₂ binding (Figure 4.1).² Aresta suggested that “the strength of the Ni-CO₂ bond should decrease on increasing the acidity of the phosphorus ligand.” This meant that a very strong donor, such as the proazaphosphatrane molecule, could strengthen the Ni-CO₂ bond, and consequently weaken the double bond of CO₂. Years later, Hillhouse³ and Lee⁴ structurally characterized the second and third mononuclear Ni-CO₂ complexes, respectively (Figure 4.1). In Hillhouse’s system, he demonstrated the reduction of CO₂ to CO on a Ni complex with bidentate diphosphines, while Lee and coworkers utilized a tridentate triphosphine ligand system with Ni. In all three systems, phosphine donors are used with a Ni(0) metal center.
In this chapter, the reactivity of Ni(0)(TPAP)(COD) complex from chapter 3 is explored with CO$_2$ in order to investigate its CO$_2$ binding and reduction activity.

4.2.2. Cu$_2$O$_2$ Complexes

The supporting ligand plays a big role in stabilizing the bis(µ-oxo)dicopper core. The characterized structures of bis(µ-oxo)dicopper complexes have been with bi- or tri-dentate nitrogen donating ligand systems. Work from Tolman and coworkers confirmed the structure of a bis(µ-oxo)dicopper complex with a tridentate N ligand. The Cu$_2$O$_2$ core was isolated in the isomeric form that is pivotal to the activation of O$_2$ (Figure 4.2). Stack later noticed that square-planar coordination geometries dominated trivalent Cu complexes; therefore, he opted for sterically demanding bidentate N ligands for isolation of Cu$_2$O$_2$ complexes (Figure 4.2). This ligand design proved useful as Stack was able to study multiple bis(µ-oxo)dicopper complexes with variations of the N-peralkylated diamine ligand. Meyer was also successful in using a bidentate ligand system and was able to structurally characterize a bis(µ-oxo)dicopper complex (Figure 4.2).
Figure 4.2. Structurally characterized Cu$_2$O$_2$ complexes with di- and tri-dentate N ligands.

Another ligand design tip from Stack was to use “bidentate strong sigma-donors” for “optimal thermodynamic stabilization of the d$^8$ Cu(III) site” in bis(µ-oxo)dicopper complexes.$^6$

The TPAP system is a strong sigma donor ligand and is flexible to coordinate in a bi-, tri- or tetradentate fashion to a transition metal ion.

4.2.3. Ir-H$_2$ Complexes

Strong sigma donating ligands have been shown to increase the rate of hydrogenation in organometallic chemistry. Bercaw and coworkers demonstrated the hydrogenation of cyclooctene to cyclooctane with an Ir(III) N-heterocyclic carbene (NHC) complex and H$_2$.\(^8\) Although they were not able to isolate the activated H$_2$ intermediate, the Ir-hydride complex was hypothesized to be the active catalyst (Figure 4.3), as most Ir catalyzed hydrogenation reactions often involve hydridoiridium(III) catalytic precursors.$^{9-11}$ Another strongly donating NHC system was used in Nozaki’s work for the hydrogenation of CO$_2$ with an Ir-PCP pincer complex (Figure 4.3). The high catalytic turnover (TON = 230,000) was “attributed to the stabilization of the cationic key transition state by the higher electron-donating nature of the PCP ligand.”\(^{12}\) Lastly, Jagirdar and coworkers used a tris(pyrazolyl)methane sulfonate complex to stabilize an Ir(III) dihydride complex, which was the active catalyst in their study of olefin hydrogenation with H$_2$.\(^{13}\) The crystal
structure displayed an octahedral geometry where two hydrides were positioned trans to two strongly donating pyrazolyl donors (Figure 4.3).

![Chemical structures](image)

**Figure 4.3.** Ir(III) complexes bearing strong sigma donor ligands.

In this chapter, the Ir(III) monohydride (IrH(TPAP)Cl) and dihydride (Ir(H)₂(TPAP)) are synthesized for their potential use as hydrogenation catalysts.

4.3. Results and Discussion

4.3.1. Reaction of Ni(TPAP)(COD) with CO₂

A solution of Ni(TPAP)(COD) (characterized in Chapter 3) in C₆H₆ was added into a Schlenk tube and filled with CO₂ gas (Scheme 4.1). The color of the solution changed from dark green to brown. A brown solid was obtained when the solvent was removed under reduced pressure.
Scheme 4.1. Proposed reactivity of CO$_2$ with Ni(TPAP)(COD).

The brown solid displayed an IR stretching frequency at 1696 cm$^{-1}$ (Figure 4.4), which is in the range of structurally characterized Ni-CO$_2$ complexes.$^{2-4}$ Multiple attempts to crystallize the brown solid via layering were unsuccessful.

Figure 4.4. IR spectrum of brown solid from the reactivity of Ni(TPAP)(COD) with CO$_2$.

After 3 days at room temperature, the brown complex decomposed and the IR stretching frequency displayed two carbonyl stretching frequencies at 1981.7 and 1906.5 cm$^{-1}$ (Figure 4.5), matching the IR stretching frequency of Ni(TPAP)(CO)$_2$ (see Chapter 3). The reduction of CO$_2$ to
CO was seen in Hillhouse’s system, where the electron rich phosphine ligands were oxidized by the oxygen of the CO₂ molecule. A similar reaction might also be possible with the TPAP system, given their strong donating ability.¹⁴ No further studies were performed to ascertain if TPAP=O was made. The ³¹P NMR signal of TPAP=O would be expected at 23.95 ppm (see Appendix B). In addition, the TPAP molecule can also react with CO₂, without the help of a transition metal ion. Verkade and coworkers previously showed the reactivity of proazaphosphatranes with CO₂ and CS₂.¹⁵,¹⁶

![Figure 4.5. IR spectra of (blue) Ni(TPAP)(CO)₂ and (red) Ni(TPAP)(COD) + CO₂ after 3 days of sitting at room temperature.](image)

**Figure 4.5.** IR spectra of (blue) Ni(TPAP)(CO)₂ and (red) Ni(TPAP)(COD) + CO₂ after 3 days of sitting at room temperature.

### 4.3.2. Synthesis and Structure of Cu(TPAP) Complex

In the glove box, [Cu(CH₃CN)₄][BF₄] and TPAP were mixed in a 1:1 ratio in acetonitrile (Scheme 4.2). After 1 day of stirring, the solution change from colorless to light yellow. A yellow
solid was isolated after acetonitrile was removed. The $^1$H NMR spectrum of the yellow solid exhibited resonances corresponding to equivalent protons from the pyridine and azaphosphatrane core, suggesting either coordination of all three pyridine donors to Cu(I) ion or a dynamic system where pyridine donors are rapidly binding and unbinding to the Cu(I) ion.

**Scheme 4.2.** Synthesis of [Cu(TPAP)]$_2$[BF$_4$]$_2$ complex.

An X-ray quality crystal of [Cu(TPAP)]$_2$[BF$_4$]$_2$ was grown by layering a solution of the yellow solid in dichloromethane with diethyl ether. The crystal structure displayed a bimetallic-Cu(TPAP) system with two Cu and two TPAP ligands, [Cu(TPAP)]$_2$[BF$_4$]$_2$, where one TPAP ligand is coordinated to one Cu(I) site through the P, and coordinated to another Cu(I) site through two pyridine Ns (Figure 4.6). Both Cu(I) ions in the crystal structure displayed a trigonal geometry, and the Cu–Cu distance is 3.018 Å. The combined data of the $^1$H NMR spectrum and crystal structure suggest the Cu(I) ion is in a different coordination environment in solution than the solid state.$^{17}$
Figure 4.6. Crystal structure of [Cu(TPAP)]₂[BF₄]₂. Thermal ellipsoids are drawn at 50% probability; hydrogen atoms and counter anions omitted for clarity.

4.3.3. Reaction of Cu(TPAP) with O₂

To a cuvette with 2.0 mmol solution of [Cu(TPAP)]₂[BF₄]₂ in acetonitrile was added 1 mL of O₂ gas at room temperature. A color change from light yellow to green occurred overnight. The green solution was analyzed by UV-vis (Figure 4.7) and EPR spectroscopy (Figure 4.8). The UV-vis spectrum of Cu(TPAP) + O₂ displayed a d-d transition band at 666 nm, characteristic of a Cu(II) metal ion. For comparison, a UV-vis spectrum of Cu(TPAP) is displayed in Figure 4.7, which showed no d-d transition band due to the full shell of the d¹⁰ Cu(I) metal ion.
Figure 4.7. UV-vis spectra of (red) Cu(TPAP) and (green) Cu(TPAP) + O₂ in CH₃CN.

An EPR measurement was performed on the green product of Cu(TPAP) + O₂ at 77K, displaying a signal centered at g = 2.07. The g value of 2.07 corresponds to an S= 1/2, one unpaired electron Cu(II) metal ion. Additional features in the EPR presented a 4-line hyperfine coupling due to I(Cu⁶³) = 3/2. The attempted crystallization of the green product proved unsuccessful as the product decomposes within days.

Figure 4.8. EPR spectrum of green product from the reaction of Cu(TPAP) with O₂ in CH₃CN at 77K.
4.3.4. Synthesis of IrH(TPAP)Cl

An IrH(TPAP)Cl complex was synthesized by stirring [Ir(COD)Cl]$_2$ (COD = 1,5-cyclooctadiene) and TPAP in a 1:1 ratio in tetrahydrofuran (Scheme 4.3). As the reaction was stirring, light orange solids precipitated out of solution. The solution was filtered through a medium fritted filter and the orange solid was washed with tetrahydrofuran. Colorless crystals were grown from a layered solution of the orange solid in dichloromethane with diethyl ether.

Scheme 4.3. Synthesis of IrH(TPAP)Cl and IrH$_2$(TPAP).

The $^1$H NMR spectrum of the colorless crystals displayed a doublet at -21.62 ppm ($J$-coupling of 16.5 Hz), which is in the region of metal hydrides. The $^{31}$P{$^1$H} NMR spectrum displayed a doublet at 66.4 ppm, with a matching $J$-coupling of 16.5 Hz to that of the metal hydride signal in the $^1$H NMR spectrum. This is consistent with other P-Ir-H $J$-coupling constant, where coupling is observed due to $^1$H resonance residing outside of the decoupling window.$^{18}$ X-ray analysis of the complex was performed and the structure revealed an octahedral coordination environment around the Ir(III) ion (Figure 4.9). The P, two pyridine Ns, and a Cl anion are coordinated to Ir(III), along with a C-H activated pyridine, where the C of the pyridine ring and a hydride are bound. The P⋯N$_{ax}$ distance is 3.22 Å, which falls closer towards the “Pro” form of azaphosphatranes.
Figure 4.9. Crystal structure of IrH(TPAP)Cl. Solvents molecules (dichloromethane and diethyl ether) and hydrogens are omitted for clarity except for H1, which was located in the difference map and refined freely.

4.3.5. Synthesis of IrH₂(TPAP)

The Ir(III)-dihydride complex, IrH₂(TPAP), was synthesized by adding LiEt₃BH (1.0 M in tetrahydrofuran) into a cold mixture of IrH(TPAP)Cl (-35°C) in tetrahydrofuran via syringe (Scheme 4.3). The solution changed color from colorless to light yellow and was stirred for one hour before adding diethyl ether, during which time a white precipitate appeared. X-ray quality crystals were grown from slow vapor diffusion of pentane into a solution of IrH₂(TPAP) in tetrahydrofuran. The structure displayed similar coordination geometry as the IrH(TPAP)Cl complex, except the Cl anion was substituted with a hydride. The P⋯Nₐx distance is 3.17 Å, similar to the P⋯Nₐx distance of IrH(TPAP)Cl, due to the same Ir(III) oxidation state (Figure 4.10).¹⁹
Figure 4.10. Crystal Structure of [IrH_2(TPAP)]. Solvents molecule (tetrahydrofuran), LiCl, and hydrogens are omitted for clarity except for H1 and H2, which were located in the difference map and refined freely.

The $^1$H NMR spectrum of crystalline IrH$_2$(TPAP) displayed two resonances in the metal-hydride region, a doublet at -3.90 ppm ($J$-coupling of 183 Hz) and a broad singlet at -21.2 ppm. The $^{31}$P{$^1$H} NMR spectrum displayed a major resonance at 105.6 ppm and smaller resonances at 72.6, 67.1 and 64.1 ppm, potentially due to unreacted starting material and impurities.

4.3.6. Reactivity of IrH(TPAP)Cl with H$_2$

No reaction was observed when H$_2$ was added directly to IrH(TPAP)Cl. The IrH(TPAP)Cl complex must be treated with AgBF$_4$ first before H$_2$ addition, in order to provide an open coordination site for H$_2$ to bind. When AgBF$_4$ was added to IrH(TPAP)Cl, grey solids appear in solution, likely due to AgCl. The solution was filtered and added into a J. Young tube, followed by the addition of H$_2$ gas. The $^1$H NMR spectrum of the reaction displayed new resonances around the metal-hydride region (Figure 4.11). In addition, the $^{31}$P{$^1$H} NMR spectrum is shifted from
66.4 ppm in IrH(TPAP)Cl to 89.6 ppm. Potential future reactions include adding CO₂ to this new Ir-hydride complex or IrH₂(TPAP).

**Figure 4.11.** ¹H NMR spectrum of IrH(TPAP)Cl + AgBF₄ + H₂ in CD₂Cl₂. Inset displays a close-up view of the hydride region.

4.4. Conclusion

4.4.1. Ni(TPAP)(COD) + CO₂

The reactivity of CO₂ with Ni(TPAP)(COD) produced a brown solid with an IR vibrational frequency consistent with a CO₂ bound Ni(0) complex. The brown solid decomposed to Ni(TPAP)(CO)₂, which demonstrates the ability of the Ni(TPAP) system to activate and reduce CO₂ to CO.
4.4.2. Cu(TPAP) + O$_2$

A Cu(TPAP) complex was synthesized and characterized. In the solid state, the Cu(TPAP) complex is a dimeric complex, with a molecular formula of [Cu$_2$(TPAP)$_2$][BF$_4$]$_2$. In solution, all three pyridine donors are equivalent at room temperature. The Cu(TPAP) complex showed O$_2$ reactivity and the product was characterized as a Cu(II) metal ion by UV-vis and EPR spectroscopies.

4.4.3. IrH(TPAP)Cl + H$_2$

The synthesis and characterization of IrH(TPAP)Cl and IrH$_2$(TPAP) are presented. The reactivity of IrH(TPAP)Cl with H$_2$ was attempted but no reactions occurred until AgBF$_4$ was added. The cleavage of the Ir-Cl bond important in order to provide an open coordination site for H$_2$ binding to the Ir(III) metal center.

4.5. Experimental Details

General Considerations

All manipulations were performed in the glovebox, as the complexes are air- and moisture-sensitive. All solvents were first purged with argon and dried using a solvent purification system. [Ir(COD)Cl]$_2$, [Cu(CH$_3$CN)$_4$][BF$_4$], Ni(0)(COD)$_2$, AgBF$_4$, CO$_2$, O$_2$ and H$_2$ were commercially purchased and used without further purification. Ni(TPAP)(COD) was synthesized according to an established procedure.$^{19}$

Physical Methods

Nuclear Magnetic Resonance (NMR) Spectroscopy: Nuclear magnetic resonance (NMR) spectra were recorded on a DRX400 with a switchable QNP probe ($^1$H) or a Bruker AVANCE 600 MHz ($^{31}$P). $^1$H NMR spectra were referenced to (tetramethylsilane) TMS using the residual proteo
impurities of the solvent; $^{31}$P{$^1$H} NMR spectroscopy experiments are referenced to an internal H$_3$PO$_4$ sample in D$_2$O or to H$_3$PO$_4$ using the Ξ scale with the corresponding $^1$H spectra or referenced to the absolute frequency of 0 ppm in the $^1$H dimension according to the Xi scale.$^{20}$

**Infrared (IR) Spectroscopy:** IR absorption was taken on a Thermo Scientific Nicolet iS5 spectrophotometer with an iD5 ATR attachment.

**Ultraviolet-visible (UV-vis):** UV-vis was collected in a 1cm fluoro cell in acetonitrile solution using Agilent Technologies Cary 60 UV-vis spectrometer and 8453 Diode-array UV-vis spectrometer equipped with Unisoku cryostat.

**Electron Paramagnetic Resonance (EPR):** Perpendicular-mode X-band electron paramagnetic resonance (EPR) spectrum was collected using a Bruker EMX spectrometer.

**X-ray Crystallography (XRC):** X-ray diffraction studies were carried out at the UCI Department of Chemistry X-ray Crystallography Facility on a Bruker SMART APEX II diffractometer. Data were collected at 88 K using Mo Kα radiation ($\lambda = 0.710$ 73 Å). The APEX2 program package was used to determine the unit cell parameters and data collection. The raw frame data was processed using SAINT and SADABS to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL program.
[Cu(TPAP)]_2[BF_4]_2: In the glove box, [Cu(CH_3CN)_4][BF_4] (40.9 mg, 0.130 mmol) was added to a solution of TPAP (58.2 mg, 0.130 mmol) in 3 mL of acetonitrile. The solution immediately turned light yellow and was stirred for 2 hours at room temperature. The solvent was removed under vacuum and the resulting yellow solid was washed with diethyl ether. The yellow solid was redissolved in dichloromethane and filtered through a glass pipette packed with a glass microfiber filter. Diethyl ether was layered on top of this solution to afford yellow crystals that were isolated in 81.18% yield. ^1H NMR (CD_3CN, 400 MHz) δ = 2.83 (m, 12H, NCH_2CH_2N), 4.03 (d, 6H, PyrCH_2N), 7.31 (t, 3H, Py), 7.39 (d, 3H, Py), 7.80 (t, 3H, Py), 8.51 (d, 3H, Py). ^31P(^1H)NMR (CD_3CN, 243 MHz) δ = -11.78.
Figure 4.12. $^1$H NMR spectrum of Cu(TPAP) complex in CD$_3$CN.

Figure 4.13. $^{31}$P($^1$H) NMR spectrum of Cu(TPAP) complex in CD$_3$CN.
**IrH(TPAP)Cl:** In the glove box, a solution of TPAP (80.0 mg, 0.223 mmol) in 5 mL tetrahydrofuran was added to a solution of [Ir(COD)Cl]₂ (61.5 mg, 0.223 mmol) in 8 mL tetrahydrofuran. An orange precipitate appeared after 30 min of stirring. The orange mixture was stirred for 1 day at room temperature. The solution was filtered through a medium fritted filter and washed with tetrahydrofuran, yielding a light orange solid. Colorless crystals were grown from a layered solution of the orange solid in dichloromethane with diethyl ether. ¹H NMR (CD₂Cl₂, 600 MHz) δ = -21.6. (d, Jₚᴴ = 6.5 Hz, P-Ir-H). ³¹P{¹H} NMR (CD₂Cl₂, 243 MHz) δ = 66.4. The yield is not reported due to the presence of solvent impurities in the ¹H NMR data.
**Figure 4.14.** $^1$H NMR spectrum of IrH(TPAP)Cl in CD$_2$Cl$_2$. Inset display close up view of hydride region.

**Figure 4.15.** $^{31}$P{$^1$H} NMR spectrum of IrH(TPAP)Cl in CD$_2$Cl$_2$. Inset display close up view of resonance.
**IrH₂(TPAP):** In the glove box, a mixture of IrH(TPAP)Cl (50.0 mg, 0.160 mmol) in 3 mL tetrahydrofuran was cooled in a -35 °C freezer for 2 hours before adding LiEt₃BH 0.2 mL, 1.0 M in tetrahydrofuran) via 1 mL syringe. The mixture went into solution and a color change to light yellow occurred within 30 minutes. After 1 h, diethyl ether was added to the solution to produce a white solid. X-ray quality crystals were grown from slow vapor diffusion of pentane into a solution of IrH₂(TPAP) in tetrahydrofuran. ¹H NMR (CD₃CN, 600 MHz) δ = -3.90. (d, P-Ir-Hₐx) and -21.2. (d, P-Ir-Hₑq). ³¹P{¹H} NMR (CD₃CN, 243 MHz) δ = 105.6. The yield is not reported due to the presence of solvent impurities in the ¹H NMR data.

![Figure 4.16](image_url)  
*Figure 4.16.* ¹H NMR spectrum of IrH₂(TPAP) in CD₂Cl₂.
Figure 4.17. $^{31}$P$\{^1$H$\}$ NMR spectrum of IrH$_2$(TPAP) in CD$_2$Cl$_2$. 
IrH(TPAP)Cl + AgBF₄ + H₂: In the glove box, a solution of AgBF₄ (80.0 mg, 0.400 mmol) in acetone was added to a solution of IrH(TPAP)Cl (103 mg, 0.401 mmol) in CD₂Cl₂. The reaction was stirred in the dark for 1 hour before filtrating through a medium fritted funnel. The collected solution was added to a J. Young tube and taken outside the box to be charged with H₂ gas. No color change occurred. Gray solids precipitated out of solution after sitting in the J. Young tube for 1 day.

Figure 4.18. $^{31}$P{¹H} NMR spectrum of [IrH(TPAP)Cl] + AgBF₄ + H₂ in CD₂Cl₂.
4.6. References


3. Anderson, J. S.; Iluc, V. M.; Hillhouse, G. L., Reactions of CO$_2$ and CS$_2$ with 1,2-Bis(ditert-butylphosphino)ethane Complexes of Nickel(0) and Nickel(I). *Inorganic Chemistry* 2010, 49 (21), 10203-10207.


APPENDIX A

Crystal Structure of

NiFe(CO)$_5$(Tris(2-pyridylmethyl)azaphosphatrane);

A Synthetic Mimic of the NiFe Hydrogenase Active Site

Incorporating a Pendant Pyridine Base

Portions of this chapter have been published:


Data in this appendix was collected by undergraduate Natvara Sutthirat under the guidance and supervision of Zachary Thammavongsy
A.1. Motivation and Specific Aims

The reaction of Ni(TPAP)(COD) \{where TPAP = [(NC₅H₄)CH₂]₃P(NC₂H₄)₂N\} with Fe(CO)₅ resulted in the isolation of the title heterobimetallic NiFe(TPAP)(CO)₅ complex dicarbonyl-tricarbonyl[2,8,9-tris(pyridin-2-ylmethyl)-2,5,8,9-tetraaza-1-phosphabicyclo[3.3.3]undecane]-iron-nickel, [FeNi(C₂₄H₃₀N₇P)(CO)₅]. Characterization of the complex by ¹H and ³¹P NMR as well as IR spectroscopies are presented. The structure of NiFe(TPAP)(CO)₅ reveals three terminally bound CO molecules on Fe(0), two bridging CO molecules between Ni(0) and Fe(0), and TPAP coordinated to Ni(0). The Ni—Fe bond length is 2.4828 (4) Å, similar to that of the reduced form of the active site of NiFe hydrogenase (2.5 Å). Additionally, a proximal pendant base from one of the non-coordinating pyridine groups of TPAP is also present. Although the involvement of a pendant base has been cited in the mechanism of NiFe hydrogenase, this moiety has yet to be incorporated in a structurally characterized synthetic mimic with key structural motifs (terminally bound CO or CN⁻ ligands on Fe). Thus, the title complex NiFe(TPAP)(CO)₅ is a unique synthetic model for NiFe hydrogenase.
A.2. Background

Rare and expensive metals such as Pt are often used to catalyze the production and oxidation of H₂ for utilization in electrolyzers or fuel cells, respectively. Because of this, the production and utilization of H₂ for clean energy applications have motivated scientists to produce efficient catalysts made from abundant metals. In nature, hydrogenase enzymes catalyze the reversible production and oxidation of H₂ with the metals Ni and Fe.¹ Inspired by nature, this work aimed to structurally mimic the active site of the NiFe hydrogenase enzyme.² NiFe hydrogenase contains a NiFe active center, where Fe is coordinated with three different types of ligand (C≡O, C≡N, and a sulfur atom) while Ni is coordinated by four cysteine residues. The C≡O, C≡N, and the sulfur-atom ligands play a role in maintaining the oxidation state of Fe(II) and stabilizing the oxidation state changes of the Ni ion during the catalytic cycle.³ Prior work in this thesis discussed the transannular interaction of bridgehead N and P atoms in the tris(2-pyridylmethyl)-azaphosphatrane (TPAP) ligand in the stabilization of metal ions in different oxidation states.⁴

A recent study by Johnson and co-workers found that the transannular interaction in azaphosphatranes plays a potential role in Pd cross-coupling reactions, where the oxidative addition event ‘is promoted due to electron donation to the metal center from transannulation’.⁵ The transannular interaction in TPAP could play a similar role in stabilizing the Ni ion.

Additionally, a study by Armstrong and collaborators found a conserved arginine residue was vital for catalysis in NiFe hydrogenase.⁶ They propose the guanidine base of arginine participates in the activation of H₂. As a result of this conserved motif, the incorporation of pendant bases into the ligand design of synthetic models of NiFe hydrogenase is important but has been
rarely observed in reported synthetic models of NiFe hydrogenase (as opposed to those of FeFe hydrogenase). In the title complex, NiFe(TPAP)(CO)$_5$, whose synthesis is illustrated in Scheme A.1, the TPAP ligand features a pendant pyridine base, providing a close structural mimic of the NiFe hydrogenase enzyme.

**Scheme A.1.** Synthesis of NiFe(TPAP)(CO)$_5$.

A.3. Results and Discussion

A.3.1. Structural Commentary

The title heterobimetallic NiFe(TPAP)(CO)$_5$ complex (Figure A.1), displays two bridging CO molecules between the Ni and Fe metal centers. Selected bond lengths and bond angles are given in Table A.1. The Fe(0) center shows a five-coordinate pseudo square-pyramidal geometry comprising three terminally bound CO and two bridging CO molecules. The $\tau_5$ value of the Fe(0) atom is 0.40, where $\tau_5 = 0$ represents an ideal square pyramidal and 1 represents an ideal trigonal–bipyramidal geometry. The Ni(0) center is also coordinated by the two bridging CO molecules and the TPAP ligand, where the two nitrogens from two pyridines and the phosphorus of the azaphosphatrane are coordinated. The Ni(0) ion displays a five-coordinated square-pyramidal geometry with a $\tau_5$ value of 0.06. The bond lengths of the CO molecules bridging between the Ni
and Fe ions are 1.1821 (16) and 1.1754 (17) Å for O1—C25 and O2—C26, respectively. These bond lengths are longer than the terminally bound CO molecules on Fe, which are 1.1509 (17), 1.148 (2) and 1.1531 (19) Å for O3—C27, O4—C28 and O5—C29, respectively. The shorter bond distances in the bridging CO molecules is indicative of π-back-bonding from the two metal centers to the bridging CO ligands. The Ni—Fe bond length is 2.4828 (4) Å, similar to the Ni—Fe bond length (2.5 Å) in the reduced state of NiFe hydrogenase.\(^8\) The distance between atoms P1 and N1 in TPAP is 3.2518 (13) Å, consistent with a fully relaxed, pro-form of azaphosphatranne.\(^9\) One pyridine group from TPAP is uncoordinated to the Ni or Fe metals. Atom N5 of the non-coordinating pyridine is not facing directly towards the metal ions, resulting in an approximate distance of 5.61 and 5.93 Å from Ni and Fe, respectively. In comparison, the arginine side chain lies less than 4.5 Å from both the Ni and Fe in NiFe hydrogenase.\(^6\)

![Figure A.1](image)

**Figure A.1.** The molecular structure of complex NiFe(TPAP)(CO)\(_5\). The displacement ellipsoids are drawn at the 50% probability level. For clarity, the hydrogen atoms have been omitted.
Table A.1. Selected geometric parameters NiFe(TPAP)(CO)$_5$ (Å, °).

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance (Å)</th>
<th>Bond</th>
<th>Distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni1—Fe1</td>
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<td>Ni1—N6</td>
<td>2.1167 (11)</td>
</tr>
<tr>
<td>Ni1—C25</td>
<td>1.8983 (13)</td>
<td>Ni1—N7</td>
<td>2.1394 (11)</td>
</tr>
<tr>
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<td>Ni1—P1</td>
<td>2.2276 (4)</td>
</tr>
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<td>155.94 (5)</td>
<td>Fe1—C26—Ni1</td>
<td>79.42 (5)</td>
</tr>
</tbody>
</table>

A.3.2. Database Survey

A search was performed to compare previously published structures of molecular NiFe bimetallic complexes that are potential biological mimics of NiFe hydrogenase. Specifically, the search was for molecular NiFe that contained three terminally bound CO or CN$^-$ ligands to Fe and any bridging ligand(s) between the Ni and Fe metal ions. This search was limited to these features because of their importance in the active site of NiFe hydrogenase. A search of the Cambridge Structural Database (CSD, Version 5.40, update November 2018), gave 32 hits with these attributes. Only 12 structures have Ni—Fe bond lengths relatively close (within 0.2 Å) to those of the reduced form of NiFe hydrogenase (2.5 Å). However, the NiFe complexes of these 12 structures [CSD refcodes: FANHEK, FANHEK01, FANGUZ, FANHAG, FANHIO and FANHUA, LAZWEP, SUQQOL, UCUXOH and UCUXUN, UQAJAZ and YOKWIE; do not feature a pendant base, which has been demonstrated by Armstrong and collaborators to play a key role in the function of NiFe hydrogenase. Structural models of NiFe hydrogenase which incorporate a pendant base but lack the three terminally bound CO or CN ligands of the NiFe hydrogenase active site can be found here [CSD refcodes: EJUSEJ and EJUSUZ, FOTKOP and QEKLAT].
A.4. Conclusion

The heterobimetallic complex, NiFe(TPAP)(CO)$_5$, was characterized by X-ray crystallography. The structure revealed a proximal pendant base from one of the non-coordinating pyridine groups of TPAP. The NiFe(TPAP)(CO)$_5$ is a rare synthetic mimic of NiFe hydrogenase where pendant bases are incorporated into the design.

A.5. Experimental Details

General Considerations

All manipulations were performed in the glovebox, as the title complex is air- and moisture-sensitive. All solvents (except for C$_6$D$_6$) were first purged with argon and dried using a solvent purification system. Iron(0) pentacarbonyl was purchased from Sigma–Aldrich and used without further purification. Ni(TPAP)(COD) was synthesized according to an established procedure.$^4$

Physical Methods

Nuclear Magnetic Resonance (NMR) Spectroscopy:

$^1$H and $^{31}$P NMR spectra were recorded on a Bruker AVANCE 600 MHz and were referenced to the residual protio solvent peak (except for $^{31}$P, which was referenced to the absolute frequency of 0 ppm in the $^1$H dimension according to the Xi scale).

Infrared (IR) Spectroscopy: IR absorption was taken on a Thermo Scientific Nicolet iS5 spectrophotometer with an iD5 ATR attachment.

Elemental analyses (EA): EA were performed on a PerkinElmer 2400 Series II CHNS elemental analyzer.

X-ray Crystallography (XRC): X-ray diffraction studies were carried out at the UCI Department of Chemistry X-ray Crystallography Facility on a Bruker SMART APEX II diffractometer. Data
were collected at 88 K using Mo Kα radiation ($\lambda = 0.71073$ Å). A pink crystal of approximate dimensions 0.230 x 0.342 x 0.354 mm was mounted in a cryo-loop and transferred to a Bruker SMART APEX II diffractometer. The APEX2 program package was used to determine the unit cell parameters and for data collection (30 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT and SADABS to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL program. The diffraction symmetry was 2/m and the systematic absences were consistent with the monoclinic space group P21/c that was later determined to be correct. The structure was solved by dual space methods and refined on F2 by full-matrix least-squares techniques. The analytical scattering factors for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. Least-squares analysis yielded wR2 = 0.0645 and Goof = 1.039 for 397 variables refined against 7655 data, R1 = 0.0249 for those 6933 data with $I > 2\sigma(I)$.
**NiFe(TPAP)(CO)$_5$**: In a glove box, a solution of TPAP (61.2 mg, 0.136 mmol) in 3 ml of tetrahydrofuran was added to a solution of bis(1,5-cyclooctadiene)nickel(0) (37.4 mg, 0.136 mmol) in tetrahydrofuran. The solution immediately turned dark forest green and was stirred for 1 h at room temperature. To this solution, iron(0) pentacarbonyl (26.6 mg, 0.136 mmol) in 3 ml of tetrahydrofuran was added. The solution turned dark orange–brown and was stirred for 1 h. The solvent was removed under reduced pressure and re-dissolved in diethyl ether. The re-dissolved product was filtered through a glass disposable Pasteur pipette packed with a 25 mm glass microfiber filter and celite (3 cm). Slow evaporation of NiFe(TPAP)(CO)$_5$ in diethyl ether lead to the formation of pink block-like crystals of the title complex (52% yield). $^1$H NMR (C$_6$D$_6$, 600 MHz): 2.45–2.58 (m, 12H, NC$_2$H$_2$N), 4.09 (s, 6H, PyrC$_2$H$_2$), 6.58 (t, 3H, Pyr), 6.96 (t, 3H, Pyr), 7.09 (t, 3H, Pyr), 8.93 (m, 3H, Pyr). $^{31}$P{$^1$H} NMR (C$_6$D$_6$, 242.94 MHz): 118.6. IR (CO): 1745, 1770, 1919 and 2001 cm$^{-1}$. Elemental Analysis for C$_{29}$H$_{30}$FeN$_7$NiO$_5$P: C, 49.61; H, 4.31; N, 13.96; found: C, 49.52; H, 4.28; N, 13.63.
Figure A.2. $^1$H NMR spectrum of NiFe(TPAP)(CO)$_5$ in C$_6$D$_6$.

Figure A.3. $^{31}$P{$^1$H} NMR spectrum of NiFe(TPAP)(CO)$_5$ in C$_6$D$_6$. 
A.6. References


APPENDIX B

 Attempted Protonation and pKₐ Measurement of
Tris(2-pyridylmethyl)azaphosphatraneoxide

Data in this appendix was collected by undergraduate Jessica Mendoza under the guidance and supervision of Zachary Thammavongsy.
**B.1. Motivation and Specific Aims**

Vanadium phosphates (VPO) are heterogenous catalysts used for the oxidation of butane to maleic anhydride, an industrially valuable chemical. A proposed mechanism by Goddard and coworkers suggest the C-H bond activation step occurs at the P=O unit\(^1\), rather than the vanadium center. This appendix describes work towards understanding the basicity of phosphine oxides in acetonitrile, particularly tris(2-pyridylmethyl)azaphosphatrane)oxide (TPAPO) and tri(benzyl)-azaphosphatrane)oxide (TBAPO).

**B.2. Background**

Theoretical work by Goddard and coworkers proposed that the terminal P=O linkages in VPO heterogenous catalysis are responsible for C–H activation at butane (Scheme B.1).\(^1\) Goddard coined the mechanism as “reduction-coupled oxo activation” (ROA) and occurs due to the strong basicity at the P=O bond that is coupled to the neighboring high-valent, oxidative V(V) centers, which undergo reduction.

**Scheme B.1. Proposed Reduction-Coupled Oxo Activation (ROA) Mechanism in VPO system.**

![Scheme B.1. Proposed Reduction-Coupled Oxo Activation (ROA) Mechanism in VPO system.](image)

The role of a strong basic P=O in VPO motivated this work on quantifying the basicity of P=O, particularly in tris(2-pyridylmethyl)azaphosphatraneoxide (TPAPO) and tris(benzyl)azaphosphatrane)oxide (TBAPO). Previous pK\(_a\) studies on general P=O with alkyl or aryl substituents indicate they are very weak bases.\(^2\) Proazaphosphatrane-oxides have been shown
to be good nucleophiles for organic catalysis due to the added stability from the transannular interaction;\textsuperscript{3} therefore, the P=O in TPAPO and TBAPO could be stronger bases, due to the general correlation between the strength of bases and nucleophiles.

**B.3. Results and Discussion**

**B.3.1. Synthesis and Characterization of tris(2-pyridylmethyl)azaphosphatraneoxide (TPAPO)**

The synthesis and characterization of tris(2-pyridylmethyl)azaphosphatraneoxide (TPAPO) was not reported by Verkade and coworkers, despite being used as an organic catalyst in their study.\textsuperscript{4} The synthesis of TPAPO followed a published procedure,\textsuperscript{5} where a slight excess of ((CH\textsubscript{3})\textsubscript{3}SiO)\textsubscript{2} is added to a solution of tris(2-pyridylmethyl)azaphosphatrane (TPAP) in benzene (Scheme B.2).

**Scheme B.2. Synthesis of tris(2-pyridylmethyl)azaphosphatraneoxide (TPAPO).**

![Synthesis of TPAPO scheme]

After work up, a white solid is obtained and characterized by \textsuperscript{1}H and \textsuperscript{31}P{\textsuperscript{1}H} NMR spectroscopy. The \textsuperscript{31}P{\textsuperscript{1}H} NMR spectrum displayed a resonance at 23 ppm, closely matching \textsuperscript{31}P{\textsuperscript{1}H} NMR spectrum of tris(benzyl)azaphosphatraneoxide (24 ppm).\textsuperscript{5}
B.3.2. Protonation study of tris(2-pyridylmethyl)azaphosphatraneoxide (TPAPO)

Verkade and coworkers attempted the protonation of the methyl substituted Verkade’s Superbase with HCl (pK_a = 10.3 in acetonitrile) but the data and discussion were brief. In this study, HBF_4 (pK_a = 1.8 in acetonitrile) and p-toluenesulfonic acid (TsOH, pK_a = 8.5 in acetonitrile) are used to protonate TPAPO. Excess HBF_4 was added to TPAPO in acetonitrile (Scheme B.3) to approximate the pK_a of [TPAPOH]^+.

Scheme B.3. Proposed reactivity of tris(2-pyridylmethyl)azaphosphatraneoxide (TPAPO) with HBF_4.

![Proposed reactivity of tris(2-pyridylmethyl)azaphosphatraneoxide (TPAPO) with HBF_4.]

After the solvent was removed under reduced pressure, a white solid is obtained. The $^{31}\text{P}^{(1)}\text{H}$ NMR spectrum of the white solid displayed four resonances at 20.0, 16.9, 14.1 and 10.9 ppm (Figure B.1).
The multiple resonances could correspond to protonation at the P=O oxygen, the N$_{py}$ and/or the N$_{ax}$. These are all possible sites of protonation due to the pK$_a$ of pyridinium (pK$_a$ = 12.53 in acetonitrile) and tertiary amines (Et$_3$NH, pK$_a$ = 18.82). The pK$_a$ of the P=O oxygen is not measured but is proposed to be the protonation site in tris(methyl)azaphosphatrane(oxide)$_3$.$^3$ The resonance at 14.1 ppm in the $^{31}$P{$^{1}$H} NMR spectrum is the largest resonance, and is close to the resonance in the $^{31}$P NMR spectrum of Verkade’s proposed protonated methyl substituted azaphosphatraneoxide at 14.6 ppm.

Due to the difficulty of accurately measuring 1 equivalent of HBF$_4$, TsOH is used. A 1:1 ratio of TPAPO and TsOH is mixed together in acetonitrile (Scheme B.4). After the solvent is removed under reduced pressure, a white solid was obtained.
Scheme B.4. Proposed reactivity of tris(2-pyridylmethyl)azaphosphatraneoxide (TPAPO) with TsOH.

The $^{31}$P{$^1$H} NMR spectrum of the white solid displayed a major resonance at 1.64 ppm in CD$_3$CN (Figure B.2) and the disappearance of the P=O signal at 23 ppm. This data could signify a complete conversion to the protonated form TPAPO; however, P=O in proazaphosphatranes are known to be good nucleophiles that could attack electrophilic sites, such as the S in TsOH.$^3$

Figure B.2. $^{31}$P{$^1$H} NMR spectrum of tris(2-pyridylmethyl)azaphosphatraneoxide (TPAPO) + TsOH in CD$_3$CN.
B.3.3. Protonation study of tris(benzyl)azaphosphatraneoxide (TBAPO)

The benzyl version of azaphosphatrane lacks the basic pyridine N site and limits the possible sites of protonation. The synthesis of tris(benzyl)azaphosphatraneoxide (TBAPO) is outlined in previous publication from Verkade and coworkers. The addition of excess HBF₄ to TBAPO in acetonitrile is performed (Scheme B.5). After removal of solvent under reduced pressure, a white solid is obtained.

**Scheme B.5.** Reactivity of tris(benzyl)azaphosphatraneoxide (TBAPO) with HBF₄ or TsOH.

![Proposed Reaction Scheme](image)

The $^{31}$P{¹H} NMR spectrum of the white solid displayed a single resonance at 14.7 ppm (Figure B.3) This resonance is very close to the $^{31}$P NMR spectrum reported for Verkade’s proposed protonated methyl substituted azaphosphatraneoxide at 14.6 ppm.³ By switching to the benzyl version of azaphosphatrane, there are now less protonation sites to account for and less resonances in the $^{31}$P{¹H} NMR spectrum compared to the addition of HBF₄ to TPAPO.
Once again, due to the difficulty of accurately measuring 1 equivalent of HBF₄, TsOH was used. A 1:1 ratio of TBAPO and TsOH was mixed in acetonitrile (Scheme B.5). After removal of solvent under reduced pressure, a white solid was obtained. The $^{31}$P{$^1$H} NMR spectrum of the white solid displayed resonances at 21.0 and 15.7 ppm in CD$_3$CN (Figure B.4). The resonance at 21.0 ppm maybe the original TBAPO (24 ppm), but shifted due to potential hydrogen bonding interaction with nearby protonated TBAPO or TsOH. The appearance of both TBAPO and protonated TBAPO in the $^{31}$P{$^1$H} NMR spectrum would indicate an incomplete reaction, potentially due to similar pKₐ between the protonated TBAPO and TsOH in CD$_3$CN.

Figure B.3. $^{31}$P{$^1$H} NMR spectrum of tris(benzy)azaphosphatraneoxide (TBAPO) + HBF₄ in CD$_3$CN.
The protonation study of tris(2-pyridylmethyl)azaphosphatraneoxide (TPAPO) and tris(benzy)azaphosphatraneoxide (TBAPO) with HBF₄ and TsOH was performed. The $^{31}$P{$^1$H} NMR spectra displayed shifts consistent with a protonated P=O in both azaphosphatraneoxides when HBF₄ was used, however, the addition of TsOH to TPAPO resulted in a $^{31}$P{$^1$H} NMR spectrum that suggests nucleophilic addition to the electrophilic S of TsOH. Furthermore, the $pK_a$ of the protonated TBAPO may be close to that of TsOH.
B.5. Experimental Details

General Considerations

All manipulations were performed outside the glovebox. All solvents were first purged with argon and dried using a solvent purification system. The compound, \((\text{CH}_3)_3\text{SiO})_2\), was provided by the Borovik group and used without further purification. \(p\)-toluenesulfonic acid and \(\text{HBF}_4\bullet\text{Et}_2\text{O}\) (48% w/w) were commercially purchased and used without further purification.

Physical Methods

**Nuclear Magnetic Resonance (NMR) Spectroscopy:** Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AVANCE 600 MHz \((^1\text{H}, ^{13}\text{C} \text{ and } ^{31}\text{P})\) \(^1\text{H}\) NMR spectra were referenced to (tetramethylsilane) TMS using the residual proton signal of the solvent and \(^{31}\text{P}\) NMR spectra were referenced to an internal \(\text{H}_3\text{PO}_4\) sample in \(\text{D}_2\text{O}\).
Tris(2-pyridylmethyl)azaphosphatraneoxide (TPAPO): A solution of \(((\text{CH}_3)_3\text{SiO})_2\) (35.0 mg, 0.19 mmol) in 5 mL of benzene was added to a solution of tris(2-pyridylmethyl)azaphosphatrane (79.0 mg, 0.17 mmol) in 6 mL of benzene. After the solution was stirred for 1 day, the solvent was removed under reduced pressure, yielding a white solid. $^1\text{H} \text{NMR (CD}_3\text{CN, 600 MHz) } \delta = 2.82$ (t, 6H, NCH$_2$CH$_2$NP), 2.96 (m, 6H, NCH$_2$CH$_2$NP), 4.33 (d, 6H, PyCH$_2$N), 7.22 (m, 3H, Py), 7.76 (s, 6H, Py), 8.48 (d, 3H, Py). $^{31}\text{P}\{^1\text{H}\} \text{ (CD}_3\text{CN, 243 MHz) } \delta = 23.95$.

**Figure B.5.** $^1\text{H} \text{ NMR spectrum of tris(2-pyridylmethyl)azaphosphatraneoxide (TPAPO) in CD}_3\text{CN.}
Figure B.6. $^{31}P\{^1H\}$ NMR spectrum of tris(2-pyridylmethyl)azaphosphatraneoxide (TPAPO) in CD$_3$CN.
Tris(2-pyridylmethyl)azaphosphatraneoxide (TPAPO) + HBF₄: 20 drops of HBF₄ (48% w/w) were added to a solution of tris(2-pyridylmethyl)azaphosphatrane in benzene. After the solution was stirred for 1 day, the solvent was removed under reduced pressure yielding a white solid. $^{31}\text{P} \{^1\text{H}\} (\text{CD}_3\text{CN}, 243 \text{ MHz}) \delta = 20.0, 16.9, 14.1$ and 10.9.

Tris(2-pyridylmethyl)azaphosphatraneoxide (TPAPO) + TsOH : TsOH (16.1 mg, 0.08 mmol) in acetonitrile was added to a solution of tris(2-pyridylmethyl)azaphosphatrane (37.0 mg, 0.08 mmol) in acetonitrile. After the solution was stirred for 1 day, the solvent was removed under reduced pressure yielding a white solid. $^{31}\text{P} \{^1\text{H}\} (\text{CD}_3\text{CN}, 243 \text{ MHz}) \delta = 12.9, 7.8, 1.64, -19.1$ and -38.8.

Tris(benzyl)azaphosphatraneoxide (TBAPO) + HBF₄: 20 drops of HBF₄ (48% w/w) were added to a solution of tris(benzyl)azaphosphatrane in benzene. After the solution was stirred for 1 day, the solvent was removed under reduced pressure yielding a white solid. $^{31}\text{P} \{^1\text{H}\} (\text{CD}_3\text{CN}, 243 \text{ MHz}) \delta = 14.7$.

Tris(benzyl)azaphosphatraneoxide (TBAPO) + TsOH : TsOH (15.4 mg, 0.08 mmol) in acetonitrile was added to a solution of tris(benzyl)azaphosphatrane (36.8 mg, 0.08 mmol) in acetonitrile. After the solution was stirred for 1 day, the solvent was removed under reduced pressure yielding a white solid. $^{31}\text{P} \{^1\text{H}\} (\text{CD}_3\text{CN}, 243 \text{ MHz}) \delta = 21.0$ and 15.7.
B.6. References

APPENDIX C

Coordination Complexes of Phosphine Ligands without Transannular Interactions

Portions of this chapter have been published:

C.1. Motivation and Specific Aims

Ligand scaffold without the bicyclic cage frame in TPAP was designed and coordinated to Co(II) metal ions. These complexes were structurally characterized and compared with [Co(II)(TPAP)(CH3CN)][BF4]2. The ligands without the bicyclic cage frame were designed in order to compare future reactivity studies with transition metal TPAP analogues.

C.2. Background

The role of transannular interactions in transition metal complexes was outlined in the introduction of chapter 3. In this appendix, the transition metal complexes of tris(2-pyridylmethyl)aminophosphine (TPMAP) and tris(2-pyridylethyl)aminophosphine (TPEAP) are described. Both TPMAP and TPEAP ligands lack the transannular interaction of the P-Nax bond in comparison to TPAP (Chart C.1).

Chart C.1. Ligand with Bicyclic Caged Framed (TPAP) and without (TPMAP & TPEAP).
C.3. Results and Discussion

C.3.1. Synthesis of Co(II) Complexes of Tris(2-pyridylmethyl)aminophosphine (TPMAP)

The ligand, TPMAP, was synthesized following a published procedure. One equivalent of TPMAP in dichloromethane was combined with one equivalent of [Co(CH$_3$CN)$_6$][BF$_4$]$_2$ in acetonitrile (Scheme C.1). Electrospray ionization mass spectrum (ESI-MS) of the reaction mixture reveals the presence of the [Co(TPMAP)$_2$]$^{2+}$ ion and an absence of the [Co(TPMAP)]$^{2+}$ ion. The isolated product [Co(TPMAP)$_2$][BF$_4$]$_2$ was precipitated and washed with diethyl ether to afford a green solid in 32.5% yield.

Scheme C.1. Coordination of TPMAP with [Co(CH$_3$CN)$_6$][BF$_4$]$_2$.

[Co(TPMAP)$_2$][BF$_4$]$_2$ was analyzed by single crystal X-ray diffraction (Figure C.1). The crystal structure contains two 6-coordinate [Co(TPMAP)$_2$]$^{2+}$ complexes in the asymmetric unit. In each TPMAP ligand, only two pyridines and the central phosphorus donor are coordinated, leaving one pyridine unbound to the Co(II) center. This binding mode is similar to what was previously observed with Cr(III), Fe(II), and Ru(II).
Figure C.1. Crystal structure of [Co(TPMAP)$_2$][BF$_4$)$_2$. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms and counter anions are omitted for clarity. Adapted with permission from Thammavongsy, Z.; Khosrowabadi Kotyk, J. F.; Tsay, C.; Yang, J. Y. *Inorg. Chem.* **2015**, *54*, 11505-11510. Copyright 2015 American Chemical Society.

C.3.2. Synthesis of Tris(2-pyridylethyl)aminophosphine (TPEAP)

The ligand, TPEAP, which has an additional methylene linker compared to TPMAP, is a closer analogue of TPAP due to the potential 6-membered chelate ring formation. TPEAP was synthesized by mixing 2-pyridinemethanamine and tris(dimethylamino)phosphine in a 6:1 ratio at room temperature followed by the addition of KO'Bu in tetrahydrofuran (Scheme C.2). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of TPEAP displayed one resonance at 125.6 ppm. The $^1\text{H}$ NMR spectrum contained impurities consistent to the starting material 2-pyridinemethaneamine, which can impact potential metallation reactions. Care must be taken with the ratio of the starting materials to regulate the amount of impurities found in the product.
Scheme C.2. Synthesis of tris(2-pyridylethyl)aminophosphine (TPEAP).

C.3.3. Synthesis of Co(II) Complexes of Tris(2-pyridylethyl)aminophosphine (TPEAP)

One equivalent of TPEAP in dichloromethane was combined with one equivalent of [Co(CH$_3$CN)$_6$][BF$_4$]$_2$ in acetonitrile (Scheme C.3). The solution exhibited a color change from light pink to brown. After solvent was removed under reduced pressure, a brown solid was isolated in 61.19% yield. X-ray quality crystals were grown from layering a solution of the brown solid in dichloromethane with diethyl ether.

Scheme C.3. Coordination of TPEAP with [Co(CH$_3$CN)$_6$][BF$_4$]$_2$. 

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178
The crystal structure contains two 5-coordinate \([\text{Co(TPEAP)(CH}_3\text{CN)}]^{2+}\) complexes in the asymmetric unit (Figure C.2). Unlike TPMAP, the TPEAP version coordinates to the Co(II) ion in a tetradentate fashion. The \(\tau_5\) value of \([\text{Co(TPEAP)(CH}_3\text{CN)}][\text{BF}_4]\)_2 is 0.274 (average of both complexes in unit cell), where a value of 0 represents an ideal square pyramid, and a value of 1 represents an ideal trigonal bipyramid. Comparing the \(\tau_5\) value of \([\text{Co(TPEAP)(CH}_3\text{CN)}][\text{BF}_4]\)_2 and \([\text{Co(TPAP)(CH}_3\text{CN)}][\text{BF}_4]\)_2 (\(\tau_5 = 0.418\)), the geometry of the \([\text{Co(TPEAP)(CH}_3\text{CN)}][\text{BF}_4]\)_2 is more square pyramidal than \([\text{Co(TPAP)(CH}_3\text{CN)}][\text{BF}_4]\)_2, potentially due to the non-bicyclic cage frame that would restrict coordination to a more C\(_3\) symmetric complex. The Co–P distance in \([\text{Co(TPEAP)(CH}_3\text{CN)}][\text{BF}_4]\)_2 is 2.147 Å (average of both complexes in unit cell) which is similar to that of \([\text{Co(TPAP)(CH}_3\text{CN)}][\text{BF}_4]\)_2 (Co–P = 2.1693(7) Å).

Figure C.2. Crystal structure of \([\text{Co(TPEAP)(CH}_3\text{CN)}][\text{BF}_4]\)_2. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms and counter anions are omitted for clarity.
C.4. Conclusion

Co(II) complexes of TPMAP and TPEAP (non-bicyclic analogue of TPAP) were synthesized and structurally characterized. The additional methylene linker in TPEAP (compared to TPMAP) provided flexibility for tetradentate coordination to a Co(II) ion. TPEAP displayed tetradentate chelation in \([\text{Co(TPEAP)(CH}_3\text{CN)}][\text{BF}_4]_2\), just like TPAP in \([\text{Co(TPAP)(CH}_3\text{CN)}][\text{BF}_4]_2\).

C.5. Experimental Details

General Considerations

All manipulations were performed in the glovebox, as all complexes are air- and moisture-sensitive. All solvents were first purged with argon and dried using a solvent purification system. 2-pyridinemethanamine, KOtBu, tris(dimethylamino)phosphine were commercially purchased and used without further purification. Ni(TPAP)(COD) was synthesized according to an established procedure.\(^4\) \([\text{Co(CH}_3\text{CN)}_6][\text{BF}_4]_2\)\(^5\) and TPMAP\(^1\) were synthesized according to published procedures.

Physical Methods

Nuclear Magnetic Resonance (NMR) Spectroscopy: Nuclear magnetic resonance (NMR) spectra were recorded on a DRX400 with a switchable QNP probe (\(^1\text{H}\) and \(^31\text{P}\)) or a Bruker AVANCE 600 MHz (\(^1\text{H}\) and \(^31\text{P}\)). \(^1\text{H}\) NMR spectra were referenced to (tetramethylsilane) TMS using the residual proteo impurities of the solvent; \(^31\text{P}\{^1\text{H}\}\) NMR spectroscopy experiments are referenced to the absolute frequency of 0 ppm in the \(^1\text{H}\) dimension according to the Xi scale.\(^6\)

X-ray Crystallography (XRC): X-ray diffraction studies were carried out at the UCI Department of Chemistry X-ray Crystallography Facility on a Bruker SMART APEX II diffractometer. Data
were collected at 88 K using Mo Kα radiation (λ = 0.710 73 Å). A full sphere of data was collected for each crystal structure. The APEX2 program suite was used to determine unit-cell parameters and to collect data. The raw frame data were processed and absorption corrected using the SAINT and SADABS programs, respectively, to yield the reflection data files. Structures were solved by direct methods using SHELXS and refined against F2 on all data by full-matrix least-squares with SHELXL-97.

For the structure of [Co(TPMA)2][BF4]2, checkCIF reports one level B alert (PLAT214_ALERT_2_B) due to a high ratio of maximum to minimum anisotropic displacement parameters (ADPs) for atom F2B, which can signify a substitutional or positional disorder. As this atom is in the minor part of a disordered BF4 anion, the identity of which is not in question.

[Co(TPMA)2][BF4]2: In the glovebox, [Co(CH3CN)6][BF4]2 (61.3 mg, 0.128 mmol) was added to a solution of TPMA (45.1 mg, 0.128 mmol) in 3 mL of dichloromethane. The solution immediately turned dark green and was stirred for 6 h at room temperature. The solvent was removed under reduced pressure, and the resulting green solid was washed with diethyl ether. The green solid was re-dissolved in acetonitrile and filtered through a glass pipet packed with a glass microfiber filter. Slow vapor diffusion with diethyl ether afforded green crystals. ESI-MS (m/z): [M − BF4 ]+ Calculation for C36H42BCoF8N12P2, 850.25; Found, 850.17. UV-vis (CH3CN) λmax, nm (ε): 230 (49377), and 290 (18654). Analytical Calculation for C36H42B2Cl3CoF8N12P2·(CH2Cl2)1.5: C, 42.14; H, 4.13; N, 15.92. Found: C, 42.30; H, 4.26; N, 15.79. μeff (solution) = 2.11 μB
**Tris(2-pyridylethyl)aminophosphine (TPEAP):** In a Schlenk flask, 2-pyridinemethanamine (200 mg, 1.64 mmol), tris(dimethylamino)phosphine (44.5 mg, 0.273 mmol) and 15 mL of tetrahydrofuran were added. The reaction was stirred for 4 days at room temperature, under N₂. The reaction mixture was brought into the glove box and was added KOtBu (0.061 mg, 0.54 mmol). A color change was observed from colorless to pink and stirred for 1 day. The reaction was filtered through a medium fritted funnel. The filtrate was collected, and the solvent was removed under reduced pressure. The solid was redissolved in acetonitrile and refiltered through a medium fritted funnel to remove excess potassium tert-butoxide. The filtrate was collected, the solvent was removed under reduced pressure, and the solid was redissolved in tetrahydrofuran and layered with pentane. After 1 day of standing, the solution was decanted from crystalline potassium tert-butoxide. The solvent from the filtrate was removed under reduced pressure to afford the product as a colorless oil. ¹H NMR (CD₃CN, 400 MHz) δ = 2.51 (d, 9H, NCH₃), 4.18 (d, 6H, PyrCH₂N), 7.18 (m, 3H, Py), 7.40 (d, 3H, Py), 7.68 (m, 3H, Py), 8.49 (d, 3H, Py). ³¹P{¹H}NMR (CD₃CN, 162 MHz) δ = 125.6.
Figure C.3. $^1$H NMR spectrum of tris(2-pyridylethyl)aminophosphine (TPEAP) in CD$_3$CN.

Figure C.4. $^{31}$P{$^1$H}NMR spectrum of tris(2-pyridylethyl)aminophosphine (TPEAP) in CD$_3$CN.
[Co(TPEAP)(CH₃CN)][BF₄]₂: In the glovebox, a solution of [Co(CH₃CN)₆][BF₄]₂ (42.6 mg, 0.0889 mmol) in 3 mL acetonitrile was added to a solution of TPEAP (35.1 mg, 0.0889 mmol) in 3 mL of dichloromethane. The solution turned brown and was stirred for 1 day at room temperature. The solvent was removed under reduced pressure, and the resulting brown solid was washed with diethyl ether. The green solid was re-dissolved in dichloromethane and filtered through a glass pipet packed with a glass microfiber filter. A layering system of diethyl ether/dichloromethane afforded red crystals.

C.6. References


184
APPENDIX D

Attempted Synthesis of an Fe-Sulfur-Carbide Cluster
D.1. Motivation and Specific Aims

Cluster chemistry is a rich subset of inorganic chemistry since Albert Cotton first used the word “cluster” to describe multimetallic complexes in the 1960s.\textsuperscript{1} One of the motivations driving inorganic chemists to pursue these synthetic challenges is the importance cluster complexes play in biology. There is great interest in a synthetic mimic of the FeMocofactor (FeMoco) in the molybdenum nitrogenase enzyme due to the recent identification of the carbide interstitial atom.\textsuperscript{2,3} The work detailed in this appendix describes efforts to synthesize an Fe-carbide cluster containing sulfur ligands.

D.2. Background

In 2011, the mysterious interstitial atom was revealed in the nitrogenase’s FeMocofactor (FeMoco) as a tetraanionic carbon.\textsuperscript{2,3} Although chemists have not yet synthesized a FeMoco mimic containing all components of the active site (Fe, S, and a carbide), some groups have published related complexes in hopes of shedding light on the role some of these atoms play in the active site.\textsuperscript{4} Holland and coworkers came close to incorporating relevant atoms of FeMoco with their Fe-bis(thiolate)arene ligand system, where the arene system is illustrated as a carbide (Figure D.1).\textsuperscript{5} Their electron rich Fe-bis(thiolate)arene complex binds N\textsubscript{2}, where Holland and coworkers found the breaking of an Fe-S bond, from an exogenous sulfur ligand, to be an important step before N\textsubscript{2} binding. Holm synthesized a tris-pyrazolyborate capping ligand on an Fe\textsubscript{3}S\textsubscript{3} cluster group on W (Figure D.1). The Fe\textsubscript{3}S\textsubscript{3} cluster contains a light atom, N, presenting a unique synthetic pathway to potentially incorporate other light atoms (i.e. carbon).\textsuperscript{6} Recently, Bendix and coworkers developed a new methodology to incorporate a carbide center in a Fe\textsubscript{2}Ru cluster
complex. Although this system is missing sulfur ligands, the rare presence of a carbide center provides a solid foundation for more synthetic modifications in pursuit of a more structurally complete synthetic model of FeMoco.

**Figure D.1.** Structurally characterized Fe complexes containing either sulfur or carbide-like components as partial FeMoco synthetic mimics.

This appendix describes efforts to decorate a well-known Fe-carbide carbonyl cluster with sulfur ligands to generate the first synthetic model that incorporates all three components of FeMoco (Fe, S, and carbide atom).

**D.3. Results and Discussion**

The starting point of this study was the cluster $\text{[Me}_4\text{N}]_2[\text{Fe}_6(\text{CO})_{16}\text{C}^2]$ which was synthesized following a procedure by Churchill. The composition was confirmed by $^{13}$C NMR and IR spectroscopy. The carbide is located downfield in the $^{13}$C NMR spectrum, at 484 ppm and the IR spectrum display two major CO vibrational frequency at 1863 and 1727 cm$^{-1}$. Despite the difference in geometry between the $\text{[Me}_4\text{N}]_2[\text{Fe}_6(\text{CO})_{16}\text{C}^2]$ cluster and the FeMoco active site, the closest Fe-C distance measured by X-ray diffraction is quite similar, at 1.9 Å and 2.0 Å, for $\text{[Me}_4\text{N}]_2[\text{Fe}_6(\text{CO})_{16}\text{C}^2]$ and FeMoco, respectively.

187
The addition of sulfur atoms to $[\text{Me}_4\text{N}]_2[\text{Fe}_6(\text{CO})_{16}\text{C}^2]$ was attempted through the addition of various sulfur compounds to $[\text{Me}_4\text{N}]_2[\text{Fe}_6(\text{CO})_{16}\text{C}^2]$ in acetonitrile or tetrahydrofuran (Table D.1). These reactions were motivated by Holm’s Fe$_4$S$_4$ cluster work with sulfur ligand exchange.$^{11}$

**Table D.1.** Attempted substitution of carbonyl with sulfur reagents in $[\text{Me}_4\text{N}]_2[\text{Fe}_6(\text{CO})_{16}\text{C}^2]$.

<table>
<thead>
<tr>
<th>Number</th>
<th>Sulfur Reagent</th>
<th>Ratio (Cluster:Sulfur)</th>
<th>Condition</th>
<th>Solvent</th>
<th>Duration (day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$S_8$</td>
<td>1:4.5</td>
<td>Room Temperature</td>
<td>THF</td>
<td>1 day</td>
</tr>
<tr>
<td>2</td>
<td>$S_8$</td>
<td>1:4.5</td>
<td>UV-Lamp Room Temperature</td>
<td>CH$_3$CN</td>
<td>1 day</td>
</tr>
<tr>
<td>3</td>
<td>$\text{cyclohexyl SH}$</td>
<td>1:20</td>
<td>Room Temperature</td>
<td>CH$_3$CN</td>
<td>2 days</td>
</tr>
<tr>
<td>4</td>
<td>$\text{cyclohexyl SH}$</td>
<td>1:20</td>
<td>UV-Lamp Room Temperature</td>
<td>CH$_3$CN</td>
<td>1 day</td>
</tr>
<tr>
<td>5</td>
<td>$\text{cyclopropane SH}$</td>
<td>1:18</td>
<td>Room Temperature</td>
<td>CH$_3$CN</td>
<td>2 days</td>
</tr>
<tr>
<td>6</td>
<td>$\text{cyclopropane SH}$</td>
<td>1:22</td>
<td>UV-Lamp Room Temperature</td>
<td>CH$_3$CN</td>
<td>1 days</td>
</tr>
<tr>
<td>7</td>
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<td>1:20</td>
<td>Room Temperature</td>
<td>CH$_3$CN</td>
<td>2 days</td>
</tr>
<tr>
<td>8</td>
<td>$\text{cyclopentadiene SH}$</td>
<td>1:17</td>
<td>UV-Lamp Room Temperature</td>
<td>CH$_3$CN</td>
<td>1 days</td>
</tr>
<tr>
<td>9</td>
<td>$\text{cyclopentadiene SH}$</td>
<td>1:17</td>
<td>Room Temperature</td>
<td>CH$_3$CN</td>
<td>2 days</td>
</tr>
<tr>
<td>10</td>
<td>$\text{cyclopentadiene SH}$</td>
<td>1:20</td>
<td>UV-Lamp Room Temperature</td>
<td>CH$_3$CN</td>
<td>1 days</td>
</tr>
</tbody>
</table>
The reactions under a UV-lamp (365 nm) did produce a color change, resulting in the isolation of a brown or red brown solid. However, all reactions produced IR spectra with CO stretches that matched the vibrational spectra of the starting material. Infrared spectra of the isolated products from all the reactions can be found in the Experimental Details.

Reactions run at room temperature did not display a color change from purple (except with S₈). The reaction of [Me₄N]₂[Fe₆(CO)₁₆C²⁻] with S₈ in tetrahydrofuran (row 1 in Table D.1) produced a brown solid. Washing the brown solid with diethyl ether resulted in an orange yellow solution, in which colorless crystals formed upon slow evaporation of the diethyl ether. IR spectrum of the colorless crystals displayed CO vibrational frequencies at higher wavenumber (2082 and 1998 cm⁻¹) than the starting material (1863 and 1727 cm⁻¹ of [Me₄N]₂[Fe₆(CO)₁₆C²⁻]).

X-ray analysis of the colorless crystals displayed a Fe₅(CO)₁₅C, which is consistent with previous structures of Fe₅(CO)₁₅C (Figure D.2).⁹ It is documented that the [Me₄N]₂[Fe₆(CO)₁₆C²⁻] cluster can undergo chemical oxidation via the oxidative elimination of {Fe(CO)ₘ(X)ₙ} units.¹² However, the IR stretching frequency of the Fe₅(CO)₁₅C produced in this appendix do not match that of previous published Fe₅(CO)₁₅C (2015, 1975 and 1945 cm⁻¹).⁹
Figure D.2. Crystal structure of Fe₅(CO)₁₅C. Thermal ellipsoids are drawn at 50% probability.

D.4. Conclusion

The cluster, [Me₄N]₂[Fe₆(CO)₁₆C²⁻] was mixed with various sulfur reagents in order to produce a Fe-S-Carbide cluster that would mimic the FeMoco active site of nitrogenase. The reaction of [Me₄N]₂[Fe₆(CO)₁₆C²⁻] with S₈ (row 1 in Table D.1) produced crystal structures that identified as the Fe₅(CO)₁₅C cluster. However, the IR spectrum displayed CO vibrational frequencies that are not consistent with the literature values of a Fe₅(CO)₁₅C cluster.
D.5. Experimental Details

General Considerations
All manipulations were performed in the glovebox, as the clusters can undergo oxidative elimination. All solvents were first purged with argon and dried using a solvent purification system. Methyl disulfide, 4-fluorothiophenol, 2-methyl-1-propanethiol and benzyl mercaptan were provided from the Rychnovsky lab at UCI and used without further purification. Na(Hg), Mn$_2$(CO)$_{10}$, Fe(CO)$_5$ and S$_8$ were commercially purchased and used without further purification.

Physical Methods

Infrared (IR) Spectroscopy: In a glove box, the IR absorption was taken on a Thermo Scientific Nicolet iS5 spectrophotometer with an iD5 ATR attachment.

UV-Lamp Condition: All experiments with a UV-Lamp were conducted in the Evans’ lab. In a hood with aluminum foil covered windows is a Hanovia medium-pressure 450 W (254 nm) mercury vapor lamp (PC451050/ 610741). The 5.5 in. long lamp was clamped to hang inside a 13 in. × 1.5 in. diameter cavity of a double-walled quartz water cooling jacket. Samples were placed on a stir plate, placed on one side of the lamp.

General Reaction: In the glove box, the neat sulfur reagent was added to a solution of [Me$_4$N]$_2$[Fe$_6$(CO)$_{16}$C$_2$] in 10 mL of THF. The mixture was stirred for either 1 d (UV-Lamp) or 2 d (no UV-Lamp). The solvent was then removed under reduced pressure to obtain a solid. For reactions with UV-light, the reaction vial (20 mL scintillation vial) was sealed with electrical tape and brought outside the box. After the reaction was finished, the solvent was removed under reduced pressure before analyzing the solid by IR spectroscopy in the glovebox.
(1) Solid S\textsubscript{8} (45.0 mg) was added to a solution of [Me\textsubscript{4}N\textsubscript{2}Fe\textsubscript{6}(CO)\textsubscript{16}C\textsubscript{2}-] (36.8 mg) in THF. The purple mixture was stirred for 1 day, during which time the color changed from purple to brown. Solvent was removed under reduced pressure to obtain a brown solid. The brown solid was extracted with diethyl ether to give an orange yellow solution. X-ray quality crystals were grown from the slow evaporation of diethyl ether.

Figure D.3. IR spectra of (red, top) [Me\textsubscript{4}N\textsubscript{2}Fe\textsubscript{6}(CO)\textsubscript{16}C\textsubscript{2}-] and the product of (blue, bottom) [Me\textsubscript{4}N\textsubscript{2}Fe\textsubscript{6}(CO)\textsubscript{16}C\textsubscript{2}-] + S\textsubscript{8}.
(2) Solid $S_8$ (52.9 mg) was added to a solution of $[\text{Me}_4\text{N}]_2[\text{Fe}_6(\text{CO})_{16}C^2\text{]}$ (43.3 mg) in $\text{CH}_3\text{CN}$. The purple mixture was stirred for 1 day under UV light, during which time the color changed from purple to red-brown.

**Figure D.4.** IR spectra of (red, top) $[\text{Me}_4\text{N}]_2[\text{Fe}_6(\text{CO})_{16}C^2\text{]}$ and the product of (blue, bottom) $[\text{Me}_4\text{N}]_2[\text{Fe}_6(\text{CO})_{16}C^2\text{]} + S_8$ under UV light.
(3) PhCH$_2$SH (53.7 mg) was added to a solution of [Me$_4$N]$_2$[Fe$_6$(CO)$_{16}$C$_2$] (25.5 mg) in CH$_3$CN. The purple mixture was stirred for 1 day at room temperature. No color change occurred.

Figure D.5. IR spectra of (red, top) [Me$_4$N]$_2$[Fe$_6$(CO)$_{16}$C$_2$] and the product of (blue, bottom) [Me$_4$N]$_2$[Fe$_6$(CO)$_{16}$C$_2$] + PhCH$_2$SH.
(4) PhCH$_2$SH (52.9 mg) was added to a solution of Me$_4$N$\textsubscript{2}$[Fe$_6$(CO)$_{16}$C$_2$]$^-$ (43.3 mg) in CH$_3$CN. The purple mixture was stirred for 1 day under UV light, during which time the color changed from purple to red-brown.

![Figure D.6. IR spectra of (red, top) $[\text{Me}_4\text{N}]_2[\text{Fe}_6(\text{CO})_{16}\text{C}_2^-]$ and the product of (blue, bottom) $[\text{Me}_4\text{N}]_2[\text{Fe}_6(\text{CO})_{16}\text{C}_2^-] + \text{PhCH}_2\text{SH}$ under UV light.](image-url)
(5) iPrSH (42.2 mg) was added to a solution of [Me₄N]₂[Fe₆(CO)₁₆C²⁻] (24.2 mg) in CH₃CN. The purple mixture was stirred for 1 day at room temperature. No color change occurred.

Figure D.7. IR spectra of (red, top) [Me₄N]₂[Fe₆(CO)₁₆C²⁻] and the product of (blue, bottom) [Me₄N]₂[Fe₆(CO)₁₆C²⁻] + iPrSH.
(6) iPrSH (72.5 mg) was added to a solution of \([\text{Me}_4\text{N}]_2[\text{Fe}_6(\text{CO})_{16}^2\text{C}_2^-]\) (34.2 mg) in CH$_3$CN. The purple mixture was stirred for 1 day under UV light, during which time the color changed from purple to red-brown.

**Figure D.8.** IR spectra of (red, top) \([\text{Me}_4\text{N}]_2[\text{Fe}_6(\text{CO})_{16}^2\text{C}_2^-]\) and the product of (blue, bottom) \([\text{Me}_4\text{N}]_2[\text{Fe}_6(\text{CO})_{16}^2\text{C}_2^-] + \text{iPrSH}\) under UV light.
(7) $p$-FC$_6$H$_4$SH (69.6 mg) was added to the solution of [Me$_4$N]$_2$[Fe$_6$(CO)$_{16}$C$_2^-$] (26.0 mg) in CH$_3$CN. The purple mixture was stirred for 1 day at room temperature. No color change occurred.

**Figure D.9.** IR spectra of (red, top) [Me$_4$N]$_2$[Fe$_6$(CO)$_{16}$C$_2^-$] and the product of (blue, bottom) [Me$_4$N]$_2$[Fe$_6$(CO)$_{16}$C$_2^-$] + $p$-FC$_6$H$_4$SH.
(8) $p$-FC$_6$H$_4$SH (64.5 mg) was added to a solution of [Me$_4$N]$_2$[Fe$_6$(CO)$_{16}$C$_2^-$] (28.4 mg) in CH$_3$CN. The purple mixture was stirred for 1 day under UV light, during which time the color changed from purple to red-brown.

![IR spectra](image)

Figure D.10. IR spectra of (red, top) [Me$_4$N]$_2$[Fe$_6$(CO)$_{16}$C$_2^-$] and the product of (blue, bottom) [Me$_4$N]$_2$[Fe$_6$(CO)$_{16}$C$_2^-$] + $p$-FC$_6$H$_4$SH under UV light.
(9) Me₂S₂ (41.9 mg) was added to a solution of [Me₄N]₂[Fe₆(CO)₁₆C²⁻] (25.0 mg) in CH₃CN. The purple mixture was stirred for 1 day at room temperature. No color changed occurred.

**Figure D.11.** IR spectra of (red, top) [Me₄N]₂[Fe₆(CO)₁₆C²⁻] and the product of (blue, bottom) [Me₄N]₂[Fe₆(CO)₁₆C²⁻] + Me₂S₂.
(10) Me₂S₂ (64.5 mg) was added to a solution of [Me₄N]₂[Fe₆(CO)₁₆C²⁻] (28.4 mg) in CH₃CN. The purple mixture was stirred for 1 day under UV light, during which time the color changed from purple to red-brown.

Figure D.12. IR spectra of (red, top) [Me₄N]₂[Fe₆(CO)₁₆C²⁻] and the product of (blue, bottom) [Me₄N]₂[Fe₆(CO)₁₆C²⁻] + Me₂S₂ under UV light.
D.6. References

APPENDIX E

CH₄ Activation Study with Fe(depe)₂ Derivatives
E.1. Motivation and Specific Aims

Methane is used as a resource for the production of many important industrialized chemicals such as ammonia, methanol and acetic acid.\(^1\) Unfortunately, this process proceeds through a very energy intensive pathway (700 - 1100 °C) via the steam reforming of methane.\(^1\) Therefore, efforts to directly convert methane to valuable chemicals such as methanol\(^2\) are highly sought after and is the motivation of this project.

One of the challenges with direct conversion of methane is the activation of the strong C-H bond. There are many approaches possible for C-H bond activation; this appendix describes attempts to activate the C-H bond of methane by heterolysis in a base-assisted pathway.

E.2. Background

Methane is inert due to its strong C-H bond (BDE = 105 kcal/mol\(^-1\)) and its high lying LUMO and low lying HOMO.\(^3\) Although C-H bond cleavage is possible at high temperatures under atmospheric conditions, combustion of methane is not controlled and produces undesirable products. The first step towards functionalization is activating the C-H bond of methane. This can be challenging due to two reasons; the inertness of the C-H bond and competing reactions once the oxidized product is formed.\(^4\) Examples of C-H bond activation of methane by metal complexes are categorized into 5 classes,\(^5\) which exclude some approaches that are not directly related to metal-CH\(_3\) bond formation. These classes are detailed below and outlined in Scheme E.1.
Scheme E.1. Categories of C-H activation of methane. a) oxidative addition, b) σ-bond metathesis, c) electrophilic activation, d) 1,2 addition and e) metalloradical.

\[
\begin{align*}
\text{a} & \quad L_nM + H \xrightarrow{\text{CH}_3} L_nM\text{CH}_3 \\
\text{b} & \quad L_nM^{\text{CH}_3} + H \xrightarrow{\text{CH}_3} L_nM\text{CH}_3 \\
\text{c} & \quad L_nM^{\text{X}} + H \xrightarrow{\text{CH}_3} L_nM\text{C}^+ \xrightarrow{\text{CH}_3} L_nM\text{CH}_3 + X \\
\text{d} & \quad L_nM\text{X} + H \xrightarrow{\text{CH}_3} L_nM\text{XCH}_3 \\
\text{e} & \quad 2L_nM + H \xrightarrow{\text{CH}_3} L_nM\text{CH}_3 + L_nMH
\end{align*}
\]

E.2.1. Oxidative Addition

These complexes feature electron rich, low-valent late transition metal centers with low-coordination numbers. The low-coordination number allows space for the addition of both carbon and hydrogen from methane while the highly electron rich metal center can easily undergo two electron oxidation. Examples can be seen with metals such as Re, Fe, Os, and Ir. Early examples of oxidative addition of methane involve a Cp*Ir(CO) complex, under 20 atm of methane using light at room temperature. The drawback of this system is the use of expensive precious metals.
E.2.2. Sigma-Bond Metathesis

These complexes feature electron poor, high-valent early transition metal centers. The process goes through a net zero oxidation state change. In all but one case, a reversible reaction occurs in which alkyl fragments interchange with no further methane functionalization. Examples include metals in group 3, lanthanides and actinides. The first example of σ-bond metathesis focuses on the lanthanide complex, Cp²LuCH₃, which showed a reversible methane activation at 70 °C.

E.2.3. 1,2-Addition

Similar to σ-bond metathesis, 1,2-addition features electron-poor, high-valent, and typically early transition metal centers. However, they have a unique feature that incorporates metal-ligand multiple bonds. The addition of methane does not change the oxidation state of the metal and examples can be seen with Zr, V, Ti and W metals. The transient imido complex, [(tBu₃SiNH)₂Zr=NSi₃Bu₃] incorporates methane and other aliphatic C-H bonds in high yields (99%). However, the resulting product is relatively unreactive and does not undergo subsequent functionalization.

E.2.4. Metalloradicals

These complexes feature two metal centers that can homolytically split the C-H bond in methane. Rh(II) is an example of a metal capable of metalloradicals, which oxidize to Rh(III) upon the addition of the alkyl or hydrogen atom. A porphyrin Rh dimer was shown to slowly activate methane after 15 days at 40 °C with 40% conversion.
E.2.5. Electrophilic Activation

Electrophilic activation of methane was pioneered by Shilov using square planar Pt(II) complexes and can now be seen with other late metals such as Pd, Co, Hg and Tl. The reaction conditions for Shilov’s chemistry usually involve strong polar mediums (such as water or an anhydrous strong acid) at 100 °C. Additionally, this chemistry suffers from an expensive sacrificial oxidant [Pt(IV)]. However, this system is catalytic, oxidizing methane to methanol or chloroform.

E.2.6. Base Assisted Activation for C-H Activation

Similar to electrophilic activation, this work described in this appendix aims to activate C-H bonds by employing a base and a metal center to facilitate base-assisted heterolytic cleavage of the C-H bond. The base used in this work is 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, pKa 24.3 in acetonitrile). A few examples of base-assisted C-H activation involve sp² and sp³ carbons, but none involve methane. Recent work from Darensbourg and colleagues utilizes a pendant base amine to assist in the intramolecular cleavage of an sp³ C-H bond in an iron complex.

E.3. Results and Discussions

E.3.1. Synthesis of [FeCl(CO)(depe)₂]Cl

Following a literature procedure, two equivalent of bis(diethylphosphino)ethane (depe) were added to FeCl₂ in THF to isolate the product, FeCl₂(depe)₂ as a green solid. CO gas was then added to the solution of FeCl₂(depe)₂ in ethanol. The color changed from green to orange after dissolution in ethanol and then to orange-yellow when CO gas was added to
generate the complex, $[\text{FeCl(CO)(depe)}_2]\text{Cl}$ (Scheme E.2). $[\text{FeCl(CO)(depe)}_2]\text{Cl}$ displayed a CO vibrational frequency peak in the solution-IR (dichloromethane) at 1915 cm$^{-1}$, matching the literature value.$^{31}$ The $^{31}\text{P}$ NMR spectrum of $[\text{FeCl(CO)(depe)}_2]\text{Cl}$ had a single resonance at 65.97 ppm, also matching the previously reported value.$^{31}$

**Scheme E.2.** Synthesis of FeCl$_2$(depe)$_2$ and [FeCl(CO)(depe)$_2$]Cl.

**E.3.2. Reactivity with CH$_4$**

Following the literature procedure, $[\text{FeCl(CO)(depe)}_2]\text{Cl}$ undergoes a salt metathesis with 2 equivalents of AgSbF$_6$ in CD$_2$Cl$_2$ to obtain a bright orange-yellow solution (Scheme E.3). The proposed structure of $[\text{Fe(SbF}_6\text{(CO)(depe)}_2]\text{(SbF}_6\text{)}$ is in line with other structurally characterized $[\text{Fe(CO)(X)(depe)}_2]\text{(X)}$ complex, where X is BF$_4$ or OTf. The solution containing $[\text{Fe(SbF}_6\text{(CO)(depe)}_2]\text{(SbF}_6\text{)}$ was filtered into a J. Young tube and sealed. A $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{Fe(SbF}_6\text{(CO)(depe)}_2]\text{(SbF}_6\text{)}$ displayed three resonances at 64.7, 64.3 and 64.1 ppm. The weak Fe-F bond presented an opportunity for CH$_4$ binding, as it was demonstrated previously that H$_2$ can bind to Fe in this system.$^{31}$ CH$_4$ gas was then added to the J. Young tube but no color change was observed (Scheme E.3). In addition, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum was unchanged from $[\text{Fe(SbF}_6\text{(CO)(depe)}_2]\text{(SbF}_6\text{)}$.
E.3.3. Reactivity with CH₄ and DBU

The addition of an external base (DBU) was added to achieve the base assisted activation of CH₄. The goal was to produce the [Fe(CH₃)(depe)₂] complex and a [DBU-H] molecule. The characterization of a Fe-CH₃ complex of the Fe(depe)₂ system was previously published and can help identify if a Fe-CH₃ bond was formed. The J. Young tube was filled with [FeCl(CO)(depe)₂]Cl, 1.5 equiv DBU, 2.5 equiv of AgSbF₆ and CH₄ gas (Scheme E.4). The ³¹P NMR spectrum of product showed a major resonance at 70.0 ppm, which is consistent with the controlled experiment of DBU addition (without CH₄) to the proposed [Fe(SbF₆)(CO)(depe)₂](SbF₆). Thus, it appears DBU binds directly to the iron complex, inhibiting any direct CH₄ interaction. R. H. Morris has noted the importance of using less nucleophilic bases in these systems to prevent ligation to the Fe center. One method to circumvent this issue is to use a sterically bulky base, where access to the Fe center would be hindered.
**Scheme E.4.** Reactivity of [FeCl(CO)(depe)$_2$]Cl with CH$_4$ and DBU.

**E.4. Conclusions**

Base assisted C-H bond activation was attempted with [FeCl(CO)(depe)$_2$]Cl, DBU, CH$_4$ and SbF$_6$. No reaction was observed for CH$_4$ activation, potentially due to the formation of an Fe-DBU bond that may prevent CH$_4$ from accessing the Fe center of [Fe(CO)(depe)$_2$](SbF$_6$)$_2$. Future work with this system could utilize a bulkier base, such as the tertbutyl functionalized Verkade’s Superbase, in order to inhibit coordination.

**E.5. Experimental Details**

**General Considerations**

All manipulations were performed in the glovebox or on a Schlenk line, as the complex is moisture-sensitive. All solvents were first purged with argon and dried using a solvent purification system. Bis(diethylphosphino)ethane (depe), FeCl$_2$, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), and CH$_4$ were commercially purchased and used without further purification. AgSbF$_6$ was generously donated from the Pronin Lab from UCI and used without further purification. Complexes [FeCl$_2$(depe)$_2$], [FeCl(CO)(depe)$_2$]Cl, and [Fe(SbF$_6$)(CO)-(depe)$_2$](SbF$_6$)$_2$ were synthesized using published procedures.$^{31}$
Physical Methods

Nuclear Magnetic Resonance (NMR) Spectroscopy: Nuclear magnetic resonance (NMR) spectra were recorded on a DRX400 with a switchable QNP probe (\(^1\)H and \(^{31}\)P) or a Bruker AVANCE 600 MHz (\(^1\)H and \(^{31}\)P). \(^1\)H NMR spectra were referenced to (tetramethylsilane) TMS using the residual proteo impurities of the solvent; \(^{31}\)P\{\(^1\)H\} NMR spectroscopy experiments are referenced to an internal standard (PPh\(_3\) in toluene).

Reactivity with CH\(_4\): In the glove box a solution of AgSbF\(_6\) (7.3 mg, 21 nmol) in CD\(_2\)Cl\(_2\) was added to a solution of [FeCl\(_2\)depe\(_2\)] (5.0 mg, 8.8 nmol) in CD\(_2\)Cl\(_2\). An immediate white precipitate formed and the color changed from light yellow to bright orange-yellow. The solution was filtered through a pipette packed with filter paper into a J. Young tube with an inner tube filled with PPh\(_3\) in toluene as an internal standard. The J. Young tube was taken out of the glove box and subject to three freeze-pump-thaw cycles before CH\(_4\) was introduced. \(^{31}\)P\{\(^1\)H\}NMR (CD\(_2\)Cl\(_2\), 243 MHz) \(\delta = 64.7, 64.4, 64.1,\) and 63.5 ppm.
Figure E.1. $^1$H NMR spectrum of [Fe(CO)(depe)$_2$]Cl + AgSbF$_6$ + CH$_4$ in CD$_2$Cl$_2$.

Figure E.2. $^{31}$P{$^1$H} NMR spectrum of [Fe(CO)(depe)$_2$]Cl + AgSbF$_6$ + CH$_4$ in CD$_2$Cl$_2$. 
Reactivity with CH₄ and DBU: In the glove box 2 μL of DBU was added via microsyringe to a J. Young tube with [Fe(SbF₆)(CO)(depe)₂](SbF₆) in CD₂Cl₂. The J. Young tube was taken out of the glove box and subject to three freeze-pump-thaw cycles before CH₄ (~1 atm) was introduced. No color change was observed when CH₄ was introduced. ³¹P{¹H} NMR (CD₂Cl₂, 243 MHz) δ = 71.9, 71.81, 70.0, 65.5, 65.2, 64.1, 63.5, 51.8, 51.7, and 49.8 ppm.

Figure E.3. ¹H NMR spectrum of [Fe(CO)(depe)₂]Cl + AgSbF₆ + CH₄ + DBU in CD₂Cl₂.
**Figure E.4.** $^{31}$P{$^1$H} NMR spectrum of [Fe(CO)(depe)$_2$]Cl + AgSbF$_6$ + CH$_4$ + DBU in CD$_2$Cl$_2$. 
E.6. References