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UNIVERSITY OF ALBERTA

PYRAZOLYL - METHANE AND -BORATE COMPLEXES OF  
MOLYBDENUM AND RHENIUM

BY



SHAUN DUHAIME

A THESIS SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND  
RESEARCH IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR  
THE DEGREE OF MASTER OF SCIENCE.

DEPARTMENT OF CHEMISTRY

EDMONTON, ALBERTA

SPRING 1995



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| Gerontology             | 0351 |
| History                 |      |
| General                 | 0578 |

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| Medieval                         | 0581 |
| Modern                           | 0582 |
| Black                            | 0328 |
| African                          | 0331 |
| Asia, Australia and Oceania      | 0332 |
| Canadian                         | 0334 |
| European                         | 0335 |
| Latin American                   | 0336 |
| Middle Eastern                   | 0333 |
| United States                    | 0337 |
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| Law                              | 0398 |
| Political Science                |      |
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| International Law and Relations  | 0616 |
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| Individual and Family Studies    | 0628 |
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| Food Science and Technology  | 0359 |
| Forestry and Wildlife        | 0478 |
| Plant Culture                | 0479 |
| Plant Pathology              | 0480 |
| Plant Physiology             | 0817 |
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| Wood Technology              | 0746 |
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| Anatomy                      | 0287 |
| Biostatistics                | 0308 |
| Botany                       | 0309 |
| Cell                         | 0379 |
| Ecology                      | 0329 |
| Entomology                   | 0353 |
| Genetics                     | 0369 |
| Limnology                    | 0793 |
| Microbiology                 | 0410 |
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| Neuroscience                 | 0317 |
| Oceanography                 | 0416 |
| Physiology                   | 0433 |
| Radiation                    | 0521 |
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| Biophysics                   |      |
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| Human Development              | 0758 |
| Immunology                     | 0982 |
| Medicine and Surgery           | 0564 |
| Mental Health                  | 0347 |
| Nursing                        | 0569 |
| Nutrition                      | 0570 |
| Obstetrics and Gynecology      | 0380 |
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| Therapy                        | 0354 |
| Ophthalmology                  | 0355 |
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| Pharmacy                       | 0572 |
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| Analytical                           | 0486 |
| Biochemistry                         | 0487 |
| Inorganic                            | 0488 |
| Nuclear                              | 0738 |
| Organic                              | 0490 |
| Pharmaceutical                       | 0491 |
| Physical                             | 0494 |
| Polymer                              | 0495 |
| Radiation                            | 0754 |
| Mathematics                          | 0405 |
| Physics                              |      |
| General                              | 0605 |
| Acoustics                            | 0986 |
| Astronomy and Astrophysics           | 0606 |
| Atmospheric Science                  | 0608 |
| Atomic                               | 0748 |
| Electronics and Electricity          | 0607 |
| Elementary Particles and High Energy | 0798 |
| Fluid and Plasma                     | 0759 |
| Molecular                            | 0609 |
| Nuclear                              | 0610 |
| Optics                               | 0752 |
| Radiation                            | 0756 |
| Solid State                          | 0611 |
| Statistics                           | 0463 |
| Applied Sciences                     |      |
| Applied Mechanics                    | 0346 |
| Computer Science                     | 0984 |

|                            |      |
|----------------------------|------|
| Engineering                |      |
| General                    | 0537 |
| Aerospace                  | 0538 |
| Agricultural               | 0539 |
| Automotive                 | 0540 |
| Biomedical                 | 0541 |
| Chemical                   | 0542 |
| Civil                      | 0543 |
| Electronics and Electrical | 0544 |
| Heat and Thermodynamics    | 0348 |
| Hydraulic                  | 0545 |
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| Marine                     | 0547 |
| Materials Science          | 0794 |
| Mechanical                 | 0548 |
| Metallurgy                 | 0743 |
| Mining                     | 0551 |
| Nuclear                    | 0552 |
| Packaging                  | 0549 |
| Petroleum                  | 0765 |
| Sanitary and Municipal     | 0554 |
| System Science             | 0790 |
| Geotechnology              | 0428 |
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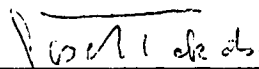
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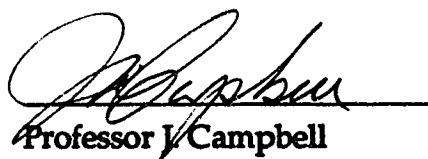
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Professor W. A. G. Graham  
Supervisor



Professor J. Takats



Professor J. Campbell

Date: November 16, 1994

## ABSTRACT

The synthesis and characterization of pyrazolylalkane rhenium and pyrazolylborate molybdenum and rhenium complexes using 3-trifluoromethyl-5-methylpyrazole (HPf), have been investigated in an effort to define more closely the effect that the 3-CF<sub>3</sub> group exhibits on the size and electronic properties of the tris(3-trifluoromethyl-5-methylpyrazol-1-yl)borate (HBPf<sub>3</sub>) and bis(3-trifluoromethyl-5-methylpyrazol-1-yl)methane (H<sub>2</sub>CPf<sub>2</sub>) ligands.

The bispyrazolylalkane H<sub>2</sub>CPf<sub>2</sub> was synthesized and reacted with [Re(CO)<sub>4</sub>(μ-Br)]<sub>2</sub> to give *fac*-H<sub>2</sub>CPf<sub>2</sub>Re(CO)<sub>3</sub>Br (2). The stereochemistry of 2 was established by an X-ray structure. Reaction of 2 with PMe<sub>3</sub> and PMe<sub>2</sub>Ph resulted in the substitution of the pyrazolylalkane ligand by two phosphines affording *fac*-Re(CO)<sub>3</sub>(PR<sub>2</sub>R')<sub>2</sub>Br.

Reaction of the tris(3-trifluoromethyl-5-methylpyrazol-1-yl)borate ligand (HBPf<sub>3</sub>) with [Re(CO)<sub>4</sub>(μ-Br)]<sub>2</sub> resulted in HBPf<sub>3</sub>Re(CO)<sub>3</sub> (5), for which a crystal structure was determined. Photolysis of 5 in tetrahydrofuran substituted one CO, forming HBPf<sub>3</sub>Re(CO)<sub>2</sub>THF (6). The reaction of 6 with PMe<sub>3</sub> resulted in the substitution of the THF, while 6 reacted with Br<sub>2</sub> and CCl<sub>4</sub> to produce the air-stable seventeen-electron radicals HBPf<sub>3</sub>Re(CO)<sub>2</sub>X (X = Br, Cl), for which magnetic moments were measured.

The complex [Et<sub>4</sub>N]<sup>+</sup> [HBPf<sub>3</sub>Mo(CO)<sub>3</sub>]<sup>-</sup> (10) has been synthesized, and oxidized to the air-stable seventeen-electron radical HBPf<sub>3</sub>Mo(CO)<sub>3</sub><sup>•</sup>. The seven-coordinate hydride HBPf<sub>3</sub>Mo(CO)<sub>3</sub>H was synthesized and its infrared spectrum appeared consistent with a 3:4 coordination geometry (C<sub>s</sub> symmetry). However, its NMR spectrum suggested a C<sub>3v</sub> symmetrical intermediate (3:3:1 coordination geometry) as only a singlet was observed for

the three pyrazole rings, even at  $-80^{\circ}\text{C}$ . It is suggested that the molecule is fluxional at this temperature. The reaction of **10** with various nitrosonium salts has revealed a solvent dependency in the yield of  $\text{HBPf}_3\text{Mo}(\text{CO})_2(\text{NO})$  (**13**). Reaction of **13** with bromine, methanol and ethanol afforded stable sixteen-electron molybdenum complexes of the form  $\text{HBPf}_3\text{Mo}(\text{NO})\text{X}_2$  ( $\text{X} = \text{Br}, \text{OMe}, \text{OEt}$ ).



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## TABLE OF CONTENTS

| CHAPTER |  | PAGE |
|---------|--|------|
| 1       | INTRODUCTION .....   | 1    |
|         | Section 1 Organometallic Chemistry .....                           | 2    |
|         | Section 2 Polypyrazolyborates .....                                | 3    |
|         | Section 3 18 Electron Formalism .....                              | 6    |
|         | Section 4 Synergic Bonding .....                                   | 10   |
|         | Section 5 The Nitrosyl Ligand .....                                | 11   |
|         | Section 6 Paramagnetic Complexes .....                             | 15   |
|         | References .....   | 18   |
| 2       | PYRAZOLYLALKANE RHENIUM COMPLEXES .....                            | 21   |
|         | Section 1 Introduction .....                                       | 22   |
|         | Section 2 Synthesis and Properties of $H_2CPf_2$ .....             | 24   |
|         | Section 3 Synthesis and Reactions of<br>$H_2CPf_2Re(CO)_3Br$ ..... | 28   |
|         | Section 4 Experimental .....                                       | 38   |
|         | References .....   | 46   |
| 3       | SYNTHESIS AND REACTIVITY OF $HBPf_3Re(CO)_3$ .....                 | 49   |
|         | Section 1 Introduction .....                                       | 50   |
|         | Section 2 Synthesis and Properties of $HBPf_3Re(CO)_3$ .....       | 52   |
|         | Section 3 The Reactivity of $HBPf_3Re(CO)_3$ .....                 | 56   |
|         | Section 4 The Reactivity of $HBPf_3Re(CO)_2(THF)$ .....            | 59   |
|         | Section 5 Experimental .....                                       | 63   |

|   |   |     |
|---|---|-----|
|   | References .....  | 75  |
| 4 | SYNTHESIS AND REACTIVITY OF $\text{HBPf}_3\text{Mo}(\text{CO})_3^-$ .....                                       | 77  |
|   | Section 1 Introduction .....  | 78  |
|   | Section 2 Synthesis and Reactions of<br>$[\text{Et}_4\text{N}]^+ [\text{HBPf}_3\text{Mo}(\text{CO})_3]^-$ ..... | 80  |
|   | Section 3 The Chemistry of $\text{HBPf}_3\text{Mo}(\text{CO})_2(\text{NO})$ .....                               | 90  |
|   | Section 4 Experimental .....  | 95  |
|   | References .....  | 100 |
| 5 | SUMMARY AND CONCLUSIONS .....   | 103 |
|   | References .....  | 107 |

## LIST OF TABLES

| TABLE            |   | PAGE |
|------------------|---|------|
| <b>CHAPTER 1</b> |   |      |
| 1-1              | Electrons Donated by Ligands to a Metal Center.....   | 10   |
| <b>CHAPTER 2</b> |   |      |
| 2-1              | <sup>13</sup> C{ <sup>1</sup> H} NMR Data for H <sub>2</sub> CPf <sub>2</sub> .....   | 26   |
| 2-2              | <sup>1</sup> H NMR Data for H <sub>2</sub> CPf <sub>2</sub> Re(CO) <sub>3</sub> Br .....  | 34   |
| 2-3              | Drying Reagents for Solvents .....  | 38   |
| 2-4              | Crystal Data and Details of Structure Refinement for<br>H <sub>2</sub> CPf <sub>2</sub> Re(CO) <sub>3</sub> Br.....   | 43   |
| 2-5              | Atomic Coordinates and Equivalent Isotropic Displacement<br>Parameters for H <sub>2</sub> CPf <sub>2</sub> Re(CO) <sub>3</sub> Br.....                                      | 44   |
| 2-6              | Bond Lengths for H <sub>2</sub> CPf <sub>2</sub> Re(CO) <sub>3</sub> Br.....  | 45   |
| 2-7              | Bond Angles for H <sub>2</sub> CPf <sub>2</sub> Re(CO) <sub>3</sub> Br.....   | 45   |
| <b>CHAPTER 3</b> |   |      |
| 3-1              | Comparisons of Crystal Structure Data for<br>HBPz <sub>3</sub> Re(CO) <sub>3</sub> , HBPz <sub>3</sub> *Re(CO) <sub>3</sub> and HBPf <sub>3</sub> Re(CO) <sub>3</sub> ..... | 54   |
| 3-2              | Magnetic Moments of Paramagnetic Compounds<br>8 and 9 .....   | 63   |
| 3-3              | Pascal's Constants .....  | 69   |
| 3-4              | Crystal Data and Details of Structure Refinement for<br>HBPf <sub>3</sub> Re(CO) <sub>3</sub> .....   | 71   |

|     |  |    |
|-----|--|----|
| 3-5 | Atomic Coordinates and Equivalent Isotropic Displacement<br>Parameters for $\text{HBPf}_3\text{Re}(\text{CO})_3$ ..... | 72 |
| 3-6 | Bond Lengths for $\text{HBPf}_3\text{Re}(\text{CO})_3$ .....   | 73 |
| 3-7 | Bond Angles for $\text{HBPf}_3\text{Re}(\text{CO})_3$ .....  | 74 |

#### CHAPTER 4

|     |  |    |
|-----|--|----|
| 4-1 | $^1\text{H}$ and $^{19}\text{F}$ NMR Data for $\text{Pf}$ , $\text{HBPf}_3$ , and $\text{HBPf}_3\text{Mo}(\text{CO})_3^-$ .... | 81 |
| 4-2 | Comparison of Carbonyl Stretching Frequencies for Some<br>17-Electron Molybdenum Compounds .....                               | 82 |
| 4-3 | Stretching Frequencies of Molybdenum Nitrosyl<br>Complexes .....   | 93 |

## LIST OF FIGURES

| FIGURE    |   | PAGE |
|-----------|---|------|
| CHAPTER 1 |   |      |
| 1-1       | Comparison of Cp and HBPz <sub>3</sub> Ligands .....  | 4    |
| 1-2       | Numbering of Pyrazole Ring .....  | 5    |
| 1-3       | Molecular Orbital Diagram for an Octahedral Complex .....   | 7    |
| 1-4       | Metal to Carbonyl Bonding Interaction .....   | 11   |
| 1-5       | Molecular Orbital Diagram for Nitric Oxide .....  | 12   |
| 1-6       | Linear and Bent NO Complexes .....  | 13   |
| 1-7       | Resonance Structures for Linear and Bent NO .....   | 14   |
| CHAPTER 2 |   |      |
| 2-1       | Boat Conformation of H <sub>2</sub> BPz <sub>2</sub> M .....  | 23   |
| 2-2       | The H <sub>2</sub> CPf <sub>2</sub> Ligand .....  | 25   |
| 2-3       | <sup>1</sup> H NMR of H <sub>2</sub> CPf <sub>2</sub> .....   | 27   |
| 2-4       | Possible Stereochemical Conformations for<br>H <sub>2</sub> CPf <sub>2</sub> Re(CO) <sub>3</sub> Br ..... | 29   |
| 2-5       | Infrared Spectrum of H <sub>2</sub> CPf <sub>2</sub> Re(CO) <sub>3</sub> Br .....                         | 30   |
| 2-6       | Possible Chair Conformation of H <sub>2</sub> CPf <sub>2</sub> Re(CO) <sub>3</sub> Br .....               | 31   |
| 2-7       | ORTEP view of H <sub>2</sub> CPf <sub>2</sub> Re(CO) <sub>3</sub> Br .....                                | 33   |
| 2-8       | Inversion of Boat Conformation .....  | 35   |
| CHAPTER 3 |   |      |
| 3-1       | ORTEP view of HBPf <sub>3</sub> Re(CO) <sub>3</sub> .....   | 55   |

|     |   |    |
|-----|---|----|
| 3-2 | Partial Charges on Carbon Atoms in Pz, Pz* and Pf ..... | 58 |
|-----|---|----|

#### CHAPTER 4

|     |  |    |
|-----|--|----|
| 4-1 | Possible Geometries for $\text{HBPf}_3\text{Mo}(\text{CO})_3\text{H}$ .....              | 84 |
| 4-2 | Faller's Proposed Intermediate to Explain Fluxionality .....                             | 85 |
| 4-3 | Infrared Spectrum of $\text{HBPf}_3\text{Mo}(\text{CO})_3\text{H}$ .....                 | 86 |
| 4-4 | Room Temperature $^1\text{H}$ NMR of $\text{HBPf}_3\text{Mo}(\text{CO})_3\text{H}$ ..... | 87 |
| 4-5 | Methods for Synthesizing $\text{HBPf}_3\text{Mo}(\text{CO})_2\text{NO}$ .....            | 89 |

## LIST OF SCHEMES

### CHAPTER 3

|     |   |    |
|-----|---|----|
| 3-1 | Possible Mechanisms for Rhenium Radical Formation ..... | 62 |
|-----|---|----|

### CHAPTER 4

|     |   |    |
|-----|---|----|
| 4-1 | Mechanistic Proposal for the Formation of Dialkoxy<br>Products..... | 94 |
|-----|---|----|



## LIST OF ABBREVIATIONS

|                                 |  |
|---------------------------------|--|
| Me                              | methyl   |
| Et                              | ethyl  |
| Ph                              | phenyl   |
| Cp                              | $\eta^5$ -cyclopentadienyl   |
| Cp*                             | $\eta^5$ -pentamethylcyclopentadienyl  |
| Pz                              | pyrazole   |
| Pz*                             | 3,5-dimethylpyrazole   |
| Pf                              | trifluoromethylmethylpyrazole  |
| HBPz <sub>3</sub>               | trishydrido(pyrazol-1-yl)borate anion  |
| HBPz* <sub>3</sub>              | tris(3,5-dimethylpyrazol-1-yl)borate anion   |
| HBPf <sub>3</sub>               | tris(3-trifluoromethyl-5-methylpyrazol-1-yl)borate anion                                     |
| H <sub>2</sub> CPf <sub>2</sub> | bis(3-trifluoromethyl-5-methylpyrazol-1-yl)methane   |
| allyl                           | CH <sub>2</sub> CHCH <sub>2</sub>  |
| THF                             | tetrahydrofuran  |
| APT                             | attached proton test   |
| $\eta$                          | descriptor for hapticity   |
| $\delta$                        | chemical shifts in NMR (ppm)   |
| NMR                             | nuclear magnetic resonance   |
| IR                              | infrared   |
| MS                              | mass spectroscopy  |
| $\mu$                           | denotes a bridging ligand, or designates micro- (eg. $\mu\text{mol} = 10^{-6} \text{ mol}$ ) |
| $\nu$                           | denotes stretching frequency   |

## **CHAPTER 1**

### **INTRODUCTION**

## Section 1

### ORGANOMETALLIC CHEMISTRY

In 1827, the synthesis of  $K^+[(C_2H_4)PtCl_3]^-$  by Zeise<sup>1</sup> marked the beginning of a new genre of chemical compound which incorporated aspects of both organic and transition metal chemistry. Not surprisingly, these complexes became known as organometallic compounds, representing their unique make-up. Interest in them has developed greatly since that time, in part because of organometallic chemistry's practical applications in organic and industrial use. Their main distinguishing feature is the presence of at least one metal-to-carbon bond, and this provides the generally accepted definition of an organometallic compound.<sup>2</sup>

Zeise's discovery was followed by Schutzenberger's synthesis<sup>3</sup> of  $[PtCl_2(CO)_2]$  in 1868, which marked the first metal carbonyl to be made. Then in 1890 Mond,<sup>4</sup> while studying the corrosion of the nickel valves in the reaction vessels, discovered  $Ni(CO)_4$ . This discovery led to a method for the purification of nickel metal.

It was not until the 1930's that Hieber<sup>5</sup> began his systematic research on metal carbonyl chemistry. Soon after, Sidgwick<sup>6</sup> established the 18 electron formalism, which could be used when considering structural possibilities. Ideas of bonding<sup>7</sup> were not fully developed, and would remain simplistic until the 1950's.

Up to that time, many practical and insightful discoveries had been made. However, organometallic chemistry was not evolving at a rapid rate. Then, in 1951, Kealy and Pauson's discovery of ferrocene<sup>8</sup> sparked new interest into the field. While its true structure was not deduced until the

following year, the unique sandwich structure and reactivity attracted immense interest to the field. As well, it aided in the formation of present day bonding theories. Since then, the cyclopentadienyl ligand has been examined extensively to explore its effect on the chemistry of other metal carbonyl and nitrosyl compounds. One of the more interesting compounds is  $\text{CpIr}(\text{CO})_2$  which was found to activate the C-H bonds in methane.<sup>9</sup>

Organometallic compounds have also proven to be useful in the area of catalysis, and have become a part of such processes as polymerizations, hydrogenations, and hydroformylations. As well, they have become a useful part of organic chemistry, creating carbon to carbon bonds while maintaining chemoselectivity and synthesizing otherwise inaccessible organic compounds.

Consequently, the area of organometallic chemistry has, and continues to expand into a flourishing division of chemistry.

## Section 2

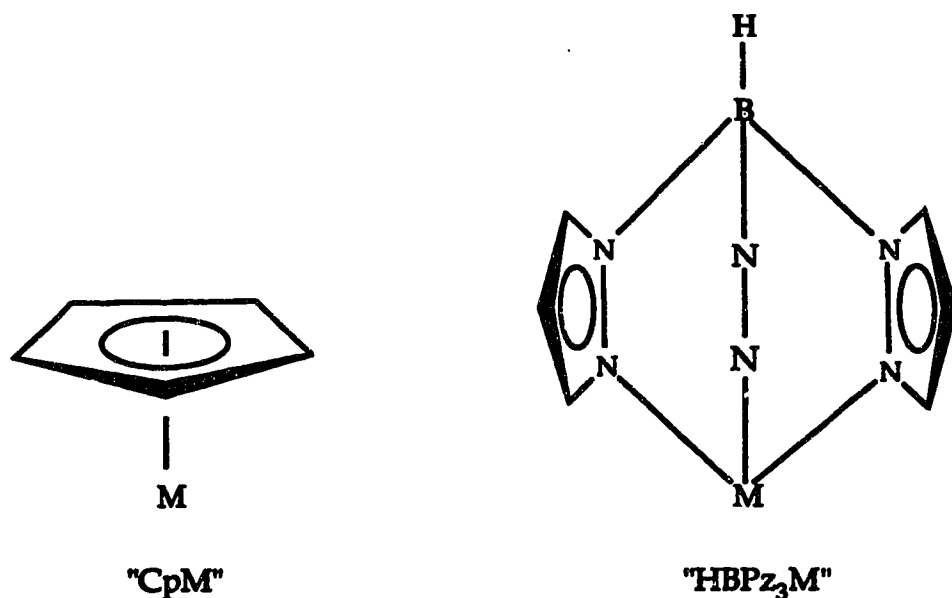
### POLYPYRAZOLYLBORATES

Pyrazolylborates were first introduced by Trofimenko<sup>10</sup> in 1967. Since then, extensive investigations into their chemistry on nearly all the transition metals<sup>11</sup> has been accomplished. One attractive feature is their relatively facile synthesis. In principle, heating an excess of pyrazole with  $\text{KBH}_4$  until the theoretical number of moles of hydrogen are released (equation (1-1)),



gives the desired ligand. It has also been possible to synthesize bis- and tetrakispyrazolylborates by similar methods.<sup>11a-d</sup>

When trispyrazolylborates were first introduced, comparisons to the Cp and Cp\* ligands were made.<sup>12</sup> Both ligands donate six electrons to the metal center, possess a uninegative charge, and occupy (at least formally) three coordination sites on the metal center. This comparison is illustrated in Figure 1-1, where the third pyrazole, going into the page and viewed edge on, is denoted as N-N.



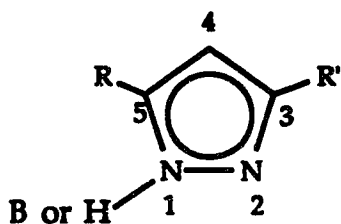
**Figure 1-1. Comparison of Cp and HBPz<sub>3</sub> Ligands**

Electronic and steric differences between the two ligands do exist. For example, while many seven coordinate CpMoL<sub>4</sub> complexes<sup>13</sup> are known, there have been few reported for trispyrazolylborate analogues.<sup>14</sup> Also, while many dinuclear Cp complexes are formed, few have been identified for the pyrazolylborates.<sup>15</sup> These observations have been attributed to the shielding of the metal from further attack by the larger pyrazolylborate ligand.

Interestingly, the trispyrazolylborate ligand has 10 positions (nine carbon positions and one boron position) which can be altered, while Cp has only five.<sup>11a-d</sup> Consequently, the electron richness and steric requirements of the pyrazolylborate can be easily altered, and this should facilitate new and unique chemistry.

While such immense possibilities exist, the most frequently used pyrazolylborates are the hydrotris(pyrazol-1-yl)borate (HBPz<sub>3</sub>) and the (3,5-dimethylpyrazol-1-yl)borate (HBPz\*<sub>3</sub>) ligands, due mainly to their commercial availability. However, exploration of other homo- and heteropyrazolylborates is increasing.<sup>11d</sup>

In 1974, McCurdy used the unsymmetrical MePzH pyrazole<sup>16</sup> to synthesize its corresponding trispyrazolylborate and determined that the reaction was regiospecific. (Figure 1-2 illustrates the numbering scheme of the pyrazole ligand). Trofimenko<sup>17</sup> has also synthesized "second generation" ligands by incorporating large groups, such as t-butyl, mesityl and isopropyl, capable of shielding the metal center of the first row transition metals, in the 3-position of the pyrazole. While it would seem that the unsymmetrical pyrazoles could result in trispyrazolylborates with a mixture of substituents



**Figure 1-2. Numbering of Pyrazole Ring**

in the 3- and 5-positions, this has only been found with one of the second generation ligands.<sup>18</sup> It was believed that the boron would attack the least

sterically hindered nitrogen first.<sup>16</sup> However, for the  $[\text{HB}(\text{Pr}^i\text{MeC}_3\text{N}_2\text{H})_3]^-$  ligand, the isopropyl group ( $\text{Pr}^i$ ) does not exclusively occupy the 3-position. Experimental results indicate that approximately 80% of the ligand formed placed the isopropyl group in the 3-position, the remaining 20% have two pyrazoles with the isopropyl in the 3-position and the third in the 5-position.<sup>18</sup>

Another interesting ligand is (3-trifluoromethyl-5-methylpyrazol-1-yl)borate<sup>19</sup>, first prepared in this group by Richard Krentz. It has been shown to promote C-H activation when on rhodium centers, and has provided unique insight into the coordinative stability of alkenes. For example,  $\eta^2$ -ethylene complexes are usually the thermally favored isomer. However, on some of Krentz's complexes this stability is reversed, and on heating, the hydridovinyl isomer is formed.<sup>19a</sup> Consequently, the effect of this ligand on other metal centers is of interest.

### Section 3

#### 18 ELECTRON FORMALISM

The 18 electron rule was first proposed by Sidgwick<sup>6</sup> in 1934 and it has proven to be a useful method of predicting a compound's stability and reactivity. The rule refers to the number of electrons which surround the metal center, and can be rationalized by looking at the compound's molecular orbital diagram. (Figure 1-3)

Transition metals contain five  $nd$  orbitals ( $n$  being the quantum number), three  $(n + 1)p$  orbitals, and one  $(n + 1)s$  orbital. For octahedral

complexes, the six ligand  $\sigma$  orbitals of  $a_{1g}$ ,  $e_g$  and  $t_{1u}$  symmetry will interact with the orbitals of the transition metal with similar symmetry, to result in six bonding and six antibonding interactions. The bonding interactions result in a lowering of the energy of both the free ligand and the metal center orbitals, while the antibonding orbitals are higher in energy than both. Figure 1-3 indicates that the  $t_{2g}$  set of d orbitals of the transition metal will be nonbonding because there are no ligand orbitals of the appropriate symmetry.

Each of the six ligands can be considered to provide two electrons, thus filling the  $t_{1u}$ ,  $a_{1g}$ , and  $e_g$  orbitals. When the metal has a  $d^6$  valence electron count, six more electrons will come from the metal center, and these will fill

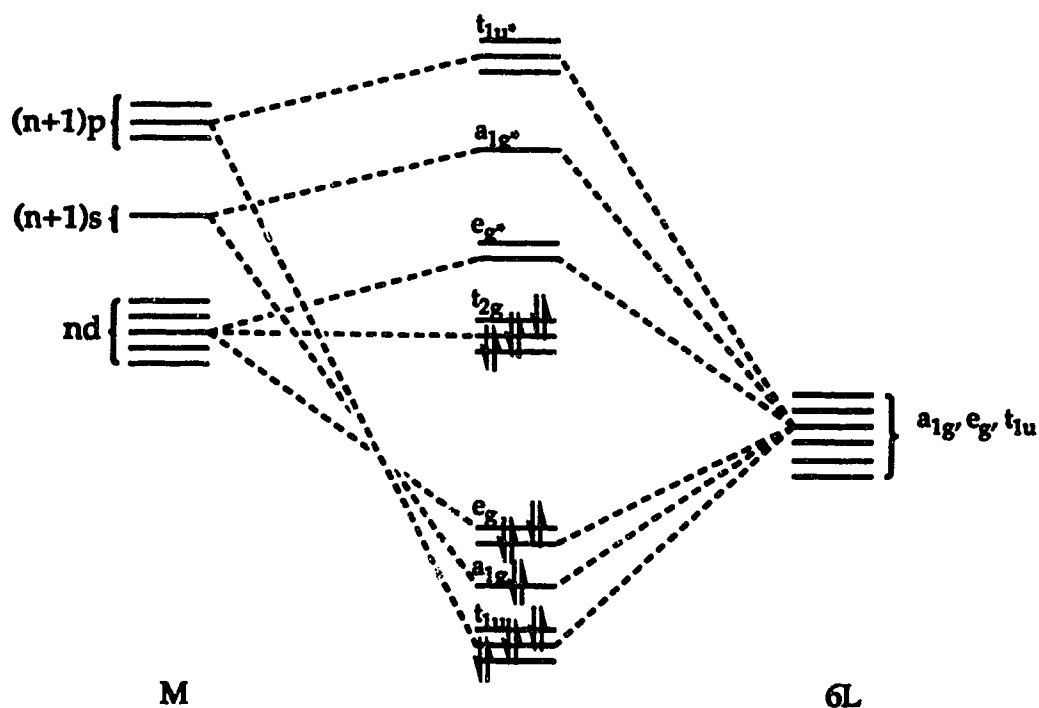


Figure 1-3. Molecular Orbital Diagram for an Octahedral Complex

the  $t_{2g}$  nonbonding orbitals. As a result, 18 electrons will be present, but no electrons will occupy the antibonding orbitals, which would destabilize the



complex. Stability can be obtained as long as there are no empty, low lying orbitals into which electrons can be easily promoted or which can be subject to nucleophilic attack. Therefore, if less than 18 electrons are present, loss of stability could occur.

Exceptions to the 18 electron rule do exist. Metals surrounded by four ligands ( $ML_4$ ) having a  $d^8$  electronic configuration can acquire a stable square planar geometry, due to the d orbitals beginning to enter the core, providing less of a contribution to the metal-to-ligand bond. As well, early transition metals do not always conform to the rule. Normally, metal centers will coordinate to either 4 or 6 ligands. However, steric repulsions can prevent complexes from attaining 18 electrons. For example,  $[Ti(H_2O)_6]^{3+}$  contains only 13 electrons because steric effects prevent additional ligands from approaching the metal center. As well, d and p orbitals of early transition metals can be too high in energy, causing them to play a reduced role in bonding.<sup>2b</sup>

Steric effects can also play an important role in the formation of stable complexes with less than 18 electrons. The 17-electron radical  $HBPz^*_3Mo(CO)_3^*$  has been synthesized<sup>20</sup> and found to be quite air stable. Also, Chapter 4 will present 16-electron complexes of the form  $HBPf_3Mo(NO)XY$  (where  $HBPf_3$  is the tris(3-trifluoromethyl-5-methylpyrazol-1-yl)borate ligand, and  $X = Y = \text{halogen or fluoride}$ ) which are air stable. One possible explanation<sup>21</sup> for this stability is the size of the pyrazolylborate ligand, and its ability to prevent dimerization and to protect the metal center from further attack.

There are two methods for counting electrons around the metal center. One method assumes the metal to be in the zero oxidation state with the

neutral ligands contributing the appropriate number of electrons while ligands such as bromine are considered one electron radicals. For example:

|  | <u>Ligand</u>                  | <u>Electrons Donated</u> |
|--|--------------------------------|--------------------------|
| HBPz <sub>3</sub> Mo(CO) <sub>3</sub> Br | HBPz <sub>3</sub> <sup>•</sup> | 5                        |
|  | Mo                             | 6                        |
|  | 3xCO                           | 6                        |
|  | Br <sup>•</sup>                | <u>1</u>                 |
|  |                                | 18                       |

The pyrazolylborate ligand and the halide are considered to be a radical species, thereby donating only five and one electrons respectively, while the metal center is in the zero oxidation state, possessing six electrons. With each CO donating two electrons, the total count is eighteen.

Alternatively, the second method does not consider bromine or the pyrazolylborate ligand to be a radical, but two and six electron-donating anions, thereby placing the metal center in the two oxidation state.

|  | <u>Ligand</u>                  | <u>Electrons Donated</u> |
|--|--------------------------------|--------------------------|
| HBPz <sub>3</sub> Mo(CO) <sub>3</sub> Br | HBPz <sub>3</sub> <sup>-</sup> | 6                        |
|  | Mo (II)                        | 4                        |
|  | 3xCO                           | 6                        |
|  | Br <sup>-</sup>                | <u>2</u>                 |
|  |                                | 18                       |

Since both methods yield the same result, they are both equally viable, with the choice being based on convenience or custom. Table 1 indicates the number of electrons donated by various ligands.

**Table 1-1. Electrons Donated by Ligands to a Metal Center**

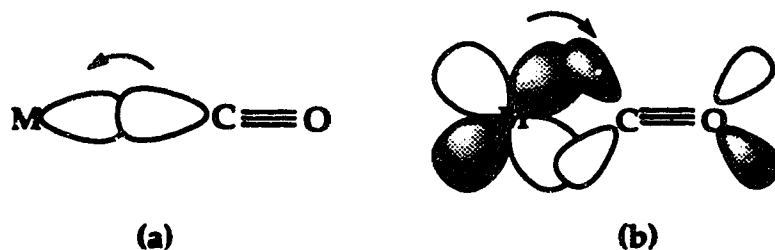
| Number of Electrons Donated | Example Ligands  |
|-----------------------------|--|
| 1                           | Halide and alkyl radicals  |
| 2                           | $\text{NO}^+$ , Halide $^-$ , $\text{R}^-$ , $\text{CO}$ , $\text{PR}_3$ |
| 3                           | $\text{NO}$ , $\eta^3$ - allyl $^\cdot$                                  |
| 4                           | $\eta^4$ - $\text{C}_4\text{R}_4$ , $\eta^3$ - allyl $^-$                |
| 5                           | $\text{Cp}^\cdot$  |
| 6                           | $\text{Cp}^-$ , $\eta^6$ - $\text{C}_6\text{H}_6$                        |
| 7                           | $\eta^7$ - $\text{C}_7\text{H}_7^\cdot$                                  |
| 8                           | $\eta^8$ - $\text{C}_8\text{H}_8$  |

#### Section 4

#### SYNERGIC BONDING

The interaction of the metal center and some ligands is described as synergic bonding because bonding results from the donation of electrons from the ligand to the metal, and the back donation of electrons from the metal center to the ligand. However, the degree of sigma donation compared to  $\pi$  acceptor ability for ligands can vary widely. For example, in  $\text{PR}_3$  groups the more electronegative the R group, the greater the  $\pi$  acceptor ability of the phosphine ligand. This is a result of the lowering in energy of empty d-orbitals. As well, some ligands (for example, halogens) are  $\pi$  donors. The sigma and  $\pi$  interaction is pictured in Figure 1-4. The  $\sigma$  orbital on the carbonyl will donate a pair of electrons to the metal center (a), while the filled metal d orbital will back donate electrons into the empty  $\pi^*$  orbital of the

carbonyl (b). Consequently, the carbon-oxygen bond order will decrease as a larger population of electrons begins to enter the antibonding orbital, while the M-C bond will strengthen.<sup>7</sup>



**Figure 1-4. Metal to Carbonyl Bonding Interaction**

A convenient method of determining the extent of M-CO back donation is by observing the position of the CO stretching bands in the infrared. Free CO exhibits an infrared band at  $2143\text{ cm}^{-1}$ . However, as the C-O bond order decreases, due to increasing electron density in the  $\pi^*$  orbital, the frequency of the CO bands also decrease. In general, terminal CO stretching frequencies are found in the  $2140 - 1800\text{ cm}^{-1}$  region, while bridging CO groups have frequencies in the  $1850 - 1700\text{ cm}^{-1}$  region.<sup>22</sup>

## **Section 5**

### **THE NITROSYL LIGAND**

Nitric oxide, like CO, is a  $\pi$  acid ligand capable of forming bonds to transition metals. However, its chemistry is distinct from that of the carbonyl. For example, unlike the carbonyl ligand, NO can bind through either end. Although no isonitrosyl linkages (M-ON) have yet been conclusively

determined, complexes have been characterized which contain an  $\eta^2\text{-M-N-O-M'}$  structure.<sup>23</sup> The molecular orbital diagram of NO aids in understanding its unique character (Figure 1-5).<sup>24</sup>

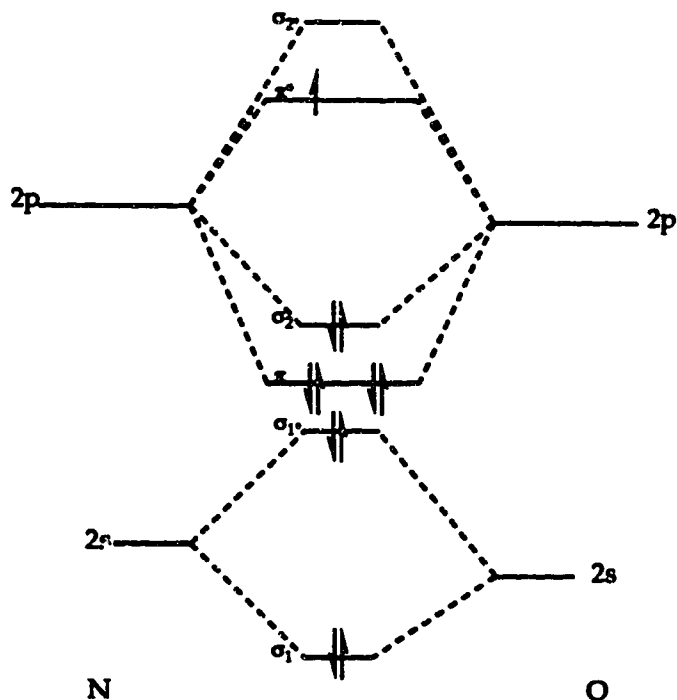


Figure 1-5. Molecular Orbital Diagram for Nitric Oxide

The NO molecule contains 15 electrons: seven from the nitrogen, and eight from the oxygen. Four of these will occupy the sigma bonding and antibonding orbitals from the interaction of the 1s orbitals. The remaining 11 electrons will be placed in the 2s and 2p orbitals. As a result, one electron must occupy the  $\pi^*$  orbital. This is in contrast to the carbonyl ligand, which contains only 14 electrons. Since CO's molecular orbital diagram is similar to nitric oxide's, its HOMO (highest occupied molecular orbital) would be the  $\sigma_2$  orbital, rather than the  $\pi^*$  orbital for NO. Therefore, the one electron in the  $\pi^*$  orbital appears to play a major role in NO's unusual behaviour.

Bonding of NO to a metal center occurs through the same synergic bonding model used to describe the bonding in CO. There will be donation to the metal through the sigma orbital, and the filled d orbital on the metal will backdonate to the  $\pi^*$  of the NO. However, due to the extra electron in the  $\pi^*$  orbital, an unusual feature also occurs. While terminal CO's are always found to be two electron donors, terminal NO's have been documented to donate either one or three electrons to the metal center, depending on their geometry.<sup>25</sup> Figure 1-6 provides an example of complexes with linear and bent NO bonds. If NO forms a linear bond with the metal (Figure 1-6(a))<sup>26</sup>, there will be a net three electron donation, whereas if NO acquires a bent

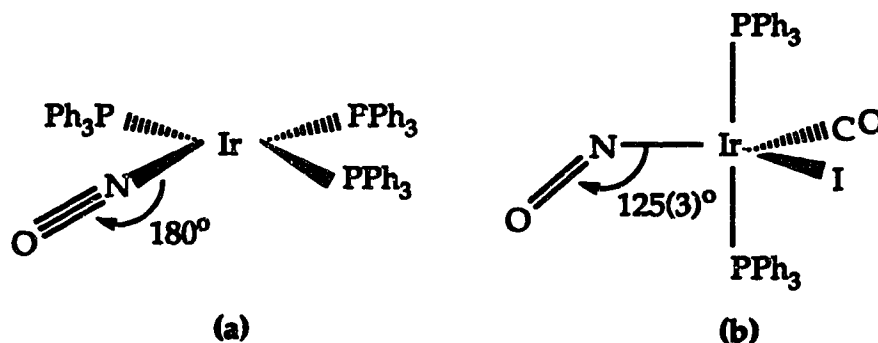


Figure 1-6. Linear and Bent NO Complexes

conformation (Figure 1-6(b))<sup>27</sup>, only one electron is donated. The linear NO interaction is explained by assuming it to be isoelectronic (containing the same number of electrons) with CO by considering it to be the  $\text{NO}^+$  species. Therefore, once NO approaches the metal center, it donates an electron (forming  $\text{NO}^+$ ) and a lone pair thereby donating three electrons. However, in the bent conformation, the metal will donate an electron to the NO, forming  $\text{NO}^-$ , and then the NO will donate the lone pair. As a result, the net donation is only one electron.

Infrared spectroscopy is a useful tool in determining bond order changes, and for CO, it can be useful in establishing if terminal or bridging CO's are present. For nitrosyls, which conform to similar bonding modes as carbonyls, more electron donation from the metal center into the  $\pi^*$  orbital results in a weakening of the N-O bond, resulting in a decrease in its infrared stretching frequency. However, it is not possible to conclusively determine the presence of a linear, bridging or bent nitrosyl from the infrared spectrum. This is a consequence of a wide overlapping infrared region for linear, bent and bridging nitrosyls due to N-O bond orders of both one and two being able to exist. This is illustrated by the valence bond resonance structures in Figure 1-7.<sup>24</sup>

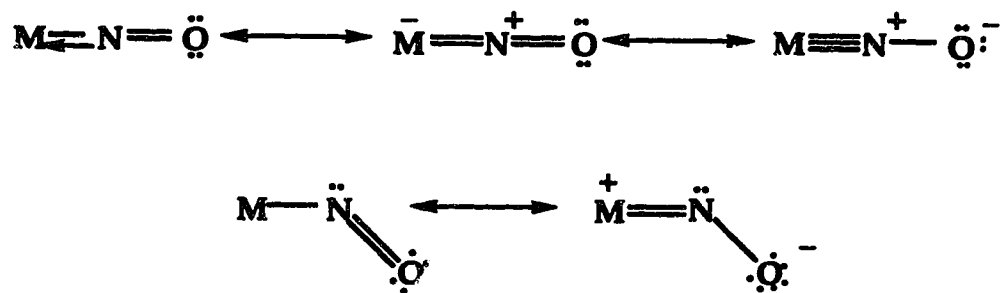


Figure 1-7. Resonance Structures for Linear and Bent NO

Despite the strong similarity with CO, it is important to keep in mind that since N is more electronegative than C, NO will be a better  $\pi$  acceptor ligand than CO. This means that the M-N bond will be strong and the N-O bond will be relatively weak. This is in contrast to CO, where the M-C bond is usually weak, but the C-O bond is quite strong. The importance of this feature lies in predicting the chemistry of complexes containing both NO and CO. Since NO is a better  $\pi$  acid, it will provide added stability to the

complex, by widening the HOMO-LUMO gap. Consequently, metal nitrosyl chemistry is quite distinct from that of the metal carbonyl.

## Section 6

### PARAMAGNETIC COMPLEXES

Complexes containing one or more unpaired electrons are said to be paramagnetic. Even in the absence of a magnetic field, these compounds have a permanent magnetic moment due to their net spin and orbital angular momenta.<sup>28</sup> Although some paramagnetic complexes are easy to predict - such as radicals - others can contain even numbers of electrons and still be paramagnetic. For example,  $\text{HBPz}_3\text{Re}(\text{CO})(\text{Cl})_2$  contains 16 electrons, yet it is paramagnetic.<sup>29</sup>

#### Measurement of Magnetic Susceptibility

While conventional NMR data is difficult to obtain for paramagnetic species, other useful information, such as the number of unpaired electrons per unit weight or mole, can be determined by employing NMR techniques.<sup>30</sup> Many methods for determining magnetic susceptibility are available.<sup>31</sup> Only the Evans method<sup>32</sup>, which conveniently uses NMR instrumentation and is practical for small quantities of solutions, will be employed in this thesis.



Commercial apparatus designed for use of the Evans method was available in the form of a Wilmad Special Stem Coaxial Insert (196 mm long tube - the top 154 mm has an OD (outer diameter) = 4 mm while the stem has an OD = 2 mm) which was inserted into a standard 178 mm (OD = 5 mm) NMR tube. The inner tube contains a known quantity of compound and internal standard, dissolved in an appropriate deuterated solvent, while the outer tube contains the same internal standard, at the same concentration as the inner tube, dissolved in the same solvent. Two separate lines, both referring to the internal standard, will be observed in the NMR. The line at higher frequency results from the paramagnetic solution.<sup>31b</sup>

The mass susceptibility,  $\chi_g$ , is determined using equation (1-2), where  $\Delta\nu$  is the difference between the two lines, in Hz,  $\nu$  is the probe frequency,  $m$  is the mass of substance per mL of solution,  $\chi_o$  is the mass susceptibility of the solvent,  $d_o$  is the density of the solvent, and  $d_g$  is the density of the solution. The molar susceptibility,  $\chi$  ( $\text{cm}^3 \text{mol}^{-1}$ ), is determined

$$\chi_g = \frac{3\Delta\nu}{2\pi\nu m} + \chi_o + \frac{\chi_o(d_o - d_g)}{m} \quad (1-2)$$

by multiplying  $\chi_g$  by the complex's molecular weight. This value is composed of paramagnetic and diamagnetic contributions (1-3). The  $\chi_{\text{dia}}$  value is determined using Pascal's constants (Table 3-2). Therefore,  $\chi_{\text{para}}$  can be determined.

$$\chi = \chi_{\text{para}} + \chi_{\text{dia}} \quad (1-3)$$

For transition metal complexes, the effective magnetic moment,  $\mu_{\text{eff}}$  is usually used, equation (1-4), where  $\chi$  is the paramagnetic contribution ( $\chi_{\text{para}}$ ).

$$\mu_{\text{eff}} = 2.828(\chi T)^{0.5} \text{ (Bohr Magnetron, BM)} \quad (1-4)$$

This formula incorporates Curie's law, which stipulates that the magnetic susceptibility must vary inversely with the absolute temperature, yielding a constant value.<sup>30</sup>

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## **CHAPTER 2**

### **PYRAZOLYLALKANE RHENIUM COMPLEXES**

## Section 1

### INTRODUCTION

The introduction of the pyrazolylborate ligand has resulted in a wealth of new and interesting complexes.<sup>1</sup> Since then, attempts to vary the electronic and steric properties of the pyrazoles, and, consequently, of the borate ligand, have provided many interesting results.

One variant of the pyrazolylborate ligand is the pyrazolylalkane analogue,  $R_nC(Px)_{4-n}$  (where R= hydrogen or an organic group, and Px represents any pyrazole). Investigations<sup>2</sup> since their introduction in 1970 have revealed that they closely resemble the pyrazolylborate ligand in coordinative behavior. Trofimenko suggested<sup>2</sup> that it would be possible to predict the reactivity of the pyrazolylborate ligand if the pyrazolymethane chemistry were known. However, the properties of the analogous pyrazolylalkane ligands have been less extensively investigated, and therefore are of particular interest.

As with the pyrazolylborate ligand, both the bis- and trispyrazolylalkanes can be synthesized. However, depending on the size of the substituents on the pyrazole ring, synthesis of the trisubstituted ligand may not be possible. For example, the tris(3,5-bis(trifluoromethyl)pyrazol-1-yl)borate is apparently unstable due, presumably in part, to the steric hindrance of the  $CF_3$  groups in the 5-position.<sup>3</sup> In view of the low yields obtained in the preparation of tris(3,5-dimethylpyrazol-1-yl)methane,<sup>2</sup> no attempt was made to synthesize the tris(3-trifluoromethyl-5-methylpyrazol-1-yl)methane ligand.

In general, pyrazolylalkane chemistry is rather similar to that of its pyrazolylborate analogues, as Trofimenko suggested. There are two main differences: (1) the pyrazolylalkane is neutral, yielding complexes with an overall charge one unit more positive than that of the borate; and (2) if hydrogen is a substituent on the methylene group, then any effect generated through coordination to the metal center may be monitored by  $^1\text{H}$  NMR. In contrast, the hydrogens on boron in pyrazolylborate ligands produce signals which are too broad to be observed, due to the quadrupolar nature of boron. As a consequence, information regarding possible conformations can be determined more readily for the alkane analogues.

For complexes of the type  $\text{R}_2\text{B}(\text{Px})_2\text{M}$  (where M is a metal center), the B-N and M-N distances and angles result in "puckering" of the ring, causing it to prefer a boat conformation (Figure 2-1). This conformation places one R group toward the metal center, providing the opportunity to interact with

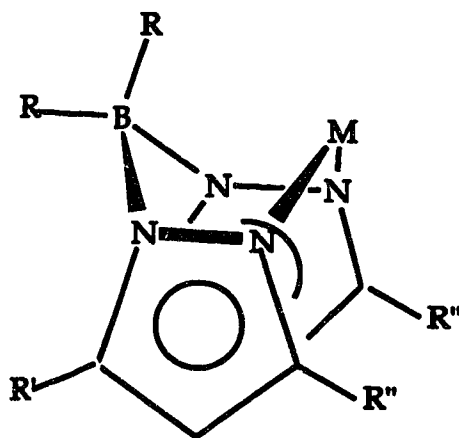


Figure 2-1. Boat Conformation of  $\text{R}_2\text{B}(\text{Px})_2\text{M}$

electron-deficient metal centers.<sup>4</sup> However, in this Chapter, only eighteen-electron complexes have been synthesized, so an interaction of this kind is not expected.

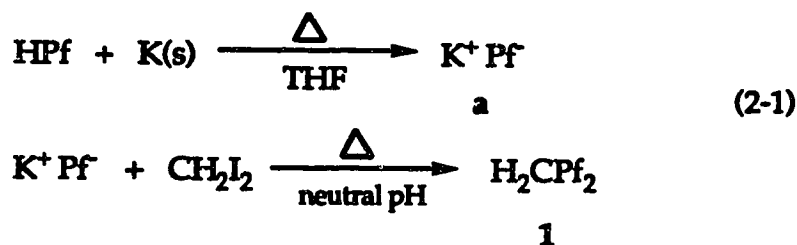


For these reasons, the synthesis of the bis(3-trifluoro-5-trimethylpyrazolyl)methane ligand,  $H_2CPf_2$  (1), was undertaken. Its reaction with  $[Re(CO)_4(\mu-Br)]_2$  has yielded  $H_2CPf_2Re(CO)_3Br$  (2), for which the crystal structure has been determined. Subsequent investigation of the reactions of 2 with  $PMe_3$  and  $PPh_3$  has provided interesting results and information regarding some properties of the ligand.

## Section 2

### SYNTHESIS AND PROPERTIES OF $H_2CPf_2$ (1)

The compound 3-trifluoromethyl-5-methylpyrazole (HPf) has been synthesized by various groups,<sup>5</sup> and was first reported in 1964. Synthesis of the bis(3(5)-trifluoromethyl-5(3)-methylpyrazol-1-yl)methane ( $H_2CPf_2$ ) ligand is illustrated in equation (2-1), and is similar to the method used by Trofimenko<sup>2</sup> in preparing other pyrazolylalkanes. Addition of potassium



metal to the 3-trifluoromethyl-5-methylpyrazole solution removed the N-bound proton, and produced the pyrazolide nucleophile **a**. Reaction of **a** with diiodomethane was very slow (requiring over 50h), and was continued until a

neutral pH was obtained. Following trituration and recrystallization, **1** was obtained as a white solid.

The  $\text{CF}_3$  and  $\text{CH}_3$  groups in **1** could be positioned in either the 3- or 5-positions since the pyrazolide anion is, in principle, an ambident nucleophile. However, spectroscopic data indicate the formation of only one, symmetrical compound. It has been speculated<sup>6</sup> that the proposed transition state for the synthesis of the pyrazolylborate ligand favors attack at the least favored nitrogen. However, Krentz<sup>3</sup> has shown, by means of X-ray structures, that in the reaction of  $\text{HPf}$  with  $\text{KBH}_4$ , only the tris(3-trifluoromethyl-5-methylpyrazoly-1-yl)borate ligand is obtained. This, in conjunction with the successful crystal structure determination of  $\text{H}_2\text{CPf}_2\text{Re}(\text{CO})_3\text{Br}$ , seems to support the assumption that the  $\text{CF}_3$  group resides in the 3-position.

The  $\text{H}_2\text{CPf}_2$  ligand is shown in Figure 2-2, and its  $^{13}\text{C}$  data are compiled in Table 2-1. The C-F coupling constants are within the 265 - 290 Hz

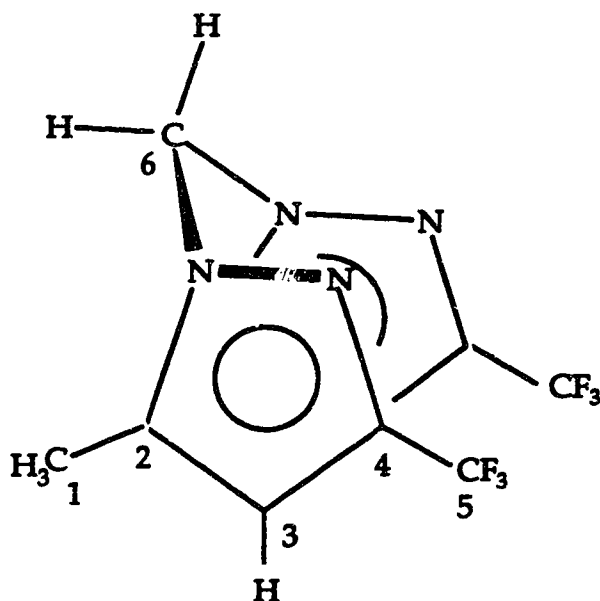


Figure 2-2. The  $\text{H}_2\text{CPf}_2$  Ligand

range for a CF<sub>3</sub> group attached to an aromatic compound, while the two-bond C-F coupling value is consistent with values found in fluorinated alkanes (22 - 61 Hz).<sup>7</sup>

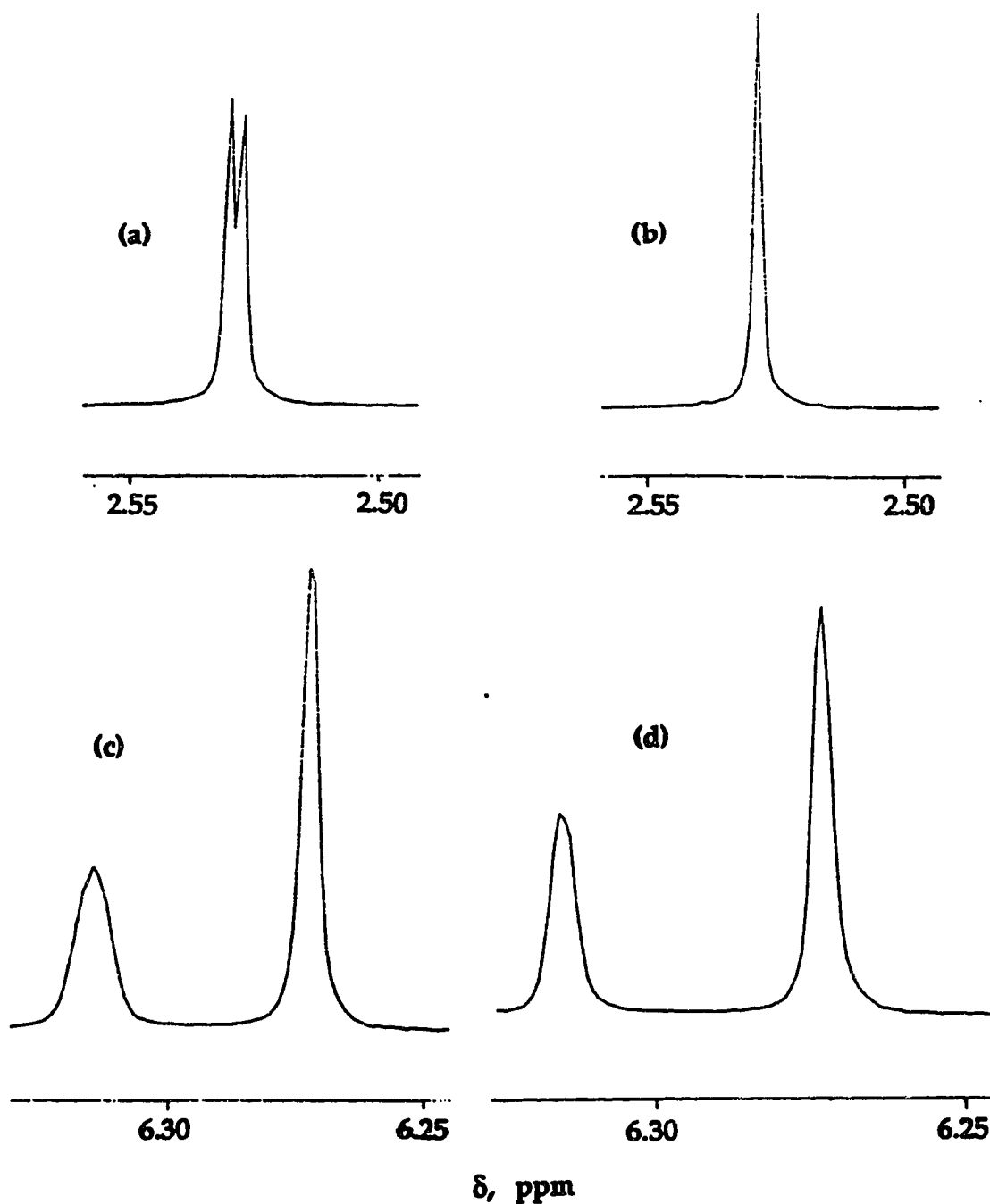
Table 2-1. <sup>13</sup>C {<sup>1</sup>H} NMR Data for H<sub>2</sub>CPf<sub>2</sub><sup>a</sup>

| Shift (δ) | Multiplicity | Assignment | Coupling (Hz) |
|-----------|--------------|------------|---------------|
| 11.38     | s            | C1         | -             |
| 61.11     | s            | C6         | -             |
| 105.79    | s            | C3         | -             |
| 122.90    | q            | C5         | 270           |
| 143.52    | q            | C4         | 36            |
| 144.46    | s            | C2         | -             |

a. In CD<sub>3</sub>NO<sub>2</sub>

At ambient temperatures, the <sup>1</sup>H NMR exhibited three peaks: a doublet at δ 2.53 ppm (J = 0.8 Hz) and two singlets at δ 6.28 and δ 6.32 ppm. Although the doublet can be assigned to the 5-methyl group on the pyrazole ring, further investigation was necessary to unambiguously assign the two singlets to the hydrogens on carbon 3 or 6 (Figure 2-2).

Assignment of these peaks was aided by the coupling observed. Irradiation of the doublet at δ 2.53 ppm should sharpen the peak to which it is coupled. Figure 2-3(a) and (c) show the initial spectrum, while (b) and (d) are the result of irradiation. The peak at δ 6.28 ppm retains its half-height width, while the δ 6.32 ppm peak has narrowed. Consequently, the former may be assigned to the two hydrogens on the methylene unit, and the latter to the 4-H on the pyrazole rings.



**Figure 2-3.**  $^1\text{H}$  NMR Spectrum of  $\text{H}_2\text{CPf}_2$  in  $\text{CD}_2\text{Cl}_2$ . Upper traces show methyl region (a) without irradiation and (b) with irradiation at  $\delta$  6.32. Lower traces show  $\text{CH}_2$  and pyrazole 4-H region (c) without irradiation and (d) with irradiation at  $\delta$  2.53. Peak intensities of upper and lower spectra have been arbitrarily adjusted and should not be compared.

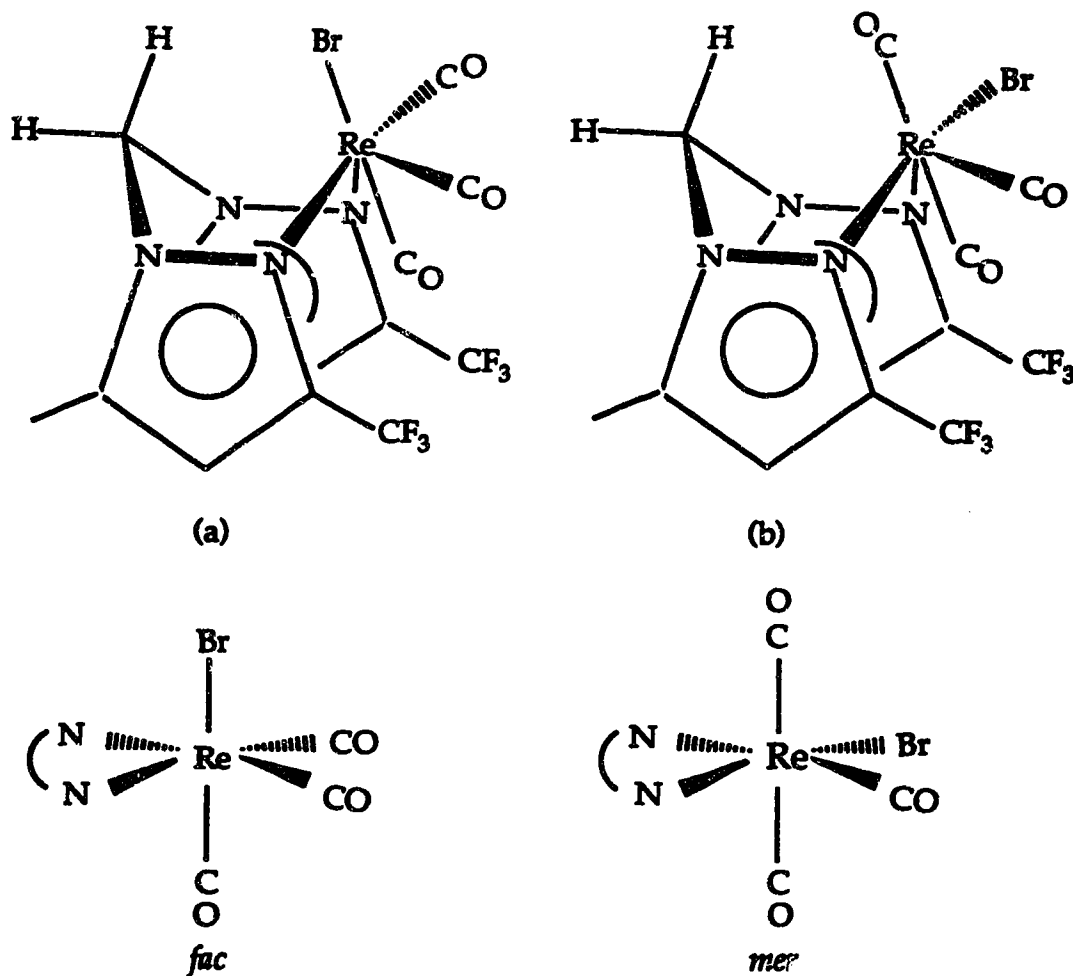
### Section 3

#### SYNTHESIS AND REACTIONS OF $\text{H}_2\text{CPf}_2\text{Re}(\text{CO})_3\text{Br}$ (2)

Refluxing **1** with  $[\text{Re}(\text{CO})_4(\mu\text{-Br})]_2$  in THF resulted in the formation of  $\text{H}_2\text{CPf}_2\text{Re}(\text{CO})_3\text{Br}$  (**2**) in approximately 55% yield (equation 2-3). This ivory complex could be recrystallized by cooling its dichloromethane solution to  $-30^\circ\text{C}$  for several days.

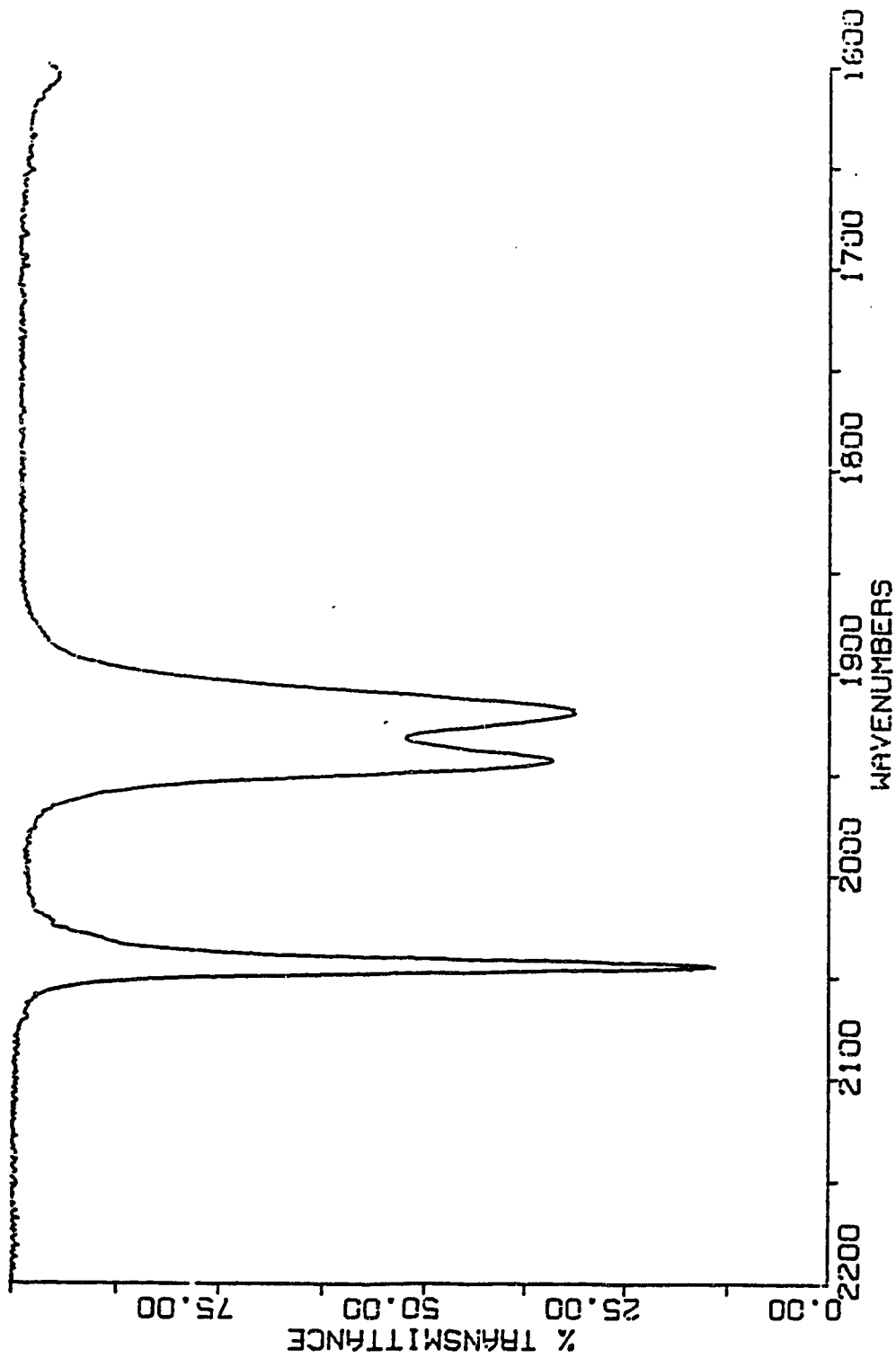


This reaction creates a six membered ring, containing four nitrogen atoms, the carbon atom of the methylene unit, and rhenium, and permits the formation of two possible geometries: one containing the bromine in the axial position, and one with bromine in an equatorial site ((a) and (b) respectively in Figure 2-4). If the bromine is in the axial position, it could either be closer to the methylene unit or to the pyrazole rings. Since the cone angles<sup>8</sup> for CO and Br are  $95^\circ$  and  $105^\circ$  respectively, it would seem likely that due to steric interactions between bromine and the  $\text{CF}_3$  groups, the bromine would prefer a position closer to the methylene unit. If it occupies an equatorial site, two enantiomers would result. For simplicity, only one axial and one equatorial illustration are presented. Below each structure is a simplified representation which identifies each as having *fac* or *mer* stereochemistry at the rhenium center.



**Figure 2-4. Possible Stereochemical Conformations for  $\text{H}_2\text{CPf}_2\text{Re}(\text{CO})_3\text{Br}$**

The infrared spectrum of 2 (Figure 2-5) exhibited three carbonyl stretching bands within the  $2200 - 1600 \text{ cm}^{-1}$  region. Having the bromine in the axial position (a) creates a mirror plane, resulting in  $C_s$  symmetry, while (b), containing no plane, has  $C_1$  symmetry. Unfortunately, character tables predict the presence of three bands for the carbonyl ligands for both symmetry groups:  $(2A' + A'')$  for  $C_s$  symmetry and  $(3A)$  for  $C_1$  symmetry groups. However, by observing the relative intensities of the infrared bands it is possible to establish with reasonable certainty whether the facial or

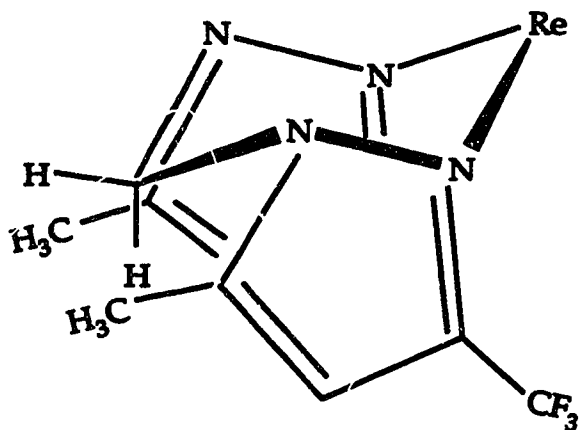


**Figure 2-5. Infrared Spectrum of  $H_2CPl_2Re(CO)_3Br$  (2) ( $CHCl_3$ )**

meridional isomer is present.<sup>9</sup> In this case, the three bands are of near equal intensity, which is consistent with the infrared spectrum of a *fac* isomer.

The <sup>19</sup>F NMR spectrum of **2** consisted of a singlet, while the <sup>1</sup>H NMR contained a doublet for the 5-Me protons and the inner two peaks of a quartet for the 4-H protons on the pyrazole rings. The presence of these multiplets is a consequence of the coupling between the 5-Me and the 4-H of the pyrazole ring. These data confirm the presence of a plane of symmetry, and suggests structure (a) to be the most plausible alternative, since (b) would place the pyrazole groups in different environments, which would result in two singlets in the <sup>19</sup>F NMR.

Organic six-membered rings usually adopt either a chair or twist conformation.<sup>10</sup> Here, though, the chair conformation is unlikely, as it would require the near planar three coordinate nitrogen to rehybridize to a pyramidal configuration, which would result in the loss of aromaticity in the pyrazole ring (Figure 2-6).



**Figure 2-6. Possible Chair Conformation of H<sub>2</sub>CPf<sub>2</sub>Re(CO)<sub>3</sub>Br**

Carbon-13 NMR data could not be obtained for all the carbon atoms of the complex due to its low solubility. However, signals for the 5-Me (11.52



ppm), CH<sub>2</sub> (58.89 ppm), and 4-CH (110.03 ppm) carbons were observed. Compared to the uncoordinated ligand, the two carbons which are part of the pyrazole show some movement downfield, with the 4-C incurring the largest shift (approximately 5 ppm), possibly as a result of the donation of electrons to the metal center upon coordination. Of the three signals observed, it would be expected that the 4-C of the pyrazole ring would undergo a largest shift since it is part of the pyrazole ring.

### X-Ray Structure of H<sub>2</sub>CPf<sub>2</sub>Re(CO)<sub>3</sub>Br (2)

Confirmation of the structure of 2 was provided by an X-ray structure (Figure 2-7) carried out by Dr. R. McDonald of the Structure Determination Laboratory of this Department. It shows a boat conformation, with the bromine in the axial position, pointing toward the methylene group. A crystallographic mirror plane is present running through the hydrogens on the methylene group, the metal center, and the axial bromine and carbonyl. This is consistent with the spectroscopic data obtained. Bond angles indicate that the rhenium has a slightly distorted octahedral conformation, while the carbon of the methylene unit has a slightly distorted tetrahedral environment.

The Re-N bond length is 2.263(5)Å, which is longer than that found in PhPPz\*<sub>2</sub>Re(CO)<sub>3</sub>Br (2.18(4)Å)<sup>11</sup> and HBPz\*<sub>3</sub>Re(CO)<sub>3</sub> (2.174Å).<sup>12</sup> The Re-Br bond length (2.6569(10)Å) is within the acceptable range of 2.469-2.769Å, while the M-C-O bond angles for 2 (175.4(9)°, 176.0(7)°) are similar to values for PhPPz\*<sub>2</sub>Re(CO)<sub>3</sub>Br (174(6)°, 171(5)°, 165(5)°), and HBPz\*<sub>3</sub>Re(CO)<sub>3</sub> (176.7(2)°, 178.7(2)°).

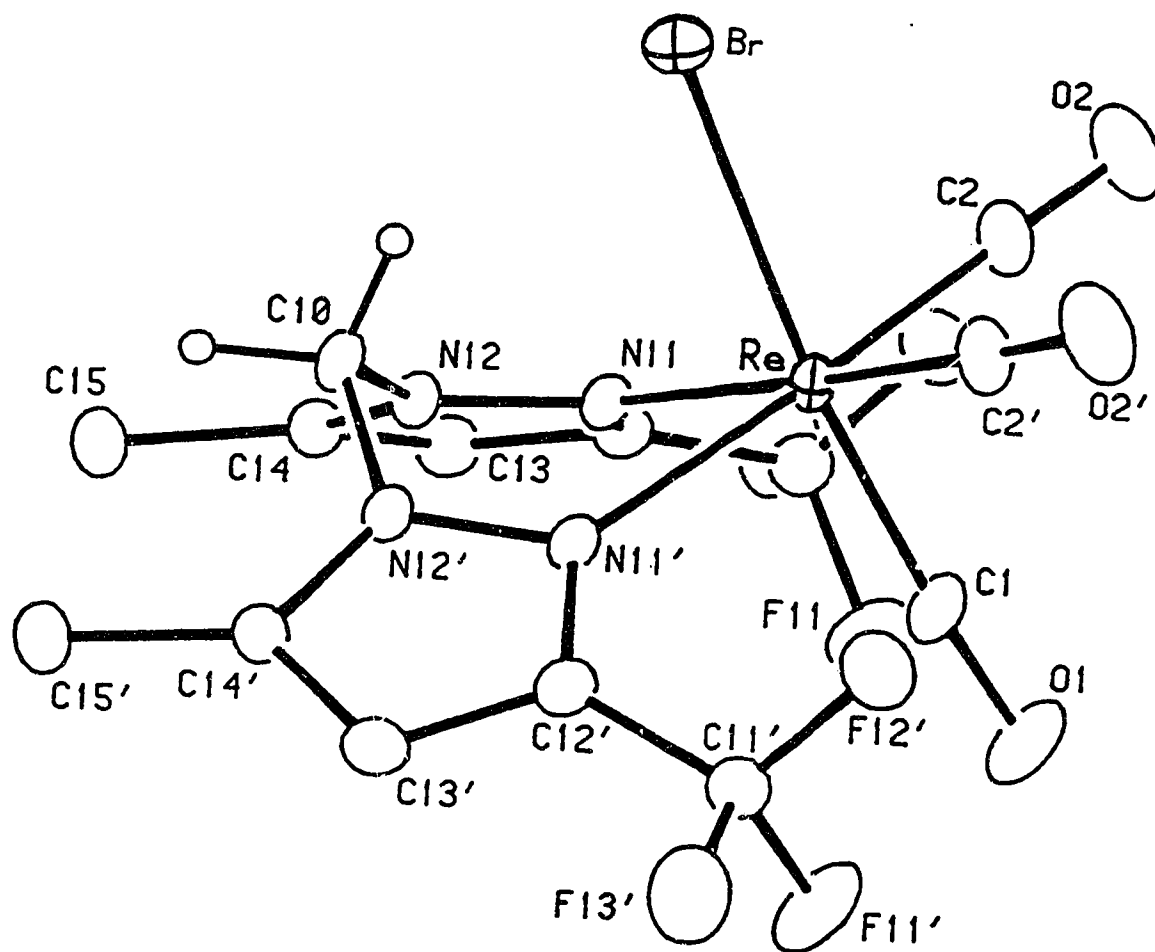


Figure 2-7. ORTEP view of  $\text{H}_2\text{CPf}_2\text{Re}(\text{CO})_3\text{Br}$  (2)

The axial hydrogen of the methylene group is 3.09Å from the rhenium center, and 2.48Å from the bromide, while the carbon and nitrogen atoms of the pyrazole rings are within 0.01Å of the two planes which incorporate them, and which meet at a 56.1° angle.

### Attempted Ring Inversion

Room temperature <sup>1</sup>H NMR data for 2 are presented in Table 2-2, and suggest a non-fluxional molecule. Storr has shown<sup>13</sup> that in some bispyrazolylgallate boat complexes a boat inversion occurs (Figure 2-8), and has proposed a pathway which includes a planar intermediate. Activation parameters between 40 - 70 KJ/mol were obtained. However, other pyrazolylgallate complexes, such as (Me<sub>2</sub>GaPz\*<sub>2</sub>)Rh(CO)(PPh<sub>3</sub>), do not

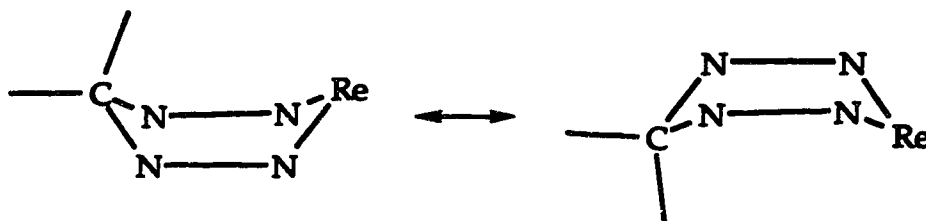
Table 2-2. <sup>1</sup>H NMR Data for H<sub>2</sub>CPf<sub>2</sub>Re(CO)<sub>3</sub>Br<sup>a</sup>

| Shift (ppm) | Assignment           | Multiplicity <sup>b</sup> | Coupling(Hz) |
|-------------|----------------------|---------------------------|--------------|
| 2.59        | 5-Me                 | d                         | 0.4          |
| 6.04        | CH <sub>2</sub> (eq) | d                         | 15           |
| 6.74        | 4-H                  | q                         | 0.4          |
| 8.78        | CH <sub>2</sub> (ax) | d                         | 15           |

a in CD<sub>2</sub>Cl<sub>2</sub>, ambient temperatures

b d = doublet, q = quartet

exhibit fluxional behavior at room temperature due, presumably (as Storr has suggested), to interactions between the substituent groups on the pyrazole ring and the PPh<sub>3</sub> group.<sup>14</sup> It is likely that ring substituents markedly influence the activation barrier.



**Figure 2-8. Inversion of Boat Conformation**

In an attempt to observe ring inversion in **2**, its  $^1\text{H}$  NMR was monitored as a solution was heated. Up to  $40\text{ }^\circ\text{C}$ , no change was observed. At  $60\text{ }^\circ\text{C}$ , new peaks began to appear, indicating the decomposition of the starting material. This was confirmed by running a subsequent room temperature spectrum and noting the continued presence of these signals. Applying Storr's postulate<sup>14</sup> that the activation barrier to reach the planar intermediate is influenced by the interaction of the pyrazole substituents with the ligand, the methyl and trifluoromethyl substituents in **2** could increase the activation barrier, so that the complex decomposed before inversion took place at an observable rate. It should be remembered, however, that in contrast to Storr's systems, inversion of **2** would result in a different and energetically less favorable isomer.

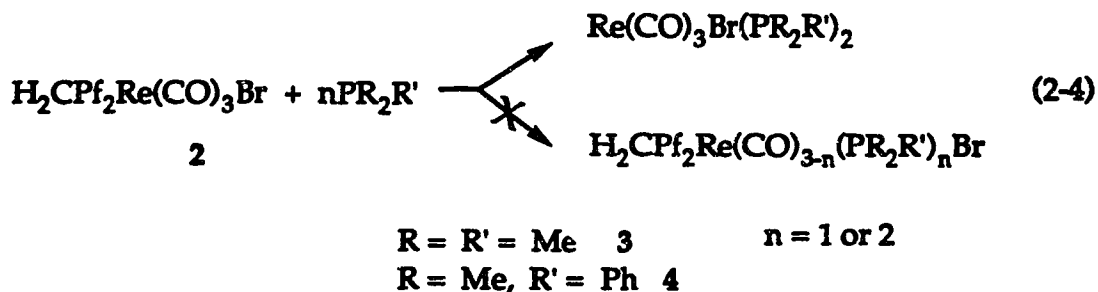
In the  $^1\text{H}$  NMR spectrum of the free ligand **1**, a singlet at  $\delta$  6.28 ppm represented the hydrogens on the methylene group. In the coordinated ligand, though, they are doublets at  $\delta$  8.79 and 6.04 ppm with a coupling constant of 15 Hz. Therefore, one proton has shifted only slightly upon coordination, while the other has moved over 2.5 ppm downfield. This coupling value is within the range 12-15 Hz for geminal hydrogen of a locked six membered ring,<sup>15</sup> however, this large downfield shift is unusual. For instance, when  $\text{H}_2\text{CPz}^*_2$  coordinates in  $\text{H}_2\text{CPz}^*_2\text{Mo}(\text{CO})_2(\pi\text{-allyl})\text{Br}$  the difference between the signals for the  $\text{CH}_2$  protons is only 0.3 ppm.<sup>16</sup> Since

one methylene hydrogen is bent toward the metal center and the bromide ligand, with distances of 3.09Å and 2.48Å respectively, one might suppose that it is being deshielded by these two groups, and consequently is found farther downfield than expected. It is also possible that there is a weak Br-H interaction, resulting in the deshielding of the proton.

### Reactions of $\text{H}_2\text{CPf}_2\text{Re}(\text{CO})_3\text{Br}$ (2)

The infrared spectrum of 2 exhibited three CO stretching bands at 2045, 1943 and 1920  $\text{cm}^{-1}$ . In view of these relatively high frequency bands, it was assumed that reaction with  $\text{PMe}_3$  or  $\text{PMe}_2\text{Ph}$  would result in the substitution of a carbonyl by the phosphine. As the phosphine was slowly added at room temperature, three new bands appeared in the infrared spectrum at lower frequency than the starting material. Although only two bands would be expected for a monosubstituted product, it may be that two carbonyls were substituted, giving a mixture of mono- and disubstituted products, or that isomers have formed. However, examination of the  $^{19}\text{F}$  NMR indicated a singlet at -63.52 ppm, which is identical to the value of the free ligand 1. Therefore, reaction with the phosphine resulted in the substitution of the ligand by two phosphine molecules (equation (2-4)). Attempts to rigorously control the stoichiometry in order to observe an  $\eta^1\text{-(H}_2\text{CPf}_2\text{)}$  intermediate, or product, were not successful.

Compounds 3 and 4 have been previously synthesized by Singleton.<sup>17</sup> A comparison of infrared band intensities and values indicated the formation of the *fac* isomer in each instance. A mass spectrum was also obtained as further proof of their identity.



Loss of the bispyrazolylmethane ligand when other nonchelating ligands are present has been previously observed.<sup>16,18</sup> It has been proposed<sup>18b</sup> that the displacement of the bispyrazolylalkane is a result of favorable energetics. That is, the pyrazolylalkane, once dissociated, is able to adopt a more stable (less strained) configuration requiring less energy. Thermochemical data for complexes of the form  $\text{L}_2\text{Mo}(\text{CO})_4$  have indicated that when L is 1,10-phenanthroline, the complex is 5 kcal/mol more stable than when L is 2, 2'-bipyridine.<sup>19</sup> While the displaced bipyridine can revert to a preferred conformation of lower energy, no such energy gain would be realized for the phenanthroline ligand.

The crystal structure of **2** indicates only a slightly distorted tetrahedral conformation around the methylene group ( $111.0(6)^\circ$  vs  $109.5^\circ$ ), with the two pyrazole rings pointing away from one another. Consequently, Lobbia's suggestion that the ligand's facile displacement could be due, in part, to its adoption of a less strained (lower energy) conformation, is not likely important in this case. Entropy would not be the driving force for the reaction since three reactant molecules react to form two product molecules. Thus it appears to be a matter of relative ligand-metal bond energies. The X-ray structure of **2** indicated longer Re-N bond lengths, possibly as a result of the  $\text{CF}_3$  groups on the pyrazole rings. This suggests a reduced Re-N bond

strength, with the result that the Re-CO bonds are stronger and less prone to substitution.

## **Section 4**

### **EXPERIMENTAL**

All manipulations were carried out under an inert atmosphere of prepurified argon, using standard Schlenk techniques.  $[\text{Re}(\text{CO})_4(\mu\text{-Br})_2]$  was synthesized according to literature methods.<sup>20</sup> Complexes showed oxygen sensitivity in solution, but solids could be handled in air for prolonged periods of time, without decomposition. The HPf ligand was synthesized according to Krentz.<sup>3</sup>

#### **General Techniques**

Solvents were dried according to Table 2-3, under argon, and from the appropriate drying reagent. Acetonitrile was distilled over phosphorous pentoxide prior to storage over the calcium hydride. Deuterated solvents were dried by the same method as the regular solvent, and were stored over molecular sieves. All other solvents were either stored over molecular sieves, or used as received from suppliers.

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**Table 2-3. Drying Reagents for Solvents**


---

| Solvent         | Drying Reagent            |
|-----------------|---------------------------|
| Dichloromethane | Calcium Hydride           |
| Acetonitrile    | Calcium Hydride           |
| Hexane          | Na-K alloy                |
| Benzene         | Potassium metal           |
| Methanol        | Drierite                  |
| Tetrahydrofuran | Sodium metal/benzophenone |
| Nitromethane    | Calcium Chloride          |

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Glassware was cleaned using a KOH-Ethanol solution, followed by treatment with an HCl solution and was then dried in a 160 °C oven, prior to use.

Infrared spectra were obtained using an Nicolet MX-1 FTIR spectrometer, scanning over the 2200 - 1600  $\text{cm}^{-1}$  region, with a 0.5 mm KBr cell. Unless otherwise specified, proton, fluorine, and carbon NMR were collected at ambient temperatures using Bruker WH-200, Bruker AM-300 and Bruker AM-400 spectrometers. Samples were either septa sealed under argon or flame sealed under vacuum.

Elemental analyses were carried out by the Microanalytical Laboratory of this department. Mass spectra were recorded on an A.E.I. MS-12 Spectrometer.

#### Preparation of $\text{H}_2\text{C}(3\text{-CF}_3\text{-5-MePz})_2$ (1)

Potassium metal (3.15 g, 80.6 mmol) in 150 mL THF was added to HPf (15.00 g, 99.9 mmol) in 100 mL THF and refluxed overnight. After removing the orange solution from heat and cooling,  $\text{CH}_2\text{I}_2$  (3.12 mL, 11.6 mmol) was



added. This solution was refluxed for approximately 52 hours, at which time, the pH was neutral (determined by using pH paper). The THF was removed by the rotary evaporator, and the residue triturated in 10 mL heptane. The solution was filtered, and the precipitate washed with heptane (5 x 5 mL) yielding a white solid (5.31 g, 44%).

Characterization: MS, 120 °C/70 eV (m/e, rel. int.): M<sup>+</sup> (312, 76), M-Pf<sup>+</sup> (162, 100), Pf<sup>+</sup> (150, 3). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 2.53 (d, 6H, <sup>4</sup>J<sub>H-H</sub> = 0.6 Hz), 6.28 (s, 2H), 6.32 (s, 2H). <sup>19</sup>F NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ -63.53 (s, 6F). <sup>13</sup>C APT NMR (CD<sub>3</sub>NO<sub>2</sub>): δ 11.38 (s, CH<sub>3</sub>), 61.11 (s, CH<sub>2</sub>), 105.79 (s, CH), 122.90 (q, CF<sub>3</sub>, J<sub>C-F</sub> = 270 Hz), 143.52 (q, C-CF<sub>3</sub>, <sup>2</sup>J<sub>C-F</sub> = 36 Hz), 144.46 (s, C-CH<sub>3</sub>). Anal. Calcd for C<sub>11</sub>H<sub>10</sub>N<sub>4</sub>F<sub>6</sub>: C 42.32, H 3.23, N 17.94. Found: C 42.23, H 3.23, N 17.87.

#### Synthesis of H<sub>2</sub>C(3-CF<sub>3</sub>-5-MePz)<sub>2</sub>Re(CO)<sub>3</sub>Br (2)

H<sub>2</sub>C(3-CF<sub>3</sub>-5-MePz)<sub>2</sub> (176.8 mg, 0.566 mmol) was added to a solution of [Re(CO)<sub>4</sub>Br]<sub>2</sub> (202.2 mg, 0.267 mmol) in 10 mL THF, and refluxed overnight. The solvent was removed under vacuum, leaving a yellow precipitate, which was dissolved in a small quantity of CH<sub>2</sub>Cl<sub>2</sub> and filtered through Celite. The filtrate was stored at -30 °C, resulting in the formation of ivory crystals. (213.0 mg, 57%).

Characterization: IR(CH<sub>2</sub>Cl<sub>2</sub>): 2045 (vs), 1943 (vs), 1920 (vs) νCO. MS, +ve FAB (m/e, rel. int.): M<sup>+</sup> (662, 21), M-CO<sup>+</sup> (634, 8), M-2CO<sup>+</sup> (606, 1), M-Br<sup>+</sup> (583, 57), M-3CO<sup>+</sup> (578, 15). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 2.59 (d, 6H, <sup>4</sup>J<sub>H-H</sub> = 0.4 Hz), 6.04 (d, 1H, <sup>1</sup>J<sub>H-H</sub> = 15 Hz), 6.74 (q, 2H), 8.78 (d, 1H). <sup>19</sup>F NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ -59.89 (s, 6F), -63.59 (s, 3F). <sup>13</sup>C APT NMR (CD<sub>3</sub>NO<sub>2</sub>): δ 11.95 (s,

CH<sub>3</sub>), 58.89 (s, CH<sub>2</sub>), 110.03 (s, CH). Anal. Calcd for C<sub>14</sub>H<sub>10</sub>N<sub>4</sub>F<sub>6</sub>O<sub>3</sub>BrRe: C 25.39, H 1.52, N 8.46, Br 12.06. Found: C 25.44, H 1.55, N 8.02, Br 12.27.

### Synthesis of Re(CO)<sub>3</sub>(PMe<sub>3</sub>)<sub>2</sub>Br (3)

To H<sub>2</sub>CPf<sub>2</sub>Re(CO)<sub>3</sub>Br (30 mg, 75.5 μmol) in 20 mL CH<sub>2</sub>Cl<sub>2</sub> was added PMe<sub>3</sub> (7.8 μL, 75.4 μmol). The solution was stirred for approximately 20h, at which time the infrared indicated that the reaction had not gone to completion. An additional 7.8μL of PMe<sub>3</sub> was added, and stirred for an additional 2h. The solution was concentrated, layered with hexanes, and stored at -30°C. A tan colored precipitate was isolated.

Characterization: IR (CHCl<sub>3</sub>): 2032 (s), 1950 (s), 1986 (s) νCO. MS, 220 °C/70 eV (m/e, rel. int.): M<sup>+</sup> (502, 23), M-CO<sup>+</sup> (474, 46), M-2CO<sup>+</sup> (446, 75), M-3CO<sup>+</sup> (417, 21).

### Synthesis of Re(CO)<sub>3</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>Br (4)

To a solution of H<sub>2</sub>CPf<sub>2</sub>Re(CO)<sub>3</sub>Br (27.2 mg, 41.1 μmol) in 20 mL THF was added dropwise a solution of PMe<sub>2</sub>Ph (0.33 mL, 232 μmol) in 10 mL THF until no starting material could be seen in the IR. (approximately 2.5 mL of the PMe<sub>2</sub>Ph solution was added) The solvent was removed under vacuum, leaving behind a white/yellow crystalline solid. This was dissolved in CH<sub>2</sub>Cl<sub>2</sub>, layered with hexanes, and stored at -26 °C. A sand colored precipitate formed.

Characterization: IR (CHCl<sub>3</sub>): 2033 (s), 1953 (s), 1899 (s)  $\nu$ CO. MS, 230 °C/70 eV (m/e, rel. int.): M<sup>+</sup> (626, 21), M-CO<sup>+</sup> (598, 58), M-2CO<sup>+</sup> (570, 82), M-Br<sup>+</sup> (547, 15).

### X-Ray Structure of H<sub>2</sub>CPf<sub>2</sub>Re(CO)<sub>3</sub>Br (2)

The X-ray crystallographic study was carried out by Dr. R. McDonald of the Structure Determination Laboratory of this Department. This section and the tables are adapted from his report.

Suitable crystals of 2 were grown by the slow evaporation of CH<sub>2</sub>Cl<sub>2</sub> at room temperature. A crystal of dimensions 0.24 x 0.21 x 0.20 mm was obtained, having a P2<sub>1</sub>/m space group.

The structure was solved using a three dimensional Patterson synthesis which gave the positional parameters for the Re atom. The remaining non-hydrogen atoms were located by the usual combination of least squares refinement and difference Fourier synthesis.

Refinement of atomic parameters were carried out by full matrix least-squares techniques on F<sub>o</sub> minimizing the function

$$\sum w (|F_o| - |F_c|)^2$$

and the weighting factor w is given by

$$w = 4F_o^2 / \sigma^2(F_o)^2$$

All hydrogen atoms were included at their idealized calculated distances, assuming C-H distances of 0.94 Å.

In the final cycle, 139 parameters were refined using 1738 observations having  $I > 2\sigma(I)$ . The final agreement factors were:

$$R_1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|} = 0.0322$$

$$R_2 = \left[ \frac{\sum w (|F_o| - |F_c|)^2}{\sum w F_o^2} \right]^{1/2} = 0.0794.$$

**Table 2-4. Crystal Data and Details of Structure Refinement for  $H_2CPf_2Re(CO)_3Br$**

#### A. Crystal Data

$C_{14}H_{10}BrF_6N_4O_3Re$ ; FW = 662.37  
 Crystal dimensions (mm): 0.24 X 0.21 X 0.20  
 monoclinic space group  $P2_1/m$  (No. 11)  
 $a$  (Å) = 7.3483(10)  $b$  (Å) = 14.660(2)  $c$  (Å) = 8.8043(7)  
 $V$  (Å<sup>3</sup>) = 941.8(2)  $Z = 2$   $\rho_{calcd}$  (Mg/m<sup>3</sup>) = 2.336  $\mu$  (mm<sup>-1</sup>) = 8.654

#### B. Data Collection and Refinement Conditions

|  |   |
|--|---|
| Radiation ( $\lambda$ [Å])                       | Mo $K\alpha$ (0.71073)                                    |
| $F_{000}$  | 620   |
| Data collection $\theta$ range (deg)             | 2.33 to 25.00   |
| Index ranges                                     | $-1 \leq h \leq 8, -1 \leq k \leq 17, -10 \leq l \leq 10$ |
| Reflections collected                            | 2346  |
| Independent reflections                          | 1738 ( $R_{int} = 0.0273$ )                               |
| Refinement method                                | Full-matrix least-squares on $F^2$                        |
| Data/restraints/parameters                       | 1738/0/139  |
| Goodness-of-fit on $F^2$                         | 1.082   |
| Final $R$ indices ( $I > 2s(I)$ )                | $R_1 = 0.0322, wR_2 = 0.0794$                             |
| $R$ indices (all data)                           | $R_1 = 0.0367, wR_2 = 0.0819$                             |
| Largest diff. peak and hole (e Å <sup>-3</sup> ) | .952 and -1.015   |

**Table 2-5. Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for  $\text{H}_2\text{CPf}_2\text{Re}(\text{CO})_3\text{Br}$**

| Atom  | <i>x</i> | <i>y</i> | <i>z</i>  | <i>U</i> <sub>eq</sub> |
|-------|----------|----------|-----------|------------------------|
| Re    | -1175(1) | 2500     | -7242(1)  | 38(1)                  |
| Br    | -3522(1) | 2500     | -5167(1)  | 59(1)                  |
| F(11) | 2108(7)  | 603(4)   | -8696(5)  | 90(2)                  |
| F(12) | -541(6)  | 194(4)   | -8338(5)  | 76(1)                  |
| F(13) | 1709(9)  | -641(3)  | -7566(6)  | 93(2)                  |
| O(1)  | 1008(13) | 2500     | -9956(8)  | 88(3)                  |
| O(2)  | -3838(8) | 1160(4)  | -8981(7)  | 86(2)                  |
| N(11) | 695(6)   | 1490(3)  | -5884(5)  | 38(1)                  |
| N(12) | 1459(6)  | 1685(3)  | -4448(5)  | 38(1)                  |
| C(1)  | 241(14)  | 2500     | -8877(10) | 54(2)                  |
| C(2)  | -2802(9) | 1636(5)  | -8310(7)  | 56(2)                  |
| C(10) | 897(12)  | 2500     | -3695(8)  | 43(2)                  |
| C(11) | 1166(8)  | 226(5)   | -7700(7)  | 51(2)                  |
| C(12) | 1431(8)  | 682(4)   | -6187(7)  | 43(1)                  |
| C(13) | 2638(8)  | 375(4)   | -4960(7)  | 47(1)                  |
| C(14) | 2648(7)  | 1033(4)  | -3861(6)  | 42(1)                  |
| C(15) | 3752(8)  | 1106(5)  | -2328(6)  | 54(2)                  |

*U*<sub>eq</sub> is defined as one third of the trace of the orthogonalized *U*<sub>ij</sub> tensor.

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**Table 2-6. Bond Lengths (Å) for H<sub>2</sub>C(Pf)<sub>2</sub>Re(CO)<sub>3</sub>Br**


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|             |            |             |           |             |          |
|-------------|------------|-------------|-----------|-------------|----------|
| Re–C(1)     | 1.874(9)   | F(13)–C(11) | 1.332(9)  | N(12)–C(10) | 1.451(6) |
| Re–C(2)     | 1.911(7)   | O(1)–C(1)   | 1.161(11) | C(11)–C(12) | 1.483(8) |
| Re–N(11)    | 2.263(5)   | O(2)–C(2)   | 1.144(8)  | C(12)–C(13) | 1.389(8) |
| Re–Br       | 2.6569(10) | N(11)–C(12) | 1.341(8)  | C(13)–C(14) | 1.366(8) |
| F(11)–C(11) | 1.303(7)   | N(11)–N(12) | 1.351(6)  | C(14)–C(15) | 1.494(7) |
| F(12)–C(11) | 1.313(7)   | N(12)–C(14) | 1.355(7)  |             |          |

---

**Table 2-7. Bond Angles (deg) for H<sub>2</sub>C(Pf)<sub>2</sub>Re(CO)<sub>3</sub>Br**


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|                   |           |                    |          |
|-------------------|-----------|--------------------|----------|
| C(1)–Re–C(2)      | 89.7(3)   | O(2)–C(2)–Re       | 176.0(7) |
| C(2)′–Re–C(2)     | 83.0(4)   | N(12)–C(10)–N(12)′ | 111.0(6) |
| C(2)–Re–N(11)′    | 177.5(2)  | F(11)–C(11)–F(12)  | 106.5(6) |
| C(1)–Re–N(11)     | 92.8(3)   | F(11)–C(11)–F(13)  | 106.7(6) |
| C(2)–Re–N(11)     | 97.5(2)   | F(12)–C(11)–F(13)  | 105.4(6) |
| N(11)′–Re–N(11)   | 81.8(2)   | F(11)–C(11)–C(12)  | 112.9(6) |
| C(1)–Re–Br        | 173.3(3)  | F(12)–C(11)–C(12)  | 114.6(5) |
| C(2)–Re–Br        | 85.4(2)   | F(13)–C(11)–C(12)  | 110.1(5) |
| N(11)–Re–Br       | 92.28(10) | N(11)–C(12)–C(13)  | 111.5(5) |
| C(12)–N(11)–N(12) | 103.9(4)  | N(11)–C(12)–C(11)  | 124.3(5) |
| C(12)–N(11)–Re    | 135.0(4)  | C(13)–C(12)–C(11)  | 123.8(6) |
| N(12)–N(11)–Re    | 121.0(3)  | C(14)–C(13)–C(12)  | 105.7(5) |
| N(11)–N(12)–C(14) | 112.6(5)  | N(12)–C(14)–C(13)  | 106.2(5) |
| N(11)–N(12)–C(10) | 119.5(5)  | N(12)–C(14)–C(15)  | 123.4(6) |
| C(14)–N(12)–C(10) | 127.8(5)  | C(13)–C(14)–C(15)  | 130.3(6) |
| O(1)–C(1)–Re      | 175.4(9)  |                    |          |

Primed atoms are related to unprimed ones via the symmetry transformation  $x, 1/2-y, z$ .

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## **CHAPTER 3**

### **SYNTHESIS AND REACTIVITY OF $\text{HBPf}_3\text{Re}(\text{CO})_3$**

## Section 1

### INTRODUCTION

Since their introduction in 1967, pyrazolylborates<sup>1</sup> have been used to synthesize compounds of nearly all the transition metals.<sup>2</sup> Due primarily to their large size, they have been instrumental in providing stability to otherwise sensitive compounds, creating enzyme models and anchoring the metal to provide support while performing reactions on the complex's other coordination sites.<sup>2d</sup>

Comparisons of the chemistry of the cyclopentadienyl (Cp) and pentamethylcyclopentadienyl (Cp\*) ligands to that of the pyrazolylborate ligand are of interest, as they provide the opportunity to study the effect of the steric and electronic components of the pyrazolylborate on the metal center. As the 3-, 4- and 5-positions of the pyrazoles are altered (Figure 1-2), so are the steric and electronic properties of the pyrazolylborate. This is one of the main tenets of Trofimenko's "second generation" pyrazolylborates.<sup>3</sup>

The (3-trifluoromethyl-5-methylpyrazol-1-yl)borate (HBPF<sub>3</sub>) ligand was synthesized in this group by Richard Krentz,<sup>4</sup> and has exhibited interesting properties. On rhodium centers, it has altered the usual relative thermochemical stability of hydridovinyl and  $\eta^2$ -ethylene complexes, and it has activated the C-H bonds in benzene and cyclohexane, as well as the Si-H bond in HSiR<sub>3</sub> (R=Cl, Me).<sup>4b</sup> Consequently, the use of HBPF<sub>3</sub> on other metal centers was of interest.

Although pyrazolylborate chemistry on Group six metals has been extensively investigated, very little focus has been placed on those in Group seven, especially rhenium. Due principally to their commercial availability,

most investigations have involved only the HBPz<sub>3</sub> and HBPz\*<sub>3</sub> ligands. Therefore, using the HBPf<sub>3</sub> ligand provided the opportunity to compare its steric and electronic differences to that of the other two pyrazolylborates.

The syntheses<sup>5</sup> and crystal structures<sup>6</sup> of HBPz<sub>3</sub>Re(CO)<sub>3</sub> and HBPz\*<sub>3</sub>Re(CO)<sub>3</sub> have been reported. Therefore, a structure of HBPf<sub>3</sub>Re(CO)<sub>3</sub> would aid in determining the extent that steric effects play in its chemistry as compared to the other two ligands. Also, the reactivity of pyrazolylboraterhenium tricarbonyl complexes differs from that of the Cp analogues. For instance, the reaction of CpRe(CO)<sub>3</sub> with Br<sub>2</sub> yielded the seven-coordinate CpRe(CO)<sub>2</sub>Br<sub>2</sub> complex.<sup>7</sup> However, when bromine is reacted with the HBPz\*<sub>3</sub> analogue, bromination at the 4-position of the pyrazole results.<sup>5b</sup> While steric effects may prevent the formation of the seven-coordinate pyrazolylborate complex, some other property may also account for the unusual substitution reaction observed. The presence of the electron-withdrawing CF<sub>3</sub> group in the 3-position of the HBPf<sub>3</sub> ligand may provide insight into the chemistry observed.

Previous rhenium chemistry using the HBPz<sub>3</sub> and HBPz\*<sub>3</sub> ligands has mainly involved the photochemistry of the tricarbonyl complex.<sup>5a,6b</sup> Photolysis in a coordinating solvent (tetrahydrofuran) has resulted in the substitution of one carbonyl with a solvent molecule, while subsequent chemistry has demonstrated the facile substitution of the solvent ligand with various other donor ligands. Consequently, the photochemistry of HBPf<sub>3</sub>Re(CO)<sub>3</sub>, and its subsequent reactions with PPh<sub>3</sub> and PMe<sub>3</sub> has been studied in this work. Stable seventeen-electron paramagnetic species have also been synthesized by reacting the THF adduct with Br<sub>2</sub> and CCl<sub>4</sub>. Their effective magnetic moments have been measured and will be presented.

## Section 2

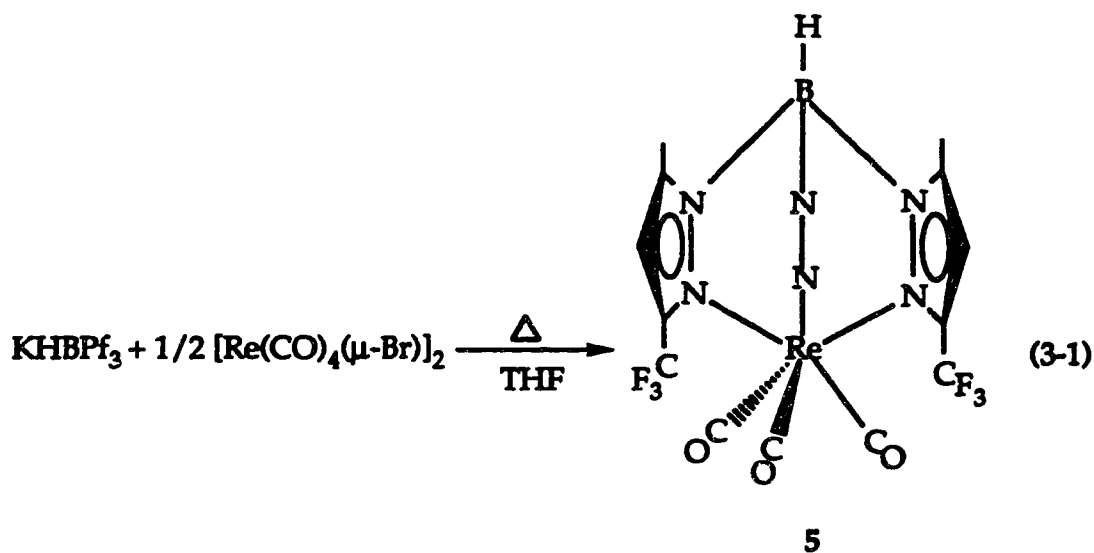
### SYNTHESIS AND PROPERTIES OF $\text{HBPf}_3\text{Re}(\text{CO})_3$ (5)

The preparation of 3-trifluoromethyl-5-methylpyrazole (HPf) was first reported<sup>8</sup> in 1964. However, its use in synthesizing the tris(3-trifluoromethyl-5-methylpyrazol-1-yl)borate ligand ( $\text{HBPf}_3$ ) was not reported until 1989 by Graham and Krentz.<sup>4</sup> The reaction leading to the  $\text{HBPf}_3$  ligand is regiospecific: all three  $\text{CF}_3$  groups occupy the same position in the borate ligand. That position was shown by X-ray crystallography to be the 3-position,<sup>4b</sup> which appears consistent with McCurdy's speculation of the formation of a less sterically-hindered transition state.<sup>9</sup> Attempts to purify the ligand have been only partly successful, therefore, for reaction purposes, an excess is used.

The preparation of 5 was similar to McCleverty's synthesis of the  $\text{HBPz}^*_3$  analogue.<sup>5b</sup> A tetrahydrofuran solution containing  $\text{KHBPf}_3$  and  $[\text{Re}(\text{CO})_4(\mu\text{-Et})]_2$  was refluxed until starting material bands had disappeared, and new bands at 2044 and 1937  $\text{cm}^{-1}$  were present. The solvent was removed and the oily residue washed with methanol, yielding  $\text{HBPf}_3\text{Re}(\text{CO})_3$  as a white, microcrystalline precipitate, in low yield (equation (3-1)).

The carbonyl stretching frequencies of 5 are approximately 20 and 30 wavenumbers higher than each  $\nu_{\text{CO}}$  value found in  $\text{HBPz}_3\text{Re}(\text{CO})_3$  and  $\text{HBPz}^*_3\text{Re}(\text{CO})_3$  respectively. This suggests that the  $\text{HBPf}_3$  ligand is less electron-donating to the metal center, presumably due to the presence of the electron-withdrawing  $\text{CF}_3$  groups on the pyrazole ring. Proton and fluorine NMR are indicative of a compound with  $\text{C}_{3v}$  symmetry as the  $^1\text{H}$  spectrum

contains only two singlets, one for the 5-Me group and one for the 4-H proton, while there is only a singlet in the  $^{19}\text{F}$  spectrum.



The synthesis of  $\text{HBPz}^*_3\text{Re}(\text{CO})_3$  using  $[\text{Re}(\text{CO})_4(\mu\text{-Cl})_2]^{5b}$  and  $[\text{Re}(\text{CO})_4(\mu\text{-Br})_2]^{6b}$  resulted in the formation of the by-products  $(\text{HPz}^*)_2\text{Re}(\text{CO})_3\text{Cl}^{5b}$  and  $(\text{OMe})_2\text{B}(\text{Pz}^*)_2\text{Re}(\text{CO})_3^{6b}$  respectively. McCleverty<sup>5b</sup> postulated that the formation of the rhenium chloride product may have resulted from the decomposition of the  $\text{HBPz}^*_3$  ligand by some rhenium species formed in solution. However, Gan<sup>6b</sup> only observed the dimethoxide complex, and speculated that while it may have formed from the decomposition of the pyrazolylborate ligand, it may also have resulted from the substitution of the two hydrogens attached to boron in  $\text{H}_2\text{B}(\text{Pz}^*)_2$ , which was present as an impurity in the  $\text{HBPz}^*_3$  ligand.

In the preparation of 5, other infrared bands were noted in the 2200 - 1600  $\text{cm}^{-1}$  region. Attempts to isolate these products using the methods employed by McCleverty and Gan were unsuccessful. Addition of chloroform did afford a white precipitate, but it appeared to be the result of

decomposition as its infrared spectrum exhibited six carbonyl stretching bands and the  $^1\text{H}$  and  $^{19}\text{F}$  NMR contained numerous peaks, among which only unreacted  $\text{KHBPf}_3$  was identified.

### X-Ray Structure of $\text{HBPf}_3\text{Re}(\text{CO})_3$ (5)

The crystal structures of the  $\text{HBPz}_3\text{Re}(\text{CO})_3$  and  $\text{HBPz}^*_3\text{Re}(\text{CO})_3$  complexes have already been determined.<sup>6</sup> Therefore, a structure of the  $\text{HBPf}_3\text{Re}(\text{CO})_3$  analogue would provide the opportunity to compare the ligands. Table 3-1 compares some bond length and angle values for the analogous  $\text{HBPz}_3$  and  $\text{HBPz}^*_3$  ligand to that of 5. In most cases, it appears that similar values are present in the three complexes.

**Table 3-1. Comparisons of Crystal Structure Data for  $\text{HBPz}_3\text{Re}(\text{CO})_3$ ,  $\text{HBPz}^*_3\text{Re}(\text{CO})_3$  and  $\text{HBPf}_3\text{Re}(\text{CO})_3$ \***

| Bond/ Angle               | $\text{HBPz}_3\text{Re}(\text{CO})_3$ | $\text{HBPz}^*_3\text{Re}(\text{CO})_3$ | $\text{HBPf}_3\text{Re}(\text{CO})_3$ |
|---------------------------|---------------------------------------|---|---------------------------------------|
| M-CO <sub>avg</sub> (Å)   | 1.82(3)                               | 1.911(5)                                | 1.909(7)                              |
| M-N <sub>avg</sub> (Å)    | 2.22(2)                               | 2.172(3)                                | 2.217(6)                              |
| N-N <sub>avg</sub> (Å)    | 1.38(3)                               | 1.387(5)                                | 1.360(8)                              |
| 3-C-4-C (Å)               | 1.38(4)                               | 1.399(7)                                | 1.391(9)                              |
| 5-C-4-C (Å)               | 1.37(4)                               | 1.386(7)                                | 1.368(9)                              |
| N(11)-Re-C(1) (°)         | 91.7(9)                               | 95.0(2)                                 | 93.8(2)                               |
| Re-C-O <sub>avg</sub> (°) | 175(2)                                | 176.8(5)                                | 177.3(7)                              |

\* average values were determined by taking into account all bonds present

The molecular structure of 5, shown in Figure 3-1, may be described as a slightly distorted octahedron with  $\text{C}_{3v}$  symmetry. This is consistent with spectroscopic data. Coincidentally, a crystallographic mirror plane includes





the metal center, one Pf group, and one carbonyl. Symmetry related atoms are assigned the "prime" value. Although the HBPf<sub>3</sub> ligand can be bidentate in some cases,<sup>4b</sup> it is tridentate here, allowing the complex to satisfy the 18 electron rule.

As with the HBPz\*<sub>3</sub> analogue<sup>6</sup> the rhenium center is within the pocket made by the presence of the CF<sub>3</sub> groups in the 3-position on the pyrazole rings. This illustrates one important feature of pyrazolylborate chemistry which is not found with the planar cyclopentadienyl rings.

The Re-N<sub>avg</sub> bond length for **5** is 2.217(6)Å, which is similar to the value obtained in the HBPz<sub>3</sub>Re(CO)<sub>3</sub> analogue (2.22(2)Å) but longer than the value in the HBPz\*<sub>3</sub>Re(CO)<sub>3</sub> complex (2.174(6)Å). The bond length variances may be related to the electron richness of the pyrazolylborates.

Bond angles between the carbonyls and the trans pyrazole for **5** are 178.1(2) and 176.9(3)°, which are consistent with values obtained for HBPz\*<sub>3</sub>Re(CO)<sub>3</sub> (176.7(2), 178.7(2)°) and close to values for HBPz<sub>3</sub>Re(CO)<sub>3</sub> (171.9(9), 171.2(9), 167.9(8)°).

### Section 3

#### THE REACTIVITY OF HBPf<sub>3</sub>Re(CO)<sub>3</sub> (**5**)

##### Photolysis

Photolysis of **5** in tetrahydrofuran results in the loss of one CO and the coordination of one solvent molecule to form HBPf<sub>3</sub>Re(CO)<sub>2</sub>THF (**6**). During the photolysis, the colorless solution of **5** turns yellow-orange. Although

attempts to determine the species responsible for this coloration have failed, it has been suggested<sup>6b</sup> that it is due to decomposition products, as **6** and the corresponding HBPz<sub>3</sub> and HBPz\*<sub>3</sub> analogues are light yellow.

The infrared spectrum of the tetrahydrofuran solution exhibits two carbonyl stretching bands, at 1934 and 1855 cm<sup>-1</sup>, which are approximately 80 cm<sup>-1</sup> below that found in **5**. This indicates increased electron donation from the metal center to the carbonyl ligands, decreasing the bond order of the C-O bond. This would be the result of the donation of electrons through the oxygen in the THF molecule, which is not a  $\pi$ -acceptor ligand. The <sup>1</sup>H spectrum exhibits peaks in a 2:1 ratio for the 5-Me protons and two unresolved peaks (also in a 2:1 ratio) for the 4-H protons on the pyrazole ring, while the <sup>19</sup>F NMR contains only a singlet. Although peaks in a 2:1 ratio would be expected in the <sup>19</sup>F NMR, the singlet is probably a result of coincidentally overlapping peaks.

Interestingly, if the solutions of **5** are similar to those for the HBPz\*<sub>3</sub>Re(CO)<sub>3</sub> analogue, the time for the reaction to occur is substantially increased, and more starting material is left intact. For example, a 1.68 mM THF solution of **5** required a photolysis time of over three hours, and only 85% conversion was obtained before excessive decomposition of product occurred. However, for the HBPz\*<sub>3</sub>Re(CO)<sub>3</sub> analogue,<sup>6b</sup> a 2.64 mM THF solution required only 20 minutes for the reaction to go to completion. The HBPz<sub>3</sub> analogue<sup>5a</sup> required less time to form when using a weaker source. This would imply higher internal filtering, caused by the formation of the yellow-orange solution formed in synthesizing **6**, compared to the HBPz\*<sub>3</sub> and HBPz<sub>3</sub> analogues.

## Halogenation

The reactivity of **5** is unique in that the direct reaction with bromine did not substitute any of the CO ligands, and did not substitute the 4-H proton of the pyrazole ring. When the HBPz\*<sub>3</sub> ligand was used, no substitution of the carbonyls was observed, but the 4-H on the pyrazolylborate ligand was substituted by the halide.<sup>5b</sup> Two explanations could account for such behavior. The HBPf<sub>3</sub> ligand contains substituents at both the 3- and 5-positions, as does the HBPz\*<sub>3</sub> ligand. However, if the CF<sub>3</sub> group is slightly larger in size than the methyl substituent, the steric difference could inhibit the approach of bromine. Secondly, the charge around the pyrazole ring is different for the HBPf<sub>3</sub> ligand than for the other two. Figure 3-1 illustrates the various partial charges on the carbon atoms of the pyrazole rings due to the presence of more electronegative atoms. For Pz and Pz\*, the charge on the 4-carbon is slightly negative, while the 4-C in Pf

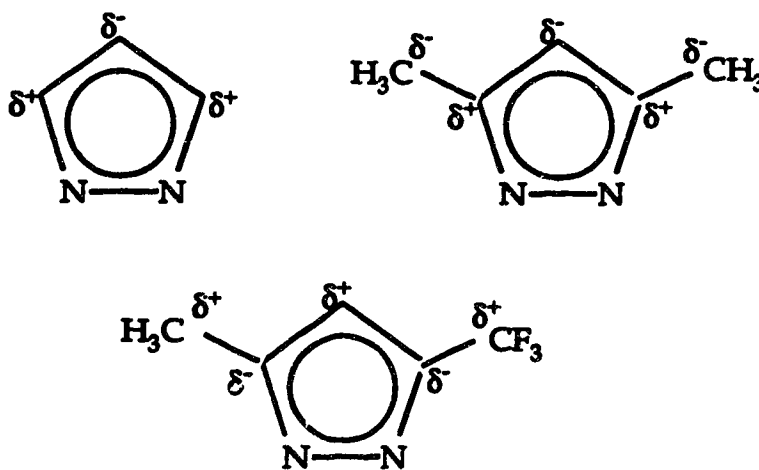


Figure 3-2. Partial Charges on Carbon Atoms in Pz, Pz\* and Pf

has a slightly positive charge. This difference in partial charges could affect the substitution of the 4-H by bromine, although the mechanism of that substitution is not known.

### **C-H Activation Attempts**

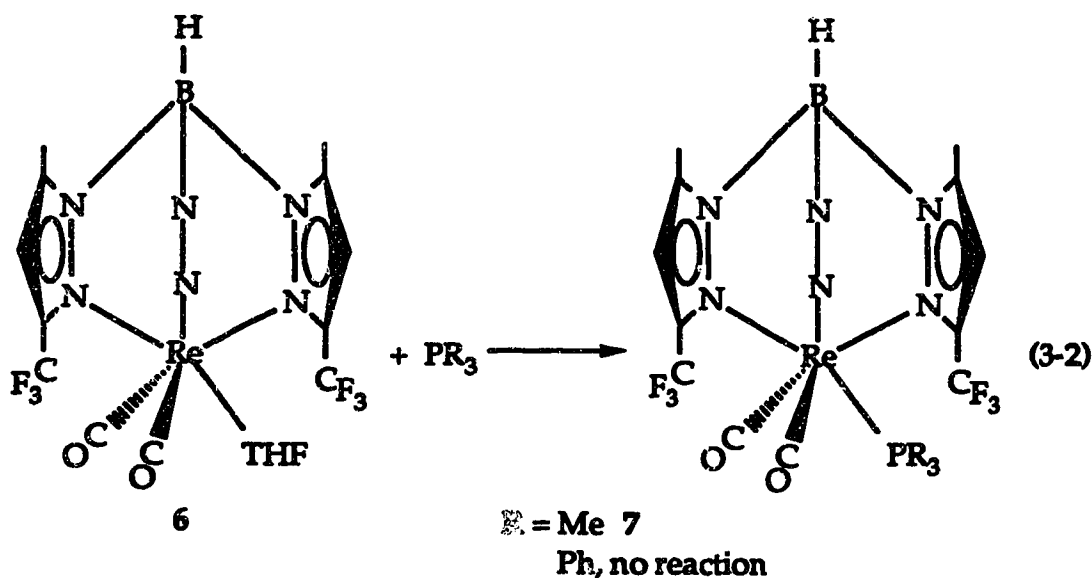
Attempts to observe C-H activation by photolysis of 5 in benzene, were unsuccessful. After several hours, the reactant bands had disappeared, but no new product bands were present in the 2200 - 1600  $\text{cm}^{-1}$  region of the infrared. It has been suggested that for  $\text{HBPz}^*_3\text{Re}(\text{CO})_3$ , the positioning of the seventh ligand would cause a large steric interaction with the 3-substituent on the pyrazolylborate ligand.<sup>6b</sup> Since the  $\text{CF}_3$  substituent in the 3-position on the pyrazoles in  $\text{HBPf}_3$  ligand is similar in size to  $\text{CH}_3$ , this result is not surprising.

## **Section 4**

### **THE REACTIVITY OF $\text{HBPf}_3\text{Re}(\text{CO})_2(\text{THF})$ (6)**

The photolysis of 5 in tetrahydrofuran led to the formation of the THF adduct 6, and this THF solution was used, without purification, for subsequent reactions. The analogous  $\text{HBPz}_3$  and  $\text{HBPz}^*_3$  complexes have demonstrated that the lability of the THF ligand provides a substitution pathway for a variety of interesting complexes.<sup>5a,6b</sup> This has also been found for 6.

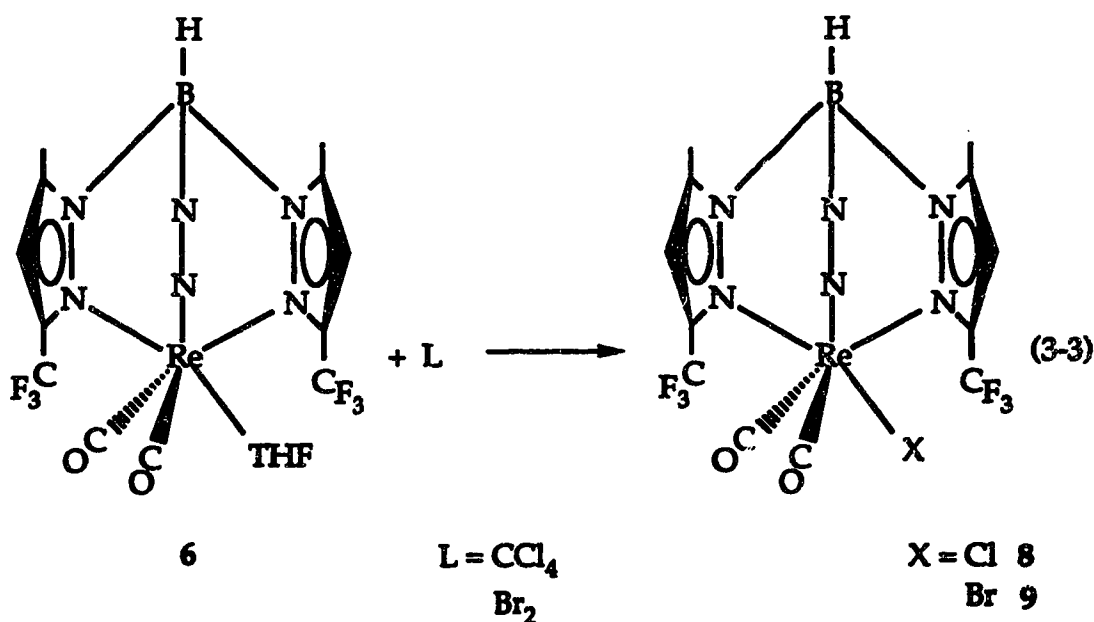
It was expected that the reaction of 6 with  $\text{PMe}_3$  and  $\text{PPh}_3$  would result in the substitution of the THF ligand, as was observed for the  $\text{HBPz}_3^{5a}$  and  $\text{HBPz}^*_3^{6b}$  analogues (equation (3-2)). Although the  $\text{PMe}_3$  complex could be made with stirring over three days, a similar reaction time saw no change in the infrared spectrum for the  $\text{PPh}_3$  reaction. Even after refluxing for 24h, little change was observed.



This difference may be a consequence of the sizes of the pyrazolylborate ligands. Due to the presence of substituents in the 3- and 5-positions of the pyrazoles in  $\text{HBPf}_3$ , its cone angle would be larger than the  $180^\circ$  value for  $\text{HBPz}_3$ , and similar to the  $224^\circ$  value for  $\text{HBPz}^*_3$ . Considering that the Tolman cone angle<sup>10</sup> for  $\text{PMe}_3$  is  $118^\circ$  while that for  $\text{PPh}_3$  is  $145^\circ$ , the steric difference created by substituting the  $\text{CH}_3$  and  $\text{CF}_3$  groups found in the 3-position of the  $\text{HBPz}^*_3$  and  $\text{HBPf}_3$  ligands can be rationalized.

## Synthesis of Paramagnetic Complexes

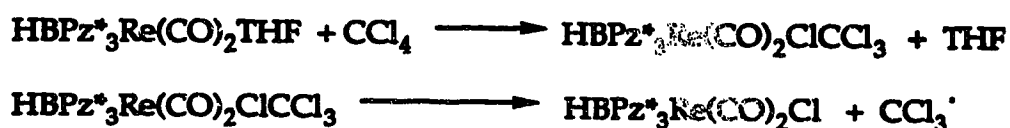
Although no reaction was observed between 5 and bromine, the reaction of 6 with  $\text{CCl}_4$  and  $\text{Br}_2$  resulted in the substitution of THF with Cl or Br, thereby forming seventeen-electron radicals, in fair yield (equation (3-3)). As was stated in Chapter 1, paramagnetic complexes do not normally provide useful NMR spectra, due to broadened signals. Through the use of Evans' method,<sup>11</sup> it is possible to determine by NMR techniques the magnetic moment of a compound, from which the number of unpaired electrons may be inferred.



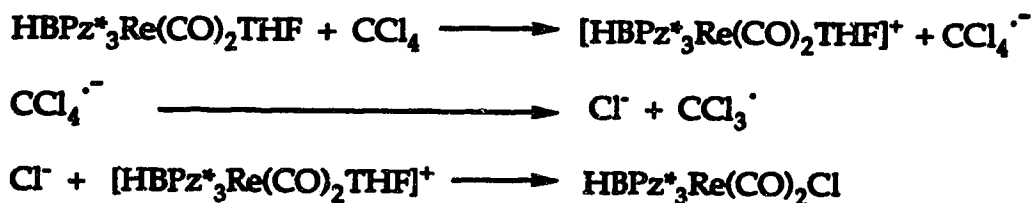
Both 8 and 9 may be left in air for several days without appreciable changes in their color or infrared spectrum. The stability added to unsaturated and radical complexes by coordination of the trispyrazolylborate ligand has been demonstrated and attributed to the size of the ligand.<sup>12</sup> Chapter 4 will describe an air- and moisture-stable seventeen-electron radical,

as well as sixteen-electron molybdenum complexes. These also exhibit remarkable stability, presumably due to the inability of other ligands to approach the metal center.

Two mechanisms for the formation of  $\text{HBPz}^*_3\text{Re}(\text{CO})_2\text{Cl}$  from the reaction of  $\text{HBPz}^*_3\text{Re}(\text{CO})_2\text{THF}$  and  $\text{CCl}_4$  have been postulated,<sup>6b</sup> and may well apply to the formation of  $\text{HBPf}_3\text{Re}(\text{CO})_2\text{Cl}$ . These are shown in Scheme 3-1.



(a)



(b)

### Scheme 3-1. Possible Mechanisms for Rhenium Radical Formation

Although the dichloro- and dibromocarbonyl products were also formed when  $\text{HBPz}^*_3\text{Re}(\text{CO})_2\text{THF}$  reacted with  $\text{CCl}_4$  and  $\text{Br}_2$ ,<sup>6b</sup> no such product was observed in similar reactions with 6. It has been suggested<sup>6b</sup> that of the two proposed mechanisms, only (b) can account for the formation of these dihalogenated species by further oxidation using  $\text{CCl}_4$ . Therefore, either the  $\text{HBPf}_3$  ligand is too large to accommodate the two bromides or  $\text{CCl}_4$  is unable to further oxidize 8 or 9 to form the dihalogenated species.

Effective magnetic moments were measured for  $\text{HBPf}_3\text{Re}(\text{CO})_2\text{X}$  ( $\text{X}=\text{Cl}, \text{Br}$ ) and are compared to analogous complexes synthesized by Gan<sup>6b</sup> in Table 3-2. For spin-only magnetic moments with one unpaired electron, values close to 1.73 BM would be obtained, which is close to the values obtained for 8 (2.02 BM) and 9 (1.94 BM) and consistent with Gan's findings. A more detailed calculation for the magnetic moment is provided in the Experimental Section.

**Table 3-2. Magnetic Moments of Paramagnetic Compounds 8 and 9<sup>a</sup>**

| Complex   | Mass<br>(mg) | Volume<br>(mL) | $\Delta\nu$<br>(Hz) | $\chi_{\text{dia}} (\times 10^6)$<br>( $\text{cm}^3 \text{mol}^{-1}$ ) | $\mu_{\text{eff}}$<br>(BM) |
|---|--------------|----------------|---------------------|--|----------------------------|
| $\text{HBPf}_3\text{Re}(\text{CO})_2\text{Cl}$ (8)          | 9.0          | 0.80           | 18.85               | -193.71  | 2.02                       |
| $\text{HBPf}_3\text{Re}(\text{CO})_2\text{Br}$ (9)          | 5.0          | 0.80           | 9.25                | -204.21  | 1.94                       |
| $\text{HBPz}^*_3\text{Re}(\text{CO})_2\text{Cl}^{\text{b}}$ |              |                |                     |  | 2.20                       |
| $\text{HBPz}^*_3\text{Re}(\text{CO})_2\text{Br}^{\text{b}}$ |              |                |                     |  | 2.37                       |

- a. All spectra were run on a 300 MHz FT NMR at 25 °C with cyclohexane as reference.  
 b. See reference 6b.

## Section 5

### EXPERIMENTAL

All reactions were carried out under an inert atmosphere of prepurified argon, using standard Schlenk techniques.  $[\text{Re}(\text{CO})_4(\mu\text{-Br})_2]$  was synthesized according to literature methods.<sup>13</sup> Complexes showed oxygen sensitivity in solution, but solids could be handled in air for prolonged periods of time without decomposition.



**Synthesis of  $\text{HBPf}_3\text{Re}(\text{CO})_3$  (5)**

$\text{KHBPf}_3$  (520 mg, 1.04 mmol) was added to a solution of  $[\text{Re}(\text{CO})_4(\mu\text{-Br})_2]$  (236 mg, 0.312 mmol) in 100 mL THF, and the solution refluxed overnight. The solvent was removed on the rotary evaporator, leaving behind a yellow oil. Methanol was added (3 x 10 mL) and the solution stirred. This yielded a white precipitate. (121 mg, 27%)

Characterization: IR (cyclohexane): 2051 (w), 1950 (w); ( $\text{CH}_2\text{Cl}_2$ ): 2045 (vs), 1937 (vs)  $\nu\text{CO}$ . MS, 200 °C 70 eV (m/e, rel. int.):  $\text{M}^+$  (730, 51),  $\text{M-CO}^+$  (702, 33),  $\text{M-2CO}^+$  (674, 9),  $\text{M-3CO}^+$  (646, 24).  $^1\text{H NMR}$  ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  2.49 (s, 9H), 6.45 (s, 3H).  $^{19}\text{F NMR}$  ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  -59.46 (s, 9F). Anal. Calcd for  $\text{C}_{18}\text{H}_{13}\text{N}_6\text{F}_9\text{ReO}_3\text{B}$ : C 29.64, H 1.80, N 11.52. Found: C 29.52, H 2.00, N 11.22.

**Synthesis of  $\text{HBPf}_3\text{Re}(\text{CO})_2\text{THF}$  (6)**

$\text{HBPf}_3\text{Re}(\text{CO})_3$  (220 mg, 0.302 mmol) in 180 mL THF was photolyzed using a high pressure mercury lamp (450 watts) with a Pyrex filter. After 3 hours, the reaction had gone to ~ 85% completion, and the originally colorless solution had become yellow-orange. Further photolysis resulted in the formation of a dark yellow-green solution whose infrared spectrum no longer exhibited product peaks. The solution was concentrated and hexanes were added, affording a precipitate. The solution was filtered and the solid washed with hexanes (3 x 5 mL) giving a light yellow precipitate. (58 mg, 25%)

Characterization: IR (THF): 1934 (s), 1855 (s)  $\nu$ CO. MS, 200 °C/70 eV (m/e, rel. int.): M-THF<sup>+</sup> (702, 3), M-2CO<sup>+</sup> (646, 2). <sup>1</sup>H NMR (THF, d<sub>8</sub>):  $\delta$  2.47 (s, 3H), 2.55 (s, 6H), 6.69 (s, 3H, contains unresolved shoulder). <sup>19</sup>F NMR (THF, d<sub>8</sub>): -59.77 (s, 9F). Anal. Calcd for C<sub>21</sub>H<sub>21</sub>N<sub>6</sub>F<sub>9</sub>BReO<sub>3</sub>: C 32.60, H 2.72, N 10.87. Found: C 32.31, H 2.53, N 10.10.

#### Synthesis of HBPf<sub>3</sub>Re(CO)<sub>2</sub>(PMe<sub>3</sub>) (7)

To a 50 mL aliquot of a freshly prepared solution of HBPf<sub>3</sub>Re(CO)<sub>2</sub>THF (made from a solution of 220 mg HBPf<sub>3</sub>Re(CO)<sub>3</sub> in 180 mL THF) was added PMe<sub>3</sub> (0.094 mL, 0.908 mmol). The yellow solution was stirred for 3 days. The solvent was removed in vacuo, and the residue dissolved in a minimum of CH<sub>2</sub>Cl<sub>2</sub>. This was chromatographed on a 1 x 20 cm Florisil (Mesh 60-100) column using CH<sub>2</sub>Cl<sub>2</sub>. The solvent was removed under vacuum, and the residue washed with hexanes (3 x 10 mL). This was dried under vacuum and yielded a cream colored precipitate. (15 mg, 23% based on 5)

Characterization: IR (Hexanes): 1963 (w), 1889 (w)  $\nu$ CO. MS 200 °C/70 eV (m/e, rel. int.): M<sup>+</sup> (778, 100), M-CO<sup>+</sup> (750, 4), M-2CO<sup>+</sup> (72, 21), M-2CO-PMe<sub>3</sub><sup>+</sup> (646, 10). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  1.43 (d, 9H, <sup>2</sup>J<sub>P-H</sub> = 7.5 Hz), 2.36 (s, 3H), 2.52 (s, 6H), 6.37 (s, 1H), 6.52 (s, 2H). <sup>19</sup>F NMR (CD<sub>2</sub>Cl<sub>2</sub>): -57.18 (s, 6F), -60.28 (s, 3F). Anal. calcd for C<sub>20</sub>H<sub>22</sub>N<sub>6</sub>F<sub>9</sub>BRePO<sub>2</sub>: C 30.90, H 2.83, N 10.81. Found: C 31.20, H 3.10, N 9.75.

### Preparation of $\text{HBPf}_3\text{Re}(\text{CO})_2\text{Cl}$ (8)

To a freshly prepared solution of  $\text{HBPf}_3\text{Re}(\text{CO})_2\text{THF}$  (50 mL of a solution prepared from 220 mg 5 in 180 mL THF) was added  $\text{CCl}_4$  (0.4 mL) and the solution was stirred for 2 days. The THF was removed under vacuum, leaving a yellow-orange precipitate. This was dissolved in  $\text{CH}_2\text{Cl}_2$  and chromatographed on a 1 x 14 cm Florisil column (60-100 mesh). The solution was concentrated, layered with hexanes and stored at  $-26\text{ }^\circ\text{C}$ . A yellow precipitate settled out. (20 mg, 32% based on 5)

Characterization: IR (THF): 2024 (s), 1914 (s)  $\nu\text{CO}$ . MS, +ve FAB (m/e, rel. int.):  $\text{M}^+$  (737, 2),  $\text{M-CO}^+$  (709, 1),  $\text{M-Cl}^+$  (701, 4),  $\text{M-2CO}^+$  (681, 2).  $^1\text{H}$  and  $^{19}\text{F}$  NMR were not obtained due to the compounds paramagnetic character. Anal. Calcd for  $\text{C}_{17}\text{H}_{13}\text{N}_6\text{F}_9\text{BReClO}_2$ : C 27.70, H 1.77, N 11.41. Found: C 28.16, H 1.95, N 10.59.  $\mu_{\text{eff}}$ : 2.02 BM (see below).

### Preparation of $\text{HBPf}_3\text{Re}(\text{CO})_2\text{Br}$ (9)

To a freshly prepared solution of 6 (75.8 mg of 5 in 150 mL THF) was added  $\text{Br}_2$  (0.0143 mL, 44.2 mg, 0.277 mmol), and the solution allowed to stir until the infrared no longer contained bands indicating the presence of 6. The solvent was removed in vacuo, leaving a brown residue. This was dissolved in  $\text{CH}_2\text{Cl}_2$ , and chromatographed on a 1 x 16 cm Florisil column (60-100 mesh). This solution was concentrated and layered with hexanes. An orange/brown precipitate formed, which was dried under vacuum. (26 mg, 32%, based on 5).  $\mu_{\text{eff}}$ : 1.94 BM (see below)

Characterization: IR (CH<sub>2</sub>Cl<sub>2</sub>): 2026 (s), 1919 (s) νCO. MS 220 °C/16 eV (m/e, rel. int.): M<sup>+</sup> (781, 29), M-CO<sup>+</sup> (753, 16), M-2CO<sup>+</sup> (725, 23), M-Br<sup>+</sup> (701, 2). <sup>1</sup>H and <sup>19</sup>F NMR were not obtained for this paramagnetic compound. Anal. Calcd for C<sub>17</sub>H<sub>13</sub>N<sub>6</sub>F<sub>9</sub>BrReBrO<sub>2</sub>: C 26.12, H 1.66, N 10.75. Found: C 26.37, H 1.64, N 9.99.

### Calculation of Effective Magnetic Moment ( $\mu_{\text{eff}}$ )

While many methods for the determination of the effective magnetic moment<sup>14</sup> exist, only Evans' method<sup>11</sup> was used in this Chapter. A Wilmad Special Stem Coaxial Insert tube (196 mm - top 154 mm has OD (outer diameter) = 4 mm and the stem has an OD = 2 mm) containing 1% cyclohexane, as reference, in CD<sub>2</sub>Cl<sub>2</sub> is placed inside a 178 mm (OD = 5 mm) NMR tube containing the sample, also dissolved in CD<sub>2</sub>Cl<sub>2</sub>, with 1% cyclohexane as reference. The following is a sample calculation for HBPf<sub>3</sub>Re(CO)<sub>2</sub>Cl (8).

Using the 300 MHz NMR spectrometer, 8 (9.0mg) was dissolved in 0.80mL CD<sub>2</sub>Cl<sub>2</sub>. Two resonances were observed at 427.46 and 408.61 Hz, at 25 °C. Therefore, in determining the molar susceptibility, equation (1-2),  $m$  is  $1.13 \times 10^{-2}$  g/mL and  $\Delta\nu$  is 18.85 Hz. The mass susceptibility of the solvent  $\chi_o$  is determined using Pascal's constants (Table 3-3), where  $\chi_H = \chi_D$ :

$$\begin{aligned} \text{H: } & 2 \times (-2.93 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}) = -5.86 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1} \\ \text{C: } & 1 \times (-6.00 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}) = -6.00 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1} \\ \text{Cl: } & 2 \times (-20.1 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}) = \underline{-40.2 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}} \\ & \chi_o (\text{CD}_2\text{Cl}_2) = -52.06 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1} \end{aligned}$$

$$\chi_g (\text{CD}_2\text{Cl}_2) = -52.06 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1} / 87 \text{ g mol}^{-1} = -0.60 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$$

Neglecting the last term of equation (1-2) due to the dilute solutions used, and substituting in the above values gives:

$$\begin{aligned} \chi_g &= \frac{3 \times 18.85}{2 \times 3.14 \times (300 \times 10^6) \times (1.13 \times 10^{-2})} - 0.60 \times 10^{-6} \\ &= 2.06 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1} \\ \chi &= 2.06 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1} \times 736.47 \text{ g mol}^{-1} \\ &= 1.52 \times 10^{-3} \text{ cm}^3 \text{ mol}^{-1} \end{aligned}$$

Using Pascal's constants, one can calculate the diamagnetic susceptibility of 8.

It was found to be  $-193.71 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ . Therefore,

$$\begin{aligned} \chi_{\text{para}} &= \chi - \chi_{\text{dia}} \\ &= 1.52 \times 10^{-3} - (-193.71 \times 10^{-6}) \\ &= 1.71 \times 10^{-3} \text{ cm}^3 \text{ mol}^{-1} \end{aligned}$$

Now, the effective magnetic moment is calculated:

$$\begin{aligned} \mu_{\text{eff}} &= 2.828 \times ((1.71 \times 10^{-3}) \times 298)^{0.5} \\ &= 2.02 \text{ BM} \end{aligned}$$

Table 3-3. Pascal's Constants

| Atom         | $\chi_A$ ( $\times 10^{-6}$<br>$\text{cm}^{-3} \text{mol}^{-1}$ ) | Atom | $\chi_A$ ( $\times 10^{-6}$<br>$\text{cm}^{-3} \text{mol}^{-1}$ ) |
|--------------|---|------|---|
| H            | -2.93   | F    | -6.3  |
| C            | -6.00   | Cl   | -20.1   |
| C (aromatic) | -6.24   | Br   | -30.6   |
| N (aromatic) | -4.61   | Re   | 67.6  |
| B            | -6.7  | Mo   | 89.0  |
| CO           | -9.8  |      |   |

### X-ray Crystal Data of $\text{HBPf}_3\text{Re}(\text{CO})_3$ (5)

The X-ray crystallographic determination was carried out by Dr. R. McDonald of this Department. The following details are adapted from his report.

A suitable crystal obtained from a  $\text{CH}_2\text{Cl}_2$ /hexane mixture, having the approximate dimensions  $0.22 \times 0.12 \times 0.11$  mm, was mounted in a non-specific orientation.

The structure was solved using standard Patterson techniques which gave the positional parameters for the Re atom. The remaining non-hydrogen atoms were located by the usual combination of least-squares refinement and difference Fourier synthesis.

Refinement of atomic parameters were carried out by full matrix least-squares techniques on  $F_o$  minimizing the function

$$\sum w (|F_o| - |F_c|)^2$$

and the weighting factor  $w$  is given by

$$w = 4F_o^2 / \sigma^2(F_o)^2$$

All hydrogen atoms were included at their idealized calculated distances, assuming C-H and B-H distances of 0.94Å.

In the final cycle, 190 parameters were refined using 2177 observations having  $I > 2\sigma(I)$ . The final agreement factors were:

$$R_1 = \Sigma |F_o| - |F_c| / \Sigma |F_o| = 0.0327$$

$$R_2 = [ \Sigma w (|F_o| - |F_c|)^2 / \Sigma w F_o^2 ]^{1/2} = 0.0790$$

**Table 3-4. Crystal Data and Details of Structure Refinement for  
HBPf<sub>3</sub>Re(CO)<sub>3</sub> (5)**

**A. Crystal Data**

**C<sub>18</sub>H<sub>13</sub>BF<sub>9</sub>N<sub>6</sub>O<sub>3</sub>Re**      **FW: 729.35**

**Crystal Dimensions: 0.22 × 0.12 × 0.11 mm**

**Monoclinic space group P2<sub>1</sub>/m (No. 11)**

**a = 8.649(1), b = 14.994(2), c = 9.328(1) Å**

**β = 100.839(8)°**

**V = 1188.1(2) Å<sup>3</sup>; Z = 2; D<sub>c</sub> = 2.039 Mg/m<sup>3</sup>**

**B. Data Collection and Refinement Conditions**

|   |  |
|---|--|
| <b>Radiation (λ [Å])</b>                              | <b>Mo Kα (0.71073)</b>                                 |
| <b>μ (mm<sup>-1</sup>)</b>                            | <b>5.218</b>   |
| <b>F<sub>000</sub></b>                                | <b>696</b>   |
| <b>Data collection θ range (deg)</b>                  | <b>2.22 to 25.00</b>                                   |
| <b>Index ranges</b>                                   | <b>-10 ≤ h ≤ 10, 0 ≤ k ≤ 17, 0 ≤ l ≤ 11</b>            |
| <b>Reflections collected</b>                          | <b>2177</b>  |
| <b>Refinement method</b>                              | <b>Full-matrix least-squares on F<sup>2</sup></b>      |
| <b>Data/restraints/parameters</b>                     | <b>2177/0/190</b>                                      |
| <b>Goodness-of-fit on F<sup>2</sup></b>               | <b>1.044</b>   |
| <b>Final R indices (I &gt; 2σ(I))</b>                 | <b>R<sub>1</sub> = 0.0327, wR<sub>2</sub> = 0.0790</b> |
| <b>R indices (all data)</b>                           | <b>R<sub>1</sub> = 0.0395, wR<sub>2</sub> = 0.0823</b> |
| <b>Largest diff. peak and hole (e Å<sup>-3</sup>)</b> | <b>1.176 and -1.251</b>                                |



**Table 3-5. Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for  $\text{HBPf}_3\text{Re}(\text{CO})_3$**

| Atom  | x        | y       | z         | $U_{\text{eq}}$ |
|-------|----------|---------|-----------|-----------------|
| Re    | 4473(1)  | 2500    | -1854(1)  | 42(1)           |
| F(11) | 1364(7)  | -403(4) | -2129(6)  | 113(2)          |
| F(12) | 1673(10) | 755(4)  | -3250(6)  | 142(3)          |
| F(13) | 3568(8)  | -74(6)  | -2582(9)  | 157(3)          |
| F(21) | 8641(6)  | 1803(5) | -1921(7)  | 119(2)          |
| F(22) | 10465(6) | 2500    | -578(9)   | 91(2)           |
| O(1)  | 5840(6)  | 1112(4) | -3669(6)  | 76(1)           |
| O(2)  | 1605(9)  | 2500    | -4314(9)  | 77(2)           |
| N(11) | 3499(5)  | 1501(3) | -507(5)   | 45(1)           |
| N(12) | 3617(5)  | 1666(3) | 944(5)    | 45(1)           |
| N(21) | 6492(7)  | 2500    | -7(8)     | 49(2)           |
| N(22) | 6196(8)  | 2500    | 1371(8)   | 49(2)           |
| C(1)  | 5336(7)  | 1621(5) | -2952(7)  | 54(2)           |
| C(2)  | 2646(11) | 2500    | -3380(11) | 53(2)           |
| C(11) | 2338(9)  | 272(5)  | -2173(9)  | 72(2)           |
| C(12) | 2710(7)  | 726(4)  | -758(7)   | 52(1)           |
| C(13) | 2326(8)  | 399(4)  | 526(8)    | 59(2)           |
| C(14) | 2914(7)  | 1007(4) | 1582(7)   | 56(2)           |
| C(15) | 2802(9)  | 995(5)  | 3165(7)   | 67(2)           |
| C(21) | 8921(11) | 2500    | -1069(13) | 65(3)           |
| C(22) | 8058(9)  | 2500    | 151(11)   | 52(2)           |
| C(23) | 8748(10) | 2500    | 1617(12)  | 62(3)           |
| C(24) | 7554(10) | 2500    | 2388(12)  | 58(2)           |
| C(25) | 7610(13) | 2500    | 3967(12)  | 83(3)           |
| B     | 4462(11) | 2500    | 1624(11)  | 46(2)           |

$U_{\text{eq}}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

---

**Table 3-6. Bond Lengths (Å) for HBPf<sub>3</sub>Re(CO)<sub>3</sub>**


---

|             |           |             |           |
|-------------|-----------|-------------|-----------|
| Re-C(1)     | 1.905(7)  | N(12)-B     | 1.525(7)  |
| Re-C(2)     | 1.917(10) | N(21)-C(22) | 1.335(10) |
| Re-N(21)    | 2.210(7)  | N(21)-N(22) | 1.358(10) |
| Re-N(11)    | 2.220(5)  | N(22)-C(24) | 1.364(11) |
| F(11)-C(11) | 1.323(8)  | N(22)-B     | 1.561(12) |
| F(12)-C(11) | 1.280(10) | C(11)-C(12) | 1.470(10) |
| F(13)-C(11) | 1.301(9)  | C(12)-C(13) | 1.391(9)  |
| F(21)-C(21) | 1.308(8)  | C(13)-C(14) | 1.368(9)  |
| F(22)-C(21) | 1.328(11) | C(14)-C(15) | 1.498(9)  |
| O(1)-C(1)   | 1.154(8)  | C(21)-C(22) | 1.473(14) |
| O(2)-C(2)   | 1.129(11) | C(22)-C(23) | 1.386(14) |
| N(11)-C(12) | 1.345(8)  | C(23)-C(24) | 1.365(14) |
| N(11)-N(12) | 1.361(7)  | C(24)-C(25) | 1.46(2)   |
| N(12)-C(14) | 1.355(8)  |             |           |

Table 3-7. Bond Angles (deg) for HBPf<sub>3</sub>Re(CO)<sub>3</sub>

|                   |          |                    |           |
|-------------------|----------|--------------------|-----------|
| C(1)'-Re-C(1)     | 87.5(4)  | N(21)-N(22)-B      | 120.0(7)  |
| C(1)-Re-C(2)      | 87.3(3)  | C(24)-N(22)-B      | 128.4(8)  |
| C(1)'-Re-N(11)    | 178.1(2) | O(1)-C(1)-Re       | 177.1(6)  |
| C(1)-Re-N(11)     | 93.8(2)  | O(2)-C(2)-Re       | 177.6(9)  |
| C(1)-Re-N(21)     | 95.0(2)  | F(12)-C(11)-F(13)  | 105.7(9)  |
| C(2)-Re-N(11)     | 94.2(2)  | F(12)-C(11)-F(11)  | 105.3(7)  |
| C(2)-Re-N(21)     | 176.9(3) | F(13)-C(11)-F(11)  | 105.4(7)  |
| N(11)'-Re-N(11)   | 84.9(2)  | F(12)-C(11)-C(12)  | 115.6(7)  |
| N(21)-Re-N(11)    | 83.5(2)  | F(13)-C(11)-C(12)  | 113.1(7)  |
| C(12)-N(11)-N(12) | 105.7(5) | F(11)-C(11)-C(12)  | 110.9(7)  |
| C(12)-N(11)-Re    | 135.9(4) | N(11)-C(12)-C(13)  | 110.5(6)  |
| N(12)-N(11)-Re    | 118.3(3) | N(11)-C(12)-C(11)  | 125.1(6)  |
| C(14)-N(12)-N(11) | 110.4(5) | C(13)-C(12)-C(11)  | 124.4(6)  |
| C(14)-N(12)-B     | 129.4(6) | C(14)-C(13)-C(12)  | 105.6(5)  |
| N(11)-N(12)-B     | 120.2(5) | N(12)-C(14)-C(13)  | 107.8(6)  |
| C(22)-N(21)-N(22) | 105.3(7) | N(12)-C(14)-C(15)  | 124.1(6)  |
| C(22)-N(21)-Re    | 136.3(7) | C(13)-C(14)-C(15)  | 128.1(6)  |
| N(22)-N(21)-Re    | 118.4(5) | F(21)'-C(21)-F(21) | 106.0(10) |
| N(21)-N(22)-C(24) | 111.6(7) | F(21)-C(21)-F(22)  | 105.6(6)  |
| F(21)-C(21)-C(22) | 114.0(6) | F(22)-C(21)-C(22)  | 110.9(9)  |
| N(21)-C(22)-C(23) | 110.4(9) | N(21)-C(22)-C(21)  | 124.5(9)  |
| C(23)-C(22)-C(21) | 125.2(8) | C(24)-C(23)-C(22)  | 107.0(8)  |
| N(22)-C(24)-C(23) | 105.7(9) | N(22)-C(24)-C(25)  | 124.1(9)  |
| C(23)-C(24)-C(25) | 130.2(9) | N(12)'-B-N(12)     | 110.2(7)  |
| N(12)-B-N(22)     | 109.6(5) |                    |           |

Primed atoms are related to unprimed ones via the symmetry transformation  $x, 1/2-y, z$ .

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## CHAPTER 4

### SYNTHESIS AND REACTIVITY OF $[\text{HBPf}_3\text{Mo}(\text{CO})_3]^-$

## Section 1

### INTRODUCTION

Pyrazolylborate chemistry has been extended to nearly all the transition metals, with the largest emphasis involving the Group six triad. However, most investigations have involved the use of the HBPz<sub>3</sub> and HBPz\*<sub>3</sub> ligands. Therefore, it was of interest to use the tris(3-trifluoromethyl-5-methylpyrazol-1-yl)borate ligand, and observe the effects of this electronically and sterically unique ligand.

It has been possible to synthesize [Et<sub>4</sub>N]<sup>+</sup> [HBPf<sub>3</sub>Mo(CO)<sub>3</sub>]<sup>-</sup>, and, as with its other pyrazolylborate analogues, it has provided an excellent starting point for the synthesis of new complexes. Also, the effect of the CF<sub>3</sub> groups in altering the electron donating power of the ligand can be established by comparing CO stretching frequencies with those of analogous compounds.

In solution there is no evidence for dissociation of the [CpMo(CO)<sub>3</sub>]<sub>2</sub> dimer to radical monomer, although the radical species can be produced by irradiation. With the 3,5-disubstituted pyrazolylborate ligands, though, the size of the ligand can inhibit the formation of the dimer, and stabilize the seventeen-electron radical.<sup>1</sup> In this Chapter, we report the synthesis and properties of HBPf<sub>3</sub>Mo(CO)<sub>3</sub><sup>-</sup>, as well as a comparison of its unusual thermal and air stability with those of the HBPz<sub>3</sub> and HBPz\*<sub>3</sub> analogues.

While complexes of the general formula CpMoL<sub>4</sub> and Cp\*MoL<sub>4</sub> (where L is a monodentate ligand) are common in cyclopentadienyl chemistry,<sup>2</sup> seven-coordinate pyrazolylborate compounds are less frequently encountered.<sup>1a,3</sup> This has mainly been attributed to the hybridization of the orbitals of the pyrazolylboratemolybdenum dicarbonyl fragment as compared

to those of  $\text{CpMo(CO)}_2$ , and to the steric factors involved. Syntheses of  $\text{HBPz}_3\text{Mo(CO)}_3\text{H}^{1c,4}$  and  $\text{HBPz}^*_3\text{Mo(CO)}_3\text{H}^{3a}$  have been reported, and similar procedures have been used in this work to synthesize  $\text{HBPf}_3\text{Mo(CO)}_3\text{H}$ . This complex exhibits interesting spectroscopic behavior, and appears to be fluxional.

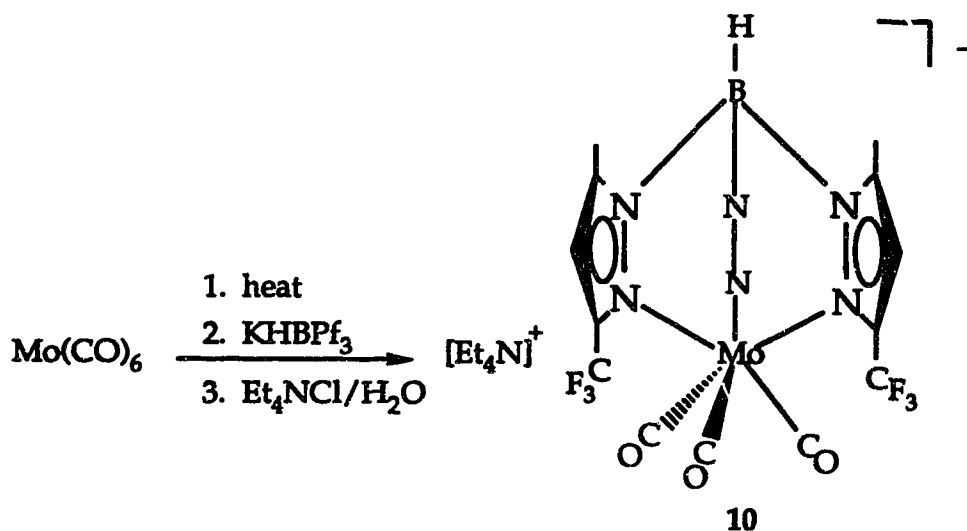
Transition metal nitrosyl chemistry has expanded greatly over the last 30 years and a recent book discusses the formation, characteristics and structures of many metal nitrosyl compounds.<sup>5</sup> McCleverty and coworkers<sup>6</sup> have synthesized numerous molybdenum and tungsten nitrosyl alkoxides of the form  $\text{HBPz}^*_3\text{Mo(NO)(X)(Y)}$  (where X = halide, alkoxide; Y = alkoxide) and have noted the remarkable stability of these 16-electron complexes. This stability has been attributed to the size of the pyrazolylborate ligand preventing the approach of another ligand to relieve the metal of its unsaturation. The  $\text{HBPf}_3$  ligand, having, presumably, a similar cone angle to that of the  $\text{HBPz}^*_3$  ligand, should also provide stability to these complexes. X-ray structures of dialkoxo metal nitrosyl complexes have indicated short Mo-O bonds due to increased  $p\pi \rightarrow d\pi$  interaction to compensate for the decrease in electron density around the unsaturated metal center.<sup>6a,b</sup> In this work, complexes of the form  $\text{HBPf}_3\text{Mo(NO)(Y)}_2$  (Y = halide, alkoxide) have been synthesized and are discussed in Section 3.



## Section 2

### SYNTHESIS AND REACTIONS OF $[\text{Et}_4\text{N}]^+ [\text{HBPf}_3\text{Mo}(\text{CO})_3]^-$

Much trispyrazolylborate chemistry has been carried out on the molybdenum metal center. However, no complexes using the  $\text{HBPf}_3$  ligand have been synthesized. Use of the anions  $[\text{HBPz}_3\text{Mo}(\text{CO})_3]^-$  and  $[\text{HBPz}^*_3\text{Mo}(\text{CO})_3]^-$  has led to many new and interesting compounds. Consequently, a logical starting point was the synthesis of the analogous molybdenum tricarbonyl anion,  $[\text{Et}_4\text{N}]^+ [\text{HBPf}_3\text{Mo}(\text{CO})_3]^-$  (10). When excess  $\text{KHBPf}_3$  was added to the tris(acetonitrile)molybdenum tricarbonyl precursor, the resulting solution showed only two infrared carbonyl stretching bands ( $1911$  and  $1777 \text{ cm}^{-1}$ ). Addition of aqueous  $\text{Et}_4\text{NCl}$  ( $\sim 0.8 \text{ M}$ ) resulted in the formation of yellow crystals in good yield (equation (4-1)).



NMR data are consistent with a species of  $\text{C}_{3v}$  symmetry as the  $^1\text{H}$  NMR spectrum shows a singlet for the 4-H proton and for the 5-methyl

group, as well as in the  $^{19}\text{F}$  nmr at  $\delta$  -59.50 ppm. NMR data for  $\text{HPf}$ ,  $\text{HBPf}_3$  and **10** are listed in Table 4-1. Coordination to the metal deshields the 5-Me and 4-H protons ( $\Delta\delta \sim 0.4$  ppm) and fluorines ( $\Delta\delta \sim 6.5$  ppm) of the

|   | $^1\text{H}$                 |                | $^{19}\text{F}$              |
|---|------------------------------|----------------|------------------------------|
|   | $\delta$ (5- $\text{CH}_3$ ) | $\delta$ (4-H) | $\delta$ (3- $\text{CF}_3$ ) |
| $\text{Pf}$   | 2.35                         | 6.36           | -63.01                       |
| $\text{HBPf}_3^-$                                     | 2.16                         | 6.17           | -66.09                       |
| $\text{HBPf}_3\text{Mo}(\text{CO})_3^-$ ( <b>10</b> ) | 2.50                         | 6.43           | -59.50                       |

All spectra run in acetone  $d_6$ , 200 MHz, ambient temperature.

pyrazolylborate ligand. Similar shifts in the  $^{19}\text{F}$  NMR are found in all the molybdenum compounds presented in this Chapter.

#### Oxidation of $[\text{Et}_4\text{N}]^+ [\text{HBPf}_3\text{Mo}(\text{CO})_3]^-$ (**10**)

The oxidation of **10** using  $[\text{Cp}_2\text{Fe}]^+ [\text{BF}_4]^-$  in acetonitrile led to the formation of the red, crystalline 17-electron radical  $\text{HBPf}_3\text{Mo}(\text{CO})_3^\cdot$  (**11**) in good yield. Although a  $^1\text{H}$  NMR spectrum containing three very broad peaks was obtained for the  $\text{HBPz}^*_3\text{Mo}(\text{CO})_3^\cdot$  analogue,<sup>7</sup> no signals at all could be observed in the  $^1\text{H}$  NMR of **11**. However, infrared and mass spectra as well as an adequate elemental analysis were obtained. An effective magnetic moment of 2.24 BM, which is indicative of one unpaired electron, was measured using the Evans method.<sup>8</sup>

Infrared spectroscopy for this dark red complex indicated the presence of two CO stretching bands at 2031 and 1908  $\text{cm}^{-1}$ , consistent with a complex having  $C_{3v}$  symmetry. A comparison of these infrared values to those of 10 indicates an increase of nearly 120  $\text{cm}^{-1}$ . A comparison to the HBPz\*<sub>3</sub>, HBPz<sub>3</sub> and Cp analogues is presented in Table 4-2.

**Table 4-2. Comparison of Carbonyl Stretching Frequencies for Some 17-Electron Molybdenum Radicals**

| Complex  | $\nu_{\text{CO}}$ ( $\text{cm}^{-1}$ ) <sup>a</sup> |
|--|---|
| $\text{CpMo}(\text{CO})_3^{\cdot}$                 | 1920 (m), 1845 (w) <sup>b</sup>                     |
| $\text{HBPz}_3\text{Mo}(\text{CO})_3^{\cdot}$      | 2010 (s), 1885 <sup>c</sup>                         |
| $\text{HBPz}^*_3\text{Mo}(\text{CO})_3^{\cdot}$    | 1998 (s), 1864 (vs) <sup>d</sup>                    |
| $\text{HBPf}_3\text{Mo}(\text{CO})_3^{\cdot}$ (11) | 2025 (s), 1901 (s)                                  |

- a. All spectra run in  $\text{CH}_2\text{Cl}_2$  at room temperature.  
 b. In THF at 81K. (possibly THF-solvated)<sup>9</sup>  
 c. See reference 1a.  
 d. See reference 7.

From these data, it is possible to estimate the relative degree of back donation to the carbonyl ligands. As electrons begin to fill the  $\pi^*$  orbital of the carbonyl ligand, the C-O bond will weaken, and a lower infrared CO stretching frequency will result. In Table 4-2, the highest  $\nu_{\text{CO}}$  value is obtained for the HBPf<sub>3</sub> radical. Therefore the HBPf<sub>3</sub> ligand is the poorest electron donor to the metal center. The presence of the CF<sub>3</sub> group on the pyrazole rings could account for the trend observed. With the high electronegativity of the fluorine, less electron density will be supplied by the ligand to the metal center, which in turn will have less electron density to donate to the carbonyls.

Complex 11 also exhibits remarkable stability. Crystals left at room temperature in an open container exhibited no decomposition over a six month period. Such high stability has also been noted for the  $\text{HBPz}^*_3\text{Mo}(\text{CO})_3^-$  complex,<sup>7</sup> and contrasts the air-sensitive nature of the  $\text{HBPz}_3\text{Mo}(\text{CO})_3^-$  complex, which showed decomposition even when stored under nitrogen.<sup>1b</sup> The added stability for the  $\text{HBPz}^*_3$  complex has been attributed to the presence of the substituent in the 3-position of the pyrazole ring.<sup>7</sup> It was proposed that this substituent blocks the access to the metal center needed by an incoming ligand and prevents a facile pathway for decomposition. Since the  $\text{HBPf}_3$  ligand possesses a substituent in the 3-position which is similar in size to the methyl group on the  $\text{HBPz}^*_3$  ligand, it would seem reasonable to expect a similar result.

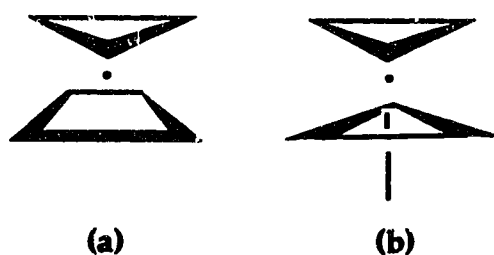
#### **$\text{HBPf}_3\text{Mo}(\text{CO})_3\text{H}$ (12)**

The addition of concentrated HCl to an acetonitrile solution of 10 resulted in the formation, in good yield, of an analytically pure light-yellow microcrystalline precipitate 12. Experimental results suggest that the hydrogen is more acidic rather than hydridic. For example, the need to use a strong acid to form this complex suggests that the anion, 10, is a weak base. This differs from the  $[\text{CpMo}(\text{CO})_3]^-$  anion, which required only acetic acid to form the weak acid  $\text{CpMo}(\text{CO})_3\text{H}$ .<sup>10</sup> Also, when 12 is dissolved in tetrahydrofuran or dimethylformamide, the infrared spectrum exhibits bands for 10 as well as 12, while in nitromethane, only bands representing 10 are observed. Therefore, an acid-base equilibrium must exist between the hydride and the solvent. The acidity of hydrides of this type may account for

Curtis and Shiu's unsuccessful attempts to react  $\text{HBPz}_3\text{Mo}(\text{CO})_3\text{H}$  with trityl.<sup>3c</sup>

Seven-coordinate complexes are of interest because they can provide useful information about mechanistic pathways for both associative and dissociative reactions.<sup>11</sup> Although seven-coordinate cyclopentadienylmolybdenum complexes are common, they are rarely formed when the sterically demanding pyrazolylborate ligand is present. Therefore, the synthesis of seven-coordinate pyrazolylborate compounds has presented interesting questions about possible geometry and fluxionality.

Through the use of  $^{13}\text{C}$  NMR, it has been shown that the majority of cyclopentadienylmolybdenum compounds exhibit the four-legged piano stool (3:4 geometry) arrangement<sup>2</sup> (Figure 4-1(a)). With pyrazolylborate complexes, though, it was hoped that due to the size of the ligand it would be possible to observe complexes adopting either a 3:4 or 3:3:1 geometry (Figure 4-1(b)). Both possibilities are known to exist. Storr has

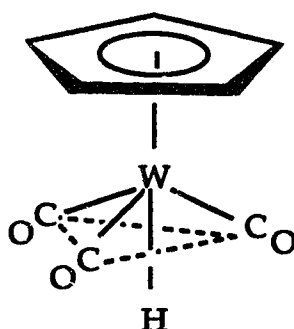


**Figure 4-1. Possible Geometries for  $\text{HBPf}_3\text{Mo}(\text{CO})_3\text{H}$**

**(a). 3:4 (capped trigonal prism) (b). 3:3:1 (capped octahedron)**

crystallographically determined that  $[\text{MeGaPz}_3]\text{Mo}(\text{CO})_3\text{SnPh}_3$  adopts a 3:3:1 geometry,<sup>12</sup> while Curtis<sup>3c</sup> has shown that  $\text{HBPz}_3\text{Mo}(\text{CO})_3\text{Br}$  adopts a 3:4 geometry.

Interestingly, Faller<sup>13</sup> found that when a sample of  $\text{CpW}(\text{CO})_3\text{H}$  ( $^{13}\text{C}$  enriched) was cooled below  $-70^\circ\text{C}$ , two  $^2J_{(\text{H}-\text{W}-^{13}\text{CO})}$  coupling constants were observed consistent with a 3:4 conformation; when the sample was warmed above  $-70^\circ\text{C}$ , only one value was observed. In order to explain the results above  $-70^\circ\text{C}$ , he proposed that an intermediate of 3:3:1 geometry formed, placing all the carbonyls in the same environment on a time averaged basis (Figure 4-2).



**Figure 4-2. Faller's Proposed Intermediate to Explain Fluxionality**

Many seven-coordinate complexes are known to be fluxional due to minimal energy differences between the idealized geometries (capped octahedron, pentagonal bipyramid, and capped trigonal prism).<sup>11,14</sup> Therefore, to observe fluxional behavior in  $\text{HBPf}_3\text{Mo}(\text{CO})_3\text{H}$  (22) would not be surprising.

Similar to the experimental findings for the analogous  $\text{HBPz}_3$  and  $\text{HBPz}^*_3$  molybdenum hydride complexes,<sup>1c, 3a, 4</sup> 12 also appears to be fluxional. Its infrared spectrum (Figure 4-3) exhibits three carbonyl stretching bands, suggesting a complex having  $C_s$  symmetry (3:4 conformation), and excluding a  $C_{3v}$  (3:3:1) structure. However,  $^1\text{H}$  (Figure 4-4) and  $^{19}\text{F}$  NMR spectra even at  $-80^\circ\text{C}$  showed singlets for the 5-Me and 4-H protons on the

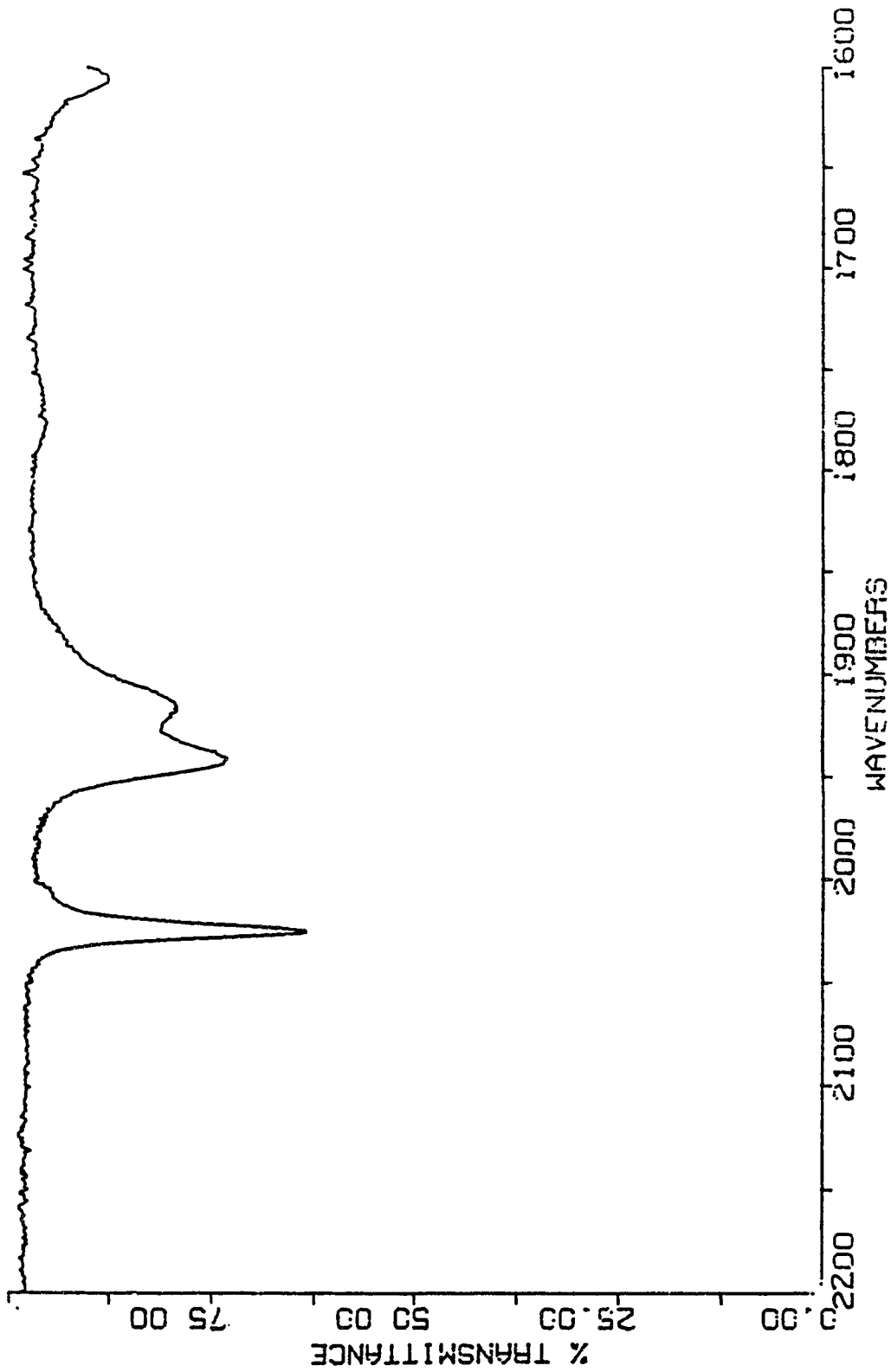


Figure 4-3. Infrared Spectrum of  $\text{HBPf}_3\text{Mo}(\text{CO})_3\text{H}$  (12) ( $\text{CH}_2\text{Cl}_2$ )

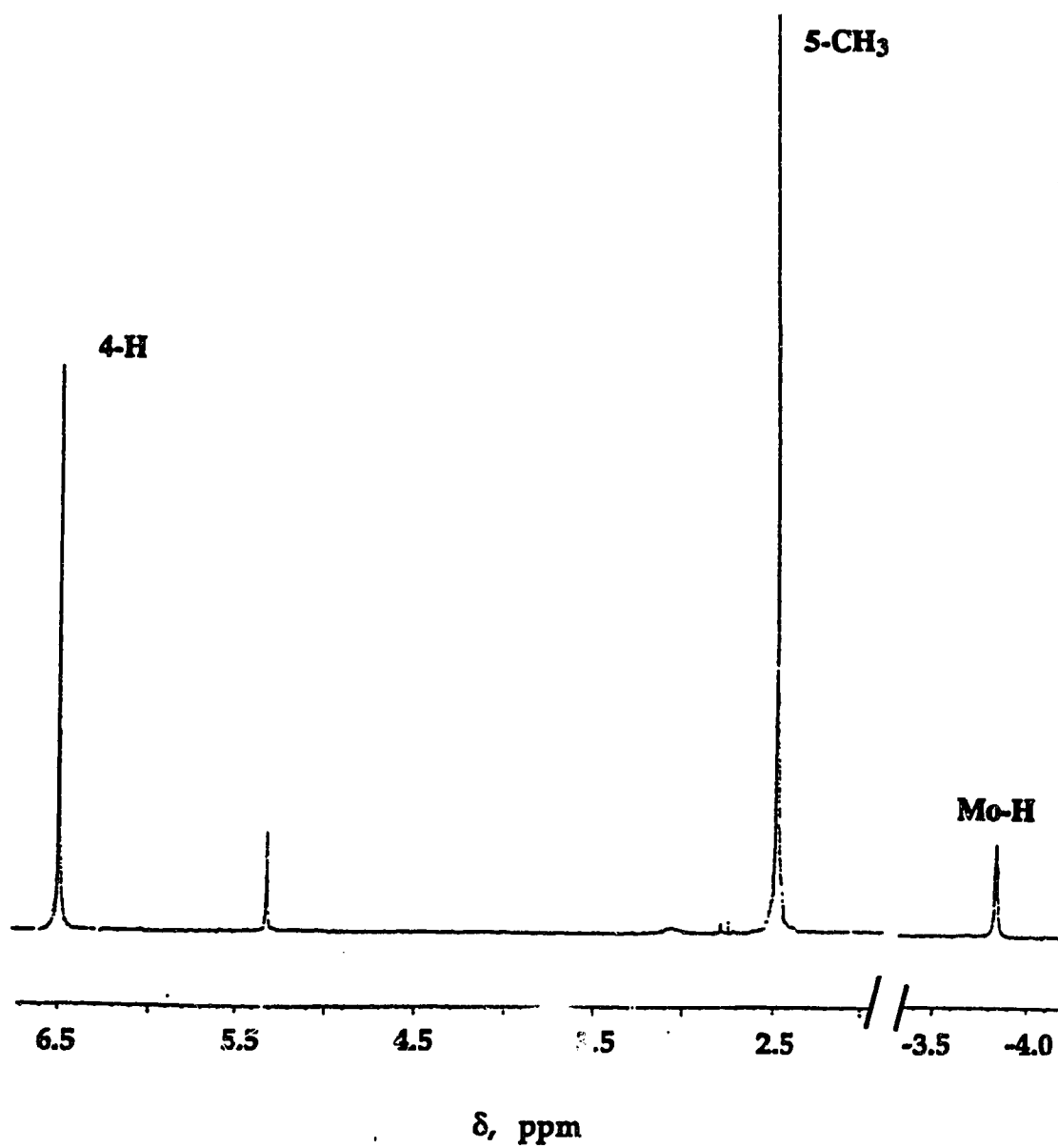


Figure 4-4. Room Temperature  $^1\text{H}$  NMR of  $\text{HBPf}_3\text{Mo}(\text{CO})_3\text{H}$  (12)

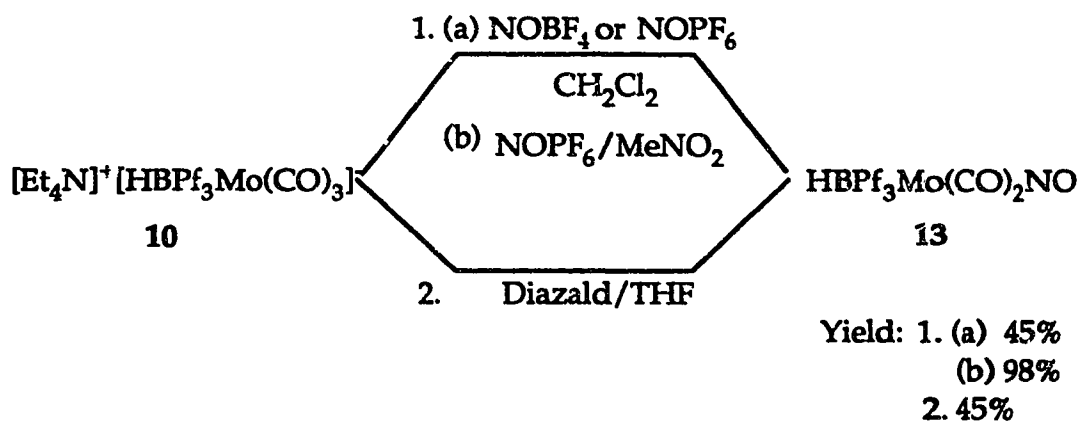


pyrazole rings. This suggests a complex having a time averaged  $C_{3v}$  symmetry (3:3:1 geometry). For the  $HBPz_3$  and  $HBPz^*_3$  analogues, it has been suggested<sup>3c</sup> that the barrier for interconversion of the ligands in the basal plane of a 3:4 structure is less for pyrazolylborate complexes than the analogous Cp compounds, and that the 3:3:1 conformation is a viable intermediate for this fluxional process. This would also explain the results observed for 12.

Curtis<sup>3c</sup> synthesized  $HBPz_3Mo(CO)_3Br$  and also noted  $C_s$  symmetry in the infrared and  $C_{3v}$  symmetry in the NMR. In this case, a crystal structure conclusively showed the 3:4 geometry. Using the 3:4 structure as the ground state, EHMO methods were used to calculate the energies of possible isomers. Although the 3:3:1 isomer with a CO in the capping position was lower in energy than the isomer with a capping bromide, the time averaged singlet observed in the  $^1H$  NMR spectrum can only be explained by the latter.

#### Ligand Substitution on $[HBPf_3Mo(CO)_3]^-$ (10)

Although numerous methods of replacing carbonyl ligands with nitrosyls exist,<sup>15</sup> two methods were used in this work in synthesizing  $HBPf_3Mo(CO)_2NO$  (13), and are summarized in Figure 4-5. Method 1(a) uses the nitrosyl anion salts  $NOPF_6$  and  $NOBF_4$ , dissolved in solvent and added dropwise to the dissolved anion. Using acetonitrile or methylene chloride as solvents resulted in yields of approximately 45%. Refluxing 10 in tetrahydrofuran, acidifying the solution, and then adding Diazald (N-methyl-N-nitroso-p-toluenesulfonamide) gave comparable yields. The only advantage of using Diazald was the ease of handling the substance.



**Figure 4-5. Methods for Synthesizing  $\text{HBPf}_3\text{Mo}(\text{CO})_2\text{NO}$**

As was also noted by Sweet<sup>16</sup> in synthesizing rhenium nitrosyls, use of the nitrosonium salts can be solvent dependent. For instance, by substituting nitromethane for acetonitrile, the yield of  $[\text{CpRe}(\text{CO})_2\text{NO}]^+$  increased from 80% to 91%. In this work, even greater improvement resulted: use of nitromethane increased the yield from 45% to greater than 90%.

The infrared spectrum of 13 exhibited three bands at 2041, 1963 ( $\nu\text{CO}$ ) and 1714 ( $\nu\text{NO}$ )  $\text{cm}^{-1}$ . The  $^1\text{H}$  NMR contained peaks in a 2:1 ratio for the 5-Me groups as well as the 4-H protons, while the  $^{19}\text{F}$  NMR contained peaks in a 2:1 ratio for the  $\text{CF}_3$  groups. Although the NO stretching frequency of 1714  $\text{cm}^{-1}$  could indicate the presence of either a linear or bent nitrosyl, X-ray structures for similar complexes have indicated that a linear nitrosyl is present.<sup>7</sup>

### Other Reactions

Curtis<sup>3d</sup> has synthesized  $\eta^2$ -acyl complexes by reacting  $[\text{HBPz}_3\text{Mo}(\text{CO})_3]^-$  with MeI or  $[\text{Me}_3\text{O}]^+[\text{BF}_4]^-$ . He postulated that their

formation could be the result of the preference of the complex for coordination number six, due to the hybridization of the orbitals of the  $\text{HBPz}_3\text{Mo}(\text{CO})_2$  fragment. In this work, when  $[\text{Et}_4\text{N}]^+ [\text{HBPf}_3\text{Mo}(\text{CO})_3]^-$  was reacted with  $\text{MeI}$  or  $[\text{Me}_3\text{O}]^+ [\text{BF}_4]^-$ , no change was observed in the 2200 - 1600  $\text{cm}^{-1}$  region of the infrared. This lack of reactivity could be a consequence of the size of the  $\text{HBPf}_3$  ligand preventing the  $\eta^2$ -acyl from forming. It is also possible that the presence of the electron withdrawing  $\text{CF}_3$  groups causes complex 10 to be a poorer nucleophile than with the  $\text{HBPz}_3$  ligand. This would inhibit its interaction with the other reactants.

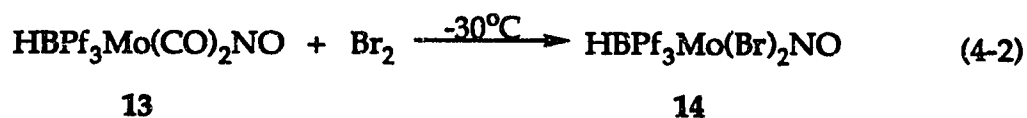
### Section 3

#### THE CHEMISTRY OF $\text{HBPf}_3\text{Mo}(\text{CO})_2\text{NO}$ (13)

The reactions of  $\text{LMo}(\text{CO})_2(\text{NO})$  complexes (where  $\text{L} = \text{HBPz}_3$  and  $\text{HBPz}^*_3$ ) have been well investigated. McCleverty<sup>7</sup> demonstrated the ability of these compounds to form air stable, 16-electron molybdenum complexes of the form  $\text{HBPz}^*_3\text{Mo}(\text{X})(\text{Y})(\text{NO})$  ( $\text{X} = \text{halide, alkoxide, Y} = \text{halide, alkoxide}$ ). Reaction of the dihalide complexes with alcohols resulted in mono- and disubstitution of the halogens. As a result, the chemistry of 13 was of interest in order to determine if similar results would be obtained with a less electron-donating pyrazolylborate ligand, and if steric differences between the ligands would affect the chemistry involved.

## Halogenation

Synthesis of  $\text{HBPf}_3\text{Mo}(\text{NO})(\text{Br})_2$  (**14**) was accomplished by adding a solution of  $\text{Br}_2$  dropwise, at  $-30^\circ\text{C}$ , to a methylene chloride solution of  $\text{HBPf}_3\text{Mo}(\text{NO})(\text{CO})_2$  (equation (4-2)). The yellow solution slowly turned red-brown, and the infrared spectrum no longer contained bands for **13**. The



red-brown product was obtained in good yield by recrystallization from methylene chloride and hexanes. The  $^1\text{H}$  NMR spectrum showed two signals in 2:1 ratio for the 5-Me protons, as well as the 4-H protons, while the infrared spectrum exhibited one nitrosyl stretching band at  $1658\text{ cm}^{-1}$ .

## Ligand Substitution

Reaction of **14** with methanol or ethanol resulted in the formation of the bisalkoxy complexes  $\text{HBPf}_3\text{Mo}(\text{NO})(\text{OR})_2$  ( $\text{R} = \text{Me}$  (**15**),  $\text{Et}$  (**16**)), as violet and pink solids respectively. Although **14** could be stored in an open container for prolonged periods of time with no indication of decomposition, it was remarkably reactive. When a methylene chloride solution of **14** was layered with methanol or ethanol, a gradual color change occurred. When methanol was added, the solution slowly turned from the original orange-brown color to blue, purple and finally to violet over a period of several minutes. The infrared spectrum contained only one NO stretching band,

while the  $^1\text{H}$  NMR spectrum showed peaks in 2:1 ratio for the 5-Me and 4-H protons.

For the ethanol solution, the initially formed deep purple color exhibited infrared bands for starting material and product, and a small band mid-way between the two, presumably due to a monoethoxy intermediate. With continued stirring, the solution turned light pink. The  $^1\text{H}$  NMR also contained peaks in a 2:1 ratio for the 5-Me and 4-H protons on the pyrazole ring. This differs from the chemistry of both the  $\text{HBPz}_3$  and  $\text{HBPz}^*_3$  molybdenum nitrosyl analogues. In both those instances, only monosubstitution occurred. Disubstitution resulted only upon addition of base, or after prolonged refluxing.

There are two possible explanations for the differing reactivities of  $\text{HBPz}^*_3$ ,  $\text{HBPz}_3$ , and  $\text{HBPf}_3\text{Mo}(\text{X})_2\text{NO}$  complexes. The first deals with the size each ligand. For both the unsubstituted and dimethyl pyrazolylborate ligands, the diiodo complex could be synthesized. However, attempts to synthesize the analogous  $\text{HBPf}_3$  complex were unsuccessful. This might imply that the  $\text{HBPf}_3$  ligand is sterically more demanding. Therefore, it is possible that the dibromo complex **14** is also causing steric strain in the molecule, causing it to substitute the halides with the smaller alkoxide groups.

Although molybdenum prefers to form 18-electron complexes, both the dihalide and dialkoxy complexes contain 16 electrons. Consequently, the unsaturated metal center would prefer coordination with the alkoxy groups, as they are better  $\pi$  electron donating ligands. The effect of replacing a CO with an oxygen bound ligand was observed in the lowering of the CO bands in **5** when one CO was substituted with a THF molecule. Table 4-3 presents infrared data for the three 16-electron  $\text{HBPf}_3\text{Mo}(\text{X})_2\text{NO}$  complexes. Legzdins

and Richter-Addo<sup>17</sup> indicated that the positions of  $\nu\text{NO}$  bands within similar complexes are indicative of the degree of electron donation from the metal to the nitrosyl  $\pi^*$  orbital. Consequently, the complex containing the most electron-donating ligand (OEt) has the lowest  $\nu\text{NO}$  band, while the dihalide complex has the least electron donation to the antibonding orbital.

**Table 4-3. Stretching Frequencies of Molybdenum Nitrosyl Complexes**

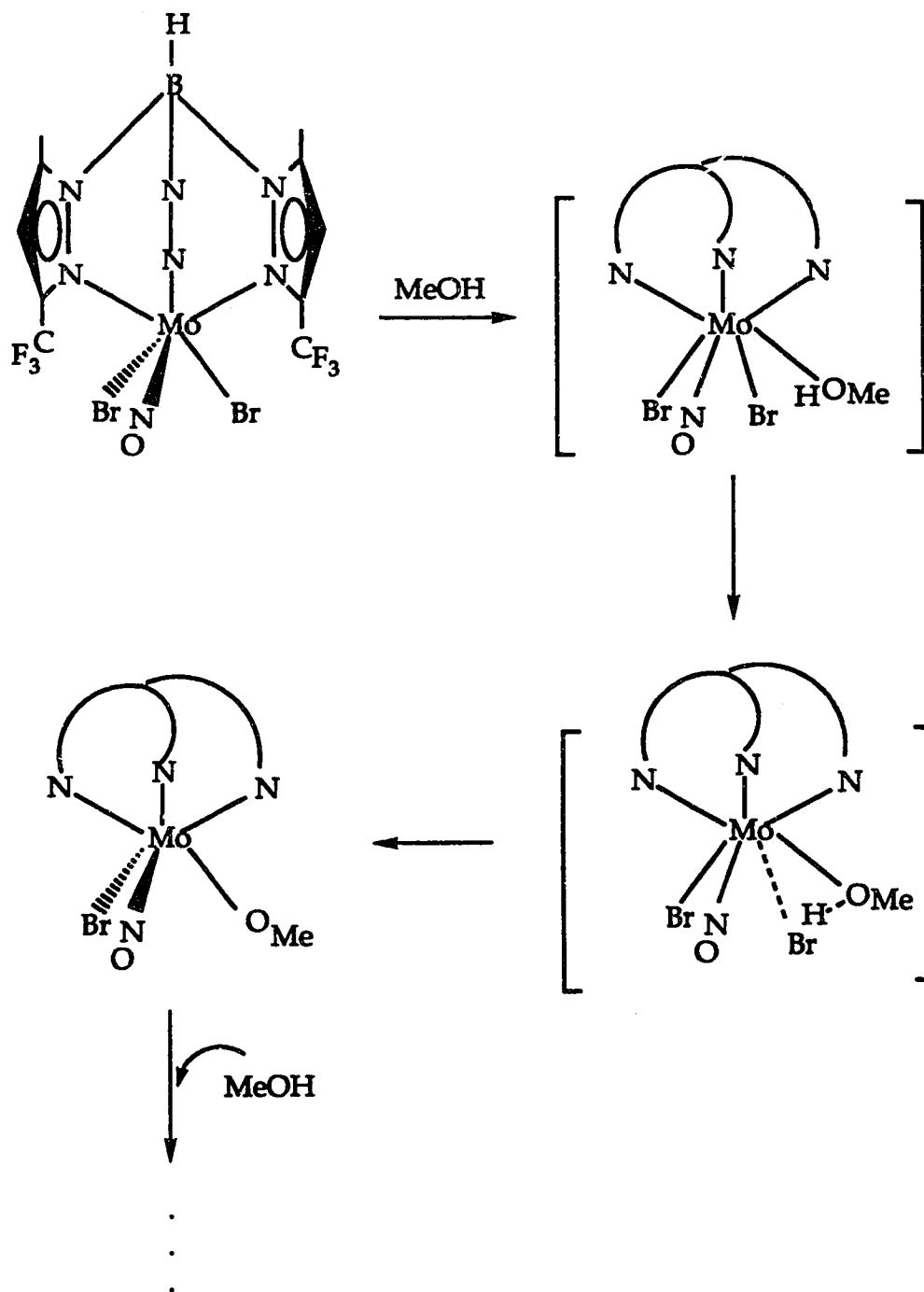
| Complex  | $\nu\text{NO}$ ( $\text{cm}^{-1}$ ) |
|--|-------------------------------------|
| HBPf <sub>3</sub> Mo(Br) <sub>2</sub> NO (14)  | 1758 <sup>a</sup>                   |
| HBPf <sub>3</sub> Mo(OMe) <sub>2</sub> NO (15) | 1685 <sup>b</sup>                   |
| HBPf <sub>3</sub> Mo(OEt) <sub>2</sub> NO (16) | 1676 <sup>a</sup>                   |

a. Recorded in CH<sub>2</sub>Cl<sub>2</sub> solvent.

b. Recorded in CHCl<sub>3</sub> solvent.

Therefore, the alkoxy groups are able to provide extra electron donation to the unsaturated metal center.

A schematic reaction pathway associated with the formation of the dialkoxy complexes is illustrated in Scheme 4-1. The lone pairs on the oxygen can attach to the metal center, creating a seven-coordinate, 18-electron, intermediate. The acidic hydrogen on methanol will be in close proximity to the bromide ligand, and could result in the loss of HBr. This monosubstituted product is presumably the one observed in the infrared spectrum of HBPf<sub>3</sub>Mo(NO)(OEt)<sub>2</sub> as a band observed mid-way between the starting material and the product. Repeating this scheme would result in the formation of the disubstituted product.



**Scheme 4-1. Mechanistic Proposal for the Formation of Dialkoxy Products**

## Section 4

### EXPERIMENTAL

All manipulations were carried out under an inert atmosphere using standard Schlenk techniques. Other solvents were used as received from suppliers. Deaeration of solvent was accomplished by bubbling argon through the solvent using a gas dispersion tube of porosity A or B for 20 minutes prior to use.

#### Preparation of $[\text{Et}_4\text{N}]^+ [\text{HBPf}_3\text{Mo}(\text{CO})_3]^-$ (10)

A sample of  $\text{Mo}(\text{CO})_6$  (581 mg, 2.23 mmol) dissolved in 120 mL acetonitrile was refluxed for 23h.  $\text{KHBPf}_3$  (1.850 g, 3.72 mmol) was added, and the solution refluxed for 4h. Once the solution was concentrated to approximately 2/3 the original volume,  $\text{Et}_4\text{NCl}$  (6.104 g, 36.9 mmol) in 55 mL deaerated water was introduced. This resulted in the formation of a yellow oil which, after storing at 5 °C overnight, afforded yellow crystals. (1.055 g, 61%).

Characterization: IR (MeCN): 1913 (vs), 1780 (vs)  $\nu_{\text{CO}}$  ( $\text{CH}_2\text{Cl}_2$ ): 1980 (vs), 1777(vs). MS, -ve FAB (m/e, rel. int.):  $\text{M}^-$  (639, 28),  $\text{M-CO}^-$  (611, 2),  $\text{M-3CO}^-$  (555, 1),  $\text{HBPf}_3^-$  (459, 60),  $\text{Mo}(\text{CO})_3^-$  (180, 5).  $^1\text{H}$  NMR (acetone  $d_6$ ):  $\delta$  1.40 (t of t, 12 H), 2.50 (s, 9H), 3.50 (q, 8H), 6.43 (s, 3H).  $^{19}\text{F}$  NMR (acetone  $d_6$ ):  $\delta$  -59.50 (s, 9F). Anal. Calcd for  $\text{C}_{26}\text{H}_{33}\text{F}_9\text{N}_7\text{O}_3\text{BMo}$ : C 40.59, H 4.32, N 12.74. Found: C 40.71, H 4.37, N 12.66.



### Synthesis of $\text{HBPf}_3\text{Mo}(\text{CO})_3^+$ (11)

Ferrocenium tetrafluoroborate (24.0 mg, 88.4  $\mu\text{mol}$ ) in 10 mL  $\text{CH}_2\text{Cl}_2$  was added to a solution of **10** (68 mg, 88.4  $\mu\text{mol}$ ) in 20 mL  $\text{CH}_2\text{Cl}_2$ . The solution slowly turned red, and red crystals could be seen on standing. These were filtered and dried in vacuo (30 mg, 52%).  $\mu_{\text{eff}} = 2.24 \text{ BM}$ .

Characterization: IR(Hexanes): 2031 (s), 1908 (m, vbr)  $\nu\text{CO}$ . MS, +ve FAB (m/e, rel. int.):  $\text{M}^+$  (641, 2),  $\text{M-CO}^+$  (613, 3),  $\text{M-2CO}^+$  (587, 10),  $\text{M-3CO}^+$  (557, 6). Anal. Calcd for  $\text{C}_{18}\text{H}_{13}\text{N}_6\text{F}_9\text{BMoO}_3$ : C 33.83, H 2.05, N 13.15. Found: C 34.07, H 1.93, N 12.95.  $^1\text{H}$  NMR and  $^{19}\text{F}$  NMR were not obtained.

### Synthesis of $\text{HBPf}_3\text{Mo}(\text{CO})_3\text{H}$ (12)

Concentrated HCl (0.170 mL) was added to **10** (108 mg, 0.168  $\mu\text{mol}$ ) in 5 mL MeCN. A light-yellow precipitate immediately formed. This was isolated and dried in vacuo. (215 mg, 50%)

Characterization: IR(THF): 2041 (vs), 1941 (vs), 1915 (vs) (KBr): 2027 (m), 1940 (m), 1928 (m)  $\nu\text{CO}$ . MS, 180  $^\circ\text{C}/16 \text{ eV}$  (m/e, rel. int.):  $\text{M}^+$  (640, 43),  $\text{M-CO}^+$  (612, 60),  $\text{M-2CO}^+$  (584, 12),  $\text{M-3CO}^+$  (556, 100).  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  -3.84 (s, 1H), 2.47 (s, 9H), 6.50 (s, 3H).  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ ): -59.08 (s, 9F). Anal. Calcd for  $\text{C}_{18}\text{H}_{14}\text{N}_6\text{F}_9\text{BMoO}_3$ : C 33.78, H 2.20, N 13.13. Found: C 33.80, H 2.01, N 12.85.

### Synthesis of $\text{HBPf}_3\text{Mo}(\text{CO})_2(\text{NO})$ (13)

(a). A sample of 10 (502 mg, 0.652 mmol) in 120 mL nitromethane, was cooled to  $-30\text{ }^\circ\text{C}$ .  $\text{NOPF}_6$  (177 mg, 1.01 mmol) in 20 mL nitromethane was added dropwise until the infrared spectrum indicated complete conversion to product. The solution was stored at  $-20\text{ }^\circ\text{C}$  for 2 days, by which time a yellow precipitate had formed. The precipitate was separated and dried under vacuum. The remaining solvent was stripped on the rotary evaporator, leaving a yellow-orange precipitate. This was recrystallized with a  $\text{CH}_2\text{Cl}_2$ -MeOH (1:1) mixture yielding a yellow precipitate (409 mg, 98%).

Characterization: IR (Hexanes): 2041 (w,  $\nu\text{CO}$ ), 1963 (w,  $\nu\text{CO}$ ), 1714 (w,  $\nu\text{NO}$ ). MS, 250  $^\circ\text{C}$ /70 eV (m/e, rel. int.):  $\text{M}^+$  (643, 2),  $\text{M-CO}^+$  (615, 10),  $\text{M-NO}^+$  (613, 8),  $\text{M-2CO}^+$  (587, 55),  $\text{M-NO-2CO}^+$  (557, 9).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  2.48 (s, 3H), 2.51 (s, 6H), 6.42 (s, 1H), 6.48 (s, 2H).  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -59.97 (s, 6F), -58.74 (s, 3F). Anal. Calcd for  $\text{C}_{17}\text{H}_{13}\text{N}_7\text{F}_9\text{MoO}_3\text{B}$ : C 31.85, H 2.04, N 15.29. Found: C 31.78, H 2.06, N 14.60.

(b). A sample of  $\text{Mo}(\text{CO})_6$  (1.14g, 4.34 mmol) and  $\text{KHBPf}_3$  (3.2207g, 6.47 mmol) were added to 200 mL dry MeCN and refluxed overnight. Acetic acid (8 mL) was added and the solution was stirred for 3 hours. Then, Diazald (0.92g, 4.34 mmol) was added and the solution stirred overnight. The solvent was removed under vacuum and the black residue dissolved in dry methanol. After several days, a yellow precipitate formed. This was filtered off and dried under vacuum. (1.25 g, 45%)

### Synthesis of $\text{HBPf}_3\text{Mo}(\text{Br})_2\text{NO}$ (14)

Bromine (65.2 mg, 0.021 mL, 0.408 mmol), in 10 mL  $\text{CH}_2\text{Cl}_2$ , was added dropwise to a  $-30\text{ }^\circ\text{C}$  solution of 13 (261 mg, 0.408 mmol) in 50 mL  $\text{CH}_2\text{Cl}_2$ . After the addition was complete, the solution was allowed to warm slowly to room temperature, and was stirred overnight. The solvent was concentrated to half its original volume and layered with hexanes, yielding an orange-brown precipitate (294 mg, 97%).

Characterization: IR( $\text{CH}_2\text{Cl}_2$ ): 1758 (vs,  $\nu\text{NO}$ ). MS 200  $^\circ\text{C}/70\text{ eV}$  (m/e, rel. int.):  $\text{M}^+$  (745, 24),  $\text{M-NO}^+$  (715, 32),  $\text{M-Br}^+$  (665, 8),  $\text{M-NO-Br}^+$  (635, 11).  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  2.48 (s, 6H), 2.61 (s, 3H), 6.62 (s, 2H), 6.66 (s, 1H).  $^{19}\text{F}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  -59.73 (s, 6F), -55.63 (s, 3F). Anal. Calcd for  $\text{C}_{15}\text{H}_{13}\text{N}_7\text{F}_9\text{BMoBr}_2\text{O}$ : C 24.19, H 1.76, N 13.16, Br 21.45. Found: C 24.34, H 1.76, N 12.59, Br 21.62.

### Synthesis of $\text{HBPf}_3\text{Mo}(\text{OMe})_2\text{NO}$ (15)

A sample of 14 (35.1 mg, 40.3  $\mu\text{mol}$ ) in 10 mL  $\text{CH}_2\text{Cl}_2$  was layered with 10 mL MeOH. The color progressed from red-orange to dark green to blue to dark purple. The solution was slightly concentrated, and stored at  $-30\text{ }^\circ\text{C}$ , where purple crystals appeared. These were filtered and dried under vacuum (21.1 mg, 81%).

Characterization: IR( $\text{CHCl}_3$ ): 1685 (s)  $\nu\text{NO}$ . MS, +ve FAB (m/e, rel. int.):  $\text{M}^+$  (649, 7),  $\text{M-OMe}^+$  (618, 19),  $\text{M-2OMe}^+$  (587, 2).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  2.46 (s, 9H), 5.04 (s, 6H), 6.41 (s, 1H), 6.49 (s, 2H).  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -60.18

(s, 6F), -60.65 (s, 3F). Crystallization incorporated 2.5 mole  $\text{CH}_2\text{Cl}_2$ . Anal. Calcd for  $\text{C}_{17}\text{H}_{19}\text{N}_7\text{F}_9\text{BMoO}_3 \cdot 2.5\text{CH}_2\text{Cl}_2$ : C 30.66 H 2.91, N 14.58. Found: C 30.54, H 2.67, N 14.29.

#### Synthesis of $\text{HBPf}_3\text{Mo}(\text{OEt})_2\text{NO}$ (16)

To 14 (37.5 mg, 50.4  $\mu\text{mol}$ ) in 10 mL  $\text{CH}_2\text{Cl}_2$  was added 1.5 mL EtOH (99.9%) and the solution allowed to stir. The solution color changed from orange/brown to deep purple in minutes. The solution was stirred overnight, at which time the color had become a paler purple. An infrared spectrum exhibited bands at 1716 (monosubstituted species) and 1675 (16)  $\text{cm}^{-1}$  in a 1:1 ratio. Continued stirring led to the formation of a pink solution. The solvent was removed under vacuum, leaving a pink solid. (20.4 mg, 60%)

Characterization: IR ( $\text{CH}_2\text{Cl}_2$ ): 1676 (m),  $\nu\text{NO}$ . MS 200  $^\circ\text{C}/70$  eV (m/e, rel. int.):  $\text{M}^+$  (677, 28),  $\text{M-NO}^+$  (647, 22),  $\text{M-OEt}^+$  (632, 2).  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  1.28 (t, 3H,  $J_{\text{H-H}} = 7.2$  Hz), 2.47 (s, 6H), 2.51 (s, 3H), 5.34 (q, 2H), 6.45 (s, 1H), 6.53 (s, 2H).  $^{19}\text{F}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  -59.61 (s, 3F), -60.62 (s, 6F). Anal. Calcd for  $\text{C}_{19}\text{H}_{23}\text{N}_7\text{F}_9\text{BMOO}_3$ : C 33.79, H 3.41, N 14.52. Found: C 33.71, H 3.56, N 12.80.

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## **CHAPTER 5**

### **SUMMARY AND CONCLUSIONS**



Ligands containing the 3-trifluoromethyl-5-methylpyrazolyl group (HPf) have been studied. Reaction of HPf with diiodomethane afforded the new bis(3-trifluoromethyl-5-methylpyrazol-1-yl)methane ligand ( $\text{CH}_2\text{Pf}_2$ ) (1), which reacted with  $[\text{Re}(\text{CO})_4(\mu\text{-Br})]_2$  to produce *fac*- $\text{CH}_2\text{Pf}_2\text{Re}(\text{CO})_3\text{Br}$  (2). Reaction of 2 with  $\text{PMe}_3$  or  $\text{PMe}_2\text{Ph}$  has resulted in the substitution of the ligand 1 by two phosphine groups, forming the *fac*- $\text{Re}(\text{CO})_3(\text{PR}_2\text{R}')_2\text{Br}$  isomer. This displacement of the chelated ligand is thought to be a result of weaker Re-N bonds, in relation to the Re-CO bonds, in 2. Weaker Re-N bonds could be due to the presence of the electron withdrawing  $\text{CF}_3$  groups on the pyrazole ring.

As a continuation of this project, it would be useful to synthesize the  $\text{H}_2\text{CPz}^*_2$  (bis(3,5-dimethylpyrazol-1-yl)methane) and  $\text{H}_2\text{CPz}_2$  (bispyrazolylmethane) analogues of 2, and react them with various phosphine groups in order to determine the role the electron donating (withdrawing) substituents play in the chemistry observed.

The chemistry of the  $\text{HBPf}_3$  ligand, synthesized by Graham and Krentz,<sup>1</sup> has now been expanded to rhenium and molybdenum metal centers. The rhenium complex  $\text{HBPf}_3\text{Re}(\text{CO})_3$  (5) was prepared, and exhibited no reaction when stirred with bromine. This is in contrast with the chemistry observed for the  $\text{HBPz}^*_3$  analogue, where the 4-H of the pyrazole ring, was substituted by a bromide.<sup>2</sup> This could be a result of the size of the substituents on the pyrazole ring, or due to the partial charges on the 4-C in 3-trifluoromethyl-5-methylpyrazole, as compared to the dimethyl and unsubstituted pyrazole analogues. The synthetic application arising from substitution of the 4-hydrogen (in complexes where it occurs) appears to have received little attention. It might provide a convenient avenue to otherwise inaccessible functionally substituted pyrazolylborates.

Photolysis of **5** in THF has resulted in the substitution on one CO to form  $\text{HBPf}_3\text{Re}(\text{CO})_2\text{THF}$  (**6**). Reaction of **6** with  $\text{Br}_2$  and  $\text{CCl}_4$  resulted in the formation of the air-stable seventeen-electron radicals  $\text{HBPf}_3\text{Re}(\text{CO})_2\text{X}^\bullet$  ( $\text{X} = \text{Br}, \text{Cl}$ ). The measurement of their effective magnetic moments indicated a single unpaired electron.

In the case of molybdenum,  $\text{HBPf}_3$  was used to synthesize  $[\text{Et}_4\text{N}]^+ [\text{HBPf}_3\text{Mo}(\text{CO})_3]^-$  (**10**). The oxidation of **10** with ferrocenium ion resulted in the formation of the seventeen-electron radical  $\text{HBPf}_3\text{Mo}(\text{CO})_3^\bullet$  (**11**), which exhibited unusual air stability. This stability has been attributed in a related case to the large size of the pyrazolylborate ligand, which protects the metal center from the approach of another ligand.<sup>3</sup>

The addition of concentrated HCl to **10** formed the seven-coordinate complex  $\text{HBPf}_3\text{Mo}(\text{CO})_3\text{H}$  (**12**). Although its infrared spectrum exhibited three carbonyl stretching bands, consistent with  $\text{C}_s$  symmetry (3:4 coordination geometry), its NMR spectrum indicated the equivalence of the three pyrazoles. As in the earlier work of Curtis<sup>4</sup> on  $\text{HBPz}_3\text{Mo}(\text{CO})_3\text{Br}$ , it would appear that **12** is fluxional, with a 3:3:1 geometry as a likely transition state or intermediate, in an averaging process. This would explain the appearance of a singlet for the three pyrazoles.

Reaction of **10** with nitrosonium salts resulted in the formation of  $\text{HBPf}_3\text{Mo}(\text{CO})_2\text{NO}$  (**13**). A marked increase in the yield of **13** occurred if nitromethane was used as the solvent, instead of acetonitrile or dichloromethane. It was also possible to synthesize **13** by acidifying a tetrahydrofuran solution of **10** and adding Diazald. The reaction of **13** with bromine resulted in the substitution of the carbonyls with bromide, forming  $\text{HBPf}_3\text{Mo}(\text{Br})_2\text{NO}$  (**14**). Although **14** is a sixteen-electron complex, it exhibits air and thermal stability. It is, however, very reactive. Layering a methylene

chloride solution of **14** with methanol or ethanol results in the substitution of the bromides by two alkoxides. This differs from the reaction of the analogous HBPz<sub>3</sub> and HBPz\*<sub>3</sub> complexes, where only monosubstitution occurs.<sup>5</sup> This may be due to the metal center attempting to compensate for its unsaturated state as the alkoxide ligands are better  $\pi$  electron-donating ligands than the bromides.

It would be interesting to react **14** with various ligands, such as t-butyl alcohol, in an attempt to substitute only one bromide ligand, forming a chiral complex. It might then be possible to substitute the remaining bromide with an alkyl group. It would also be interesting to investigate the possibility of synthesizing a dialkyl product. Legzdins<sup>6</sup> has found that CpMo(NO)R<sub>2</sub> complexes (R = CH<sub>2</sub>SiMe<sub>3</sub>, CH<sub>2</sub>CMe<sub>3</sub>, CH<sub>2</sub>CMe<sub>2</sub>Ph, Ph, p- or o-tolyl) can be formed using R<sub>2</sub>Mg-dioxane. However, the final products exhibit some air or thermal instability. He has shown<sup>7</sup> that by increasing the size of the substituents on the Cp ring, greater stability can be achieved. Therefore, the larger trispyrazolylborate ligand should provide added stability to complexes with smaller R groups.

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