# STRUCTURAL CHARACTERIZATION AND CATALYTIC ACTIVITY OF RHODIUM PYRAZOLYLBORATE COMPLEXES IN ALKYNE HYDROTHIOLATION 

by
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#### Abstract

A series of hydrobis- and hydrotris(pyrazolyl)borate bis(triphenylphosphine) rhodium (I) complexes were synthesized and structurally characterized. These complexes are of the general form $\left[\mathrm{Bp}^{\mathrm{R}} \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}\right]\left\{\mathrm{Bp}^{\mathrm{R}}=\mathrm{H}_{2} \mathrm{BR}{ }_{2}, \mathrm{R}^{\prime}=3\right.$, 5-dimethylpyrazolyl (2), pyrazolyl (3) $\}$, and $\left[\mathrm{Tp}^{\mathrm{R}} \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}\right]\left\{\mathrm{Tp}^{\mathrm{R}}=\mathrm{HBR}^{\prime}{ }_{3}, \mathrm{R}^{\prime}=3,5\right.$-dimethylpyrazolyl (1), pyrazolyl (4), 3-methylpyrazolyl (5), 3-phenylpyrazolyl (6), or 3-phenyl-5-methylpyrazolyl (7)\}. Wilkinson's catalyst, $\left[\mathrm{ClRh}\left(\mathrm{PPh}_{3}\right)_{3}\right]$, and the corresponding potassium salt of the ligands were mixed together in THF or toluene to produce known complexes 1-4 and new complexes 5-7. Both solid state and solution phase characterization were carried out for these complexes. The X-ray crystal structures were obtained for complexes 2, 4 and 5-7. All showed approximate square planar geometry with coordination of two pyrazolyl rings. IR spectroscopy ( KBr pellet) was performed on complexes 1,2 and 4-7 and the BH stretching frequencies were in the range of $\kappa^{2}$-coordination. ${ }^{1} \mathrm{H}$ and ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectroscopy was performed on all seven complexes and variable temperature NMR spectroscopy for complexes 1 and 4-7 to examine the solution phase structures of these complexes. Complexes 1-7 were then used in alkyne hydrothiolation reactions with alkyl thiols as catalysts and their activities were examined. It was found that tris(pyrazolyl)borate complexes were superior to bis(pyrazolyl)borate complexes. As well, tris(pyrazolyl)borate rhodium complexes with substitution at the 3 - and 5-positions on the pyrazolyl rings gave the best selectivity and yields, favoring the branched alkyl vinyl sulfides. Thus, complexes 1 and 7 have shown to be effective catalysts in alkyne hydrothiolation when using alkyl thiols to give regioselectively the branched isomer. A


general method to produce branched alkyl vinyl sulfides has been discovered and will be presented in the body of this thesis.

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## List of Symbols and Abbreviations

| A | angstroms ( $10^{-10}$ meters) |
| :---: | :---: |
| app d | apparent doublet |
| bim | bis(1-methylimidazol-2-yl)methane |
| bpm | bis(pyrazolyl-1-yl)methane |
| $\mu$ | mu, micro |
| br | broad |
| calcd | calculated |
| CO | carbonyl |
| cat. | catalyst |
| cm | centimeters |
| $J$ | coupling constant |
| Cy | cyclohexane |
| COD | cyclooctadiene |
| Cp | cyclopentadienyl |
| - | degrees |
| ${ }^{\circ} \mathrm{C}$ | degrees Celcius |
| D | deuterium |
| DCE | 1,2-dichloroethane |
| Bp | dihydrobis(pyrazolyl)borate |
| DMSO | dimethylsulfoxide |
| PyP | 1-(2-diphenylphosphino)ethylpyrazolyl |
| d | doublet |
| dd | doublet of doublets |
| dq | duroquinone |
| EI | electron impact |
| $E$ | entgegen |
| equiv. | equivalents |
| Et | ethyl |
| $v$ | frequency |
| $\delta$ | gamma |
| GC | gas chromatography |
| GCMS | gas chromatography-mass spectroscopy |
| g | gram |
| Hz | hertz |
| HRMS | high resolution mass spectroscopy |
| h | hours |
| Tp | hydrotris(pyrazolyl)borate |
| IR | infrared |


| $i$ | iso |
| :---: | :---: |
| $i-\operatorname{Pr}$ | isopropyl |
| $\kappa$ | kappa |
| K | kelvin |
| kcal | kilocalorie |
| L | liter |
| LRMS | low resolution mass spectroscopy |
| m/z | mass/charge |
| MALDI | matrix-assisted laser desorption/ionization |
| MHz | mega hertz |
| Me | methyl |
| DCM | dichloromethane |
| $\mu \mathrm{L}$ | microliter |
| mg | milligram |
| mL | milliliter |
| mmol | millimole |
| min | minutes |
| M | molar ( $\mathrm{mol} \mathrm{L}^{-1}$ ) |
| mol | mole |
| m | multiplet |
| IMes | $N, N$-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene |
| nbd | norbornadiene |
| $n$ | normal |
| NMR | nuclear magnetic resonance |
| ORTEP | Oakridge Thermal Ellipsoid Plot |
| ppm | parts per million |
| Ph | phenyl |
| p | pi |
| pip | piperidine |
| PPB | polypyrazolylborate |
| pz | pyrazolyl |
| q | quartet |
| rt | room temperature |
| SEM | scanning electron microscopy |
| s | singlet |
| $t$ | tertiary |
| t | triplet |
| THF | tetrahydrofuran |
| tempo | 2,2,6,6-tetramethylpiperidine- N -oxyl |
| $\mathrm{PMe}_{3}$ | trimethylphosphine. |


| $\mathrm{PPh}_{3}$ | triphenylphosphine |
| :--- | :--- |
| t | triplet |
| UV | ultra violet |
| VT | variable temperature |
| $Z$ | zusammen |

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## "If we knew what it was we were doing, it wouldn't be called research, would it?" -Albert Einstein-

## Chapter 1 - Introduction

### 1.1 Background

Sulfur is ubiquitous in nature, bioactive molecules and synthetic materials, some of which include penicillins, cephalosporin and Singulair. As well, sulfur compounds can be used as synthetic precursors or as reagents for methodology and thus it is important to have efficient methods to produce sulfur containing molecules. ${ }^{1}$

Transition metal catalyzed reactions are efficient methods of forming $\mathrm{C}-\mathrm{X}(\mathrm{X}=$ heteroatom) bonds. However, sulfur compounds have been known to poison metal catalysts due to their strong coordinating properties, which can prevent catalytic reactions from occurring. ${ }^{2}$ It is for this reason that reactions of thiols have not been as extensively studied as amines, alcohols and phosphines in transition metal catalyzed reactions.

However, some examples of catalytic reactions using thiols have still been investigated. One example is alkyne hydrothiolation in which a thiol reacts across an acetylene $\pi$-bond forming vinyl sulfide products (see Scheme 1.1).


Scheme 1.1. Alkyne hydrothiolation

Vinyl sulfides are important as they can be used as synthetic intermediates in total synthesis, ${ }^{\text {lb }}$ as well as precursors to many functionalized molecules (see Scheme 1.2). ${ }^{3}$


Scheme 1.2. Vinyl sulfide utility

One example is the oxidation of these vinyl sulfides to sulfoxides. The sulfoxide moiety is present in many pharmaceutical drugs ${ }^{4}$ and sulfoxides are also potential ligands for a variety of transition metals. ${ }^{\mathrm{le}, 5}$ Chiral variants have the potential for use in catalytic asymmetric transformations. ${ }^{\mathrm{le}, 4}$

A variety of methods including radical, ${ }^{6}$ nucleophilic ${ }^{7}$ and metal catalyzed ${ }^{8}$ hydrothiolation have been developed for C-S bond formation. However, these methods are generally used for aryl thiols with radical reactions giving a mixture of linear isomers and nucleophilic reactions giving the $Z$-isomer. Moreover, at the outset of this thesis project, alkyl thiols were reported as being unreactive in metal catalyzed hydrothiolation with Pd- and Rh-based catalysts. ${ }^{8 f, g}$ Thus, the limited substrate scope, selectivity and reaction conditions demand improvement.

The alkyne hydrothiolation reaction catalyzed by transition metal catalysts can hypothetically be carried out without any waste products in comparison with substitution reactions giving the same vinyl sulfide products. This $100 \%$ atom economy is favorable as it satisfies the requirements of green chemistry by minimizing waste and maximizing efficiency. ${ }^{9}$

### 1.2 Hydrothiolation Reactions

The main products obtained from alkyne hydrothiolation reactions are the branched (Markovnikov) and $E$ - and Z-linear (anti-Markovnikov) isomers. The $E$ - and $Z$-linear products can be obtained from radical, ${ }^{6}$ nucleophlic ${ }^{7}$ and metal catalyzed conditions. ${ }^{8 b, h, o}$ The branched product can be obtained from nucleophilic addition of sulfur to Michaeltype acceptors (vinylpyridinium cations) ${ }^{7 \mathrm{~d}}$ and metal catalyzed reactions. ${ }^{8 d-g, i-n, p}$ However, the majority of examples report the use of aryl thiols. In comparison, alkyl thiols have not been as widely explored. A selective method for the formation of Z-linear vinyl sulfides was reported in $2005 ;{ }^{7 \mathrm{e}}$ however, general methods for the stereo- and regiocontrolled synthesis of branched and E-linear alkyl vinyl sulfides remain elusive. The above methods will be discussed in further detail throughout the remainder of this chapter.

### 1.2.1 Radical Hydrothiolation

Radical hydrothiolation has been investigated and found to give predominantly the linear isomers. The ratio of the $E$ - and $Z$-linear isomers seems to depend on the ratio of thiol to alkyne. ${ }^{6 \mathrm{a}, \mathrm{b}}$ These free radical additions progress via a chain reaction mechanism and can occur in the presence of UV irradiation or chemical initiators. ${ }^{6 b}$ One such reaction involves 1-dodecyne and benzene thiol catalyzed by $\mathrm{Et}_{3} \mathrm{~B}$ to give a mixture of $E$ and Z-linear products (see Scheme 1.3). ${ }^{6 \mathrm{~d}}$ This reaction works well for both aromatic and aliphatic alkynes with aromatic thiols but methanol must be used as an additive to increase the yield when aliphatic thiols are employed. ${ }^{6 \mathrm{~d}}$


Scheme 1.3. Radical addition of a thiol to an acetylene

### 1.2.2 Nucleophilic Hydrothiolation

To obtain the $Z$-linear hydrothiolation product, nucleophilic hydrothiolation can be used. Base mediated reactions with ethanol produced the $Z$-linear products in moderate to good yields (65-87\%) for aryl and aliphatic alkynes and aryl and alkyl thiols. ${ }^{7 \mathrm{a}}$ Kondoh and coworkers tested cesium carbonate in base mediated hydrothiolation with aryl alkynes and alkyl thiols. They reported high selectivities favoring in the Z-linear isomer in good yields. ${ }^{7 e}$ A radical inhibitor, 2,2,6,6-tetramethylpiperidine-N-oxyl (TEMPO), was used to prevent the radical reaction from occurring. When aryl thiols were employed they were found to give poor yields. In the absence of base, a radical reaction occurs which is completely inhibited by the radical inhibitor. ${ }^{7 \mathrm{e}}$

### 1.2.3 Transition Metal-Catalyzed Hydrothiolation

The first example of transition metal-catalyzed hydrothiolation was reported in 1976 by Newton and coworkers using a molybdenum catalyst. They studied the addition of benzene thiol to dimethyl acetylenedicarboxylate and obtained a $25 \%$ yield of a 19:1 mixture of the $E$ and $Z$ products (see Scheme 1.4). ${ }^{8 \mathrm{a}}$


Scheme 1.4. First example of transition metal-catalyzed hydrothiolation

### 1.2.3-1 Intramolecular Hydrothiolation

In 2000, Gabriele and coworkers showed the only example of Pd-catalyzed cycloisomerization of (Z)-2-en-4-yne-1-thiols to give thiophenes. ${ }^{8 c} \mathrm{PdI}_{2}$ was used as the catalyst, along with two equivalents of KI. The proposed mechanism involves activation of the alkyne by $\operatorname{Pd}(\mathrm{II})$, intramolecular nucleophilic attack by the thiol, followed by protonolysis and finally aromatization (see Scheme 1.5).


Scheme 1.5. Proposed mechanism for cycloisomerization

### 1.2.3-2 Intermolecular Hydrothiolation

## a) E-linear and Z-linear Products

In 1999, Ogawa and coworkers discovered that Wilkinson's catalyst, $\mathrm{ClRh}\left(\mathrm{PPh}_{3}\right)_{3}$, gave a mixture of the branched and E-linear isomers, favoring the latter, when 1-octyne was reacted with benzene thiol. This was further explored using a variety of aliphatic and aromatic alkynes with benzene thiol in ethanol; after 20 hours the reactions gave predominantly the $E$-linear isomers in good to excellent yields (62-97\%). ${ }^{8 \mathrm{~g}}$ They also
reported that under the same conditions using alkyl thiols, namely cyclohexanethiol, the reaction did not proceed and only the starting materials were recovered. Our research group has recently discovered that although Wilkinson's catalyst was reported as ineffective at catalyzing hydrothiolation reactions with alkyl thiols, ${ }^{8 f, g}$ it does in fact catalyze this reaction producing predominantly the $E$-linear isomer with good regioselectivity. ${ }^{80}$ Ogawa and coworkers postulated that the reaction proceeds via migratory insertion into the Rh-H bond on the basis of mechanistic studies (see Scheme 1.6). ${ }^{8 \mathrm{~g}, \mathrm{o}}$ ( Nb Proposed mechanisms will be presented as they appear in the literature and have not been subject to further interpretation)


Scheme 1.6. Possible pathway for $\mathrm{ClRh}\left(\mathrm{PPh}_{3}\right)_{3}$-catalyzed hydrothiolation

Burling and coworkers reported in 2003 that bidentate $\mathrm{N}, \mathrm{N}$ - and $\mathrm{P}, \mathrm{N}$-ligands on rhodium(I) and iridium(I) make active catalysts for hydrothiolation of alkynes giving predominantly the linear isomers. ${ }^{8 h}$ They synthesized and structurally characterized a
wide range of complexes: $\left[\mathrm{M}(\mathrm{bim})(\mathrm{CO})_{2}\right] \mathrm{BPh}_{4}, \quad\left[\mathrm{M}(\mathrm{bpm})(\mathrm{CO})_{2}\right] \mathrm{BPh}_{4}$, $[\mathrm{M}(\mathrm{PyP})(\mathrm{COD})] \mathrm{BPh}_{4},\left[\mathrm{M}(\mathrm{PyP})(\mathrm{CO})_{2}\right] \mathrm{BF}_{4}$ and $[\mathrm{M}(\mathrm{PyP})(\mathrm{CO}) \mathrm{Cl}]$, where $[\mathrm{bim}=\operatorname{bis}(1-$ methylimidazol-2-yl)methane; bpm $=$ bis(pyrazolyl-1-yl)methane; $\quad \mathrm{PyP}=1-(2-$ diphenylphosphino)ethylpyrazolyl; $\mathrm{M}=\mathrm{Ir}$ or Rh ). It was found that the metal complexes with mixed $\mathrm{P}, \mathrm{N}$ ligand systems were better catalysts for hydrothiolation than the corresponding complexes with $\mathrm{N}, \mathrm{N}$ ligand systems. It was also reported that iridium complexes were more effective than the corresponding rhodium complexes; as well, cationic complexes were better then their neutral analogues. Phenylacetylene, propargyl alcohol and 1-pentyne were reacted with benzene thiol. The Z-linear isomer predominates with all catalysts for phenylacetylene, the $E$-linear isomer predominates with propargyl alcohol and a 1:1 mixture of linear isomers is found for 1-pentyne. These reactions were carried out at temperatures ranging from $25-55^{\circ} \mathrm{C}$ and alkyl thiols were not tested in the substrate scope.

Recently, an article on anti-hydrothiolation of 1-alkynylphosphines using $\mathrm{Pd}(\mathrm{OAc})_{2}$ with both alkyl and aryl thiols has been reported. ${ }^{8 \mathrm{e}}$ These reactions proceed in ethanol at room temperature with high stereo- and regioselectivity giving the ( $Z$ )-1-phosphino-2-thio-1-alkene after 1 hour. Kondoh and coworkers postulated mechanism involves the reaction between palladium and the alkyne giving the corresponding palladium(1alkynylphosphine) complex. The thiol can then attack the triple bond (activated by its coordination to palladium) to give an intermediate that can be protonated, resulting in the phosphine sulfide product and the original palladium species (see Scheme 1.7).


Scheme 1.7. Possible pathway for $\mathrm{Pd}(\mathrm{OAc})_{2}$-catalyzed anti-hydrothiolation of
1-alkynylphosphines

## b) Isomerization and Bis(arylthio)alkene Products

In 1999 Ogawa and coworkers examined the catalytic activity of a variety of palladium complexes in hydrothiolation reactions. When $\mathrm{PdCl}_{2}(\mathrm{PhCN})_{2}$ was used as a catalyst with terminal alkynes with propargylic hydrogens, the isomerized internal vinyl sulfide product was formed predominantly in a $1: 1$ diastereomeric mixture. ${ }^{8 \mathrm{~g}}$ The catalytic cycle proposed by Ogawa and coworkers is shown in Scheme 1.8. This cycle involves ligand exchange with PhSH to form the active catalyst $\left[\mathrm{Pd}(\mathrm{SPh}) \mathrm{ClL}_{n}\right]$. This catalyst adds to the alkyne giving the vinylic palladium intermediate which is then protonated using PhSH , followed by double bond isomerization to give a cationic intermediate. The allylpalladium intermediate forms and finally the isomerized product is
released leading back to the active catalyst. This reaction requires heating to $80^{\circ} \mathrm{C}$ for 20 hours and only benzene thiol was examined.


Scheme 1.8. Possible pathway for $\mathrm{PdCl}_{2}\left(\mathrm{PhCN}_{2}\right)_{2}$-catalyzed hydrothiolation

When Ogawa and coworkers employed $\mathrm{Pd}\left(\mathrm{PPh}_{3}\right)_{4}$ as a catalyst for the reaction of 1octyne with benzene thiol they observed $10-15 \%$ of an unexpected product, the bis(phenylthio)alkene, as well as the branched, $E$ - and $Z$-linear products and a small amount of the isomerized product (see Scheme 1.9). ${ }^{8 \mathrm{~g}}$ No explanation was provided for the unexpected product or how to avoid its formation.


Scheme 1.9. Formation of a bis(phenylthio)alkene

## c) Branched Product

In 1992 Ogawa and coworkers compared a variety of transition metal catalysts for the reaction of 1 -octyne with benzene thiol. ${ }^{8 f}$ They found that $\mathrm{Pd}(\mathrm{OAc})_{2}$ gave predominantly the branched isomer in reasonable yields (55-85\%) for a variety of terminal aliphatic alkynes with aryl thiols. However, these reactions required heating at $67^{\circ} \mathrm{C}$ for 12-16 hours. They also reported a postulated reaction mechanism involving the following steps: ligand exchange, coordination of the alkyne, migratory insertion followed by trapping of the vinyl product and regeneration of the catalyst (see Scheme 1.10).


Scheme 1.10. Possible pathway for $\mathrm{Pd}(\mathrm{OAc})_{2}$-catalyzed hydrothiolation

In 1994, Bäckvall and coworkers found that $\mathrm{Pd}(\mathrm{OAc})_{2}$ catalyzes the addition of benzene thiol to conjugated enynes. ${ }^{8 b}$ This reaction formed the branched diene in moderate yields (41-75\%) and gave complete selectivity of addition to the alkyne over the alkene. A range of terminal enynes were examined; all required elevated temperatures of $50^{\circ} \mathrm{C}$ and $14-18$ hour reaction times. The use of alkyl thiols was not reported. The corresponding sulfoxide derivatives were prepared in $60-67 \%$ yields using oxone in a methanol-water solution at $0^{\circ} \mathrm{C}$ for 10 minutes to 3 hours, longer reaction times led to the formation of the corresponding sulfone products (see Scheme 1.11).


Scheme 1.11. Hydrothiolation of conjugated enynes and oxidation to sulfoxides

In 2005, Beletskaya and coworkers began investigating Ni complexes as catalysts for alkyne hydrothiolation in attempts to improve regioselectivity of the branched product. ${ }^{8 i}$ Nickel was chosen as it is relatively inexpensive and had not been extensively studied for these types of reactions. They used $\mathrm{NiCl}_{2}$ and a $2: 1$ thiol:alkyne ratio to examine benzene thiol with a range of alkynes (alkyl thiols were not reported). The reactions gave good to excellent yields (60-85\%) with 7:1 to $18: 1$ selectivity favoring the branched:linear isomers. It was found that the presence of triethylamine facilitated the formation of the branched product. Activated alkynes such as phenylacetylene and
methyl propiolate gave poor yields and low selectivity of the branched product. These reactions were done at elevated temperatures $\left(80-100{ }^{\circ} \mathrm{C}\right)$ for $2.5-6$ hours. Beletskaya and coworkers also examined the effects of phosphine and phosphite ligands on catalytic activity. They found that phosphite ligands increased the formation of the bis(phenylthio)alkene side-product (the same product observed by Ogawa and coworkers in $1999^{8 \mathrm{~g}}$ ) and that triphenylphosphine addition hindered the production of the branched product.

In order to prevent the formation of the isomerized internal vinyl sulfide and $Z$ bis(arylthio)alkene products, Beletskaya and coworkers developed another Ni catalyst which had N -heterocyclic carbene ligands. ${ }^{8 \mathrm{k}}$ They found that the $\mathrm{CpNi}(\mathrm{IMes}) \mathrm{Cl}[\mathrm{Cp}=$ cyclopentadienyl; IMes $=N, N$-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene] was a good catalyst for alkyne hydrothiolation using aryl thiols. A range of alkynes and aryl thiols were examined and found to give $61-87 \%$ yields with excellent selectivity favoring the branched isomer. The isomerization product and the bis(arylthio)alkene product were not formed during these reactions. Optimized reaction conditions required elevated temperatures $\left(80^{\circ} \mathrm{C}\right)$ for 5 hours. Their proposed mechanistic cycle (see Scheme 1.12) involves the chloride initially being replaced by a thiolate ion, this intermediate was isolated, characterized and proposed to be the active catalyst in the cycle. Next, the alkyne inserts into the $\mathrm{Ni}-\mathrm{S}$ bond forming another intermediate which is trapped with an aryl thiol to give the branched product, regenerating the active catalyst.




Scheme 1.12. Possible pathway for $\mathrm{CpNi}(\mathrm{IMes}) \mathrm{Cl}$-catalyzed hydrothiolation

Then in 2006, Beletskaya and coworkers reported the catalytic ability of $\mathrm{Ni}(\mathrm{acac})_{2}$ under solvent-free conditions. ${ }^{81}$ In comparison to $\mathrm{Pd}(\mathrm{OAc})_{2}$, the reaction between 1 heptyne and benzene thiol went to $99 \%$ conversion in high selectivity favoring the branched product in only 30 minutes. They optimized the conditions to minimize the formation of side products and found that reaction temperature, catalyst loading and ratio of thiol to alkyne were all factors. Temperatures between $25-40^{\circ} \mathrm{C}, 2 \mathrm{~mol} \%$ catalyst and a 2:1 thiol:alkyne ratio were found to give the highest selectivity of the branched isomer and lowest isomerization product yields. The active catalyst was found to be an insoluble polymer, $\left[\mathrm{Ni}(\mathrm{SPh})_{2}\right]_{\mathrm{n}}$, which was studied using light and scanning electron microscopy (SEM) and found to be built of nanosized structural units. Using a series of
stoichiometric reactions they proposed a catalytic cycle that involves replacement of the acac ligands with PhS ligands, alkyne insertion into the $\mathrm{Ni}-\mathrm{S}$ bond and protonolysis by PhSH to yield the branched isomer and regenerate the active catalyst (see Scheme 1.13). Aryl thiols were investigated in hydrothiolation reactions and found to give good yields (50-87\%) in relatively short reaction times ( $8 \mathrm{~min} .-3.5 \mathrm{~h}$ ). This was an important advance as it uses solvent free conditions, satisfying some requirements of green chemistry as there is less waste. However, the purification process to separate the products still required the use of solvents but the overall amount of solvent used is presumably less than a reaction where solvent is present. In a later paper in 2006, Beletskaya and coworkers reported that a 1:1 ratio of thiol:alkyne, with dropwise addition of the alkyne, gave an, on average $18 \%$ higher yield of the branched product in comparison to a $2: 1$ ratio of thiol:alkyne. ${ }^{8 j}$ When the benzene thiol is in excess it is postulated to trap the intermediate leading to the formation of the branched product. Thus using the dropwise addition method ensures an excess of thiol and although this method is more tedious it decreases the amount of thiol required.



Scheme 1.13. Possible pathway for $\left[\mathrm{Ni}(\mathrm{SPh})_{2}\right]_{\mathrm{n}}$-catalyzed hydrothiolation

Earlier this year Beletskaya and coworkers reported that palladium nanoparticles were capable of catalyzing hydrothiolation reactions with both aryl and alkyl thiols. ${ }^{8 \mathrm{~d}}$ $\mathrm{Pd}(\mathrm{OAc})_{2}$ was dissolved in the alkyne and this solution was then reacted with the thiol to give the Pd nanoparticles with organic ligands (see Scheme 1.14).
$\mathrm{Pd}(\mathrm{OAc})_{2}+\mathrm{R}^{\prime} \longrightarrow \underset{\substack{\text { in alkyne }}}{\substack{\text { solution of } \\ \mathrm{Pd}(\mathrm{OAc})_{2}}} \xrightarrow[-\mathrm{HOAc}]{\mathrm{RSH}}\left[\mathrm{Pd}^{-}-\begin{array}{c}\mathrm{SR} \\ \mathrm{SR}\end{array}\right] \longrightarrow\left[\mathrm{Pd}(\mathrm{SR})_{2}\right]_{n}$
Scheme 1.14. Preparation of Pd nanoparticles

The reaction of aryl thiols with a variety of functionalized terminal alkynes gave excellent yields ( $>95 \%$ ) with high selectivities. With alkyl thiols the yields were slightly lower but high selectivities were still obtained. Using a series of stoichiometric reactions
with the Pd nanoparticle catalysts, Beletskaya and coworkers postulated the reaction followed the same mechanistic pathway shown in Scheme 1.13. The cycle involves ligand exchange from $\mathrm{Pd}(\mathrm{OAc})_{2}$ to $\left[\mathrm{Pd}(\mathrm{SR})_{2}\right]_{\mathrm{n}}$, followed by alkyne coordination, alkyne insertion into the Pd-S bond and finally protonolysis by RSH to give the branched product and regeneration of the catalyst. This paper was an important contribution as it was the second reported selective addition of alkyl thiols to alkynes; the first report will be discussed later in this chapter.

The transition metal catalysts that have been shown to give predominantly the branched product include: $\operatorname{Pd}(\mathrm{OAc})_{2},{ }^{8 \mathrm{~b}, \mathrm{f}, \mathrm{g}} \mathrm{NiCl}_{2},{ }^{8 \mathrm{i}} \mathrm{Ni}(\mathrm{acac})_{2},{ }^{81} \mathrm{CpNi}(\mathrm{IMes}) \mathrm{Cl},{ }^{8 \mathrm{k}}$ and $\left[\operatorname{Pd}(\mathrm{SR})_{2}\right]_{\mathrm{n}} .{ }^{8 \mathrm{~d}}$ All of these catalysts were shown to be effective when using aryl thiols but alkyl thiols were only explored using $\left[\operatorname{Pd}(\mathrm{SR})_{2}\right]_{\mathrm{n}}$.

### 1.3 Polypyrazolylborates

Polypyrazolylborate (PPB) ligands have been reported in the literature for over 40 years with the first communication published in 1966 by Trofimenko. ${ }^{10}$ They are a well defined ligand system that have caught the interest of many researchers because they are versatile, relatively easy to synthesize and can influence stereochemical outcomes. ${ }^{11}$

PPBs are made up of a tetra-substituted boron anion with two or more pyrazolyl substituents. Tris- and tetrapyrazolylborates are also commonly referred to as scorpionates as their binding motif mimics that of a scorpion capturing its prey. Two claws are represented by the pyrazolyl rings and the overreaching tail is another substituent on the boron atom. PPB complexes are usually at least bidentate forming a six membered ring comprised of two bridging pyrazolyl groups, the boron atom and the
metal center. This $\mathrm{B}(\mu-\mathrm{pz})_{2} \mathrm{M}$ ring is found predominately in the boat configuration which gives the third substituent on the boron the potential to bind to the metal centre, forming a tridentate species (Figure 1.1). ${ }^{11}$


Figure 1.1. Boat conformation and agostic interactions in a PPB complex

There are two major groups of PPBs: homoscorpionates $\left(\mathrm{R}^{\prime} \mathrm{Tp}^{\mathrm{R}}\right)[\mathrm{Tp}=$ tris(pyrazolyl)borate] and heteroscorpionates ( $\mathrm{R}^{\prime} \mathrm{R}^{\prime \prime} \mathrm{Bp}^{\mathrm{R}}$ ) $[\mathrm{Bp}=$ bis(pyrazolyl)borate $]$, where $R^{\prime} / R^{\prime \prime}=H$, alkyl, aryl or pyrazolyl groups and $R$ can be any substituent at the 3-, 4- and/or 5-positions of the pyrazolyl ring. Homoscorpionates are the more commonly used PPBs. These PPBs have the potential to bind either bidentate $\left(\kappa^{2}\right)$ or tridentate $\left(\kappa^{3}\right)$; when bound in a $\kappa^{2}$ manner the uncoordinated and coordinated pyrazolyl groups can exchange rapidly, which can be observed via NMR spectroscopy. ${ }^{11}$

These ligands have very lengthy names and thus an abbreviation system has been developed. Curtis proposed for homoscorpionates the use of Tp in place of $\left[\mathrm{HB}(\mathrm{pz})_{3}\right]^{-}$ and the use of $\mathrm{Tp} *$ in place of $\left[\mathrm{HB}(3,5 \text {-dimethylpyrazol-1-yl) }]^{-12}\right.$. In accordance with this nomenclature heteroscorpionates $\left[\mathrm{H}_{2} \mathrm{~B}(\mathrm{pz})_{2}\right]^{-}$are named Bp . The substituents on the pyrazolyl ring are denoted by superscripts. The 3-substituent comes first, followed by a

5 -substituent. The 4 -substituent is denoted with the number 4 preceding the substituent. Finally non-hydrogen groups on the boron are written before the abbreviation; see Table 1.1 for some examples.

Table 1.1. Abbreviation system for PPBs

| Compound Name | Abbreviation |
| :---: | :---: |
| $\left[\mathrm{HB}(3-\text { phenyl-5-methylpyrazol-1-yl) }]^{-}\right.$ | $\mathrm{Tp}^{\mathrm{Ph}, \mathrm{Me}}$ |
| $\left[\mathrm{HB}(3-\text { methylpyrazol-1-yl })_{3}\right]^{-}$ | $\mathrm{Tp}^{\mathrm{Me}}$ |
| $\left[\mathrm{HB}(3 \text {-isopropyl-4-bromopyrazol-1-yl) }]_{3}\right]^{-}$ | $\mathrm{Tp}^{\mathrm{iPr}, 4 \mathrm{Br}}$ |
| $\left[\mathrm{Et}_{2} \mathrm{~B}(\text { pyrazolyl-1-yl })_{2}\right]^{-}$ | $\mathrm{Et}_{2} \mathrm{Bp}$ |

The PPB ligands are often compared to cyclopentadienyl ( Cp ) ligands. Tp and Cp ligands have many similarities, such as similar metal complexes, having a -1 charge, donating six electrons and having the potential to occupy three coordination sites. However, there are also many differences associated with these common ligand sets. For example, they have different point groups, Tp has the potential for more substitution variations, Tp alkali metal salts are air stable where Cp salts are not and Tp can form neutral analogues with carbon. The huge versatility of PPBs makes them attractive compounds to study. Substitution on the pyrazolyl rings allows one to tune the electronics and sterics which can potentially alter the metal-ligand interaction and thus change the coordination environment.

### 1.3.1 Denticity of Pyrazolylborate Ligands

### 1.3.1-1 $\kappa^{2}$ and $\kappa^{3}$ Binding Modes

It has been well established in the literature that the denticity of poly(pyrazolyl)borate ligands can differ from $\kappa^{0}$, in which the PPB acts as a counterion, to $\kappa^{3}$, depending on the number of pyrazolyl rings attached to the boron, substituents on these rings and the participation of side chains in agostic interactions. ${ }^{13}$ This flexible coordination geometry contributes to the unique properties of the pyrazolylborate motif and can influence reactivity. Rhodium tris(pyrazolyl)borates typically exist in an equilibrium between four isomers, A-D (Figure 1.2). ${ }^{8 \mathrm{p}}$.


A


B


C


D

Figure 1.2. Isomeric forms of tris(pyrazolyl)borate rhodium complexes

Isomers $\mathbf{A}$ and $\mathbf{B}$ are both 16 -electron square planar species, where $\mathbf{C}$ and $\mathbf{D}$ are both 18 electron species with trigonal bipyramidal and square pyramidal geometries, respectively. The equilibrium between these isomeric forms depends upon the substitution on the pyrazolyl rings (see Scheme 1-15, type $\mathbf{A}$ for numbering of the pyrazolyl ring substituents) as well as bulkiness of the ancillary ligands (L). The trends in isomer preference are: bulky substituents in the 3-position of the pyrazolyl and bulky ancillary ligands favor forms $\mathbf{A}$ and $\mathbf{B}$, whereas smaller substituents on the pyrazolyl and less
bulky ancillary ligands favor the $\mathbf{C}$ and $\mathbf{D}$ isomers. Isomer $\mathbf{A}$ is favored over $\mathbf{B}$ when there are bulky substituents in the 3-position. Isomer $\mathbf{B}$ is favored over $\mathbf{A}$ when there are smaller substituents in the 3-position and substituents in the 5-position enhance this preference. ${ }^{14}$

### 1.3.1-2 $\kappa^{0}$ to $\kappa^{3}$ Coordination: PPBs as Counterions or with Agostic Interactions

Tris(pyrazolyl)borate ligands often act as spectator ligands, but can also be "noninnocent" because of changes in denticity. $\kappa^{2}$ and $\kappa^{3}$ tris(pyrazolyl)borate complexes are well established in the literature, although $\kappa^{0}$ and $\kappa^{1}$ complexes are not as well known. For example, in 2000 Paneque and coworkers reported the synthesis of a $\kappa^{1}$ complex. Treatment of $\kappa^{3}-\mathrm{Tp} * \mathrm{Rh}\left(\mathrm{C}_{2} \mathrm{H}_{4}\right)\left(\mathrm{PMe}_{3}\right)$ with 5-6 equivalents of $\mathrm{PMe}_{3}$ at $20^{\circ} \mathrm{C}$ for $<1$ hour produced a new complex $\kappa^{1}-\mathrm{Tp} * \mathrm{Rh}\left(\mathrm{PMe}_{3}\right)_{3}$ (see Scheme 1.15). ${ }^{15}$ The crystal structure of the $\kappa^{1}-\mathrm{Tp} * \mathrm{Rh}\left(\mathrm{PMe}_{3}\right)_{3}$ complex showed no agostic interactions as the $\mathrm{Rh}-\mathrm{H}(\mathrm{B})$ distance was $2.59(4) \AA$ (which is too long to be considered a bonding interaction). The $\kappa^{2}$ complex was not detected in this reaction but can be synthesized by dropwise addition of 1 equivalent of $\mathrm{PMe}_{3}$ to the $\kappa^{3}$ complex. They also found that the $\mathrm{Tp} *$ ligand completely dissociated upon heating to $120{ }^{\circ} \mathrm{C}$ for 6 hours and hypothesized that it formed $\left[\mathrm{Rh}\left(\mathrm{PMe}_{3}\right)_{4}\right] \mathrm{Tp}{ }^{*}$ (effectively, $\left.\kappa^{0}-\mathrm{Tp}^{*}\right)$. Unfortunately, this species decomposed upon workup and therefore full characterization could not be obtained. However, they did manage to show that the bis-hydrido complex $\left(\kappa^{3}-\mathrm{Tp}\right) \mathrm{Rh}(\mathrm{H})_{2}\left(\mathrm{PMe}_{3}\right)$ forms $\left(\kappa^{2}-\right.$ $\mathrm{Tp}) \mathrm{Rh}(\mathrm{H})_{2}\left(\mathrm{PMe}_{3}\right)_{2}$ complex upon heating at $50^{\circ} \mathrm{C}$ for 2 hours. Additional heating at this temperature for 8 hours gives $\left[\mathrm{Rh}(\mathrm{H})_{2}\left(\mathrm{PMe}_{3}\right)_{4}\right] \mathrm{Tp}$. These assignments were confirmed by NMR spectroscopy and X-ray analysis. The molecular structure shows that the closest

Rh-N distance was $4.627 \AA$, which is much larger than the van der Waals radius. ${ }^{15}$ This contribution was important as it is the first time the denticity changes of the $\mathrm{Tp}{ }^{*}$ and Tp ligands from $\kappa^{3}$ to $\kappa^{0}$ were observed. Until this point the only $\kappa^{1}$ complexes known were Ni complexes with bulky hydrotris(3-tert-butylpyrazolyl)borate ligands and $\kappa^{0}$ complexes were unprecedented. ${ }^{16}$


Scheme 1.15. $\kappa^{3}$ to $\kappa^{1}$ binding modes

In 2000, Herberhold and coworkers synthesized $\mathrm{Tp} * \mathrm{Rh}\left\{\mathrm{P}_{\left.\left(\mathrm{C}_{7} \mathrm{H}_{7}\right)_{3}\right\} \text { which had an }}\right.$ interesting $\kappa^{2} N, H$ binding mode. ${ }^{17}$ One pyrazolyl ring is attached to the metal centre and there is also an agostic interaction with the B-H hydrogen and the metal centre. The Rh$\mathrm{H}(\mathrm{B})$ distance was $1.789(7) \AA$ (two independent molecules were found per unit cell differing only in $\mathrm{Rh}-\mathrm{H}(\mathrm{B})$ distance, the second being $1.899(7) \AA$ ) which is close to a typical Rh-H bond distance of $1.55 \AA$. Through X-ray crystallography, ${ }^{1} \mathrm{H},{ }^{11} \mathrm{~B},{ }^{13} \mathrm{C},{ }^{31} \mathrm{P}$ and ${ }^{103} \mathrm{Rh}$ NMR spectroscopy the geometry of the Rh-H-B bridged complex with two uncoordinated pyrazolyl rings was established, demonstrating $\kappa^{2} N, H$ binding (Figure 1.3).


Figure 1.3. $\kappa^{2} N, H$ binding mode

Other binding modes have been mentioned throughout the literature, including: $\kappa^{3} N, N, H$ seen in $\mathrm{Tp} * \mathrm{Ru}\left(\mathrm{CH}_{3}\right)(\mathrm{COD}),{ }^{18} \mathrm{Bp}^{(\mathrm{CF} 3) 2} \mathrm{Ru}(\mathrm{H})\left(\mathrm{PPh}_{3}\right)_{2}$ and $\mathrm{Bp}{ }^{(\mathrm{CF} 3) 2} \cdot \mathrm{Ru}(\mathrm{H})(\mathrm{COD})$ and a $\kappa^{2} N, H$ in $\mathrm{Bp}^{(\mathrm{CF} 3) 2} \mathrm{RuH}\left(\mathrm{H}_{2}\right)\left(\mathrm{PCy}_{3}\right)_{2}$ which was proposed to be due to the different cone angles of the phosphines. ${ }^{19}$ However, these binding modes have not been observed in any rhodium pyrazolylborate complexes.

### 1.3.2 Characterization Methods

The interconversion and fluxional processes between isomers A-D makes the solution phase assignment of $\mathrm{Tp}^{\mathrm{R}}$ denticity very difficult. ${ }^{20}$ Solvent effects must also be taken into consideration as it has been noted that the equilibrium between forms of pyrazolylborate rhodium complexes can be shifted by changing the polarity of the solvent. $\mathrm{Tp}^{i \mathrm{Pr}, 4 \mathrm{Br}} \mathrm{Rh}(\mathrm{CO})_{2}$ and $\mathrm{Tp}^{\mathrm{Me}} \mathrm{Rh}(\mathrm{CO})_{2}$ were found to be in an equilibrium between $\mathbf{A}$ and $\mathbf{B} / \mathbf{C}$ where the $\mathbf{B} / \mathbf{C}$ forms were favored in solvents having a higher dipole moment. ${ }^{13}$ Also, $\mathrm{Tp}^{\mathrm{Ph}} \mathrm{Rh}(\mathrm{COD})$ exists in forms $\mathbf{A}$ and $\mathbf{B}$ and as the solvent becomes more polar the equilibrium shifts towards form $\mathbf{B}$. ${ }^{21}$ However, other pyrazolylborate rhodium
complexes such as $\mathrm{Tp}^{\mathrm{CF3}, \mathrm{Me}} \mathrm{Rh}(\mathrm{CO})_{2}$ and $\mathrm{Tp}^{i \mathrm{Pr}} \mathrm{Rh}(\mathrm{COD})$, have been examined and no solvent effects were found. ${ }^{14,20 a}$

A number of techniques have been used to determine denticity, including infrared (IR) spectroscopy, variable temperature and multinuclear NMR spectroscopy. In 2001, Connelly and coworkers reported what was believed to be the first rhodium hydrotris(pyrazolyl)borate complex, $\mathrm{Tp} * \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}$, where the unbound pyrazolyl ring is frozen on the NMR timescale at $-80^{\circ} \mathrm{C}$. They observed that the three pyrazolyl rings and phosphorous atoms became inequivalent as the temperature was decreased. This phenomenon was attributed to the fixed orientation of the unbound pyrazolyl ring. ${ }^{22}$ Other $\mathrm{Tp}^{\mathrm{R}} \mathrm{ML}_{2}$ complexes have shown only a single set of pyrazolyl resonances at both room temperature and low temperature. This has been documented in the literature and some examples include $\mathrm{Tp} * \mathrm{Rh}\left(\mathrm{C}_{2} \mathrm{H}_{4}\right)_{2}{ }^{23}$ and $\mathrm{Tp} * \mathrm{Rh}[\mathrm{CN} \text {-(neopentyl) }]_{2}{ }^{24}$, possibly indicating that these complexes are present in only one isomeric form with fast exchange of the pyrazolyl rings or that the interconversion between isomers is too fast for the NMR time scale.

The exchange rates of the pyrazolyl rings were examined in 1982 by Cocivera and coworkers working with $\left[\mathrm{B}(\mathrm{pz})_{4}\right] \mathrm{RhL}[\mathrm{L}=$ duroquinone (dq), 1,5-cyclooctadiene (COD) and norbornadiene (nbd)]. They postulated that the rate of exchange is dependent upon the strength of the rhodium diene interaction. Therefore with more electron-donating dienes, the exchange between uncoordinated and coordinated pyrazolyl groups increases, indicating the Rh-N bond strength decreases. ${ }^{25}$ Other examples demonstrate that equilibration between $\kappa^{2}$ and $\kappa^{3}$ can be seen using variable temperature NMR spectroscopy. For example, $\mathrm{Tp}^{\text {Menth }} \mathrm{R} h(\mathrm{CO})_{2}$, gave a $1: 1: 1$ ratio for the pyrazolyl
resonances in the ${ }^{1} \mathrm{H}$ NMR spectrum with an additional singlet at low temperature. ${ }^{26}$ They attribute the 1:1:1 peaks to form $\mathbf{A}$ and the forth peak as an equilibrium between forms $\mathbf{B}$ and $\mathbf{C}$ or $\mathbf{B}$ and $\mathbf{D}$ accounting for the singlet due to fast exchange making the pyrazolyl rings appear equivalent on the NMR time scale. It seems that each complex behaves differently in solution and therefore careful analysis is required to determine what isomers and/or fluxional processes are occurring in each case.

Akita and coworkers have shown that IR stretching frequencies, particularly the $v(B-H)$ values, seem to be diagnostic of $\kappa^{2}$ and $\kappa^{3}$ binding modes. The solution and solid state structures of $\kappa^{3}$ complexes generally show higher frequencies in the IR spectrum. ${ }^{20 a}$ This was shown for $\left(\kappa^{3}-\mathrm{Tp}^{\mathrm{iPr}}\right) \mathrm{ML}_{n}$-type $(\mathrm{M}=\mathrm{Mn}, \mathrm{Fe}, \mathrm{Co}, \mathrm{Ni}, \mathrm{Cu}, \mathrm{Rh})$ complexes where the $v(\mathrm{~B}-\mathrm{H})$ bands are between $2527-2554 \mathrm{~cm}^{-1}$ and the $\left(\kappa^{2}-\mathrm{Tp}^{\mathrm{iPr}}\right) \mathrm{ML}_{n}$-type $(\mathrm{M}=\mathrm{Ru}, \mathrm{Rh}$, Pd) complexes had $v(\mathrm{~B}-\mathrm{H})$ bands between 2471-2486 $\mathrm{cm}^{-1} .{ }^{20 a}$ However $\left(\kappa^{3}-\mathrm{Tp}^{\mathrm{R}}\right) \mathrm{ML}_{n^{-}}$ type $(\mathrm{M}=\mathrm{Zn}, \mathrm{Ru}, \mathrm{Cu}, \mathrm{Ni}, \mathrm{Co}, \mathrm{Fe}, \mathrm{Rh}, \mathrm{Ni}, \mathrm{In})$ complexes have shown $\mathrm{v}(\mathrm{B}-\mathrm{H})$ bands between $2476-2552 \mathrm{~cm}^{-1}$ which show overlap with $\left(\kappa^{2}-\mathrm{Tp}^{R}\right) \mathrm{ML}_{n}$-type complexes. This overlap has been attributed to the substituents on the pyrazolyl ring; an increase in the electron donating ability of these substituents caused a shift toward higher wavenumbers in the IR spectrum. ${ }^{20 a}$ In general B-H stretching frequencies $<2480 \mathrm{~cm}^{-1}$ indicate $\kappa^{2}$ binding while $\mathrm{B}-\mathrm{H}$ stretching frequencies $>2480$ indicate $\kappa^{3}$ binding. ${ }^{20 a}$
${ }^{103}$ Rh NMR spectroscopy has been employed to differentiate between forms A to D as there are expected to be large chemical shift differences between 16 and 18 electron species. Venanzi and coworkers used this technique and found that $\kappa^{2}$ complexes typically had a lower chemical shift ( $\delta$ 947-1374) versus $\kappa^{3}$ complexes ( $\delta 1475-1777$ ). ${ }^{13}$ However, no solid state ${ }^{103}$ Rh NMR measurements have been carried out to determine the
limiting value of chemical shift of a $\kappa^{3}$ species, thus other methods must also be used to characterize the forms present in solution.

If the complex of interest has olefinic carbons, ${ }^{13} \mathrm{C}$ NMR spectroscopic data can be used to provide evidence towards $\kappa^{2}$ and $\kappa^{3}$.species. This is based on the $\pi$-backbonding ability, as the 18 electron $\kappa^{3}$ species should have higher $\pi$-backbonding ability in comparison to the 16 electron $\kappa^{2}$ species. Thus, the olefinic carbons should be shifted upfield for the $\kappa^{3}$ species. To confirm this hypothesis, the ${ }^{13} \mathrm{C}$ solid-state NMR spectrum was taken of a known $\kappa^{3}$ species. The X-ray structure of $\mathrm{Tp}^{\mathrm{Me}} \mathrm{Rh}(\mathrm{NBD})$ shows trigonal bipyramidal geometry and it gave upfield chemical shifts in agreement with the solution state spectra. ${ }^{13}$
${ }^{15} \mathrm{~N}$ NMR spectroscopy is also used to determine the denticity of the pyrazolylborate ligands. The uncoordinated versus coordinated nitrogen atoms of the pyrazolyl rings give significantly different chemical shifts. Nitrogen atoms on uncoordinated pyrazolyl rings give an approximate chemical shift of $\delta-75$. In comparison, nitrogen atoms on bound pyrazolyl rings give a chemical shift around $\delta-138$. If there is fast exchange on the NMR time scale these values give an averaged approximate $\delta-117$. Therefore, if the chemical shift is more negative this indicates an equilibrium favoring the $\kappa^{3}$-form. ${ }^{27}$

Using ${ }^{11} B$ NMR spectroscopy, it was found that $\kappa^{2}$ complexes show resonances between $\delta-5.90$ and -6.99 versus $\kappa^{3}$ complexes with resonances between $\delta-8.44$ and $-9.76 .{ }^{20 c}$ These resonances appear to be independent of both solvent and charge on the metal for group 9 and 10 metals. ${ }^{20 c}$ Thus, there appears to be a strong correlation between the chemical shift of the boron atom and the denticity of the tris(pyrazolyl)borate ligand.

X-ray crystallography has been used to determine the solid state structures of rhodium pyrazolylborate complexes. ${ }^{8 n, 13-15,17,19,20 a \mathrm{a}, 21,22,24,25,27,28}$ However, X-ray structures may be dependent upon the solvent used for crystallization, the isolation method and crystal packing effects of whether these complexes adopt $\kappa^{2}$ or $\kappa^{3}$-forms in the solid state. ${ }^{14}$ For example, Cocivera and coworkers described in 1982 that $\left[\mathrm{B}(\mathrm{pz})_{4}\right] \mathrm{Rh}(\mathrm{COD})$ favored $\kappa^{2}-\kappa^{3}$ equilibrium in solution phase but crystallized as the $\kappa^{2}-$ form. ${ }^{29}$

### 1.3.3 1,2-Borotropic Shift

Depending on the position and extent of substitution of the pyrazolyl ring, rearrangements of the ligand via a 1,2-borotropic shift can occur. The occurrence of such rearrangements is attributed to a reduction in van der Waals repulsion and can be induced thermally. ${ }^{13,28 a, 30}$ This isomerization has been observed for a broad range of $\mathrm{Tp}^{\mathrm{R}} \mathrm{M}$ complexes. Rearrangements in octahedral metal complexes with the tris(pyrazolyl)borate ligand bound $\kappa^{3}$ have been well documented for transition metals: $\mathrm{Co},{ }^{31} \mathrm{Ti}^{32}{ }^{32} \mathrm{Mo}^{30}{ }^{30} \mathrm{Ni}^{31 \mathrm{~b}}$ and $\mathrm{Fe}^{31 \mathrm{~b}}$. However, square planar and tetrahedral complexes with the same rearrangement are less common; some examples are with $\mathrm{Rh},{ }^{13,33} \mathrm{Ir},{ }^{28 \mathrm{a}} \mathrm{Zn},{ }^{33} \mathrm{Cd}^{33}$ and $\mathrm{Al}^{34}$ complexes (see Scheme 1.16). The substituents at the 3-position of the pyrazolyl ring that were used in combination with the above metals include methyl, isopropyl, menthyl, mesityl, neopentyl, or 3,3-dimethylbenzyl groups. A particular example of the 1,2-borotropic rearrangement occurs in the reaction between $\left[\mathrm{Ir}_{2}(\mu-\mathrm{Cl})_{2}(\mathrm{COD})_{2}\right]$ with $\mathrm{Na}\left[\mathrm{Tp}^{\mathrm{Me}}\right]$. This reaction produced the expected $\left[\mathrm{Tp}^{\mathrm{Me}} \operatorname{Ir}(\mathrm{COD})\right]$ complex in forms $\mathbf{A}$ and B but also gave the rearranged product, $\left[\left\{\mathrm{HB}(3-\mathrm{Mepz})_{2}(5-\mathrm{Mepz})\right\} \operatorname{Ir}(\mathrm{COD})\right]$, where one
of the methyl groups is now at the 5-position of the pyrazolyl ring. Upon heating to $70^{\circ} \mathrm{C}$ for 45 minutes another rearranged product, $\left[\left\{\mathrm{HB}(3-\mathrm{Mepz})(5-\mathrm{Mepz})_{2}\right\} \operatorname{lr}(\mathrm{COD})\right]$, is observed which does not change upon further heating. ${ }^{28 a}$ The 1,2-borotropic shift typically occurs for pyrazolylborates with 3- or 3,4-substitution. ${ }^{13,31 a}$


Scheme 1.16. 1,2-Borotropic shift

### 1.3.4 Applications of PPBs

PPB metal complexes have been used in many different applications including catalytic and stoichiometric reactivity. Rhodium pyrazolylborate complexes have been studied extensively for the stoichiometric activation of $\mathrm{H}-\mathrm{X}$ bonds $(\mathrm{X}=\mathrm{H}, \mathrm{C}, \mathrm{S}$, etc. $){ }^{28 i, 35}$ Although catalytic reactions with these complexes have not been widely investigated some examples do exist. ${ }^{35 \mathrm{e}}$ These are discussed in greater detail below.

### 1.3.4-1 Stoichiometric Bond Activation Reactions

Bond activation has been studied using pyrazolylborate complexes with some examples described below. The first example of $\mathrm{C}-\mathrm{H}$ bond activation using a PPB complex was in 1987 with $\mathrm{Tp} * \mathrm{Rh}(\mathrm{CO})_{2}$ which photochemically activated both aromatic and saturated hydrocarbons at room temperature (see Scheme 1.17). ${ }^{35 a}$


Scheme 1.17. C-H bond activation

Hydrodesulfurization reactions are important as it is a process that removes sulfur from natural gas and refined petroleum products. This is done in order to reduce sulfur dioxide emissions that are the result of fuel combustion. Thiophenes are a group of aromatic sulfur containing substrates that are common in petroleum products and have been investigated in order to gain information about the hydrodesulfurization mechanism. ${ }^{36}$ It is known that thiophenes are activated (C-H and/or C-S activation) by many metals ${ }^{37}$ and by changing the ligands different reactivity has been observed. ${ }^{35 d}$ One such case was reported in 1996 when the thermodynamic stability of the products of C-H and C-S activation of thiophene by $\mathrm{Tp} * \mathrm{Rh}\left(\mathrm{C}_{2} \mathrm{H}_{4}\right)\left(\mathrm{PR}_{3}\right)$ was investigated. ${ }^{35 \mathrm{~d}}$ Under thermal conditions, the $\mathrm{C}-\mathrm{H}$ activation product was found to be preferred in contrast to the $\mathrm{Cp} * \mathrm{RhL}\left(\mathrm{L}=\mathrm{PMe}_{3}{ }^{38}\right)$ complexes which gave predominantly the $\mathrm{C}-\mathrm{S}$ activation product. However, under photochemical conditions this preference was reversed (see Scheme 1.18). ${ }^{35 \mathrm{~d}}$


Scheme 1.18. C-H and C-S bond activation

In 1997, Bergman and coworkers investigated the reactivity of $\kappa^{3}-\mathrm{Tp} * \mathrm{Rh}(\mathrm{CO})_{2}$ in an alkane solvent. They used time-resolved ultra fast infrared studies to postulate intermediate structures and the energy barriers between them. The proposed mechanism involves the loss of a CO ligand by irradiation followed by fast solvation with an alkane $(\mathrm{RH})$ solvent. This complex is then converted to the lower energy $\kappa^{2}-\mathrm{Tp} * \mathrm{Rh}(\mathrm{CO})(\mathrm{RH})$ complex with a $4.2 \mathrm{kcal} / \mathrm{mol}$ barrier. $\kappa^{2}-\mathrm{Tp}^{*} \mathrm{Rh}(\mathrm{CO})(\mathrm{RH})$ then undergoes $\mathrm{C}-\mathrm{H}$ activation with an $8.3 \mathrm{kcal} / \mathrm{mol}$ barrier and finally the third pyrazolyl ring reattaches to the rhodium to form a lower energy complex (see Scheme 1.19). ${ }^{39}$





Scheme 1.19. Possible pathway for $\mathrm{C}-\mathrm{H}$ activation reaction

### 1.3.4-2 Catalytic Reactions

Rhodium tris(pyrazolyl)borate complexes of the form $\mathrm{Tp}^{\mathrm{R} 2} \mathrm{Rh}(\mathrm{COD})(\mathrm{R}=\mathrm{H}, \mathrm{Me}, \mathrm{Et}$, $\mathrm{Ph}, i-\mathrm{Pr})$ and $\mathrm{BpRh}(\mathrm{COD})$ have been used to catalyze the polymerization of phenylacetylene (see Scheme 1.20). ${ }^{40}$ It was found that the more sterically demanding R group at the 3- and 5-positions of the pyrazolyl rings led to higher catalytic activity, suggesting that a $\kappa^{2}$ isomer is essential for catalytic activity based on the trends of pyrazolylborate complexes when varying the substituents. ${ }^{40 \mathrm{a}}$ This was further supported by the findings that the complex bearing the Bp * ligand gave higher catalytic activity towards phenylacetylene polymerization than the complex bearing the $\mathrm{Tp} *$ ligand. ${ }^{40 a}$


Scheme 1.20. Polymerization of phenylacetylene

The hydrogenation of quinoline has been examined using a range of catalyst precursors including $[\mathrm{ClRh}(\mathrm{COD})]_{2}$. Addition of NaTp leads, presumably, to TpRh(COD). After 2 hours, this complex gave $100 \%$ conversion for quinoline hydrogenation. ${ }^{41} \mathrm{Tp} * \mathrm{Rh}(\mathrm{COD})$ was also tested and found that the initial reaction rate was faster with better yields then that with $\mathrm{Tp} .^{41}$

Catalytic hydrosilylation activity of $\mathrm{Tp}^{\mathrm{Ph}, \mathrm{Mc}} \mathrm{Rh}(\mathrm{CO})_{2}$ was examined by Ganicz and coworkers in 2004 . $^{42}$ They examined the reaction between 1-octene and triethoxysilane and found that the tris(pyrazyolyl)borate rhodium catalyst was highly active. Trzeciak and coworkers have shown that rhodium bis(pyrazolyl)borate complexes $[\mathrm{RhBp}(\mathrm{CO}) \mathrm{P}]$
$\left[\mathrm{P}=\mathrm{P}\left(\mathrm{NC}_{4} \mathrm{H}_{4}\right)_{3}, \quad \mathrm{PPh}_{3}, \quad \mathrm{PCy}_{3}, \quad \mathrm{P}\left(\mathrm{C}_{6} \mathrm{H}_{4} \mathrm{OMe}-4\right)_{3}\right]$ have catalytic activity for the hydroformylation of 1-hexene, producing approximately $80 \%$ of aldehydes and $20 \%$ of 2hexene. ${ }^{43}$ Murata and coworkers have recently demonstrated the aromatic C-H borylation reaction catalyzed by hydrotris(pyrazolyl)borate complexes of rhodium and iridium. ${ }^{44}$ Most reactions were carried out with a metal complex prepared in situ. For example $[\mathrm{ClRh}(\mathrm{COD})]_{2}$ was combined with $\mathrm{KTp}, \mathrm{KBp}$ or $\mathrm{KTp}^{*}$ and added to a mixture of pinacolborane and benzene to give the corresponding phenylpinacolborane (see Scheme 1.21).


Scheme 1.21. Aromatic C-H borylation using pinacolborane

Methods for the formation of branched aryl vinyl sulfides have been reported, however general methods for the formation of branched alkyl vinyl sulfides are just surfacing. We have recently reported the first general method for metal-catalyzed alkyne hydrothiolation using alkyl thiols. ${ }^{8 \mathrm{~m}, \mathrm{p}} \mathrm{Tp} * \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2} \quad\left(\mathrm{Tp}^{*}=\right.$ hydrotris $(3,5-$ dimethylpyrazolyl)borate, Figure 1.4$)^{22,45}$ is used as the catalyst, and generates the branched isomer in good to excellent yields.


Figure 1.4. $\mathrm{Tp} * \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}$ complex

Preliminary mechanistic investigations have been carried out on $\mathrm{Tp} * \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}$ by a coworker (Bal Kang). It was found, using labeling studies with deuterated phenyl acetylene, that the branched and $E$-linear products are both obtained with syn addition. ${ }^{46}$ This indicates that the reaction likely proceeds via S-H bond activation followed by alkyne coordination, migratory insertion into the $\mathrm{Rh}-\mathrm{S}$ bond and reductive elimination giving the syn-branched product predominantly (see Scheme 1.22). The syn-E-linear isomer can be obtained from the same mechanism if one imagines the R ' group on the alkyne facing towards the tris(pyrazolyl)borate group. This is less likely due to steric interactions and hence the $E$-linear isomer is the minor product.


Scheme 1.22. Possible pathway for $\mathrm{Tp} * \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}$-catalyzed hydrothiolation

Our group has also shown that $\mathrm{Tp} * \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}$ catalyzes alkyne hydrophosphinylation (see Scheme 1.23). In hydrothiolation, this tris(pyrazolyl)borate catalyst formed the complimentary isomer to Wilkinson's catalyst (vide infra). Therefore, it was expected to produce the branched isomer for hydrophosphinylation. Although it was found that $\mathrm{Tp} * \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}$ does catalyze alkyne hydrophosphinylation, higher yields were obtained with Wilkinson's catalyst. Interestingly, both $\mathrm{Tp} * \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}$ and Wilkinson's catalyst gave the $E$-linear product. ${ }^{47}$


Scheme 1.23. Alkyne hydrophosphinylation

Misumi and coworkers have recently reported the hydrothiolation activity of $\left[\mathrm{Tp} * \mathrm{Rh}(\mathrm{SPh})_{2}(\mathrm{MeCN})\right]$ which gave predominantly the branched product. ${ }^{8 n}$ The minor product for the reaction between 4 -ethynyl anisole and benzene thiol was the $Z$-linear isomer when using $\mathrm{Tp} * \mathrm{Rh}(\mathrm{SPh})_{2}(\mathrm{MeCN})$ as a catalyst and the $E$-linear isomer when using $\mathrm{Tp} * \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}$. This can be attributed to the different mechanisms between the two catalyst systems. It was proposed by Misumi and coworkers that the $Z$-linear isomer is formed independently via a nucleophilic or radical mechanism. The formation of this isomer appeared to be dependent only on the concentration of the alkyne, whereas the formation of the branched isomer was dependent on the concentration of the thiol and the catalyst. The proposed catalytic cycle for the $\mathrm{Tp}^{*} \mathrm{Rh}(\mathrm{SPh})_{2}(\mathrm{MeCN})$ is outlined in Scheme 1.24. This cycle involves the dissociation of MeCN to give an open coordination site on the active catalyst. Next, the alkyne adds regioselectively to give a four membered ring. The X-ray structure when $\mathrm{R}=\mathrm{CH}_{2} \mathrm{Ph}$ has been obtained; however, two species are seen in the ${ }^{1} \mathrm{H}$ nuclear magnetic resonance (NMR) spectrum which are attributed to the phenyl group on the sulfur atom within the ring facing opposite directions. The four membered ring is then protonated by PhSH to give the branched product and coordination of the remaining thiolate ion regenerates the active catalyst.


Scheme 1.24. Possible pathway for $\mathrm{Tp} * \mathrm{Rh}(\mathrm{SPh})_{2}(\mathrm{MeCN})$-catalyzed hydrothiolation

### 1.4 Conclusions

Pyrazolylborate complexes have been used in many reactions, both stoichiometric and catalytic in nature. We hypothesized that rhodium pyrazolylborate complexes would be sufficiently reactive to allow catalytic reactions with alkyl thiols, which had not been successful substrates for catalytic hydrothiolation at the outset of this thesis project. The large number of existing pyrazoles and their capability to tolerate a wide range of steric and electronic modifications allowed the construction of a variety of metal pyrazolylborate complexes. The scope of this thesis involves the synthesis of a series of pyrazolylborate rhodium complexes where the number of pyrazolyl rings as well as the substituents on the pyrazolyl rings have been changed. These complexes were used in a series of alkyne hydrothiolation reactions to probe their catalytic activity. Our goal was to improve upon the present synthetic methods for the formation of branched alkyl vinyl
sulfides and to determine what components of the ligand are needed for high reactivity and selectivity in alkyne hydrothiolation reactions.
"If you find some chemistry that looks beautiful and you think it is important, you should pursue your vision-even if the circumstances are not the best... all in all, this is a vast and promising area, the riches of which are yet to be fully exploited by the scorpionate community."
$\propto$ Swiatslaw Trofimenko

# Chapter 2 - Synthesis and Structural Characterization of Pyrazolylborate Complexes 

### 2.1 Introduction

As described in Chapter 1, pyrazolylborates have been studied for over 40 years with over 2000 documented articles attributed to them. The number of known pyrazolylborates has flourished over the years as they are attractive ligands due to their versatility and their ease of synthesis. ${ }^{11}$ Rhodium pyrazolylborate complexes have been used as catalysts for a number of reactions, including polymerization of phenylacetylene, ${ }^{40}$ homogeneous hydrogenation of quinoline, ${ }^{41}$ dimerization of terminal alkynes, ${ }^{35 e}$ alkyne hydrophosphinylation, ${ }^{47}$ aromatic C-H borylation, ${ }^{44}$ hydrosilylation, ${ }^{42}$ hydroarylation, ${ }^{48}$ hydroformylation ${ }^{43}$ and alkyne hydrothiolation. ${ }^{8 m, n}$

In this study, a series of rhodium pyrazolylborate complexes were prepared and structurally characterized in order to probe their catalytic activity in alkyne hydrothiolation. The complexes selected for study are shown in Figure 2.1: $\left\{\left[\mathrm{H}_{2} \mathrm{~B}(\mathrm{pz})_{2}\right]^{-}\right.$

$$
\begin{aligned}
& =\mathrm{Bp} ;\left[\mathrm{H}_{2} \mathrm{~B}\left(3,5-\mathrm{Me}_{2}\right)_{2}\right]^{-}=\mathrm{Bp}^{\mathrm{Me} 2}=\mathrm{Bp} * ;\left[\mathrm{HB}(\mathrm{pz})_{3}\right]^{-}=\mathrm{Tp} ;\left[\mathrm{HB}\left(3,5-\mathrm{Me}_{2} \mathrm{pz}\right)_{3}\right]^{-}=\mathrm{Tp}^{\mathrm{Me} 2}= \\
& \left.\mathrm{Tp}^{*} ;\left[\mathrm{HB}(3-\mathrm{Mepz})_{3}\right]^{-}=\mathrm{Tp}^{\mathrm{Me}} ;\left[\mathrm{HB}(3-\mathrm{Phpz})_{3}\right]^{-}=\mathrm{Tp}^{\mathrm{Ph}} ;\left[\mathrm{HB}(3-\mathrm{Ph}-5-\mathrm{Mepz})_{3}\right]^{-}=\mathrm{Tp}^{\mathrm{Ph}, \mathrm{Me}}\right\} .
\end{aligned}
$$


$1\left[T p * R h\left(\mathrm{PPh}_{3}\right)_{2}\right]$

$3\left[\mathrm{BpRh}\left(\mathrm{PPh}_{3}\right)_{2}\right]$

$5\left[\mathrm{Tp}^{\mathrm{Me}} \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}\right]$

$2\left[\mathrm{Bp}{ }^{*} \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}\right]$


$6\left[\mathrm{Tp}^{\mathrm{Ph}} \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}\right]$

$7\left[\mathrm{Tp}^{\mathrm{Ph}, \mathrm{Me}} \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}\right]$

Figure 2.1. Rhodium pyrazolylborate complexes

Complexes 1-7 were selected based on the number of pyrazolyl rings as well as the substitution patterns on each pyrazolyl ring. The study of bis(pyrazolyl)borate complexes will test whether or not $\kappa^{3}$-coordination is required for reactivity and selectivity. All of the complexes will be used to investigate the effect of pyrazolyl substitution. Various techniques, described in chapter 1 , have been reported in the literature for the
characterization of rhodium pyrazolylborate complexes. The techniques that were employed in this study include variable temperature ${ }^{1} \mathrm{H}$ and ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectroscopy, X-ray crystallography and IR spectroscopy.

Phosphine-containing rhodium tris(pyrazolyl)borate complexes, $\mathrm{Tp}^{\mathrm{X}} \mathrm{Rh}\left(\mathrm{PR}_{3}\right)_{2}$, are not as well precedented in the literature as carbonyl, $\mathrm{Tp}^{\mathrm{X}} \mathrm{Rh}(\mathrm{CO})_{2}$, and olefin-containing, $\mathrm{Tp}^{\mathrm{X}} \mathrm{Rh}(\mathrm{R})_{2}\left[\mathrm{R}=\mathrm{C}_{2} \mathrm{H}_{2}, \mathrm{COD}, \mathrm{nbd}, \mathrm{dq}\right.$, etc.], complexes ${ }^{13,14,20 \mathrm{a}, 21,26,27,29}$ although a few phosphine-containing complexes have been structurally characterized. ${ }^{15,17,22,28 b-h}$ $\operatorname{Tp}^{\mathrm{R}} \mathrm{RhLL}^{\prime} \quad\left[\mathrm{Tp}^{\mathrm{R}}=\right.$ substituted pyrazolylborate; $\mathrm{L}, \mathrm{L}$ ' $=$ ancillary ligands; $\mathrm{Rh}(\mathrm{I})$ ] complexes typically exist in an equilibrium between up to four isomers (A-D), as described in Chapter 1. The interconversion between these species plays a crucial role in C-H activation reactions ${ }^{35 c, 49}$ and therefore is postulated to play a role in catalytic bond activation reactions.

### 2.2 Results and Discussion

### 2.2.1 Synthesis of Potassium Pyrazolylborate Salts

The starting materials for the synthesis of the rhodium pyrazolylborate complexes are potassium pyrazolylborate salts and Wilkinson's catalyst, $\mathrm{ClRh}\left(\mathrm{PPh}_{3}\right)_{3}$. The potassium pyrazolylborate salts $\mathrm{KTp}^{*}, \mathrm{KBp}, \mathrm{KTp}, \mathrm{KTp}^{\mathrm{Ph}}$ and $\mathrm{KTp}^{\mathrm{Ph}, \mathrm{Me}}$ are commercially available. KBp * and $\mathrm{KTp}^{\mathrm{Me}}$ were synthesized using modified literature methods. ${ }^{50}$

## Potassium dihydrobis(3,5-dimethylpyrazol-1-yl)borate [KBp*] (8) ${ }^{50 \mathrm{a}}$

KBp* (8) was used as the starting material to produce the corresponding rhodium pyrazolylborate complex $\left[\mathrm{Bp}^{*} \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}\right]$ (2). Compound 8 was prepared by melting 4.0
equivalents of 3,5 -dimethylpyrazole at $120^{\circ} \mathrm{C}$ and then adding 1.0 equivalents of potassium borohydride (see Scheme 2.1). This mixture was then heated (at temperatures not exceeding $140^{\circ} \mathrm{C}$ ) for 20 hours, after which time the slurry had become a solid white mass. Toluene was added and the white solid slightly dissolved. The resulting slurry was filtered and washed with hot toluene. Finally the solid was dried under vacuum to give a white solid. Because the ${ }^{1} H$ NMR spectrum showed extra peaks, compound $\mathbf{8}$ was dissolved in acetone and filtered to remove any potential impurities The volatiles were then removed under vacuum and the white solid was sublimed to remove excess 3,5 dimethylpyrazole. After attempted purification, $\mathrm{KBp}^{*}$ was obtained with an unidentified byproduct; this mixture was used to make complex 2.


Scheme 2.1. Synthesis of KBp*

## Potassium hydrobis(3-methylpyrazol-1-yl)borate $\left[\mathrm{KTp}^{\mathrm{Mc}}\right](9){ }^{50 b}$

$\mathrm{KTp}^{\mathrm{Me}}$ (9) was used as the starting material for the preparation of the rhodium pyrazolylborate complex $\left[\mathrm{Tp}{ }^{\mathrm{Me}} \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}\right]$ (5). Compound 9 was prepared by melting 1.0 equivalents of $\mathrm{KBH}_{4}$ with 3.3 equivalents of 3-methylpyrazole (see Scheme 2.2). This reaction mixture was heated at $190^{\circ} \mathrm{C}$ for 9 hours after which time the reaction was allowed to cool to room temperature. The solution solidified and was then filtered and
washed with benzene and petroleum ether. The solid was dried under vacuum. The ${ }^{1} \mathrm{H}$ NMR spectrum confirmed the presence of compound 9 and 3-methylpyrazole. The solid mixture was sublimed to remove any excess 3-methylpyrazole; however, this was unsuccessful and the white solid mixture, a $13: 1$ ratio of compound 9 to 3 methylpyrazolyl, was used without further purification for the preparation of complex 5.


Scheme 2.2. Synthesis of $\mathrm{KTp}^{\mathrm{Me}}$

### 2.2.2 Synthesis and Characterization of Rhodium Pyrazolylborate Complexes

Wilkinson's catalyst, $\mathrm{ClRh}\left(\mathrm{PPh}_{3}\right)_{3}$, was mixed with the corresponding potassium pyrazolylborate salt, $\mathrm{KX}(\mathrm{X}=$ pyrazolylborate ligand $)$, to produce known complexes $1,{ }^{22}$ $2,{ }^{28 \mathrm{~b}} 3^{28 \mathrm{~b}}$ and $\mathbf{4}^{28 \mathrm{c}}$ and new complexes 5, 6 and 7 (Table 2.1). These reactions were all carried out at room temperature in THF (except toluene was used for the synthesis of complex 7) and gave good-to-excellent yields (58-92\%) after workup.

Table 2.1. Synthesis of rhodium pyrazolylborate complexes 1-7

|  |  | h( $\left.\mathrm{PPh}_{3}\right)_{3} \quad \frac{\mathrm{KX}, \mathrm{TH}}{\mathrm{rt}}$ | $\xrightarrow[\mathrm{rt}]{\mathrm{KX}, \mathrm{THF}}$ | $\mathrm{XRh}\left(\mathrm{PPh}_{3}\right)_{2}$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Entry | X | Complex | Time | Yield (\%) ${ }^{\text {a }}$ | Literature |
| 1 | Tp* | Tp ${ }^{*} \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}(1)$ | 1 h | 92\% | $48 \%^{\text {b }}, 66 \%^{\text {c }}$ |
| 2 | Bp* | $\mathrm{Bp}^{*} \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}(\mathbf{2})$ | 24 h | 87\% | $80 \%{ }^{\text {d }}$ |
| 3 | Bp | $\mathrm{BpRh}\left(\mathrm{PPh}_{3}\right)_{2}(\mathbf{3})$ | 24 h | 86\% | 80\% ${ }^{\text {d }}$ |
| 4 | Tp | $\mathrm{TpRh}\left(\mathrm{PPh}_{3}\right)_{2}(4)$ | 24 h | 86\% | $66 \%{ }^{\text {e }}$ |
| 5 | Tp ${ }^{\text {Me }}$ | $\mathrm{Tp}^{\mathrm{Me}} \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}(5)$ | 4 h | 59\% | - |
| 6 | Tp ${ }^{\text {Ph }}$ | $\mathrm{Tp}^{\mathrm{Ph}} \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}(6)$ | 24 h | 83\% | - |
| 7 | $T p^{\text {Ph, Me }}$ | $\mathrm{Tp}{ }^{\mathrm{Ph}, \mathrm{Me}} \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}(7)$ | 24 h | $58 \%{ }^{\text {f }}$ | - |

[^0]
## $\mathbf{T p} * \mathbf{R h}\left(\mathbf{P P h}_{3}\right)_{\mathbf{2}}, \mathbf{1}$

Complex 1 was prepared by combining 1 equivalent of both $\mathrm{ClRh}\left(\mathrm{PPh}_{3}\right)_{3}$ and KTp * in THF and stirring for 1 hour at room temperature. We have observed that longer reaction times cause decomposition of the product. ${ }^{28 j}$ The volatiles were removed under vacuum, followed by addition of toluene and layering with hexanes. This solution was left at $-35{ }^{\circ} \mathrm{C}$ for 7 days in which time orange crystals formed. After washing with hexanes and drying under vacuum, complex 1 was obtained in $92 \%$ yield; this complex was used without further purification. Our spectral data for complex 1 is consistent with literature reports at room temperature. ${ }^{22,28 i}$ At room temperature two sets of signals in a 2:1 ratio were observed for the pyrazolyl rings in the ${ }^{1} \mathrm{H}$ NMR spectrum indicating that there are two equivalent and one inequivalent pyrazolyl rings. The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum shows a doublet indicating two equivalent phosphines at room temperature ( $\delta$
$44.04 J_{\mathrm{Rh}-\mathrm{P}}=177 \mathrm{~Hz}$ ), see Table 2.9. The equivalency of the bound pyrazolyl rings and phosphines are due to the free rotation of the unbound pyrazolyl ring. At $-85^{\circ} \mathrm{C}$ two sets of signals are still observed for the ${ }^{1} \mathrm{H}$ NMR spectrum with a $2: 1$ ratio of the pyrazolyl rings; however, Connelly reports that all pyrazolyl rings were inequivalent at $-80^{\circ} \mathrm{C}$. ${ }^{22}$ In the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum at $-85^{\circ} \mathrm{C}$ the doublet that was observed at room temperature split into two broad doublets ( $\delta 44.76, J_{\mathrm{Rh}-\mathrm{P}}=164 \mathrm{~Hz} ; \delta 41.89, J_{\mathrm{Rh}-\mathrm{P}}=180 \mathrm{~Hz}$ ). In contrast, Connelly reports two doublets of doublets. ${ }^{22}$ This difference may be due to slow rotation of the unbound pyrazolyl ring with the rotation rapid enough to give a $2: 1$ ratio of pyrazolyl rings on the ${ }^{1} \mathrm{H}$ NMR time scale in our study. This contrasts with the suggestion by Connelly that there is restricted rotation of the free pyrazolyl at low temperature, which would result in the inequivalence of the bound pyrazolyl rings and the phosphines. Also consistent with our data, Carlton and coworkers reported a doublet in the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum at room temperature that becomes broadened at $-60{ }^{\circ} \mathrm{C}$, which they attributed to the interconversion between the $\kappa^{2}$ and $\kappa^{3}$ forms. They found that the addition of phosphine at low temperature did not significantly change the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum and thus phosphine dissociation is unlikely to cause the broadening seen at lower temperatures. ${ }^{28 i}$ Therefore it is difficult to attribute the spectrum to the interconversions occurring either between forms $\mathbf{A}$ and $\mathbf{B}$ or between the $\kappa^{2}$ and $\kappa^{3}$ forms due to fast exchange on the NMR time scale. In addition, at room temperature the IR shows a single stretching frequency at $2447 \mathrm{~cm}^{-1}$ which is in the range for $\kappa^{2}$ coordination.

## $\mathbf{B p} * \mathbf{R h}\left(\mathbf{P P h}_{3}\right)_{2}, \mathbf{2}$

Complex 2 was prepared by mixing 1 equivalent $\mathrm{ClRh}\left(\mathrm{PPh}_{3}\right)_{3}$ with 1.5 equivalents of $\cdot \mathrm{KBp}^{*}$ in THF at room temperature for 24 hours. After this time the volatiles were removed, and a minimal amount of toluene was added, which was layered with hexanes. This layered mixture was allowed to sit at $-35^{\circ} \mathrm{C}$ for 7 days after which time orange crystals formed. The crystals were washed with hexanes and dried under vacuum and gave an $87 \%$ yield; the crystals were used for alkyne hydrothiolation. The ${ }^{1} \mathrm{H}$ and ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectra were mostly consistent with literature reports except in the aromatic region of the ${ }^{1} \mathrm{H}$ NMR spectrum. For the two triphenylphosphine ligands, Baena and coworkers reported three multiplets at $\delta 7.77(12 \mathrm{H}), 6.87(12 \mathrm{H}), 6.85(6 \mathrm{H})$ when carried out in $\mathrm{C}_{6} \mathrm{D}_{6}$. Our spectra show two multiplets $\delta 7.74-7.73(6 \mathrm{H})$ and $7.10-6.85(24$ $\mathrm{H})$ in $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ and therefore the discrepancies between our spectra and Baena's spectra could be due to the different solvent (Table 2.9). ${ }^{28 b}$ The ${ }^{1} \mathrm{H}$ NMR spectrum indicated the equivalence of the two pyrazolyl rings and ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum indicated equivalence of the two phosphorous atoms which is consistent with the solid state structure. The IR spectrum also showed two stretching frequencies assigned to the two boron hydrogen stretches at 2449 and $2378 \mathrm{~cm}^{-1}$, both of which were in the range for $\kappa^{2}$-coordination.

The molecular structure of 2 (Figure 2.2) determined by X-ray crystallography shows that the geometry about the central rhodium atom is approximately square planar which is typical of a $\mathrm{d}^{8}$ electronic configuration. The sum of the angles about the rhodium atom is equal to $361.13^{\circ}$, consistent with square planar geometry. $\kappa^{2}$-Coordination of the Bp* ligand is observed with coordination through one nitrogen of each pyrazolyl ring. Two bridging pyrazolyl rings, the boron atom and the rhodium metal centre make up a six
membered ring in the boat conformation. The Rh1-N1 and Rh1-N4 bond distances of 2.132(2) $\AA$ and $2.092(2) \AA$, respectively, fall within the range of other reported rhodium pyrazolylborate complexes (2.081-2.140 $\AA$ ) (Table 2.2). ${ }^{22,28 i}$ The Rh1-P1 and Rh1-P2 bond distances of $2.2202(7) \AA$ and $2.2468(7) \AA$, respectively, also fall within the range reported in the literature $(2.210-2.280 \AA) .{ }^{28, \text { ei }}$ The angle between the two phosphorous atoms $\left[95.43(3)^{\circ}\right]$ is slightly larger than that between the nitrogen atoms $\left[79.84(8)^{\circ}\right]$, which is attributed to steric interactions between the large triphenylphosphine groups maximizing the distance between each other; this is consistent with literature reports. ${ }^{22,28 b, i}$ Crystallographic data for complex $\mathbf{2}$ is given in Appendix I.


Figure 2.2. ORTEP diagram of complex 2. Thermal ellipsoids are drawn at the $50 \%$ probability level. Hydrogen atoms, except for the B-H hydrogens, and phenyl groups of $\mathrm{PPh}_{3}$ are excluded for clarity. Selected bond lengths $(\AA)$ and angles $\left({ }^{\circ}\right)$ are given in Table 2-2.

Table 2.2. Selected bond distances and angles of complex 2

| Atoms | Bond Distances $(\AA)$ or Angles $\left(^{\circ}\right)$ |
| :--- | :--- |
| Rh1-N1 | $2.132(2)$ |
| Rh1-N4 | $2.092(2)$ |
| Rh1-P1 | $2.2202(7)$ |
| Rh1-P2 | $2.2468(7)$ |
| N1-Rh1-N4 | $79.84(8)$ |
| P1-Rh1-P2 | $95.43(3)$ |
| N1-Rh1-P1 | $164.16(6)$ |
| N1-Rh1-P2 | $92.91(6)$ |
| N4-Rh1-P1 | $92.93(6)$ |
| N4-Rh1-P2 | $170.88(6)$ |

## $\operatorname{BpRh}\left(\mathbf{P P h}_{3}\right)_{2}, 3$

Complex 3 was prepared by the reaction of 1 equivalent of $\mathrm{ClRh}\left(\mathrm{PPh}_{3}\right)_{3}$ with 1.1 equivalents of KBp in THF at room temperature. After 24 hours the volatiles were removed, a minimal amount of toluene was added and layered with hexanes. This layered mixture was left at room temperature for 15 days after which time orange crystals formed. After washing with hexanes and drying under vacuum an $86 \%$ yield was obtained of complex 3. The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of these crystals was consistent with literature reports showing a doublet at $\delta 52.63\left(J_{\mathrm{Rh}-\mathrm{P}}=176 \mathrm{~Hz}\right)$, see Table 2.9. ${ }^{28 \mathrm{~b}}$ The coupling constant is typical of rhodium-phosphorous coupling. The crystals were used without further purification in alkyne hydrothiolation reactions.

## $\mathbf{T p R h}\left(\mathbf{P P h}_{3}\right)_{2}, \mathbf{4}$

Complex 4 was prepared by mixing 1 equivalent of $\mathrm{ClRh}\left(\mathrm{PPh}_{3}\right)_{3}$ with 1.5 equivalents of KTp in THF. After 24 hours at room temperature the volatiles were removed and a minimal amount of toluene was added, which was then layered with hexanes. This layered mixture was left for 12 days at $-35^{\circ} \mathrm{C}$ after which time orange crystals of complex 4 formed in an $86 \%$ yield. The crystals were washed with hexanes, dried under vacuum and were used without further purification in alkyne hydrothiolation.

The ${ }^{1} \mathrm{H}$ NMR data is consistent with that reported by Connelly and coworkers. However, both our spectra and Connelly's spectra differ from the previously reported spectra by Hill and coworkers. In our ${ }^{1} \mathrm{H}$ NMR spectrum at room temperature, two equivalent and one inequivalent pyrazolyl ring are observed. As the temperature is lowered the peaks begin to sharpen and split; however, no assignment of the $-85^{\circ} \mathrm{C}$ spectra has been possible. The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum at room temperature is consistent with both literature reports, see Table 2.9. ${ }^{22,28 \mathrm{c}}$ The room temperature ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum reported by Connelly and coworkers indicated a broad doublet at $\delta 50.9\left(J_{\mathrm{Rh}-\mathrm{P}}=\right.$ $165 \mathrm{~Hz})$; at $-40^{\circ} \mathrm{C}$ this doublet splits into two doublets of equal intensity $\delta 51.0\left(J_{\mathrm{Rh}-\mathrm{P}}=\right.$ $174 \mathrm{~Hz})$ and $\delta 49.3\left(J_{\mathrm{Rh}-\mathrm{P}}=176 \mathrm{~Hz}\right)$. At $-80^{\circ} \mathrm{C}$, the doublet at $\delta 49.3$ became broadened, whereas the other doublet remained unchanged. Based on this data Connelly, and coworkers assigned the doublet at $\delta 51.0$ to form $\mathbf{A}$ and the doublet at $\delta 49.3$ to form $\mathbf{B}$. Our room temperature ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum shows a doublet at $\delta 53.11\left(J_{\mathrm{Rh}-\mathrm{P}}=173\right.$ $\mathrm{Hz})$. At $-45^{\circ} \mathrm{C}$ this doublet splits into two doublets of unequal intensity $\left[\delta 53.60\left(J_{\mathrm{Rh}-\mathrm{P}}=\right.\right.$ $177 \mathrm{~Hz})$ and $\left.\delta 52.00\left(J_{\mathrm{Rh}-\mathrm{P}}=177 \mathrm{~Hz}\right)\right]$. At $-85^{\circ} \mathrm{C}$ our spectrum shows the doublet at $\delta$ $53.39\left(J_{\mathrm{Rh}-\mathrm{P}}=173 \mathrm{~Hz}\right)$ remains unchanged. The doublet at $\delta 51.63\left(J_{\mathrm{Rh}-\mathrm{P}}=173 \mathrm{~Hz}\right)$
decreases in intensity and broadens, and a new broad doublet at $\delta 49.16\left(J_{\mathrm{Rh}-\mathrm{P}}=172 \mathrm{~Hz}\right)$ appears. Based on comparison to Connelly's assignments the doublet at $\delta 53.39$ is assigned as form $\mathbf{A}$ and the broad doublets at $\delta 51.63$ and $\delta 49.16$ are both assigned as form $\mathbf{B}$ with restricted rotation around the pyrazolyl ring. As well, a single stretching frequency at $2392 \mathrm{~cm}^{-1}$ is seen in the room temperature IR , which is consistent with $\kappa^{2}$ coordination.

The molecular structure of complex 4 (Figure 2.3) shows square planar geometry with respect to the rhodium centre, as the sum of the angles around the rhodium atom equals $361.48^{\circ}$. The six membered ring with boron, rhodium and two bridging pyrazolyl rings is in a boat conformation. The Tp ligand is bound $\kappa^{2}$ with the third uncoordinated pyrazolyl ring facing away from the rhodium in form A configuration. The Rh1-N1 and Rh1-N4 are $2.1575(13)$ and $2.1111(13) \AA$, respectively. The Rh1-N1 bond length is in the range for square planar pyrazolylborate rhodium bis(triphenylphosphine) complexes however the Rh1-N4 bond length slightly exceeds the reported length. The Rh1-P1 $[2.2299(4) \AA]$ and Rh1-P2 [2.2558(4) $\AA$ ] bond lengths are both within literature values (Table 2.3). The angle between the two phosphorous atoms $\left[93.605(15)^{\circ}\right]$ is slightly larger then that between the nitrogen atoms $\left[83.37(5)^{\circ}\right]$, again due to the large triphenylphosphine groups maximizing the distance between themselves. Crystallographic data for complex $\mathbf{3}$ is given in Appendix II.


Figure 2.3. ORTEP diagram of complex 4. Thermal ellipsoids are drawn at the $50 \%$ probability level. Hydrogen atoms, except for the B-H hydrogen, and phenyl groups of $\mathrm{PPh}_{3}$ are excluded for clarity. Selected bond lengths $(\AA)$ and angles $\left({ }^{\circ}\right)$ are given in Table 2-3.

Table 2.3. Selected bond distances and angles of complex 4

| Atoms | Bond Distances $(\AA)$ or Angles $\left(^{\circ}\right)$ |
| :--- | :--- |
| Rh1-N1 | $2.1575(13)$ |
| Rh1-N4 | $2.1111(13)$ |
| Rh1-P1 | $2.2299(4)$ |
| Rh1-P2 | $2.2558(4)$ |
| N1-Rh1-N4 | $83.37(5)$ |
| P1-Rh1-P2 | $93.605(15)$ |
| N1-Rh1-P1 | $169.58(4)$ |
| N1-Rh1-P2 | $92.98(4)$ |
| N4-Rh1-P1 | $91.52(3)$ |
| N4-Rh1-P2 | $169.18(4)$ |

## $\mathbf{T p}{ }^{\mathrm{Me}} \mathbf{R h}\left(\mathrm{PPh}_{3}\right)_{2}, 5$

Complex 5 was prepared by combining 1 equivalent of $\mathrm{CIRh}\left(\mathrm{PPh}_{3}\right)_{3}$ with 1.6 equivalents of $\mathrm{KTp}^{\mathrm{Me}}$ in THF and stirred at room temperature for 4 hours. The volatiles were removed under vacuum, followed by addition of toluene and layering with hexanes. After 12 days at $-35^{\circ} \mathrm{C}$ the resulting orange crystals were washed with hexanes and dried under vacuum to give a $59 \%$ yield which was used without further purification.

The room temperature ${ }^{1} \mathrm{H}$ NMR spectrum shows two products in a $7: 1$ ratio. Both species have two equivalent pyrazolyl rings and one inequivalent pyrazolyl ring. The major product is presumably formed by a 1,2-borotropic shift where one of the methyl groups is now in the 5 -position to form $5^{*}:\left[\mathrm{HB}(3-\mathrm{Mepz})_{2}(5-\mathrm{Mepz})\right]^{-}=\mathrm{Tp}^{\mathrm{Me}^{*}}$, and the minor product is proposed to be complex 5 (see Scheme 2.3). From the ${ }^{1} H$ NMR spectrum for the major product, there are two possible scenarios: in one case, both 3methylpyrazolyl rings are coordinated and the 5-methylpyrazolyl ring is unbound, whereas in the other case, one 3-methylpyrazolyl ring and the 5-methylpyrazolyl ring are bound and the remaining 3-methylpyrazolyl ring is unbound. The phosphines would be equivalent in the first case and the ${ }^{31} \mathrm{P}\left\{{ }^{\prime} \mathrm{H}\right\}$ NMR spectrum would be expected to show a single resonance, appearing as a doublet due to rhodium-phosphorus coupling. The phosphines would be inequivalent in the second case and the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum would be expected to show two doublets of doublets, each with rhodium-phosphorus and phosphorus-phosphorus coupling. The room temperature ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum shows two doublets of doublets providing evidence that the second case is more probable. The solid state structure is consistent with this analysis. At $-85^{\circ} \mathrm{C}$ no assignment of the ${ }^{1} \mathrm{H}$ NMR spectrum has been possible and the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum gives the same two
doublets of doublets for each product. The IR spectrum shows a single stretching B-H frequency at $2429 \mathrm{~cm}^{-1}$, indicating $\kappa^{2}$-coordination.


Scheme 2.3. 1,2-Borotropic shift

X-ray analysis of crystals obtained from the attempted preparation of complex 5 revealed the formation of $\left[\mathrm{HB}(3-\mathrm{Mepz})_{2}(5-\mathrm{Mepz})\right] \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}\left(5^{*}\right)$. The driving force for the formation of the 1,2-borotropic shift product can be attributed to reduction of van der Waals repulsions. The molecular structure of 5* (Figure 2.4) shows an approximate square planar geometry around rhodium with the sum of the angles equal to $363.10 \AA$. The six membered ring with boron, rhodium and two bridging pyrazolyl rings is in a boat conformation. The pyrazolylborate ligand is bound $\kappa^{2}$ with the third uncoordinated pyrazolyl ring overtop of the rhodium in form $\mathbf{B}$. The X-ray structure indicates one 3methylpyrazolyl is bound and the 5-methylpyrazolyl is bound while the additional 3methylpyrazolyl is unbound. The Rh1-N1 [2.110(2) $\AA$ ] and Rh1-N4 [2.084(2) $\AA$ ] bond lengths are within the range for $\mathrm{Rh}-\mathrm{N}$ bonds reported in the literature. As well, the Rh1P1 [2.2404(7) $\AA$ ] and Rh1-P2 [2.2585(7) $\AA$ ] are also within the literature range for Rh-P bonds of complexes of this type (Table 2.4). The angle between the phosphines is larger than that between the nitrogens; this is attributed to the repulsion between the large
triphenylphosphine groups. Crystallographic data for complex 5* is given in Appendix III.


Figure 2.4. ORTEP diagram of complex 5*. Thermal ellipsoids are drawn at the $50 \%$ probability level. Hydrogen atoms, except for the B-H hydrogen, and phenyl groups of $\mathrm{PPh}_{3}$ are excluded for clarity. Selected bond lengths $(\AA)$ and angles $\left({ }^{\circ}\right)$ are given in Table 2-4.

Table 2.4. Selected bond distances and angles of complex 5*

| Atoms | Bond Distances $(\AA)$ or Angles $\left(^{\circ}\right)$ |
| :--- | :--- |
| Rh1-N1 | $2.110(2)$ |
| Rh1-N4 | $2.084(2)$ |
| Rh1-P1 | $2.2404(7)$ |
| Rh1-P2 | $2.2585(7)$ |
| N1-Rh1-N4 | $82.46(8)$ |
| P1-Rh1-P2 | $94.66(3)$ |
| N1-Rh1-P1 | $164.93(6)$ |
| N1-Rh1-P2 | $94.27(6)$ |
| N4-Rh1-P1 | $91.69(6)$ |
| N4-Rh1-P2 | $165.68(6)$ |

## $\mathbf{T p}{ }^{\mathbf{P h}} \mathbf{R h}\left(\mathbf{P P h}_{3}\right)_{2}, \mathbf{6}$

Complex 6 was prepared by mixing 1 equivalent of $\mathrm{ClRh}\left(\mathrm{PPh}_{3}\right)_{3}$ with 1.5 equivalents of $\mathrm{KTp}^{\mathrm{Ph}}$ in THF for 24 hours at room temperature. The volatiles were removed under vacuum, followed by addition of toluene and layering with hexanes. This was then left in the freezer at $-35^{\circ} \mathrm{C}$ and after 7 days orange crystals formed. After washing with hexanes and drying under vacuum an $83 \%$ yield was obtained. The ${ }^{1} \mathrm{H}$ NMR spectra at both room temperature and at $-85^{\circ} \mathrm{C}$ show a $2: 1$ ratio of pyrazolyl rings and the ${ }^{31} \mathbf{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum shows a doublet both at room temperature $(\delta 46.89, \mathrm{~d}$, $\left.J_{\mathrm{Rh}-\mathrm{P}}=178 \mathrm{~Hz}\right)$ and at $-85^{\circ} \mathrm{C}\left(\delta 46.69, \mathrm{~d}, J_{\mathrm{Rh}-\mathrm{P}}=176 \mathrm{~Hz}\right)$, see Table 2.9. This data is consistent with $\kappa^{2}$-coordination with free rotation of the free pyrazolyl ring, even at lower temperatures. There is no evidence for the 1,2-borotropic shift product as seen with complex 5. The IR spectrum shows a single stretching B-H frequency at $2426 \mathrm{~cm}^{-1}$,
indicating $\kappa^{2}$-coordination. The solid state molecular structure also supports this data (Figure 2.5).

The molecular structure shows approximate square planar geometry around the rhodium centre with the sum of the angles around rhodium equal to $359.67^{\circ}$. There is also $\kappa^{2}$-coordination of the tris(pyrazoyl)borate ligand with the uncoordinated pyrazolyl ring facing away from the rhodium in form $\mathbf{A}$. The six membered chelate ring with boron and rhodium is in the boat conformation. The Rh1-N1 [2.1240(18) $\AA$ ] and the Rh1-N4 [2.1000(18) $\AA$ ] bond lengths fall within the range of known values and so do the Rh1-P1 [2.2429(6) $\AA$ ] and Rh1-P2 [2.2618(6) $\AA$ ] bond lengths (Table 2.5). The angle between the phosphine atoms is larger then that between the nitrogen atoms; this is attributed to the repulsion between the large triphenylphosphine groups. Crystallographic data for complex 6 is given in Appendix IV.


Figure 2.5. ORTEP diagram of complex 6. Thermal ellipsoids are drawn at the $50 \%$ probability level. Hydrogen atoms, except for the B-H hydrogen, and phenyl groups of $\mathrm{PPh}_{3}$ are excluded for clarity. Selected bond lengths $(\AA)$ and angles $\left({ }^{\circ}\right)$ are given in Table 2-5.

Table 2.5. Selected bond distances and angles of complex 6

| Atoms | Bond Distances $(\AA)$ or Angles $\left(^{\circ}\right)$ |
| :--- | :--- |
| Rh1-N1 | $2.1240(18)$ |
| Rh1-N4 | $2.1000(18)$ |
| Rh1-P1 | $2.2429(6)$ |
| Rh1-P2 | $2.2618(6)$ |
| N1-Rh1-N4 | $78.99(7)$ |
| P1-Rh1-P2 | $96.31(2)$ |
| N1-Rh1-P1 | $167.28(5)$ |
| N1-Rh1-P2 | $92.53(5)$ |
| N4-Rh1-P1 | $91.82(5)$ |
| N4-Rh1-P2 | $171.38(5)$ |

## $\mathbf{T p}{ }^{\mathbf{P h}, \mathrm{Me}} \mathbf{R h}\left(\mathbf{P P h}_{3}\right)_{2}, 7$

Complex 7 was prepared by mixing 1 equivalent of $\mathrm{ClRh}\left(\mathrm{PPh}_{3}\right)_{3}$ with 1.5 equivalents of $\mathrm{KTp}^{\mathrm{Ph}, \mathrm{Me}}$ in toluene for 24 hours at room temperature. The volatiles were removed under vacuum, followed by addition of toluene and layering with hexanes. This was then left in the freezer at $-35^{\circ} \mathrm{C}$ for 7 days after which time small orange crystals formed of complex 7. These were washed with hexanes and dried under vacuum to give $58 \%$ yield. At room temperature the ${ }^{1} H$ NMR spectrum show two equivalent and one inequivalent pyrazolyl ring ( $2: 1$ ratio) which indicates $\kappa^{2}$-coordination and as the temperature is decreased to $-85^{\circ} \mathrm{C}$ all three pyazoles become inequivalent, which suggests restricted rotation of the unbound pyrazolyl ring. The ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum at room temperature shows a doublet at $\delta 48.12\left(J_{\mathrm{Rh}-\mathrm{P}}=182 \mathrm{~Hz}\right)$ and a multiplet at $\delta 43.44$ 39.33 , in a $1: 5$ ratio in deuterated methylene chloride $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}\right)$. As the temperature is
decreased, the doublet ( $\delta 48.12$ ) begins to disappear, and is completely unobservable at $85^{\circ} \mathrm{C}$. At this temperature, the multiplet becomes resolved into two doublets of doublets $\left(\delta 42.60 J_{\text {Rh-P }}=178 \mathrm{~Hz}, J_{\mathrm{P}-\mathrm{P}}=50 \mathrm{~Hz} ; \delta 39.42 J_{\text {Rh-P }}=172 \mathrm{~Hz}, J_{\mathrm{P}-\mathrm{P}},=51 \mathrm{~Hz}\right.$ ), see Table 2.9. The low temperature ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectra and corresponding chemical shift values are shown in Figure 2.6 and Table' 2.6. Two possible scenarios exist to explain these results: 1) two species are present at room temperature and at lower temperatures one predominates or 2 ) both species may be present at both room temperature and lower temperatures and one species peaks may be broadened due to restricted rotation at lower temperatures. When the NMR spectrum was taken in $d_{8}$-toluene the spectrum was similar but more convoluted. The ratio of isomers in the $d_{8}$-toluene ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ spectrum at room temperature was 1:7, which was different then that in $\mathrm{CD}_{2} \mathrm{Cl}_{2}$.


Figure 2.6. Low temperature ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectra for complex 7 observed in $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ at 162 MHz

Table 2.6. Low temperature ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectroscopic data for complex 7

| Temperature | ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR Chemical Shifts |
| :---: | :---: |
| 298 K | MIN $\delta 48.12\left(\mathrm{~d}, J_{\mathrm{Rh}-\mathrm{P}}=182 \mathrm{~Hz}\right.$ ); MAJ $\delta 43.44-39.33$ (m) |
| 273 K | MIN $\delta 48.15\left(\mathrm{~d}, J_{\mathrm{Rh}-\mathrm{P}}=180 \mathrm{~Hz}\right.$ ); MAJ $\delta 44.00-42.34(\mathrm{~m})$ |
| 253 K | MIN $\delta 48.19\left(\mathrm{~d}, J_{\mathrm{Rh}-\mathrm{P}}=180 \mathrm{~Hz}\right)$; MAJ $\delta 43.14\left(\mathrm{dd}, J_{\mathrm{Rh}-\mathrm{P}}=180, J_{\mathrm{P}-\mathrm{P}}=51\right.$ $\mathrm{Hz}), \delta 39.56\left(\mathrm{dd}, J_{\mathrm{Rh}-\mathrm{P}}=174 \mathrm{~Hz}, J_{\mathrm{P}-\mathrm{P}}{ }^{\prime}=51 \mathrm{~Hz}\right)$ |
| 233 K | MIN $\delta 48.23\left(\mathrm{~d}, J_{\mathrm{Rh}-\mathrm{P}}=180 \mathrm{~Hz}\right)$; MAJ $\delta 42.99\left(\mathrm{dd}, J_{\mathrm{Rh}-\mathrm{P}}=180, J_{\mathrm{P}-\mathrm{P}}=50\right.$ $\mathrm{Hz}), \delta 39.51\left(\mathrm{dd}, J_{\mathrm{Rl}-\mathrm{P}}{ }^{\prime}=172 \mathrm{~Hz}, J_{\mathrm{P}-\mathrm{P}}{ }^{\prime}=50 \mathrm{~Hz}\right)$ |
| 213 K | $\begin{aligned} & \mathrm{MIN} \delta 48.28\left(\mathrm{~d}, J_{\mathrm{Rh}-\mathrm{P}}=182 \mathrm{~Hz}\right) ; \text { MAJ } \delta 43.83\left(\mathrm{dd}, J_{\mathrm{Rh}-\mathrm{P}}=180, J_{\mathrm{P}-\mathrm{P}}=50\right. \\ & \mathrm{Hz}), \delta 39.47\left(\mathrm{dd}, J_{\mathrm{Rh}-\mathrm{P}}=174 \mathrm{~Hz}, J_{\mathrm{P}-\mathrm{P}}=50 \mathrm{~Hz}\right) \end{aligned}$ |
| 188 K | $\begin{aligned} & \text { MAJ } \delta 42.60\left(\mathrm{dd}, J_{\mathrm{Rh}-\mathrm{P}}=180, J_{\mathrm{P}-\mathrm{P}}=52 \mathrm{~Hz}\right), \delta 39.42\left(\mathrm{dd}, J_{\mathrm{Rh}-\mathrm{P}^{\prime}}=174 \mathrm{~Hz},\right. \\ & \left.J_{\mathrm{P}-\mathrm{P}}=52 \mathrm{~Hz}\right) \end{aligned}$ |

When the high temperature ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectra were obtained in $d_{8}$-toluene it was found that the doublet at room temperature remains unchanged and the multiplet coalesces into a doublet, see Figure 2.7 and Table 2.7 for the high temperature ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectra and corresponding chemical shift values. At temperatures reaching $100{ }^{\circ} \mathrm{C}$ this complex forms a new doublet, presumably a rhodium hydrido species based on the appearance of a hydride peak in the ${ }^{1} \mathrm{H}$ NMR spectra. Upon cooling back to room temperature three new signals, apparently doublets are observed which have not been characterized. The data for the major product supports equivalent phosphines at elevated temperatures, indicating free rotation of the unbound pyrazolyl ring and restricted rotation at lower temperatures as the phosphines become inequivalent. Thus the two species could be forms $\mathbf{A}$ and $\mathbf{B}$. Alternatively, the initial product could have partially isomerized by a 1,2 -borotropic shift; however, other data are needed to determine the identities of the products. The IR spectrum shows a single stretching B-H frequency at $2463 \mathrm{~cm}^{-1}$, indicating $\mathrm{K}^{2}$-coordination.


Figure 2.7. High temperature ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectra for complex 7 observed in $d_{8}$-toluene at 162 MHz

Table 2.7. High temperature ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectroscopic data for complex 7

| Temperature | ${ }^{31} \mathrm{P}\left\{{ }^{\text {[ }} \mathrm{H}\right\}$ NMR Chemical Shifts |
| :---: | :---: |
| 298 K before heating | MIN $\delta$ 49.29-47.99 (m); MAJ $\delta$ 45.85-40.09 (m) |
| 318 K | MIN $\delta 48.60\left(\mathrm{~d}, J_{\mathrm{Rh}-\mathrm{P}}=185 \mathrm{~Hz}\right)$; MAJ $\delta 43.44-41.44(\mathrm{~m})$ |
| 338 K | MIN $\delta 48.49\left(\mathrm{~d}, J_{\mathrm{Rh}-\mathrm{P}}=180 \mathrm{~Hz}\right)$; MAJ $\delta 42.37\left(\mathrm{~d}, J_{\mathrm{Rh}-\mathrm{P}}=178\right)$ |
| 358 K | NEW $\delta 58.06(\operatorname{app} \mathrm{~d}, J=149 \mathrm{~Hz}) ; \mathrm{MIN} \delta 48.40\left(\mathrm{~d}, J_{\mathrm{Rh}-\mathrm{P}}=181 \mathrm{~Hz}\right)$; MAJ $\delta 42.40$ (d, $J_{\text {Rh-P }}=180$ ); $\delta-1.46$ (s) |
| 373 K | NEW $\delta 57.96(\operatorname{app~d}, J=151 \mathrm{~Hz}) ;$ MIN $\delta 48.33\left(\mathrm{~d}, J_{\mathrm{Rh}-\mathrm{P}}=180 \mathrm{~Hz}\right)$; MAJ $\delta 42.40\left(\mathrm{~d}, J_{\text {Rh-P }}=178\right) ; \delta-1.13$ ( s$)$ |
| 298 K after heating | NEW $\delta 58.48(\operatorname{app~d}, J=149 \mathrm{~Hz})$; NEW $\delta 44.78(\operatorname{app~d}, J=205 \mathrm{~Hz})$; NEW $\delta 40.81$ (app d, $J=120 \mathrm{~Hz}$ ); MIN $\delta 48.55\left(\mathrm{~d}, J_{\mathrm{Rh}-\mathrm{P}}=183 \mathrm{~Hz}\right.$ ); MAJ $\delta 45.84-39.40(\mathrm{~m}) ; \delta-2.70(\mathrm{~s})$ |

The molecular structure of complex 7 (Figure 2.8) shows an approximate square planar geometry with the sum of the angles around rhodium equal to $360.26^{\circ}$. The tris(pyrazolyl)borate ligand is bound $\kappa^{2}$ with the unbound pyrazolyl above the rhodium atom in form B. The six membered chelate ring with boron and rhodium has a boat conformation. The Rh1-N1 [2.100(2) $\AA$ ], Rh1-N4 [2.140(2) $\AA$ ], Rh1-P1 [2.2683(7) $\AA$ ] and Rh1-P2 [2.2572(7) $\AA$ ] bond lengths are all within those previously reported (Table 2.8). The angle between the phosphines is larger then that between the nitrogen atoms; as with complexes 2, 4, 5 and $\mathbf{6}$, this is attributed to the repulsion between the large triphenylphosphine ligands. Crystallographic data for complex 7 is given in Appendix V.


Figure 2.8. ORTEP diagram of complex 7. Thermal ellipsoids are drawn at the $50 \%$ probability level. Hydrogen atoms, except for the B-H hydrogen, and phenyl groups of $\mathrm{PPh}_{3}$ are excluded for clarity. Selected bond lengths $(\AA)$ and angles $\left({ }^{\circ}\right)$ are given in Table 2-6.

Table 2.8. Selected bond distances and angles of complex 7

| Atoms | Bond Distances $(\AA)$ or Angles $\left(^{\circ}\right)$ |
| :--- | :--- |
| Rh1-N1 | $2.100(2)$ |
| Rh1-N4 | $2.140(2)$ |
| Rh1-P1 | $2.2683(7)$ |
| Rh1-P2 | $2.2572(7)$ |
| N1-Rh1-N4 | $77.49(8)$ |
| P1-Rh1-P2 | $94.15(3)$ |
| N1-Rh1-P1 | $173.25(6)$ |
| N1-Rh1-P2 | $92.42(6)$ |
| N4-Rh1-P1 | $96.18(6)$ |
| N4-Rh1-P2 | $167.66(6)$ |

### 2.2.3 Summary of Spectroscopic Data for Complexes 1-7

${ }^{1} \mathrm{H},{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR and IR spectroscopic data for complexes 1-7 are summarized in Table 2.9. NMR spectroscopic data are given for room temperature and $-85{ }^{\circ} \mathrm{C}$ in $\mathrm{CD}_{2} \mathrm{Cl}_{2}$. The IR spectra were taken at room temperature using KBr pellet. The IR spectra for complexes 1-7 have stretching frequencies within the normal range for $\kappa^{2}$ coordination. Also, the coupling constants are typical of rhodium-phosphorous and phosphorous-phosphorous coupling.

Table 2.9. ${ }^{1} \mathrm{H},{ }^{31} \mathrm{P}\left\{{ }^{\prime} \mathrm{H}\right\}$ NMR and IR spectroscopic data for rodium pyrazolylborate complexes ${ }^{\text {a }}$

| Complex | ${ }^{1} \mathrm{H}$ NMR | ${ }^{31} \mathrm{P}\{\mathrm{H}\}$ NMR | $\begin{aligned} & \mathrm{IR} / \mathrm{cm}^{-1} \\ & \mathrm{v}(\mathrm{BH})^{\mathrm{b}} \end{aligned}$ |
| :---: | :---: | :---: | :---: |
| $\mathrm{Tp}{ }^{*} \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}, \mathbf{1}$ |  |  |  |
| $25^{\circ} \mathrm{C}$ | $\begin{aligned} & 7.6-6.9\left(\mathrm{~m}, 30 \mathrm{H}, \mathrm{PPh}_{3}\right), 5.81(\mathrm{~s}, 1 \mathrm{H}, \mathrm{pz} \mathrm{H}), \\ & 5.27(\mathrm{~s}, 2 \mathrm{H}, \mathrm{pz} \mathrm{H}), 2.35(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH} 3), 2.27(\mathrm{~s}, \\ & \left.6 \mathrm{H}, \mathrm{CH}_{3}\right), 2.26\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}\right), 1.79(\mathrm{~s}, 6 \mathrm{H}, \\ & \left.\mathrm{CH}_{3}\right) \end{aligned}$ | $\begin{aligned} & 43.78\left(\mathrm{~d}, J_{\mathrm{Rh}-\mathrm{P}}=175\right. \\ & \mathrm{Hz}) \end{aligned}$ | 2447 |
| $-85^{\circ} \mathrm{C}$ | $\begin{aligned} & 7.7-6.7\left(\mathrm{~m}, 30 \mathrm{H}, \mathrm{PPh}_{3}\right), 5.80(\mathrm{~s}, 1 \mathrm{H}, \mathrm{pz} \mathrm{H}), \\ & 5.24(\mathrm{br} \mathrm{~s}, 2 \mathrm{H}, \mathrm{pz} \mathrm{H}), 4.35(\mathrm{brs}, 1 \mathrm{H}, \mathrm{BH}), \\ & 2.51\left(\mathrm{br} \mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}\right), 2.28\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{CH}_{3}\right), 2.22 \\ & \text { (br s, } \left.6 \mathrm{H}, \mathrm{CH}_{3}\right), 1.39\left(\mathrm{brss}, 3 \mathrm{H}, \mathrm{CH}_{3}\right) \\ & \hline \end{aligned}$ | $\begin{aligned} & 44.17\left(\mathrm{~d}, J_{\mathrm{Rh} h \mathrm{P}}=186\right. \\ & \mathrm{Hz}), 41.22\left(\mathrm{~d}, J_{\mathrm{Rh}-\mathrm{P}}=\right. \\ & 185 \mathrm{~Hz}) \end{aligned}$ |  |
| $\mathrm{Bp} * \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}, 2$ |  |  |  |
| $25^{\circ} \mathrm{C}$ | 7.74-7.73 (m, $6 \mathrm{H}, \mathrm{PPh}_{3}$ ), 7.10-6.85 (m, 24H, $\mathrm{PPh}_{3}$ ), $5.1(\mathrm{~s}, 2 \mathrm{H}, \mathrm{pz} \mathrm{H}), 2.35\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{CH}_{3}\right)$, $1.83\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{CH}_{3}\right)$ | $\begin{aligned} & 47.22\left(\mathrm{~d}, J_{\mathrm{Rh}-\mathrm{P}}=178\right. \\ & \mathrm{Hz}) \end{aligned}$ | $\begin{aligned} & 2449 \\ & 2378 \end{aligned}$ |
| $\mathrm{BpRh}\left(\mathrm{PPh}_{3}\right)_{2}, 3$ |  |  |  |
| $25^{\circ} \mathrm{C}$ | 7.61-7.50 (m, 12H, $\mathrm{PPh}_{3}$ ), 7.37 ( $\mathrm{s}, 2 \mathrm{H}, \mathrm{pz} \mathrm{H}$ ), 7.22-7.15 (m, 6H, $\mathrm{PPh}_{3}$ ), 7.10-7.00 (m, 12H, $\mathrm{PPh}_{3}$ ), $6.31(\mathrm{~s}, 2 \mathrm{H}, \mathrm{pz} \mathrm{H}), 5.53(\mathrm{~s}, 2 \mathrm{H}, \mathrm{pz} \mathrm{H})$ | $\begin{aligned} & 53.91\left(\mathrm{~d}, J_{\mathrm{Rh}-\mathrm{P}}=177\right. \\ & \mathrm{Hz}) \end{aligned}$ | - |
| $\mathrm{TpRh}\left(\mathrm{PPh}_{3}\right)_{2}, 4$ |  |  |  |
| $25^{\circ} \mathrm{C}$ | $\begin{aligned} & 8.06(\mathrm{~s}, 2 \mathrm{H}, \mathrm{pz} \mathrm{H}), 7.7-7.0\left(\mathrm{~m}, 30 \mathrm{H}, \mathrm{PPh}_{3}\right), \\ & 6.90(\mathrm{~s}, 2 \mathrm{H}, \mathrm{pz} \mathrm{H}), 6.44(\mathrm{~s}, 1 \mathrm{H}, \mathrm{pz} \mathrm{H}), 6.14(\mathrm{~s}, \\ & 2 \mathrm{H}, \mathrm{pz} \mathrm{H}), 5.97(\mathrm{~s}, 1 \mathrm{H}, \mathrm{pz} \mathrm{H}), 5.80(\mathrm{~s}, 1 \mathrm{H}, \\ & \mathrm{BH}) \end{aligned}$ | $\begin{aligned} & 53.11\left(\mathrm{~d}, J_{\mathrm{Rh}-\mathrm{P}}=173\right. \\ & \mathrm{Hz}) \end{aligned}$ | 2392 |
| $-85^{\circ} \mathrm{C}$ | $\mathrm{ND}^{\text {c }}$ | $\begin{aligned} & 53.39\left(\mathrm{~d}, J_{\mathrm{Rh} h \mathrm{P}}=173\right. \\ & \mathrm{Hz}), 51.63\left(\mathrm{~d}, J_{\mathrm{Rh}-\mathrm{P}}=\right. \\ & 172 \mathrm{~Hz}), 49.16(\mathrm{~d}, \\ & \left.J_{\mathrm{Rl}-\mathrm{P}}=172 \mathrm{~Hz}\right) \end{aligned}$ |  |
| $\mathrm{Tp}^{\mathrm{Me}} \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}, 5^{\text {c }}$ |  |  |  |
|  | Major: 7.63 (br s, 2H, pz H), 7.5-6.9 (m, 30H, $\mathrm{PPh}_{3}$ ), 6.49 (s, 1H, pz H), 5.90 (s, 2H, pz H), $5.37(\mathrm{~s}, 1 \mathrm{H}, \mathrm{pz} \mathrm{H}), 2.30\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}\right), 2.15(\mathrm{~s}$, $6 \mathrm{H}, \mathrm{CH}_{3}$ ) | $\begin{aligned} & 50.82\left(\mathrm{dd}, J_{\mathrm{Rh}-\mathrm{P}}=182\right. \\ & \left.\mathrm{Hz}, J_{\mathrm{P} \cdot \mathrm{P}}=54 \mathrm{~Hz}\right), \\ & 48.19\left(\mathrm{dd}, J_{\mathrm{Rh} . \mathrm{P}}=\right. \\ & 172 \mathrm{~Hz}, J_{\mathrm{P}-\mathrm{P}}=54 \\ & \mathrm{~Hz}) \end{aligned}$ | 2429 |
|  | Minor: 8.07 (s, 2H, pz H), 7.5-6.9 (m, 30H, $\mathrm{PPh}_{3}$ ), 6.03 (s, 1H, pz H), 5.83 ( $\mathrm{s}, 2 \mathrm{H}, \mathrm{pz} \mathrm{H}$ ), 5.14 (s, 1H, pz H), $2.20\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{CH}_{3}\right), 1.43$ (s, $3 \mathrm{H}, \mathrm{CH}_{3}$ ) | $\begin{aligned} & 54.21\left(\mathrm{dd}, J_{\mathrm{Rh} \cdot \mathrm{P}}=185\right. \\ & \left.\mathrm{Hz}, J_{\mathrm{P} \cdot \mathrm{P}}=52 \mathrm{~Hz}\right), \\ & 50.70\left(\mathrm{dd}, J_{\mathrm{Rh} \cdot \mathrm{P}^{\prime}}=\right. \\ & 172 \mathrm{~Hz}, J_{\mathrm{P} \cdot \mathrm{P}}=52 \\ & \mathrm{~Hz}) \end{aligned}$ |  |
| $-85^{\circ} \mathrm{C}$ | Major: $\mathrm{ND}^{\text {d }}$ | $\begin{aligned} & 49.93\left(\mathrm{dd}, J_{\mathrm{Rh}-\mathrm{P}}=178\right. \\ & \left.\mathrm{Hz}, J_{\mathrm{P}-\mathrm{P}}=53 \mathrm{~Hz}\right), \\ & 47.66\left(\mathrm{dd}, J_{\mathrm{Rh}-\mathrm{P}},\right. \\ & 175 \mathrm{~Hz}, J_{\mathrm{P}-\mathrm{P}},=53 \\ & \mathrm{~Hz}) \end{aligned}$ |  |

Table 2.9. ${ }^{1} \mathrm{H},{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR and IR spectroscopic data...continued

|  | Minor: $\mathrm{ND}^{\text {d }}$ | $\begin{aligned} & 53.80\left(\mathrm{dd}, J_{\mathrm{Rh}-\mathrm{p}}=182\right. \\ & \left.\mathrm{Hz}, J_{\mathrm{P}-\mathrm{P}}=54 \mathrm{~Hz}\right), \\ & 50.81\left(\mathrm{dd}, J_{\mathrm{Rh}-\mathrm{P}^{\prime}}=\right. \\ & 170 \mathrm{~Hz}, J_{\mathrm{P}-\mathrm{P}}=52 \\ & \mathrm{~Hz}) \end{aligned}$ |  |
| :---: | :---: | :---: | :---: |
| $\mathrm{Tp}^{\mathrm{Ph}} \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}, 6$ |  |  |  |
| $25^{\circ} \mathrm{C}$ | $\begin{aligned} & 8.26(\mathrm{~s}, 1 \mathrm{H}, \mathrm{pzH}), 7.97\left(\mathrm{~m}, \mathrm{pz} \mathrm{C}_{6} \mathrm{H}_{5}\right), 7.43(\mathrm{~s}, \\ & 2 \mathrm{H}, \mathrm{pz} \mathrm{H}), 7.4-6.9\left(\mathrm{~m}, 45 \mathrm{H}, \mathrm{PPh}_{3}+\mathrm{pz} \mathrm{C}_{6} \mathrm{H}_{5}\right) \\ & 6.83(\mathrm{~s}, 1 \mathrm{H}, \mathrm{pzH}), 5.75(\mathrm{~s}, 2 \mathrm{H}, \mathrm{pzH} \mathrm{H}) \end{aligned}$ | $\begin{aligned} & 46.89\left(\mathrm{~d}, J_{\mathrm{Rh}-\mathrm{P}}=178\right. \\ & \mathrm{Hz}) \end{aligned}$ | 2426 |
| $-85^{\circ} \mathrm{C}$ | $\begin{aligned} & 8.25(\mathrm{~s}, 1 \mathrm{H}, \mathrm{pz} \mathrm{H}), 7.91\left(\mathrm{~m}, \mathrm{pz} \mathrm{C}_{6} \mathrm{H}_{5}\right), 7.37(\mathrm{~s}, \\ & 2 \mathrm{H}, \mathrm{pz} \mathrm{H}), 7.4-6.9\left(\mathrm{~m}, 45 \mathrm{H}, \mathrm{PPh}_{3}+\mathrm{pz} \mathrm{C}_{6} \mathrm{H}_{5}\right), \\ & 6.81(\mathrm{~s}, 1 \mathrm{H}, \mathrm{pz} \mathrm{H}), 5.73(\mathrm{~s}, 2 \mathrm{H}, \mathrm{pz} \mathrm{H}) \end{aligned}$ | $\begin{aligned} & 46.69\left(\mathrm{~d}, J_{\text {Rht }-\mathrm{P}}=176\right. \\ & \mathrm{Hz}) \end{aligned}$ |  |
| $\mathrm{Tp}{ }^{\text {Ph,Me }} \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}, 7$ |  |  |  |
| $25^{\circ} \mathrm{C}$ | $8.27\left(\mathrm{~d}, J=8.8 \mathrm{~Hz}, 4 \mathrm{H}, \mathrm{pz} \mathrm{C}_{6} \mathrm{H}_{5}\right), 7.77(\mathrm{~d}, J=$ $\left.7.3 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{pz} \mathrm{C} \mathrm{C}_{5}\right), 7.6-6.8\left(\mathrm{~m}, 45 \mathrm{H}, \mathrm{PPh}_{3}+\right.$ pz $\mathrm{C}_{6} \mathrm{H}_{5}$ ), $6.40(\mathrm{~s}, 1 \mathrm{H}, \mathrm{pz} \mathrm{H}), 6.36(\mathrm{~s}, 2 \mathrm{H}, \mathrm{pz}$ H), $5.81(\mathrm{~s}, 1 \mathrm{H}, \mathrm{BH}), 2.51\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{CH}_{3}\right), 2.14$ ( $\mathrm{s}, 3 \mathrm{H}, \mathrm{CH}_{3}$ ) | $\begin{aligned} & 48.12\left(\mathrm{~d}, J_{\text {Rh-p }}=182\right. \\ & \mathrm{Hz}), 43.44-39.33(\mathrm{~m}) \end{aligned}$ | 2463 |
| $-85^{\circ} \mathrm{C}$ | $8.24\left(\mathrm{~d}, J=7.3 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{pz} \mathrm{C} \mathrm{C}_{6} \mathrm{H}_{5}\right), 7.76(\mathrm{~d}, J=$ $\left.7.3 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{pz} \mathrm{C} \mathrm{C}_{5}\right), 7.6-6.8\left(\mathrm{~m}, 45 \mathrm{H}, \mathrm{PPh}_{3}+\right.$ $\left.\mathrm{pz} \mathrm{C} \mathrm{C}_{6} \mathrm{H}_{5}\right), 6.38(\mathrm{~s}, 1 \mathrm{H}, \mathrm{pzH}), 6.03(\mathrm{~s}, 1 \mathrm{H}, \mathrm{pz}$ $\mathrm{H}), 5.74(\mathrm{~s}, 1 \mathrm{H}, \mathrm{BH}), 5.58(\mathrm{~s}, 1 \mathrm{H}, \mathrm{pz} \mathrm{H}), 2.47$ $\left(\mathrm{s}, 3 \mathrm{H}, \mathrm{CH}_{3}\right), 2.46\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}\right), 2.04(\mathrm{~s}, 3 \mathrm{H}$, $\mathrm{CH}_{3}$ ) | $\begin{aligned} & 42.60\left(\mathrm{dd}, J_{\mathrm{Rh}-\mathrm{P}}=178\right. \\ & \left.\mathrm{Hz}, J_{\mathrm{P}-\mathrm{P}}=50 \mathrm{~Hz}\right) \\ & 39.42\left(\mathrm{dd}, J_{\mathrm{Rh}-\mathrm{P}}=\right. \\ & 172 \mathrm{~Hz}, J_{\mathrm{P}-\mathrm{P}}=51 \\ & \mathrm{~Hz}) \end{aligned}$ |  |

### 2.3 Conclusions

Three new rhodium pyrazolylborate complexes (5*-7) and four known complexes (1-4) have been synthesized using modified literature procedures. The syntheses of known complexes 1-4 were carried out with better yields then previously reported. ${ }^{12 a, f, 13 a, 16}$ All complexes were characterized by ${ }^{1} \mathrm{H},{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR and IR spectroscopy. Complexes 2, 4 and $5 *-7$ have also been characterized by X-ray crystallography. All the X-ray structures show approximate square planar geometry. The
ease of synthesis and opportunity to examine rhodium pyrazolylborate complexes with different substituents and differing numbers of pyrazolyl rings has made these complexes interesting to study. Chapter 3 examines the alkyne hydrothiolation activity of these complexes and whether electronics and/or denticity affects their catalytic activity.

### 2.4 Experimental Procedures

### 2.4.1 General Methods

Manipulation of inorganic compounds was performed in a nitrogen-filled MBraun glovebox $\left(\mathrm{O}_{2}<2 \mathrm{ppm}\right)$. NMR spectra were recorded on Bruker Avance 300 or Bruker Avance 400 spectrometers. ${ }^{1} \mathrm{H}$ and ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectra are reported in parts per million and were referenced to residual solvent. Coupling constant values were extracted assuming first-order coupling. The multiplicities are abbreviated as follows: $\mathrm{s}=$ singlet, d $=$ doublet, $\operatorname{app} \mathrm{d}=$ apparent doublet, $\mathrm{q}=$ quartet, $\mathrm{m}=$ multiplet, $\mathrm{dd}=$ doublet of doublets. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectra were referenced to an external $85 \% \mathrm{H}_{3} \mathrm{PO}_{4}$ standard. All spectra were obtained at $25^{\circ} \mathrm{C}$, unless otherwise stated. GC spectra were recorded on a Varian CP-3800 or an HP 5890 Series II gas chromatograph. Mass spectra were recorded on a Kratos MS-50 mass spectrometer. MALDI specta were recorded on a Bruker biflex IV mass spectrometer.

### 2.4.2 Materials and Methods

Pentane, hexanes, 1,2-dichloroethane (DCE), THF and toluene were dried by passage through solvent purification columns. ${ }^{51} \mathrm{CD}_{2} \mathrm{Cl}_{2}$ and $d_{8}$-toluene were purchased in

1 g ampules and used without further purification. Wilkinson's catalyst [ $\mathrm{ClRh}\left(\mathrm{PPh}_{3}\right)_{3}$ ], $\mathrm{KBp}, \mathrm{KTp}$ and KTp * were purchased from Strem Chemicals. $\mathrm{KTp}^{\mathrm{Ph}}$ and $\mathrm{KTp}^{\mathrm{Ph}, \mathrm{Me}}$ were purchased from Acros. 3-Methylpyrazole was purchased from Lancaster. 3,5dimethypyrazole was purchased from Aldrich. $\mathrm{KBH}_{4}$ was purchased from Aldrich. All commercial reagents were used without further purification.

### 2.4.3 Synthesis of Potassium Pyrazolylborate Salts

Synthesis of KBp*. In a fumehood, 3,5-dimethylpyrazole ( $14.26 \mathrm{~g}, 148 \mathrm{mmol}$ ) was added to a 100 mL Schlenk flask, equipped with a Teflon-coated magnetic stir bar. The flask was fitted with a glass stopper and was heated to $120^{\circ} \mathrm{C}$ to melt the pyrazole ( $\mathrm{mp}=$ $\left.106-109^{\circ} \mathrm{C}\right) . \mathrm{KBH}_{4}(2.02 \mathrm{~g}, 37 \mathrm{mmol})$ was crushed with a pestle and mortar and added to the flask by spatula in small portions. The flask was then put under a flow of nitrogen and the resulting mixture was heated to $140^{\circ} \mathrm{C}$. After 20 hours, the mixture had turned into a solid white mass. Toluene ( 20 mL ) was added and the resulting slurry was filtered through a Buchner funnel and was washed with $2 \times 20 \mathrm{~mL}$ of warm $\left(60^{\circ} \mathrm{C}\right)$ toluene. The remaining white solid was dried under vacuum and then 2 mL of benzene was added. This solution was frozen and the solvent removed in vacuo to yield a fluffy white powder. To remove excess $\mathrm{KBH}_{4}$, the white powder was dissolved in acetone and filtered. The remaining solid was dried under vacuum. Excess 3,5-dimethylpyrazole was then removed by sublimation. The ${ }^{1} \mathrm{H}$ NMR spectrum showed compound $\mathbf{8}$ along with some unidentified byproduct, which was not able to be removed. ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CD}_{3} \mathrm{CN}, 300\right.$ $\mathrm{MHz})$ at $25^{\circ} \mathrm{C}$ : [Major] $5.53(\mathrm{~s}, 2 \mathrm{H}, \mathrm{pz} \mathrm{H}), 2.21\left(\mathrm{~s}, \mathrm{CH}_{3}\right), 2.08\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{CH}_{3}\right) ;$ [Minor] 5.60 $(\mathrm{s}, 0.70 \mathrm{H}), 2.21(\mathrm{~s}), 2.08(\mathrm{~s}, 2.1 \mathrm{H})$.

Synthesis of KTp ${ }^{\text {Me }}$. In a fumehood, $\mathrm{KBH}_{4}(1.0 \mathrm{~g}, 19 \mathrm{mmol})$, that had been crushed with a pestle and mortar, was added to a 50 mL double neck round bottom equipped with a Teflon-coated magnetic stir bar. 3-Methylpyrazole ( $4.9 \mathrm{~mL}, 61 \mathrm{mmol}$ ) was added in one portion via syringe. The flask was then put under a flow of nitrogen and the resulting mixture was heated to $190^{\circ} \mathrm{C}$. After 9 hours, the clear solution was cooled to room temperature and became a solid white mass. Benzene ( 10 mL ) was added and the resulting slurry was filtered through a Buchner funnel and was washed with $4 \times 20 \mathrm{~mL}$ of benzene, followed by 20 mL petroleum ether. The remaining white solid was dried under vacuum. The ${ }^{1} \mathrm{H}$ NMR spectrum showed the presence of 3-methylpyazole. To remove the excess pyrazolyl sublimation was attempted; however this was unsuccessful and the white solid mixture was used without further purification. The ratio of compound 9 to 3methylpyrazole was $13: 1 .{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CD}_{3} \mathrm{CN}, 300 \mathrm{MHz}\right)$ at $25^{\circ} \mathrm{C}$ : [Major] $7.40(\mathrm{~s}, 3 \mathrm{H}, \mathrm{pz}$ H), 5.81 (s, 3H, pz H), 2.19 (s, 9H, CH3 ); [Minor] $7.26(\mathrm{~s}, 0.24 \mathrm{H}, \mathrm{pz} \mathrm{H}), 6.01(\mathrm{~s}, 0.24 \mathrm{H}$, $\mathrm{pz} \mathrm{H}), 2.24\left(\mathrm{~s}, \mathrm{CH}_{3}\right)$. The ${ }^{1} \mathrm{H}$ NMR data was consistent with literature data except the literature reported the pyrazole hydrogens as two doublets $(\mathrm{J}=1.9 \mathrm{~Hz}, \mathrm{~J}=1.7 \mathrm{~Hz})$. It is possible the doublets were unresolved in our spectrum. ${ }^{50 b}$

### 2.4.4 Synthesis of Rhodium Pyrazolylborate Complexes

Synthesis of [Tp*Rh(PPh $\left.\mathbf{3}_{2}\right]$ (1). In the glove box, $\mathrm{ClRh}\left(\mathrm{PPh}_{3}\right)_{2}(202 \mathrm{mg}, 0.22 \mathrm{mmol})$ was weighed into a 20 mL vial equipped with a Teflon-coated magnetic stir bar. $\mathrm{KTp}^{*}$ ( $74 \mathrm{mg}, 0.22 \mathrm{mmol}$ ) and THF ( 4 mL ) were then added sequentially. The vial was covered with a plastic cap and the solution was stirred at room temperature. The solution changed color from maroon to orange within ten minutes. After stirring for 1 hour, the volatiles
were removed under reduced pressure. The residue was dissolved in toluene ( 2 mL ) and was layered with hexanes ( 8 mL ). The solution was cooled to $-35^{\circ} \mathrm{C}$; after 7 days orange crystals formed. The solution was decanted and the crystals were washed with hexanes (4 x 5 mL ). The product was dried under reduced pressure to give $187 \mathrm{mg}(92 \%)$ of an orange crystalline solid. Room temperature ${ }^{1} \mathrm{H}$ and ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR data, as well as IR data, were consistent with literature reports. ${ }^{22,28 i}$ Low temperature NMR spectra indicate equivalence of two pyrazoles, whereas Connelly reports the inequivalence of all three pyrazoles (see Results and Discussion section).

Synthesis of $\left[\mathbf{B p} * \mathbf{R h}\left(\mathbf{P P h}_{3}\right)_{2}\right]$ (2). In the glove box, $\mathrm{ClRh}\left(\mathrm{PPh}_{3}\right)_{2}(103 \mathrm{mg}, 0.11 \mathrm{mmol})$ was weighed into a 20 mL vial equipped with a Teflon-coated magnetic stir bar. $\mathrm{KBp}^{*}$ ( $39 \mathrm{mg}, 0.16 \mathrm{mmol}$ ) and THF ( 2 mL ) were then added sequentially. The vial was covered with a plastic cap and the solution was stirred at room temperature. The solution changed color from maroon to orange within ten minutes. After stirring for 24 hours, the volatiles were removed under reduced pressure. The residue was dissolved in toluene ( 2 mL ) and was layered with hexanes ( 8 mL ). The solution was cooled to $-35^{\circ} \mathrm{C}$; after 7 days orange crystals formed. The solution was decanted and the crystals were washed with hexanes ( $4 \times 5 \mathrm{~mL}$ ). The product was dried under reduced pressure to give $80 \mathrm{mg}(87 \%)$ of an orange crystalline solid. ${ }^{1} \mathrm{H}$ and ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR data, as well as IR data, were consistent with literature values. ${ }^{28 b}$

Synthesis of [ $\left.\mathbf{B p R h}\left(\mathbf{P P h}_{3}\right)_{2}\right]$ (3). In the glove box, $\mathrm{ClRh}\left(\mathrm{PPh}_{3}\right)_{2}(204 \mathrm{mg}, 0.22 \mathrm{mmol})$ was weighed into a 20 mL vial equipped with a Teflon-coated magnetic stir bar. KBp ( $44 \mathrm{mg}, 0.24 \mathrm{mmol}$ ) and THF ( 6 mL ) were then added sequentially. The vial was covered with a plastic cap and the solution was stirred at room temperature. The solution changed
color from maroon to orange within ten minutes. After stirring for 24 hours, the volatiles were removed under reduced pressure. The residue was dissolved in toluene ( 4 mL ) and was layered with hexanes $(4 \mathrm{~mL})$. The solution was left in the glovebox and after 15 days orange crystals formed. The solution was decanted and the crystals were washed with hexanes ( $4 \times 5 \mathrm{~mL}$ ).. The product was dried under reduced pressure to give 147 mg ( $86 \%$ ) of an orange crystalline solid. ${ }^{1} \mathrm{H}$ and ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR data were consistent with literature values. ${ }^{28 b}$

Synthesis of $\left[\mathbf{T p R h}\left(\mathbf{P P h}_{3}\right)_{2}\right]$ (4). In the glove box, $\mathrm{ClRh}\left(\mathrm{PPh}_{3}\right)_{2}(200 \mathrm{mg}, 0.22 \mathrm{mmol})$ was weighed into a 20 mL vial equipped with a Teflon-coated magnetic stir bar. KTp (80 $\mathrm{mg}, 0.32 \mathrm{mmol}$ ) and THF ( 3 mL ) were then added sequentially. The vial was covered with a plastic cap and the solution was stirred at room temperature. The solution changed color from maroon to orange within ten minutes. After stirring for 24 hours, the volatiles were removed under reduced pressure. The residue was dissolved in toluene ( 2 mL ) and was layered with hexanes ( 8 mL ). The solution was cooled to $-35^{\circ} \mathrm{C}$; after 12 days orange crystals formed. The solution was decanted and the crystals were washed with hexanes $(4 \times 5 \mathrm{~mL}$ ). The product was dried under reduced pressure to give $155 \mathrm{mg}(86 \%)$ of an orange crystalline solid. ${ }^{1} \mathrm{H}$ and ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR data, as well as IR data, are tabulated in Table 2.9. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR data, as well as IR data, were consistent with literature values. ${ }^{22,28 c}$ Although the ${ }^{1} H$ NMR data was consistent with Connelly's data, our data and Connelly's data were both inconsistent with Hill's data (see Results and Discussion section).

Synthesis of $\left[\mathbf{T p}{ }^{\mathbf{M e}} \mathbf{R h}\left(\mathbf{P P h}_{3}\right)_{2}\right]$ (5 and 5*). In the glove box, $\operatorname{ClRh}\left(\mathrm{PPh}_{3}\right)_{2}(101 \mathrm{mg}$, 0.11 mmol ) was weighed into a 20 mL vial equipped with a Teflon-coated magnetic stir bar. $\mathrm{KTp}^{\mathrm{Me}}(52 \mathrm{mg}, 0.18 \mathrm{mmol})$ and THF ( 2 mL ) were then added sequentially. The vial was covered with a plastic cap and mixture was stirred at room temperature. The solution changed color from maroon to orange within ten minutes. After stirring for 4 hours, the volatiles were removed under reduced pressure. The residue was dissolved in toluene (2 mL ) and was layered with hexanes ( 8 mL ). The solution was cooled to $-35^{\circ} \mathrm{C}$; after 12 days orange crystals formed. The solution was decanted and the crystals were washed with hexanes ( $4 \times 5 \mathrm{~mL}$ ). The product was dried under reduced pressure to give 56 mg (59\%) of an orange crystalline solid. ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}, 400 \mathrm{MHz}\right)$ at $25^{\circ} \mathrm{C}$ : [Major] 7.63 (br s, 2H, pz H), 7.5-6.9 (m, 30H, $\mathrm{PPh}_{3}$ ), $6.49(\mathrm{~s}, 1 \mathrm{H}, \mathrm{pz} \mathrm{H}), 5.90(\mathrm{~s}, 2 \mathrm{H}, \mathrm{pz} \mathrm{H}), 5.37(\mathrm{~s}$, $1 \mathrm{H}, \mathrm{pz} \mathrm{H}), 2.30\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}\right), 2.15\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{CH}_{3}\right)$; $[$ Minor $] 8.07(\mathrm{~s}, 2 \mathrm{H}, \mathrm{pz} \mathrm{H}), 7.5-6.9(\mathrm{~m}$, $\left.30 \mathrm{H}, \mathrm{PPh}_{3}\right), 6.03(\mathrm{~s}, 1 \mathrm{H}, \mathrm{pz} \mathrm{H}), 5.83(\mathrm{~s}, 2 \mathrm{H}, \mathrm{pz} \mathrm{H}), 5.14(\mathrm{~s}, 1 \mathrm{H}, \mathrm{pz} \mathrm{H}), 2.20\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{CH}_{3}\right)$, $1.43\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}\right) ;{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}, 162 \mathrm{MHz}\right)$ at $25^{\circ} \mathrm{C}:$ [Major] $50.82\left(\mathrm{dd}, J_{\mathrm{Rh}-\mathrm{P}}=\right.$ $\left.182 \mathrm{~Hz}, J_{\mathrm{P}-\mathrm{P}}=54 \mathrm{~Hz}\right), 48.19\left(\mathrm{dd}, J_{\mathrm{Rh}-\mathrm{P}}=172 \mathrm{~Hz}, J_{\mathrm{P}-\mathrm{P}}=54 \mathrm{~Hz}\right)$; [Minor] $54.21\left(\mathrm{dd}, J_{\mathrm{Rh}-\mathrm{P}}\right.$ $\left.=185 \mathrm{~Hz}, J_{\mathrm{P}-\mathrm{P}^{\prime}}=52 \mathrm{~Hz}\right), 50.70\left(\mathrm{dd}, J_{\mathrm{Rh}-\mathrm{P}^{\prime}}=172 \mathrm{~Hz}, J_{\mathrm{P}-\mathrm{P}^{\prime}}=52 \mathrm{~Hz}\right)$; at $-85^{\circ} \mathrm{C}$ : [Major] $49.93\left(\mathrm{dd}, J_{\mathrm{Rh}-\mathrm{P}}=178 \mathrm{~Hz}, J_{\mathrm{P}-\mathrm{P}^{\prime}}=53 \mathrm{~Hz}\right), 47.66\left(\mathrm{dd}, J_{\mathrm{Rh}-\mathrm{P}^{\prime}}=175 \mathrm{~Hz}, J_{\mathrm{P}-\mathrm{P}^{\prime}}=53 \mathrm{~Hz}\right)$; [Minor] $53.80\left(\mathrm{dd}, J_{\mathrm{Rh}-\mathrm{P}}=182 \mathrm{~Hz}, J_{\mathrm{P}-\mathrm{P}}=54 \mathrm{~Hz}\right), 50.81\left(\mathrm{dd}, J_{\mathrm{Rh}-\mathrm{P}^{\prime}}=170 \mathrm{~Hz}, J_{\mathrm{P}-\mathrm{P}}=52\right.$ Hz ). IR ( KBr Pellet) at $25{ }^{\circ} \mathrm{C}: 2429[v(\mathrm{~B}-\mathrm{H})] \mathrm{cm}^{-1}$. LRMS (EI) $\mathrm{m} / \mathrm{z}$ calcd for $\mathrm{C}_{48} \mathrm{H}_{46} \mathrm{BN}_{6} \mathrm{P}_{2} \mathrm{Rh}: \quad 882.24 ; \quad$ found: $\quad 262 \quad\left(\mathrm{PPh}_{3}, \quad \mathrm{C}_{18} \mathrm{H}_{15} \mathrm{P}\right), \quad 620 \quad\left[\mathrm{Tp}^{\mathrm{Me}} \mathrm{Rh}^{2}\left(\mathrm{PPh}_{3}\right)\right.$, $\mathrm{C}_{30} \mathrm{H}_{31} \mathrm{BN}_{6} \mathrm{PRh}$. HRMS (EI) m/z calcd for $\mathrm{Tp}^{\mathrm{Me}} \mathrm{Rh}\left(\mathrm{PPh}_{3}\right), \mathrm{C}_{30} \mathrm{H}_{31} \mathrm{BN}_{6} \mathrm{PRh}: 620.1500$; found: 620.1496. MALDI m/z calcd for $\mathrm{C}_{48} \mathrm{H}_{46} \mathrm{BN}_{6} \mathrm{P}_{2} \mathrm{Rh}$ : 882 ; found: 620,882 .


${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}, 162 \mathrm{MHz}\right)$ spectrum of complexes 5 and $\mathbf{5}^{*}$ at 298 K


[^1]Synthesis of $\left[\mathbf{T p}{ }^{\mathbf{P h}} \mathbf{R h}\left(\mathbf{P P h}_{3}\right)_{2}\right]$ (6). In the glove box, $\mathrm{ClRh}\left(\mathrm{PPh}_{3}\right)_{2}(100 \mathrm{mg}, 0.11 \mathrm{mmol})$ was weighed into a 20 mL vial equipped with a Teflon-coated magnetic stir bar. $\mathrm{KTp}^{\mathrm{Ph}}$ ( $84 \mathrm{mg}, 0.17 \mathrm{mmol}$ ) and THF ( 2 mL ) were then added sequentially. The vial was covered with a plastic cap and the solution was stirred at room temperature. The solution changed color from maroon to orange within ten minutes. After stirring for 24 hours, the volatiles were removed under reduced pressure. The residue was dissolved in toluene ( 2 mL ) and was layered with hexanes ( 8 mL ). The solution was cooled to $-35^{\circ} \mathrm{C}$; after 7 days orange crystals formed. The solution was decanted and the crystals were washed with hexanes (4 x 5 mL ). The product was dried under reduced pressure to give $96 \mathrm{mg}(83 \%)$ of an orange crystalline solid. ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}, 400 \mathrm{MHz}\right)$ at $25^{\circ} \mathrm{C}: 8.26(\mathrm{~s}, 1 \mathrm{H}, \mathrm{pz} \mathrm{H}), 7.97(\mathrm{~m}, \mathrm{pz}$ $\left.\mathrm{C}_{6} \mathrm{H}_{5}\right), 7.43(\mathrm{~s}, 2 \mathrm{H}, \mathrm{pz} \mathrm{H}), 7.4-6.9\left(\mathrm{~m}, 45 \mathrm{H}, \mathrm{PPh}_{3}+\mathrm{pz} \mathrm{C} \mathrm{C}_{6} \mathrm{H}_{5}\right), 6.83(\mathrm{~s}, 1 \mathrm{H}, \mathrm{pz} \mathrm{H}), 5.75(\mathrm{~s}$, $2 \mathrm{H}, \mathrm{pz} \mathrm{H})$; at $-85^{\circ} \mathrm{C}: 8.25(\mathrm{~s}, 1 \mathrm{H}, \mathrm{pz} \mathrm{H}), 7.91\left(\mathrm{~m}, \mathrm{pz} \mathrm{C} \mathrm{C}_{6} \mathrm{H}_{5}\right), 7.37(\mathrm{~s}, 2 \mathrm{H}, \mathrm{pz} \mathrm{H}), 7.4-6.9$ $\left(\mathrm{m}, 45 \mathrm{H}, \mathrm{PPh}_{3}+\mathrm{pz} \mathrm{C} \mathrm{C}_{6} \mathrm{H}_{5}\right), 6.81(\mathrm{~s}, 1 \mathrm{H}, \mathrm{pz} \mathrm{H}), 5.73(\mathrm{~s}, 2 \mathrm{H}, \mathrm{pz} \mathrm{H}) .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}, 162 \mathrm{MHz}\right)$ at $25^{\circ} \mathrm{C}: 46.89\left(\mathrm{~d}, J_{\mathrm{Rh}-\mathrm{P}}=178 \mathrm{~Hz}\right)$; at $-85^{\circ} \mathrm{C}: 46.69\left(\mathrm{~d}, J_{\mathrm{Rh}-\mathrm{P}}=176\right.$ Hz ). IR (KBr Pellet) at $25{ }^{\circ} \mathrm{C}: 2426[v(\mathrm{~B}-\mathrm{H})] \mathrm{cm}^{-1}$. LRMS (EI) $\mathrm{m} / \mathrm{z}$ calcd for $\mathrm{C}_{63} \mathrm{H}_{52} \mathrm{BN}_{6} \mathrm{P}_{2} \mathrm{Rh}: \quad 1068.29 ;$ found: $262 \quad\left(\mathrm{PPh}_{3}, \quad \mathrm{C}_{18} \mathrm{H}_{15} \mathrm{P}\right), \quad 806 \quad\left[\mathrm{Tp}^{\mathrm{Ph}} \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)\right.$, $\mathrm{C}_{45} \mathrm{H}_{37} \mathrm{BN}_{6} \mathrm{PRh}$. HRMS (EI) m/z calcd for $\mathrm{Tp}^{\mathrm{Ph}} \mathrm{Rh}\left(\mathrm{PPh}_{3}\right), \mathrm{C}_{45} \mathrm{H}_{37} \mathrm{BN}_{6} \mathrm{PRh}: 806.1965$; found: 806.1951. MALDI m/z calcd for $\mathrm{C}_{63} \mathrm{H}_{52} \mathrm{BN}_{6} \mathrm{P}_{2} \mathrm{Rh}$ : 1068; found: 1068.



Synthesis of $\left[\mathbf{T} \mathbf{p}^{\mathbf{P h}, M \mathrm{Ce}} \mathbf{R h}\left(\mathbf{P P h}_{3}\right)_{2}\right]$ (7). In the glove box, $\mathrm{ClRh}\left(\mathrm{PPh}_{3}\right)_{2}(101 \mathrm{mg}, 0.11$ mmol) was weighed into a 20 mL vial equipped with a Teflon-coated magnetic stir bar. $\mathrm{KTp}^{\mathrm{Ph}, \mathrm{Me}}(87 \mathrm{mg}, 0.17 \mathrm{mmol})$ and toluene $(2 \mathrm{~mL})$ were then added sequentially. The vial was covered with a plastic cap and the solution was stirred at room temperature. The solution changed color from maroon to orange within ten minutes. After stirring for 24 hours, the volatiles were removed under reduced pressure. The residue was dissolved in toluene ( 2 mL ) and was layered with hexanes ( 8 mL ). The solution was cooled to $-35^{\circ} \mathrm{C}$; after 7 days orange crystals formed. The solution was decanted and the crystals were washed with hexanes ( $4 \times 5 \mathrm{~mL}$ ).. The product was dried under reduced pressure to give $70 \mathrm{mg}(58 \%)$ of an orange crystalline solid. ${ }^{1} \mathrm{H} \mathrm{NMR}\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}, 400 \mathrm{MHz}\right)$ at $25^{\circ} \mathrm{C}: 8.27$ $\left(\mathrm{d}, J=8.8 \mathrm{~Hz}, 4 \mathrm{H}, \mathrm{pz} \mathrm{C} \mathrm{C}_{6} \mathrm{H}_{5}\right), 7.77\left(\mathrm{~d}, J=7.3 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{pz} \mathrm{C} \mathrm{C}_{5}\right), 7.6-6.8\left(\mathrm{~m}, 45 \mathrm{H}, \mathrm{PPh}_{3}+\right.$ pz C $\mathrm{C}_{6}$ ) , $6.40(\mathrm{~s}, 1 \mathrm{H}, \mathrm{pz} \mathrm{H}), 6.36(\mathrm{~s}, 2 \mathrm{H}, \mathrm{pz} \mathrm{H}), 5.81(\mathrm{~s}, 1 \mathrm{H}, \mathrm{BH}), 2.51\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{CH}_{3}\right), 2.14$ (s, $3 \mathrm{H}, \mathrm{CH}_{3}$ ); at $-85^{\circ} \mathrm{C}: 8.24\left(\mathrm{~d}, J=7.3 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{pz} \mathrm{C} \mathrm{C}_{6} \mathrm{H}_{5}\right), 7.76(\mathrm{~d}, J=7.3 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{pz}$ $\left.\mathrm{C}_{6} \mathrm{H}_{5}\right), 7.6-6.8\left(\mathrm{~m}, 45 \mathrm{H}, \mathrm{PPh}_{3}+\mathrm{pz} \mathrm{C} \mathrm{C}_{6} \mathrm{H}_{5}\right), 6.38(\mathrm{~s}, 1 \mathrm{H}, \mathrm{pz} \mathrm{H}), 6.03(\mathrm{~s}, 1 \mathrm{H}, \mathrm{pz} \mathrm{H}), 5.74(\mathrm{~s}$, $1 \mathrm{H}, \mathrm{BH}), 5.58(\mathrm{~s}, 1 \mathrm{H}, \mathrm{pz} \mathrm{H}), 2.47\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}\right), 2.46\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}\right), 2.04\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}\right)$. ${ }^{31} \mathrm{P}\left\{{ }^{\mathrm{l}} \mathrm{H}\right\} \mathrm{NMR}\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}, 162 \mathrm{MHz}\right)$ at $25^{\circ} \mathrm{C}: 48.12\left(\mathrm{~d}, J_{\mathrm{Rh}-\mathrm{P}}=182 \mathrm{~Hz}\right), 43.44-39.33(\mathrm{~m}) ;$ at $-85^{\circ} \mathrm{C}: 42.60\left(\mathrm{dd}, J_{\mathrm{Rh}-\mathrm{P}}=178 \mathrm{~Hz}, J_{\mathrm{P}-\mathrm{P}}=50 \mathrm{~Hz}\right), 39.42\left(\mathrm{dd}, J_{\mathrm{Rh}-\mathrm{P}}=172 \mathrm{~Hz}, J_{\mathrm{P}-\mathrm{P}}=51\right.$ Hz ). IR (KBr Pellet) at $25{ }^{\circ} \mathrm{C}: 2463[v(\mathrm{~B}-\mathrm{H})] \mathrm{cm}^{-1}$. LRMS (EI) $\mathrm{m} / \mathrm{z}$ calcd for $\mathrm{C}_{66} \mathrm{H}_{58} \mathrm{BN}_{6} \mathrm{P}_{2} \mathrm{Rh}: \quad 1110.33$; found: $262 \quad\left(\mathrm{PPh}_{3}, \mathrm{C}_{18} \mathrm{H}_{15} \mathrm{P}\right), 848 \quad\left[\mathrm{Tp}{ }^{\mathrm{Ph}, \mathrm{Me}} \mathrm{Rh}^{2}\left(\mathrm{PPh}_{3}\right)\right.$, $\left.\mathrm{C}_{48} \mathrm{H}_{43} \mathrm{BN}_{6} \mathrm{PRh}\right]$. HRMS (EI) $\mathrm{m} / \mathrm{z}$ calcd for $\mathrm{Tp}^{\mathrm{Ph}, \mathrm{Me}} \mathrm{Rh}\left(\mathrm{PPh}_{3}\right), \mathrm{C}_{48} \mathrm{H}_{43} \mathrm{BN}_{6} \mathrm{PRh}: 848.2435$; found: 848.2429. MALDI $\mathrm{m} / \mathrm{z}$ calcd for $\mathrm{C}_{66} \mathrm{H}_{58} \mathrm{BN}_{6} \mathrm{P}_{2} \mathrm{Rh}$ : 1110 ; found: 848.6. Elemental Analysis: calcd for $\mathrm{C}_{66} \mathrm{H}_{58} \mathrm{BN}_{6} \mathrm{P}_{2} \mathrm{Rh}$ : $\mathrm{C}, 71.36 ; \mathrm{H}, 5.26 ; \mathrm{N}, 7.57$. Found: $\mathrm{C}, 71.52 ; \mathrm{H}$, 5.42; N, 7.37.

${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}, 400 \mathrm{MHz}\right)$ spectrum of complex 7 at 298 K

${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}, 400 \mathrm{MHz}\right)$ spectrum of complex 7 at 188 K

${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}, 162 \mathrm{MHz}\right)$ spectrum of complex 7 at 298 K

${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}, 162 \mathrm{MHz}\right)$ spectrum of complex 7 at 188 K

### 2.4.5 X-ray Crystal Structures of Complexes 2, 4 and 5*-7.

Crystal intensity collection and refinement details are summarized in Appendices IV. All measurements for complexes 2, 5, $\mathbf{6}$ and 7 were made on a Bruker X8 APEX II diffractometer and all measurements for complex 4 were made on a Bruker X8 APEX diffractometer, both with graphite monochromated $\mathrm{Mo}-\mathrm{K} \alpha$ radiation. Data were collected in a series of $\phi$ and $\omega$ scans and subsequently processed with the Bruker SAINT ${ }^{52}$ software package. Data were corrected for absorption effects using the multi-scan technique (SADABS). ${ }^{53}$ The data were corrected for Lorentz and polarization effects. The structures were solved using direct methods ${ }^{54}$ and refined using SHELXTL. ${ }^{55}$ All non-hydrogen atoms were refined anisotropically, while all hydrogen atoms were placed in calculated positions and not refined, except for B-H hydrogens which were located in difference maps and refined isotropically. For complex 2 the material crystallizes with both toluene and hexane in the lattice. In this case there is a $50: 50$ mixture of toluene and hexane occupying the same space in the asymmetric unit. Mild restraints were employed to maintain reasonable geometries for both solvent molecules. For complex 4 the material crystallizes with toluene in the lattice. For complex 6 the material crystallizes with one disordered molecule of solvent, $\mathrm{C}_{5} \mathrm{H}_{12}$, in the asymmetric unit. This solvent molecule was modeled in two orientations with isotropic thermal parameters. For complex 7 the material crystallizes with disordered hexanes in the lattice. This disordered solvent molecule could not be modeled reasonably, therefore the PLATON/SQUEEZE ${ }^{56}$ program was used to correct the data for any unresolved residual electron density in the lattice. The formula and any subsequent values calculated from it reflect the presence of one
molecule of hexane in the asymmetric unit. Full details for characterization of 2,4 and 5*-7 are presented in Appendices I-V.

# Chapter 3 - Alkyne Hydrothiolation Activity of Rhodium 

## Pyrazolylborate Complexes

### 3.1 Introduction

Alkyne hydrothiolation, as previously discussed, is the reaction of a thiol across an alkyne p bond. The possible products of this reaction include the branched, $E$ - and $Z$ linear vinyl sulfides. However, reports of the internal vinyl sulfides via isomerization as well as bis(arylthio)alkene products have also been reported (see Scheme 3.1). ${ }^{8 \mathrm{~g}, \mathrm{k}}$



Scheme 3.1. Alkyne hydrothiolation

The use of aryl thiols in radical, ${ }^{6 b-d}$ nucleophilic ${ }^{7}$ and metal catalyzed ${ }^{8 b, f-i, k, m-0}$ hydrothiolation is very prevalent throughout the literature. However, the use of alkyl thiols is much more limited. Radical methods have been reported using alkyl thiols to give the $E$ - and $Z$-linear vinyl sulfides. ${ }^{6 e}$ Nucleophilic methods have also been reported giving the $Z$-linear vinyl sulfides. ${ }^{7 \mathrm{~b}}$ Michael addition reactions with aryl and alkyl thiols to give the branched vinyl sulfide product have also been reported (see Scheme 3.2). ${ }^{7 \mathrm{~d}}$

However, because this requires isomerization to the allene or internal alkyne the substrate scope is limited.


Scheme 3.2. Michael addition reactions

Alkyl thiols have been reported as ineffective when used in metal catalyzed hydrothiolation reactions. ${ }^{8 f, g}$ Since alkylthiols have a stronger S-H bond and are less acidic then arylthiols their reactivity in catalytic reactions involving S-H bond breaking is likely lower than arylthiols. We postulated that the highly electron rich pyrazolylborate complexes should be reactive enough to catalyze hydrothiolation reactions with alkylthiols. In 2005, we reported that $\mathrm{Tp} * \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}$ (1) was an effective catalyst for hydrothiolation for both alkyl and arylthiols, favoring the branched product. ${ }^{8 \mathrm{~m}}$ Recently, our group also discovered that Wilkinson's catalyst, although reportedly ineffective with
alkylthiols, ${ }^{1}$ does in fact catalyze the hydrothiolation between alkylthiols and alkynes, favoring the $E$-linear product. ${ }^{80}$. To probe what affects the catalytic activity and regioselectivity seen for complex 1 we decided to explore a range of rhodium pyrazolylborate complexes. This chapter describes studies of the ability of complexes 1-7 to catalyze hydrothiolation reactions using both alkyl and arylthiols. The electronic effects and denticity of each complex will be examined to determine if correlations exist between structure and catalytic ability and regioselectivity.

### 3.2 Results and Discussion

### 3.2.1 Procedure and Optimization of Hydrothiolation Reactions

All hydrothiolation reactions were carried out in a nitrogen-filled Vacuum Atmospheres glovebox ( $\mathrm{O}_{2}<2 \mathrm{ppm}$ ). Each complex (1-7) and 1,3,5-trimethoxybenzene (internal standard) were weighed out and dissolved in the appropriate amount of solvent. Next, 1.1 equivalents of the thiol followed by 1.0 equivalent of the alkyne were added via micropipette. The plastic cap was secured on the vial and it was brought out of the glovebox, covered in foil and stirred at room temperature, unless otherwise stated. Reactions were monitored by removing an aliquot via syringe, concentrating the sample and then taking the ${ }^{1} \mathrm{H}$ NMR spectrum. The yields are based on the olefinic peaks of the product in the ${ }^{1} \mathrm{H}$ NMR spectrum versus the 1,3,5-trimethoxybenzene peaks.

Optimization studies have previously been carried out by our group using $\mathrm{Tp} * \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}$. The best solvent system was found to be a $1: 1$ mixture of $1,2-$ dichloroethane (DCE) and toluene. It has been found that $\mathrm{Tp} * \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}$ decomposes in THF and DCE if left for prolonged times, producing a complex via orthometalation of
one of the phosphine ligands (see Scheme 3.3). ${ }^{28 j}$ The resulting complex was inactive in alkyne hydrothiolation reactions. No decomposition was found to occur when using a 1:1 ratio of DCE:toluene or when short reaction times were employed.


Scheme 3.3. Orthometalation of $\mathrm{Tp} * \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}$

As we were interested in expanding the substrate scope for hydrothiolation reactions, NMR scale reactions were more appropriate for our study to minimize the amount of reagents required. Although we had previously found that a $1: 1$ ratio of DCE:toluene was an ideal solvent, we wanted to be able to use NMR spectroscopy to determine the reaction yields. Therefore, we originally carried out NMR scale reactions in a $1: 1$ deuterated chloroform $\left(\mathrm{CDCl}_{3}\right)$ : $d_{8}$-toluene combination. This combination was found to give lower yields as well as poorer or even reverse regioselectivities as compared to the 1:1 DCE:toluene combination (Table 3.1). To more closely mimic the preparative scale reaction conditions, a $1: 1$ mixture of $\mathrm{CD}_{2} \mathrm{Cl}_{2}: d_{8}$-toluene was used. This combination was found to give better selectivities than using a $1: 1$ mixture of $\mathrm{CDCl}_{3}: d_{8}$ toluene, however, the regioselectivities were not as high as with the $1: 1$ mixture of DCE:toluene (entry 4). Therefore, reactions were carried out using 1:1 DCE:toluene and monitored with ${ }^{1} \mathrm{H}$ NMR spectroscopy by taking aliquots from the original reaction mixture. When using only DCE as a solvent the reactions seemed to produce good
selectivities; however, orthometalation could become a problem and therefore this solvent system was avoided.

Table 3.1 gives some examples of different solvent combinations used in hydrothiolation reactions. Entry 1 shows that complex 1 has lower regioselectivity (2:1 vs. $16: 1$ ) favoring the branched product and a $13 \%$ lower yield when using $1: 1 \mathrm{CDCl}_{3}: d_{8^{-}}$ toluene than with a $1: 1$ ratio of DCE:toluene. Complex 2 (entry 2 ) gave a reverse in regioselectivity and a much poorer yield when using $1: 1 \mathrm{CDCl}_{3}: d_{8}$-toluene as compared to the 1:1 DCE:toluene combination. Complex 3 (entry 3) showed the same trends as both complex 1 and complex 2 with lower yields and selectivities in the $1: 1 \mathrm{CDCl}_{3}: d_{8^{-}}$ toluene solvent system. Lastly, complex 6 (entry 4) showed similar trends with lower yields and selectivities for the $1: 1 \mathrm{CDCl}_{3}: d_{8}$-toluene combination over a $1: 1$ ratio of DCE:toluene. However, when a $1: 1$ ratio of $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ : $d_{8}$-toluene was employed, a comparable yield to the 1:1 DCE:toluene combination was observed with slightly lower selectivity ( $6: 1$ vs. 11:1) favoring the branched product (entry 4). For reactions $<100 \%$ yield, starting material accounted for the remainder of the material. As well, longer reaction times did not seem to significantly increase the yields; this is possibly due to catalyst decomposition, which can be seen in the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum.

Table 3.1. Solvent studies for complexes 1-3 and 6

${ }^{a}$ Reactions conducted with $3 \mathrm{~mol} \%$ catalyst, 1.1 equiv. thiol, 1.0 equiv. alkyne. ${ }^{b}$ Yields based on ${ }^{1} \mathrm{H}$ NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard.

### 3.2.2 Substrate Scope of Hydrothiolation Reactions

A variety of thiols and alkynes were chosen to test the substrate scope of the reaction with the different complexes. These include alkyl and arylthiols, aliphatic, aryl and internal alkynes with a variety of functionalities (see Figure 3.1). The background reactions for the alkyne and thiol combinations (without metal complex) were carried out and found to either give no reaction at all or a reaction that was significantly slower than the catalyzed reaction.
(THIOLS


Figure 3.1. Thiols and alkynes

### 3.2.3 Catalytic Activity of Complexes 1-7 in Alkyne Hydrothiolation Reactions

### 3.2.3-1 $\mathbf{T p} * \mathbf{R h}\left(\mathbf{P P h}_{3}\right)_{2}, \mathbf{1}$

The first complex that was tested for catalytic activity in alkyne hydrothiolation reactions was complex 1. This is a highly electron rich tris(pyrazolyl)borate complex with the potential to bind in a $\kappa^{3}$ configuration during the catalytic cycle. Complex $\mathbf{1}$ has methyl substituents in both the 3- and 5-positions of the pyrazolyl rings. In preliminary studies this complex was found to give good-to-excellent yields (63-93\%) using a series of aliphatic and arylthiols with aliphatic, aryl and internal alkynes. ${ }^{8 \mathrm{~m}}$ Thus, we sought to expand the substrate scope and study its reactivity further. Complex $\mathbf{1}$ was found to give good to excellent yields ( $56 \%$ to $>95 \%$ ), Table 3.2 ; the branched isomer was formed
preferentially in reactions between aliphatic thiols and aryl and aliphatic alkynes (entries 1-7 and 9). All reactions were carried out using $3 \mathrm{~mol} \%$ of catalyst, a 1.1:1 ratio of thiol to alkyne and covered with aluminum foil for precautions relating to radical-promoted hydrothiolation reactions.

Using $3 \mathrm{~mol} \%$ of complex 1, benzylthiol (10) was reacted with phenylacetylene (17) (entry 1). The reaction was monitored by ${ }^{\mathrm{I}} \mathrm{H}$ NMR spectroscopy where the appearance of new peaks in the diagnostic region for olefinic protons indicated formation of the products. Two singlets for the branched isomer (25a) at $\delta 5.51$ and $\delta 5.27$ were observed, as well as two doublets for the $E$-linear isomer (25b) at $\delta 6.77\left(J_{\mathrm{H}-\mathbf{H}^{\prime}}=15.6 \mathrm{~Hz}\right)$ and $\delta$ $6.58\left(J_{\mathrm{H}^{\prime}-\mathrm{H}}=15.5 \mathrm{~Hz}\right)$. After 2 hours at room temperature a $16: 1$ ratio of the branched: $E-$ linear products ( $\mathbf{2 5 a} \mathbf{2 5} \mathbf{2 5}$ ) was observed in a $93 \%$ yield along with an additional $\sim 5 \%$ of an unidentified byproduct. 2,2,2-trifluoroethane thiol (11) reacted with phenylacetylene to give a $3: 1$ ratio of the branched to $E$-linear isomers in a $65 \%$ yield (entry 2 ). In the previous reaction an additional $\sim 5 \%$ of the $E$-linear phenylacetylene dimer and an additional $\sim 5 \%$ of an unidentified byproduct were also observed. The reaction between benzylthiol and ethylpropiolate (22) did not give the branched isomer but instead gave a mixture of $E$ - and Z-linear isomers (entry 9). If left for prolonged reaction times, the alkyl vinyl sulfide 31a isomerized to the internal vinyl sulfide as has previously been reported (entry 7). ${ }^{8 \mathrm{~m}}$ The reaction between benzylthiol and 1-phenyl-1-propyne (24) gave a mixture of isomers in a 1:3.5 ratio and a 70\% yield (entry 11 ).

Complex 1 was found to be an excellent catalyst for hydrothiolation reactions and therefore the factors that affect its catalytic ability and regioselectivity were further investigated. This was done first by examining complexes that had no access to $\mathrm{k}^{3}$ -
coordination to test denticity effects. The complexes chosen for study were $\mathrm{Bp} * \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}$ (2) and $\mathrm{BpRh}\left(\mathrm{PPh}_{3}\right)_{2}$ (3), which both lack access to the $\kappa^{3}$ form.

Table 3.2. Substrate scope of alkyne hydrothiolation catalyzed by complex 1

| $\begin{aligned} & \text { RSH } \\ & 10-16 \end{aligned}$ | $\begin{gathered} \mathrm{R}^{1} \overline{\overline{=}} \\ 17-24 \end{gathered}$ | $\frac{3 \mathrm{~mol} \% \mathrm{Tp}^{*} \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}}{\mathrm{DCE}: \mathrm{PhCH}_{3}(1: 1), \mathrm{rt}}$ | $\begin{gathered} \mathrm{R}_{1}^{1} \\ \mathrm{RS}^{2} \\ = \\ a \end{gathered}$ | $+R_{b}^{1}=$ | $R_{c}^{1}=S R$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Entry | Thiol 1.1 equiv. | Alkyne <br> 1.0 equiv. | Time | Ratio | Yield ${ }^{\text {a }}$ |
| 1 | $\begin{gathered} \mathrm{PhCH}_{2} \mathrm{SH} \\ 10 \end{gathered}$ | $\mathrm{Ph}=$ | 2 h | $\begin{gathered} \text { 25a : 25b } \\ (16: 1) \end{gathered}$ | 93\% ${ }^{\text {b }}$ |
| 2 | $\mathrm{CF}_{3} \mathrm{CH}_{2} \mathrm{SH}$ <br> 11 | $\mathrm{Ph}=$ | 2 h | $\begin{gathered} 26 a: 26 b \\ (3: 1) \end{gathered}$ | 65\% ${ }^{\text {b,c }}$ |
| 3 |  <br> 15 | $\mathrm{Ph} \overline{=}$ <br> 17 | 2 h | 27a | 78\% |
| 4 |  <br> 13 |  | 2 h | 28a | >95\% |
| 5 |  <br> 15 |  <br> 18 | 2 h | 29a | 61\% ${ }^{\text {b }}$ |
| 6 | $\mathrm{PhSH}$ | $\begin{gathered} \mathrm{Ph}= \\ 17 \end{gathered}$ | 2 h | $\begin{gathered} 30 a: 30 b \\ (6: 1) \end{gathered}$ | 84\% dee |
| 7 | $\begin{gathered} \mathrm{PhCH}_{2} \mathrm{SH} \\ 10 \end{gathered}$ | $\begin{aligned} & n-\mathrm{C}_{6} \mathrm{H}_{13}= \\ & 19 \end{aligned}$ | 2 h | 31a | >95\% |
| 8 |  | $\mathrm{Me}_{3} \mathrm{Si}=$ <br> 21 | 2 h | 32a | $74 \%{ }^{\text {b }}$ |
| 9 | $\begin{gathered} \mathrm{PhCH}_{2} \mathrm{SH} \\ 10 \end{gathered}$ |  | 24 h | $\begin{gathered} 33 b: 33 c \\ (2.5: 1) \end{gathered}$ | 59\% ${ }^{\text {f }}$ |
| 10 |  <br> 15 |  <br> 23 | 3 h | 34a | 56\% ${ }^{\text {b }}$ |
| 11 | $\begin{gathered} \mathrm{PhCH}_{2} \mathrm{SH} \\ 10 \end{gathered}$ | $\mathrm{Ph}=\mathrm{CH}_{3}$ | 4 h | $\begin{gathered} 35 a: 35 b \\ (1: 3.5) \end{gathered}$ | 70\% |

${ }^{\text {a }}$ Yields based on ${ }^{1} \mathrm{H}$ NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. ${ }^{\text {b }}$ An additional $\sim 5-10 \%$ of an unidentified byproduct was observed. ${ }^{\text {c }}$ An additional $\sim 5 \%$ of the $E$-linear phenylacetylene dimer was observed. ${ }^{\text {d }}$ This experiment was performed by C . Cao, see ref 8 m . ${ }^{\mathrm{e}}$ Isolated yield. ${ }^{\mathrm{f}}$ Percent conversion with respect to remaining thiol.

### 3.2.3-2 Bis(pyrazolyl)borate Complexes

Preliminary mechanistic investigations using deuterated phenyl acetylene have been carried out by a coworker (Bal Kang). We postulate that the mechanism likely involves a $\mathrm{Rh}(\mathrm{I}) / \mathrm{Rh}(\mathrm{III})$ cycle, implying that $\kappa^{3}$-coordination is involved (see Scheme 3.4). To test this hypothesis, we chose to study bis(pyrazolyl)borate complexes 2 and 3, which cannot adopt $\kappa^{3}$-coordination.


Scheme 3.4. Possible pathway for $\mathrm{Tp} * \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}$-catalyzed hydrothiolation

## a) $\mathbf{B p} * \operatorname{Rh}\left(\mathbf{P P h}_{3}\right)_{2}, \mathbf{2}$

Complex 2 has the same substitution patterns on the pyrazolyl rings as complex $\mathbf{1}$, with methyl groups in both the 3- and 5-positions. However, complex 2 has one less pyrazolyl ring attached to the boron atom and thus cannot adopt $\kappa^{3}$-coordination geometry. The results of the hydrothiolation reactions for complex 2 are shown in Table
3.3. The reaction between benzylthiol and phenylacetylene gave lower selectivity [5:1 branched (25a):E-linear (25b)] and lower yield (55\%) as compared to complex 1 (entry 1). The reaction between 2,2,2-trifluoroethanethiol and phenylacetylene gave no selectivity with only a $32 \%$ conversion and an additional $\sim 5 \%$ of the $E$-linear phenylacetylene dimer was also observed (entry 2). Benzylthiol reacted with tertbutylacetylene (20) and gave solely the branched product with a poor conversion of only $28 \%$ (entry 3). Entries 4 and 5 show the reaction between benzylthiol and 1ethynylcyclohexene (23) in different solvents. This reaction gave moderate selectivity of the branched (37a) to E-linear (37b) isomers (7.5:1) when carried out in only DCE but when using a $\mathrm{CDCl}_{3}: d_{8}$-toluene (1:1) solvent combination, we saw reversal in regioselectivity to a $1: 6.5$ ratio of $\mathbf{3 7 a}: \mathbf{3 7 b}$. Like complex $\mathbf{1}$, complex 2 favored the branched isomer. However, the yields were considerably lower than with complex 1.

Table 3.3. Substrate scope of alkyne hydrothiolation catalyzed by complex 2

| RSH <br> 10-11 | $+\quad \mathrm{R}^{1}=$ | $\frac{3 \mathrm{~mol} \% \mathrm{Bp}^{\star} \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}}{\mathrm{DCE}: \mathrm{PhCH}_{3}(1: 1), \mathrm{rt}}$ |  |  | $\mathrm{SR}+\mathrm{R}_{\underline{1}}^{1} \mathrm{SR}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Entry | Thiol 1.1 equiv. | Alkyne <br> 1.0 equiv. | Time | Ratio | Yield ${ }^{\text {a }}$ Conversion ${ }^{\text {b }}$ |
| 1 | $\begin{gathered} \mathrm{PhCH}_{2} \mathrm{SH} \\ 10 \end{gathered}$ | $\mathrm{Ph}=$ | 2 h | $\begin{gathered} 25 a: 25 b \\ (5: 1) \end{gathered}$ | 55\% ${ }^{\text {a }}$ |
| 2 | $\underset{11}{\mathrm{CF}_{3} \mathrm{CH}_{2} \mathrm{SH}}$ | $\mathrm{Ph} \overline{\overline{=}}$ | 2 h | $\begin{gathered} \text { 26a : 26b } \\ (1: 1) \end{gathered}$ | $32 \%{ }^{\text {b,c }}$ |
| 3 | $\begin{gathered} \mathrm{PhCH}_{2} \mathrm{SH} \\ 10 \end{gathered}$ | $t-\mathrm{Bu}=$ | 4 h | 36a | 28\% b,d |
| 4 | $\begin{gathered} \mathrm{PhCH}_{2} \mathrm{SH} \\ 10 \end{gathered}$ |  | 24 h | $\begin{gathered} 37 \mathrm{a}: 37 \mathrm{~b} \\ (7.5: 1) \end{gathered}$ | $53 \%{ }^{\text {b,d }}$ |
| 5 | $\begin{gathered} \mathrm{PhCH}_{2} \mathrm{SH} \\ 10 \end{gathered}$ |  | 24 h | $\begin{gathered} 37 a: 37 b \\ (1: 6.5) \end{gathered}$ | $69 \%{ }^{\text {b,e }}$ |

${ }^{\text {a }}$ Yields based on ${ }^{1} \mathrm{H}$ NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. ${ }^{\mathrm{b}}$ Percent conversion with respect to remaining thiol. ${ }^{\mathrm{c}}$ An additional $\sim 5 \%$ of the $E$-linear phenylacetylene dimer was observed. ${ }^{\text {d }}$ Solvent $=\mathrm{DCE} .{ }^{\mathrm{e}}$ Solvent $=\mathrm{CDCl}_{3}: d_{8^{-}}$ toluene ( $1: 1$ ).

## b) $\mathbf{B p R h}\left(\mathbf{P P h}_{3}\right)_{2}, \mathbf{3}$

Complex 3 was synthesized using a modified literature procedure. ${ }^{8 \mathrm{~m}}$ This complex presumably adopts $\kappa^{2}$-coordination as indicated in the X-ray structure reported by Carmona and coworkers. ${ }^{28 \mathrm{~b}}$ Using complex 3, the reaction between benzylthiol and phenylacetylene gave only a $24 \%$ yield after 24 hours at room temperature with a 6:5:1 ratio of branched:E-linear:Z-linear products (Table 3.4, entry 1). The ${ }^{1} \mathrm{H}$ NMR data for 25a, 25b and 25c matches previously reported data. ${ }^{2,8 m, 57}$ Next, phenylacetylene was
added to 2,2,2-trifluoroethanethiol but no reaction took place (entry 2). The reaction between propane thiol (12) and phenylacetylene gave only a $6 \%$ combined yield of branched, E-linear and Z-linear isomers after 48 hours (entry 3 ). Benzylthiol was reacted with tert-butylacetylene and 1-ethynlcyclohexene resulting in conversions of $35 \%$ and $54 \%$, respectively (entries 4 and 5). The regioselectivity of these reactions slightly favored the $E$-linear isomers ( $\mathbf{3 6 b}$ and $\mathbf{3 7 b}$ ) over the branched isomers with $1: 2$ and $1: 3$ .selectivities, respectively. The ${ }^{1} H$ NMR spectra for $\mathbf{3 6 a}, \mathbf{3 6 b}, \mathbf{3 7 a}$ and $\mathbf{3 7 b}$ are all in agreement with literature reports. ${ }^{8 \mathrm{~m}, 0,58}$

Table 3.4. Substrate scope of alkyne hydrothiolation catalyzed by complex 3

|  | $+\quad R^{1}=$ | $\frac{3 \mathrm{~mol} \% \mathrm{BpRh}\left(\mathrm{PPh}_{3}\right)_{2}}{\mathrm{DCE}: \mathrm{PhCH}_{3}(1: 1), \text { rt }}$ |  | $+R^{1} \underbrace{}_{b}$ | $\Sigma_{S R}+R_{1}^{1} S R$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 10-12 | 17-23 |  |  | b C |
| Entry | Thiol 1.1 equiv. | Alkyne <br> 1.0 equiv. | Time |  | Ratio | Yield ${ }^{\text {a } / ~ C o n v e r s i o n ~}{ }^{\text {b }}$ |
| 1 | $\begin{gathered} \mathrm{PhCH}_{2} \mathrm{SH} \\ 10 \end{gathered}$ | $\mathrm{Ph} \overline{17}$ | 24 h | $\begin{gathered} 25 a: 25 b: 25 c \\ (6: 5: 1) \end{gathered}$ | 24\% ${ }^{\text {a }}$ |
| 2 | $\underset{11}{\mathrm{CF}_{3} \mathrm{CH}_{2} \mathrm{SH}}$ | $\mathrm{Ph} \overline{17}$ | 24 h | - | No rxn |
| 3 | $\sim_{12}^{S H}$ | $\begin{gathered} \mathrm{Ph}= \\ 17 \end{gathered}$ | 48 h | $\begin{gathered} \text { 38a : 38b } \\ (1: 1) \end{gathered}$ | 6\% ${ }^{\text {a }}$ |
| 4 | $\begin{gathered} \mathrm{PhCH}_{2} \mathrm{SH} \\ 10 \end{gathered}$ | $\begin{gathered} t-B u= \\ 20 \end{gathered}$ | 24 h | $\begin{gathered} 36 a: 36 b \\ (1: 2) \end{gathered}$ | $35 \%{ }^{\text {b }}$ |
| 5 | $\mathrm{PhCH}_{2} \mathrm{SH}$ $10$ |  | 48 h | $\begin{gathered} 37 a: 37 b \\ (1: 3) \end{gathered}$ | 54\% ${ }^{\text {b }}$ |

[^2]In these five examples, complex 3 gave low selectivity and moderate to low yields/conversions ( $8-54 \%$ ). As compared to complexes 1 and 2, which favored the branched isomer, complex 3 slightly favored the E-linear isomer. Therefore, because complexes 2 and 3 gave poor yields and selectivities they are not good choices as catalysts for hydrothiolation reactions.

### 3.2.3-3 Tris(pyrazolyl)borate Complexes

Having established that denticity plays an important role in both reactivity and selectivity, we turned our attention to the effect of pyrazolyl substitution on reactivity and selectivity. A series of tris(pyrazolyl)borate complexes with varying substitution patterns on the pyrazolyl rings were synthesized and their hydrothiolation activity examined. These complexes included $\mathrm{TpRh}\left(\mathrm{PPh}_{3}\right)_{2}$ (4), $\mathrm{Tp}^{\mathrm{Me}} \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}$ (5), $\mathrm{Tp}^{\mathrm{Ph}} \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}(6)$ and $\mathrm{Tp}{ }^{\mathrm{Ph}, \mathrm{Mc}} \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}(7)$, which will all be further discussed in detail.

## a) $\mathbf{T p R h}\left(\mathrm{PPh}_{3}\right)_{2}, 4$

Complex 4, which lacks substitution on the pyrazolyl rings, was found to give poor to moderate yields/conversions ( $<5 \%$ to $67 \%$ ) or resulted in no reaction at all when tested in hydrothiolation reactions (Table 3.5). The reaction between benzylthiol and phenylacetylene proceeded to only $7 \%$ conversion and produced solely the $Z$-linear isomer (25c) (entry 1). The reaction between 2,2,2-trifluoroethane thiol and phenylacetylene gave selectivity favoring the $E$-linear isomer over the $Z$-linear isomer in a 3:1 ratio with only a $14 \%$ combined yield (entry 4 ). When phenoxyethane thiol (13) was mixed with 4-ethynylanisole (18) and benzene thiol (16) was mixed with
phenylacetylene both showed no selectivity between the $E$ - and $Z$-linear isomers with $14 \%$ and $60 \%$ yields, respectively (entries 5 and 7). Benzylthiol reacted with ethylpropiolate (22) to give a $1: 2.5$ ratio of the $E$ - to $Z$-linear isomers in a $67 \%$ yield (entry 9). In most cases, complex 4 gave a mixture of linear isomers or just the $Z$-linear product. To ensure that the formation of the linear isomers was not due to a background radical reaction, galvinoxyl was used as a radical scavenger in several reactions (entries 3 and 8 ). The results were then compared to reactions without these radical scavenging reagents. The production of the linear isomers was not suppressed in the presence of galvinoxyl; hence, we postulate that the formation of the linear products observed for complex 4 were not due to a non-metal catalyzed radical reaction.

Table 3.5. Substrate scope of alkyne hydrothiolation catalyzed by complex 4

| $\begin{aligned} & \text { RSH } \\ & \mathbf{1 0 - 1 6} \end{aligned}$ | $+\quad R^{1}=$ | $3 \mathrm{~mol} \% \mathrm{TpRh}(\mathrm{P}$ |  | $\begin{gathered} \mathrm{R}_{1}^{1} \\ \mathrm{RS}_{a} \\ = \end{gathered}$ | $+R^{1}=$ | $R_{c}^{1} S R$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Entry | Thiol 1.1 equiv. | Alkyne 1.0 equiv. | Time |  | Ratio | Yield ${ }^{\text {a }}$ |
| 1 | $\begin{gathered} \mathrm{PhCH}_{2} \mathrm{SH} \\ 10 \end{gathered}$ | $\mathrm{Ph} \overline{17}$ | 24 h |  | 25c | $7 \%{ }^{\text {b }}$ |
| 2 | $\begin{gathered} \mathrm{PhCH}_{2} \mathrm{SH} \\ 10 \end{gathered}$ | $\mathrm{Ph} \overline{\overline{17}}$ | 2 h |  | 25c | 8\% ${ }^{\text {b,c }}$ |
| 3 | $\begin{gathered} \mathrm{PhCH}_{2} \mathrm{SH} \\ 10 \end{gathered}$ | $\mathrm{Ph} \overline{17}$ | 3 h |  | $\begin{gathered} 25 a: 25 c \\ (1: 1) \end{gathered}$ | $8 \%{ }^{\text {b,c, }}$ d |
| 4 | $\underset{11}{\mathrm{CF}_{3} \mathrm{CH}_{2} \mathrm{SH}}$ | $\mathrm{Ph} \overline{=}$ | 48 h |  | $\begin{gathered} \text { 26b : 26c } \\ (3: 1) \end{gathered}$ | 14\% |
| 5 |  |  <br> 18 | 24 h |  | $\begin{gathered} \text { 28a: 28c } \\ (1: 1) \end{gathered}$ | 14\% |
| 6 |  <br> 15 |  <br> 18 | 24 h |  | - | no rxn |
| 7 | $\begin{gathered} \mathrm{Ph}-\mathrm{SH} \\ 16 \end{gathered}$ | $\mathrm{Ph} \overline{17}$ | 24 h |  | $\begin{gathered} 30 b: 30 c \\ (1.5: 1) \end{gathered}$ | 60\% |
| 8 | $\begin{gathered} \mathrm{Ph}-\mathrm{SH} \\ 16 \end{gathered}$ | $\mathrm{Ph} \overline{17}$ | 24 h |  | $\begin{gathered} 30 b: 30 c \\ (1: 3) \end{gathered}$ | $51 \%{ }^{\text {d }}$ |
| 9 | $\begin{gathered} \mathrm{PhCH}_{2} \mathrm{SH} \\ 10 \end{gathered}$ |  | 24 h |  | $\begin{gathered} 33 b: 33 c \\ (1: 2.5) \end{gathered}$ | 67\% |
| 10 |  <br> 15 |  | 24 h |  | , - | no rxn |

${ }^{\text {a }}$ Yields based on ${ }^{1} \mathrm{H}$ NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. ${ }^{\text {b }}$ Percent conversion with respect to remaining thiol. ${ }^{\text {c }}$ Solvent $=$ DCE. ${ }^{d}$ With an additional 3 mol\% galvinoxyl.

Complex 4 gave opposite regioselectivity, favoring the linear isomers, as compared to complex 1, which favored the branched product. Thus it seems that substitution is necessary on the pyrazolyl rings for regioselectivity favoring the branched product and for higher yields.

## b) $\mathbf{T p}{ }^{\mathrm{Me}} \mathbf{R h}\left(\mathbf{P P h}_{3}\right)_{2}, \mathbf{5}$

To examine if one methyl substituent on the pyrazolyl rings would be sufficient for catalytic activity of tris(pyrazolyl)borate complexes in hydrothiolation reactions, we synthesized complex 5: This complex has a methyl group in the 3-position of each pyrazolyl ring and no substitution at the 5-position. During the attempted synthesis of 5, a mixture of two isomers was obtained. This mixture included complex 5 and complex $5^{*}$, in which one methyl group is located in the 5-, rather than the 3-position of the pyrazolyl ring. Complex $5^{*}$ was presumably formed by a 1,2 -borotropic shift as discussed in section 2.2.2 of Chapter 2. Hydrothiolation reactions were performed with the isomeric mixture.

In the hydrothiolation reactions that were tested, complex 5 favored the branched product, but with poor to moderate yields ( $<5 \%$ to $62 \%$ ) (Table 3.6). In the reaction between benzylthiol and phenylacetylene there was good selectivity, as only the branched product was formed (entry 1). However, the yield of this reaction was only $15 \%$. There was no selectivity in the reaction between 2,2,2-trifluoroethanethiol and phenylacetylene, which gave a $1: 1: 1$ ratio of all three isomers $\mathbf{2 6 a}: \mathbf{2 6 b} \mathbf{2 6 c}$ (entry 2 ). No reaction was observed between benzylthiol and the internal alkyne 1-phenyl-1-propyne (entry 9).

Table 3.6. Substrate scope of alkyne hydrothiolation catalyzed by complex 5

| $\begin{aligned} & \text { RSH } \\ & 10-15 \end{aligned}$ | $\begin{gathered} R^{1}= \\ 17-24 \end{gathered}$ | $\frac{3 \mathrm{~mol} \% \mathrm{Tp}^{\mathrm{Me}} \mathrm{Rh}(\mathrm{PP}}{\mathrm{DCE}: \mathrm{PhCH}_{3}(1: 1)}$ |  | $=+R_{b}^{1}=$ | $R_{c}^{1} \underbrace{}_{c} S R$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Entry | Thiol 1.1 equiv. | Alkyne 1.0 equiv. | Time | Ratio | Yield ${ }^{\text {a }}$ |
| 1 | $\begin{gathered} \mathrm{PhCH}_{2} \mathrm{SH} \\ 10 \end{gathered}$ | $\mathrm{Ph}=$ | 2 h | 25a | 15\% |
| 2 | $\begin{gathered} \mathrm{CF}_{3} \mathrm{CH}_{2} \mathrm{SH} \\ 11 \end{gathered}$ | $\mathrm{Ph}=$ | 2 h | $\begin{gathered} 26 a: 26 b: 26 c \\ (1: 1: 1) \end{gathered}$ | 7\% |
| 3 |  | $\mathrm{Ph} \overline{=}$ | 2 h | 27a | $16 \%{ }^{\text {b }}$ |
| 4 |  |  <br> 18 | 2 h | 28a | 49\% |
| 5 |  <br> 15 |  <br> 18 | 2 h | 29a | 62\% ${ }^{\text {b }}$ |
| 6 | $\begin{gathered} \mathrm{PhCH}_{2} \mathrm{SH} \\ 10 \end{gathered}$ | $\begin{gathered} n-\mathrm{C}_{6} \mathrm{H}_{13}= \\ 19 \end{gathered}$ | 2 h | 31a | < $5 \%$ |
| 7 |  <br> 14 | $\begin{gathered} \mathrm{Me}_{3} \mathrm{Si}= \\ 21= \end{gathered}$ | 2 h | 32a | $<5 \%{ }^{\text {b }}$ |
| 8 |  <br> 15 |  <br> 23 | 2 h | 34a | 48\% |
| 9 | $\begin{gathered} \mathrm{PhCH}_{2} \mathrm{SH} \\ \mathbf{1 0} \end{gathered}$ | $\mathrm{Ph}=\mathrm{CH}_{3}$ | 1 h | - | no rxn |

${ }^{\text {a }}$ Yields based on ${ }^{1}$ H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. ${ }^{\text {b }}$ An additional $\sim 5-15 \%$ of an unidentified byproduct was observed.

As complex 5 was used as a mixture of isomers (5 and $5^{*}$ ) we are not certain whether the low reactivity and selectivity is due to the product mixture or due to the lack
of substitution on the pyrazolyl rings. Therefore, because this complex is difficult to prepare as solely complex 5 and the mixture gives poor yields and selectivities it is not a good choice as a catalyst for hydrothiolation reactions.

## c) $\mathbf{T p}{ }^{\mathrm{Ph}} \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}, 6$

Next we decided to place a larger substituent at the 3-position. We prepared complex 6 where instead of a methyl group in the 3-position there is a phenyl group. This complex showed no indication of a 1,2-borotropic shift product in the ${ }^{1} \mathrm{H},{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR or by X-ray analysis. Complex 6 gave a range of yields from $11 \%$ to $>95 \%$ and favored the formation of the branched product in most cases (Table 3.7, entries 1-8). The reaction between benzylthiol and phenylacetylene gave an $87 \%$ yield with an $11: 1$ ratio of the branched to $E$-linear isomers (entry 1). 2,2,2-Trifluoroethane thiol reacted with phenylacetylene to give a $4: 1$ ratio of the branched to $E$-linear isomers in a $64 \%$ yield (entry 2). The reactions carried out in entries 3-8 all gave the branched product with $18 \%$ to $>95 \%$ yields. Benzylthiol reacted with 1-phenyl-1-propyne to give only an $11 \%$ yield and no selectivity was observed between isomers (entry 9). This low yield was not surprising as reactions with an internal alkyne generally gave relatively low yields with most of the complexes studied thus far.

Table 3.7. Substrate scope of alkyne hydrothiolation catalyzed by complex 6

${ }^{\text {a }}$ Yields based on ${ }^{1} \mathrm{H}$ NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. ${ }^{\text {b }}$ An additional $\sim 5-20 \%$ of an unidentified byproduct was observed. ${ }^{\mathrm{c}}$ An additional $\sim 5 \%$ of the $E$-linear phenylacetylene dimer was observed. ${ }^{\mathrm{d}}$ Solvent $=\mathrm{CD}_{2} \mathrm{Cl}_{2}$ : $d_{8}$-toluene (1:1).

The overall yields obtained with complex 6 were higher than those obtained with complex 5 but generally lower then those obtained for complex 1 . It seems if there is only
one substituent on each pyrazolyl ring, in the 3-position, a larger substituent is preferred. The larger phenyl group present in complex 6 causes it to favor adoption of form $\mathbf{A}$ over form B and this may affect its catalytic activity. However, further mechanistic investigations are required to fully understand the factors that affect the catalytic activity of these complexes.

## d) $\mathbf{T} \mathbf{p}^{\mathbf{P h}, \mathbf{M c}} \mathbf{R h}\left(\mathbf{P P h}_{3}\right)_{2}, 7$

Thus far, there appears be a correlation between the substituents in the 3- and 5position or large substituents in the 3-position and catalytic activity, as well as the potential to bind in a $\kappa^{3}$ configuration. We therefore decided to examine another rhodium tris(pyrazolyl)borate complex that had a large substituent in the 3-position and another substituent in the 5 -position to see if this complex would be superior to complex $\mathbf{1}$. We prepared complex 7 with phenyl groups at the 3-position and methyl groups at the 5position of the pyrazolyl rings. The catalytic activity of complex 7 in hydrothiolation reactions was comparable to complex 1, giving similar yields and selectivities. The results are shown in Table 3.8. The reaction between benzylthiol and phenylacetylene gave a 6:1 ratio favoring the branched over the $E$-linear isomer in a $78 \%$ yield (entry 1 ). 2,2,2-trifluoroethane thiol reacted with phenylacetylene to give a 3:1 ratio of branched to E-linear in an 84\% yield (entry 2). Entries 3-7 showed reactions between aliphatic thiols and aryl and aliphatic alkynes, which all gave predominantly the branched product in good to excellent yields ( $40->95 \%$ ). The reaction between benzylthiol and 1-phenyl-1propyne resulted in no selectivity between isomers and only $24 \%$ yield (entry 8 ). These results suggest that complexes with substituents in both the 3- and 5-positions of the
pyrazolyl rings and the ability to bind $\kappa^{3}$ outperform those complexes that do not have these factors.

Table 3.8. Substrate scope of alkyne hydrothiolation catalyzed by complex 7

| $\begin{aligned} & \text { RSH } \\ & \mathbf{1 0 - 1 5} \end{aligned}$ | $+\quad R^{1}=$ | $\frac{3 \mathrm{~mol} \% \mathrm{Tp}^{\mathrm{Ph}, \mathrm{Me}_{\mathrm{Rh}}(\mathrm{~F}}}{\mathrm{DCE}: \mathrm{PhCH}_{3}(1: 1)}$ |  |  | $+R^{1}=$ <br> b | $R_{c}^{1}=S R$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Entry | Thiol 1.1 equiv. | Alkyne 1.0 equiv. | Time |  | Ratio | Yield ${ }^{\text {a }}$ |
| 1 | $\begin{gathered} \mathrm{PhCH}_{2} \mathrm{SH} \\ 10 \end{gathered}$ | $\mathrm{Ph}=$ | 2 h |  | $\begin{gathered} \text { 25a : 25b } \\ (6: 1) \end{gathered}$ | $78 \%{ }^{\text {b }}$ |
| 2 | $\begin{gathered} \mathrm{CF}_{3} \mathrm{CH}_{2} \mathrm{SH} \\ 11 \end{gathered}$ | $\mathrm{Ph} \overline{=}$ | 2 h |  | $\begin{gathered} \mathbf{2 6 a}: \mathbf{2 6 b} \\ (3: 1) \end{gathered}$ | 84\% b,c |
| 3 |  <br> 13 |  <br> 18 | 2 h |  | 28a | >95\% |
| 4 |  <br> 15 |  <br> 18 | 2 h |  | 29a | $75 \%$ b |
| 5 | $\begin{gathered} \mathrm{PhCH}_{2} \mathrm{SH} \\ 10 \end{gathered}$ | $\begin{aligned} & n-\mathrm{C}_{6} \mathrm{H}_{13}= \\ & 19 \end{aligned}$ | 2 h |  | 31a | >95\% |
| 6 |  | $\begin{gathered} \mathrm{Me}_{3} \mathrm{Si}= \\ 21 \end{gathered}$ | 2 h |  | 32a | $40 \% \text { b }$ |
| 7 |  <br> 15 |  <br> 23 | 3 h |  | 34a | 80\% ${ }^{\text {b }}$ |
| 8 | $\begin{gathered} \mathrm{PhCH}_{2} \mathrm{SH} \\ 10 \end{gathered}$ | $\mathrm{Ph}=\mathrm{CH}_{3}$ | 1 h |  | $\begin{gathered} 35 a: 35 b \\ (1: 1) \end{gathered}$ | 24\% |

[^3]
### 3.2.3-4 Complexes 1-7 Comparative Studies

For a more direct comparison between complexes 1-7 the results for the reaction between 10 and $\mathbf{1 7}$ are summarized in Table 3.9. The results of this reaction are representative of the trends observed for complexes 1-7. It seems that for catalytic activity, substitution in the 3-position and the 5-position of the pyrazolyl rings are important. If there is solely substitution in the 3-position, a large substituent appears to be necessary. In addition, the ability to achieve $\kappa^{3}$-coordination also appears to be important as higher yields were obtained with the tris(pyrazolyl)borate complexes $\mathbf{1 , 6}$ and 7 . It is interesting to note that complex 4 has minimal catalytic activity and favors the Z-linear isomer, possibly suggesting the reaction in its presence proceeds through a different mechanism.

Table 3.9. Hydrothiolation of benzylthiol with phenylacetylene catalyzed by complexes 1-7

| $\begin{gathered} \mathrm{Ph}^{\wedge} \mathrm{SH} \\ 10 \end{gathered}$ | $\mathrm{Ph}=\frac{\mathrm{XRh}( }{\mathrm{DCE}: \mathrm{Ph}}$ |  |  |  |
| :---: | :---: | :---: | :---: | :---: |
| Entry ${ }^{\text {a }}$ | Complex | Time | Ratio | Yield ${ }^{\text {b }}$ |
| 1 | $\mathrm{Tp} \mathrm{Rh}_{\left(\mathrm{PPh}_{3}\right)_{2}}$ | 2 h | $\begin{gathered} 25 a: 25 b \\ (16: 1) \end{gathered}$ | 93\% ${ }^{\text {c }}$ |
| 2 | $\mathrm{Bp}{ }^{*} \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}$ | 2 h | $\begin{gathered} 25 a: 25 b \\ (5: 1) \end{gathered}$ | 55\% |
| 3 | $\mathrm{BpRh}\left(\mathrm{PPh}_{3}\right)_{2}$ | 24 h | $\underset{(6: 5: 1)}{25 a}: 25 \mathrm{~b}: 25 \mathrm{c}$ | 24\% |
| 4 | $\mathrm{TpRh}\left(\mathrm{PPh}_{3}\right)_{2}$ | 24 h | 25c | 7\% ${ }^{\text {d }}$ |
| 5 | $\mathrm{Tp}{ }^{\mathrm{Me}} \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}$ | 2 h | 25a | 15\% |
| 6 | $\mathrm{Tp}{ }^{\mathrm{Ph}} \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}$ | 2 h | $\begin{gathered} \text { 25a : 25b } \\ (11: 1) \end{gathered}$ | 87\% ${ }^{\text {c }}$ |
| 7 | $\mathrm{Tp}{ }^{\mathrm{Ph}, \mathrm{Me}} \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}$ | 2 h | $\begin{gathered} 25 a: 25 b \\ (6: 1) \end{gathered}$ | 78\% ${ }^{\text {c }}$ |

${ }^{a}$ Reactions conducted with $3 \mathrm{~mol} \%$ catalyst, 1.1 equiv. thiol, 1.0 equiv. alkyne. ${ }^{b}$ Yields based on ${ }^{1} \mathrm{H}$ NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. ${ }^{\text {c }}$ An additional $\sim 5-10 \%$ of an unidentified byproduct was observed. ${ }^{\text {d }}$ Percent conversion with respect to benzylthiol.

The results for the reaction between 11 and 17 (Table 3.10) are consistent with the trends seen for the reaction between 10 and 17 (Table 3.9). Complexes $\mathbf{1 , 6}$ and 7 again gave the highest yields (64-84\%) with the highest selectivity favoring the branched over the $E$-linear isomer. Furthermore, tris(pyrazolyl)borate complexes are superior to the bis(pyrazolyl)borate complexes. The reaction using 2,2,2-trifluoroethanethiol gave slightly lower selectivities and yields as compared to that using benzylthiol but the general trends remain constant.

Table 3.10. Hydrothiolation of 2,2,2-trifluoroethanethiol with phenylacetylene catalyzed by complexes 1-7

${ }^{\text {a }}$ Reactions conducted with $3 \mathrm{~mol} \%$ catalyst, 1.1 equiv. thiol, 1.0 equiv. alkyne. ${ }^{b}$ Yields based on ${ }^{1} H$ NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. ${ }^{\mathrm{c}}$ An additional $\sim 5 \%$ of the $E$-linear phenylacetylene dimer was observed. ${ }^{\text {d }}$ An additional $\sim 5 \%$ of an unidentified byproduct was observed.

### 3.2.4 Phenylacetlyene Dimerization and Other Unidentified Byproducts

Beletskaya and coworkers found when using their nickel catalysts that oligo- and polymerization reactions with the alkyne substrates occurred readily. ${ }^{81}$ Therefore they carried out a series of optimization studies in order to minimize the polymerization reactions. When using a $1: 1$ ratio of thiol:alkyne they found about $10-12 \%$ of the alkyne formed oligomers. When the ratio of thiol to alkyne was $0.5: 1$ they reported an ever higher production of the oligomer products. However, when using an excess of thiol in a

2:1 ratio of thiol:alkyne there was no detectable production of the oligomers by ${ }^{1} \mathrm{H}$ NMR spectroscopy. Therefore they concluded that it is important for the thiol to be in excess to avoid oligo- and polymerization products.

In our studies we have found that the $E$-linear phenylacetylene dimer formed in the reaction between 2,2,2-trifluoroethanethiol and phenylacetylene when using a ratio of 1.1:1 thiol:alkyne. However, this thiol is extremely volatile $\left(\mathrm{bp}=34-35^{\circ} \mathrm{C}\right)$ and thus some of this reagent may have evaporated before the reaction flask was sealed. This would result in a lack of excess thiol and could possibly lead to the formation of the dimer. Therefore, future studies with 2,2,2-trifluoroethane thiol should be carried out using an increased ratio of thiol to alkyne to determine if the ratio affects the yield of oligomerization products.

The unidentified byproducts that were observed in the hydrothiolation reactions in $5-20 \%$ yields have not been characterized. Attempts to separate the byproducts from the desired products were unsuccessful and thus far the identities of the byproducts are unknown. However, we speculate the byproduct may be the product of hydrothiolation of dimerized phenylacetylene, see Figure 3.2. This would account for the gas chromatography/mass spectroscopy data where only masses corresponding to the hydrothiolation products were observed. The postulated byproduct would have the same fragmentation pattern as the hydrothiolation products and thus it is possible for the same peaks to be observed. As well, generally three singlets in a 1:1:1 ratio are observed in the ${ }^{1} H$ NMR spectrum. These occur in the diagnostic olefinic region which is also in agreement with this structure. It must also be noted that the byproduct(s) seen in the reaction been butyl 3-mercaptopropionate and trimethylsilylacetylene do not seem to
match this interpretation with respect to the ${ }^{1} \mathrm{H}$ NMR data. Further investigations need to be carried out to fully characterize the unknown byproduct(s).


Figure 3.2. Postulated byproduct for hydrothiolation reactions

### 3.3 Conclusions

From the hydrothiolation reaction results obtained for complexes 1-7 it is clear that tris(pyrazolyl)borate complexes are superior to bis(pyrazolyl)borate complexes. Presumably the ability to adopt $\kappa^{3}$-coordination is an important factor in the catalytic cycle (see Scheme 1.22 in Chapter 1). Complexes with substitution on the pyrazolyl rings gave better yields and selectivity, favoring the branched product, than complexes lacking substitution. In addition, substitution at the 3- and 5-positions of the pyrazolyl rings enhances the catalytic ability of those complexes in comparison to substitution at only the 3-position of the pyrazolyl rings. The size of the substituent at the 3-position also seems to have a large effect on the yield. Replacement of the methyl group in complex 5 with a phenyl group in complex 6 greatly increased the yields of the hydrothiolation reactions. However, since complex 5 was used as a mixture of isomers ( 5 and $5^{*}$ ) we cannot be certain whether the poor catalytic activity is due to the product mixture or to the lack of substitution on the pyrazolyl rings. We have established that tris(pyrazolyl)borate complexes are better than bispyraozlylborate complexes and that substitution on the
pyrazolyl rings is needed for catalytic activity, however the reasons for this are still unclear. Mechanistic investigations for alkyne hydrothiolation reactions catalyzed by rhodium pyrazolylborate complexes need to be carried out to fully comprehend the effect that denticity and pyrazolyl substitution have on the catalytic activity of these complexes.

### 3.4 Experimental Procedures

### 3.4.1 General Methods

The manipulation of air and moisture sensitive organometallic compounds was carried out using standard Schlenk techniques under a positive pressure of dry nitrogen or in a nitrogen-filled Vacuum Atmospheres glovebox $\left(\mathrm{O}_{2}<2 \mathrm{ppm}\right)$. Reactions were run at room temperature $\left(20-28^{\circ} \mathrm{C}\right)$ and stirred with a Teflon-coated magnetic stir bar, unless otherwise stated. Reaction mixtures were concentrated using rotary evaporation methods combined with pumping on the vacuum line for nonvolatile compounds. A base bath composed of potassium hydroxide, isopropanol and water was used to clean glassware, followed by rinsing with deionized water and then acetone.

### 3.4.2 Reagents and Solvents

All organic reagents were obtained from commercial sources and used as received, unless otherwise stated. Hexanes and toluene were dried by passage through solvent purification columns. ${ }^{51}$ DCE was distilled and degassed prior to use. Deuterated chloroform was purified by vacuum transfer from $\mathrm{P}_{2} \mathrm{O}_{5}$ and was degassed prior to use.
$\mathrm{CD}_{2} \mathrm{Cl}_{2}$ and $d_{8}$-toluene were used from 1 g ampules and $1,3,5$-trimethoxybenzene was sublimed prior to use.

### 3.4.3 Chromatography

Flash chromatography was used to separate products as described by Still and coworkers. ${ }^{59}$ The solvent was eluted using either nitrogen or air pressure at an approximate rate of two inches per minute.

### 3.4.4 Physical and Spectroscopic Measurements

Bruker Avance $300\left({ }^{1} \mathrm{H}\right.$ at 300 MHz and ${ }^{13} \mathrm{C}$ at 75 MHz$)$ or Bruker Avance $400\left({ }^{1} \mathrm{H}\right.$ at 400 MHz and ${ }^{13} \mathrm{C}$ at 100 MHz ) magnetic resonance spectrometers were used to collect NMR spectra. Values for ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ spectra are reported as chemical shifts as parts per million ( ppm ) and were referenced to a residual solvent. Coupling constants $(J)$ are reported in Hertz (Hz) and were extracted assuming first-order coupling. Spin multiplicities are abbreviated as follows: $\mathrm{s}=$ singlet, $\mathrm{d}=$ doublet, $\mathrm{t}=$ triplet, $\mathrm{q}=$ quartet, $\mathrm{qn}=$ quintet, $\mathrm{sx}=$ sextet, $\mathrm{m}=$ multiplet. Unless otherwise indicated, all spectra were obtained at $25{ }^{\circ} \mathrm{C}$. 1,3,5-Trimethoxybenzene was used as an internal standard to determine NMR yields. GCMS data was recorded on a Varian CP-3800 or an HP 5890 Series II gas chromatograph. Mass spectra were recorded on a Kratos MS-50 mass spectrometer.

### 3.4.5 Synthesis and Characterization of Hydrothiolation Products

All of the following hydrothiolation reactions were conducted in a Vacuum Atmospheres glovebox. 20 mL or 5 mL vials were equipped with Teflon-coated magnetic stir bars. After addition of all reagents, the vials were sealed with plastic screw caps, taken out of the glovebox and covered in aluminum foil. Reactions were stirred at room temperature. All stock solutions were made with a 1:1 DCE:toluene mixture, unless otherwise stated. The reaction mixtures were concentrated under vacuum. The residue was dissolved in $\sim 1 \mathrm{~mL}$ of $\mathrm{CDCl}_{3}$ and the resulting solution was analyzed by ${ }^{1} \mathrm{H}$ NMR spectroscopy. The yields were determined using 1,3,5-trimethoxybenzene as an internal standard or the conversion was calculated based on remaining thiol. The reaction mixture was then transferred to a 20 mL vial and petroleum ether (boiling range $35-60^{\circ} \mathrm{C}$ ) was added to precipitate the rhodium complex. The solution was filtered through silica gel and the resulting solution was concentrated under vacuum. Flash chromatography $\left(\mathrm{SiO}_{2}\right.$, solvent combination for eluant) provided the product.

For each reaction, a representative experimental procedure is given. Results with each complex are tabulated after the experimental procedure, followed by characterization data or literature references.

## Reaction of Benzylthiol (10) and Phenylaceytlene (17)


$\mathrm{Tp} * \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}(17 \mathrm{mg}, 0.018 \mathrm{mmol})$ was weighed out using a spatula into a 20 mL vial. 1,3,5-Trimethoxybenzene, ( $30 \mathrm{mg}, 0.18 \mathrm{mmol}, 408 \mu \mathrm{~L}$ of a 0.44 M stock solution in a $1: 1$ DCE:toluene mixture) was added via micropipette. To this solution, benzylthiol ( $70 \mu \mathrm{~L}$, 0.60 mmol ) and phenylacetylene ( $59 \mu \mathrm{~L}, 0.54 \mathrm{mmol}$ ) were added sequentially via micropipette. After stirring for 2 hours at room temperature, the reaction was concentrated and the residue dissolved in $\mathrm{CDCl}_{3} .{ }^{1} \mathrm{H}$ NMR analysis indicated the formation of the branched (25a) and $E$-linear ( $\mathbf{2 5 b}$ ) isomers in a $16: 1$ ratio in $93 \%$ combined yield. An additional $6 \%$ yield of an unidentified product was also observed.

Table 3.11. Hydrothiolation of benzylthiol with phenylacetylene catalyzed by complexes 1-7

| Entry | Complex | Time | Ratio | Yield |
| :---: | :---: | :---: | :---: | :---: |
| 1 | $\mathrm{Tp} * \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}$ | 2 h | $\begin{gathered} 25 a: 25 b \\ (16: 1) \end{gathered}$ | 93\% ${ }^{\text {a }}$ |
| 2 | $\mathrm{Bp} * \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}$ | 2 h | $\begin{gathered} 25 a: 25 b \\ (5: 1) \end{gathered}$ | 55\% |
| 3 | $\mathrm{BpRh}\left(\mathrm{PPh}_{3}\right)_{2}$ | 24 h | $\begin{gathered} 25 a: 25 b: 25 c \\ (6: 5: 1) \end{gathered}$ | 24\% |
| 4 | $\mathrm{TpRh}\left(\mathrm{PPh}_{3}\right)_{2}$ | 24 h | 25c | $7 \%{ }^{\text {b }}$ |
| 5 | $\mathrm{Tp}{ }^{\mathrm{Me}} \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}$ | 2 h | 25a | 15\% |
| 6 | $T p^{P h} \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}$ | 2 h | $\begin{gathered} 25 a: 25 b \\ (11: 1) \end{gathered}$ | 87\% ${ }^{\text {a }}$ |
| 7 | $\mathrm{Tp}{ }^{\mathrm{Ph}, \mathrm{Me}} \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}$ | 2 h | $\begin{gathered} 25 a: 25 b \\ (6: 1) \end{gathered}$ | 78\% ${ }^{\text {a }}$ |

${ }^{\text {a }}$ An additional $\sim 5-10 \%$ of an unidentified byproduct was observed. ${ }^{\text {b }}$ Percent conversion with respect to benzylthiol.

Branched (25a): Characterization matches previously reported data. ${ }^{8 m}$ $E$-linear (25b): Characterization matches previously reported data. ${ }^{57}$ Z-linear (25c): Characterization matches previously reported data. ${ }^{2}$

$\mathrm{Tp} * \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}(17 \mathrm{mg}, 0.018 \mathrm{mmol})$ was weighed out using a spatula into a 20 mL vial. 1,3,5-Trimethoxybenzene, ( $30 \mathrm{mg}, 0.18 \mathrm{mmol}, 408 \mu \mathrm{~L}$ of a 0.44 M stock solution in a $1: 1$ DCE:toluene mixture) was added via micropipette. To this solution, 2,2,2trifluoroethanethiol ( $53 \mu \mathrm{~L}, 0.60 \mathrm{mmol}$ ) and phenylacetylene ( $59 \mu \mathrm{~L}, 0.54 \mathrm{mmol}$ ) were added sequentially via micropipette. After stirring for 2 hours at room temperature, the reaction was concentrated and the residue dissolved in $\mathrm{CDCl}_{3}$. ${ }^{1} \mathrm{H}$ NMR analysis indicated the formation of the branched (26a) and $E$-linear (26b) isomers in a $3: 1$ ratio in $65 \%$ combined yield. An additional $7 \%$ yield of an unidentified product as well as $8 \%$ of the $E$-linear phenylacetylene dimer was also observed.

Table 3.12. Hydrothiolation of 2,2,2-trifluoroethanethiol with phenylacetylene catalyzed by complexes 1-7

| Entry | Complex | Time | Ratio | Yield |
| :---: | :---: | :---: | :---: | :---: |
| 1 | $\mathrm{Tp}{ }^{*} \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}$ | 2 h | $\begin{gathered} 26 a: 26 b \\ (3: 1) \end{gathered}$ | 65\% ${ }^{\text {a,b }}$ |
| 2 | $\mathrm{Bp}{ }^{*} \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}$ | 2 h | $\begin{gathered} 26 a: 26 b \\ (1: 1) \end{gathered}$ | 32 \% ${ }^{\text {a }}$ |
| 3 | $\mathrm{BpRh}\left(\mathrm{PPh}_{3}\right)_{2}$ | 24 h | - | No rxn |
| 4 | $\mathrm{TpRh}\left(\mathrm{PPh}_{3}\right)_{2}$ | 48 h | $\begin{gathered} \text { 26b : 26c } \\ (3: 1) \end{gathered}$ | 14\% |
| 5 | $T p^{\text {Me }} \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}$ | 2 h | $\begin{gathered} 26 a: 26 b: 26 c \\ (1: 1: 1) \end{gathered}$ | 7\% |
| 6 | $\mathrm{Tp}{ }^{\mathrm{Ph}} \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}$ | 2 h | $\begin{gathered} 26 a: 26 b \\ (4: 1) \end{gathered}$ | 64\% ${ }^{\text {a,b }}$ |
| 7 |  | 2 h | $\begin{gathered} \text { 26a: 26b } \\ (3: 1) \end{gathered}$ | 84\% ${ }^{\text {a,b }}$ |

$\overline{{ }^{\text {a }} \text { An additional } \sim 5 \% \text { of the } E \text {-linear phenylacetylene dimer was observed. }{ }^{\mathrm{b}} \text { An additional }}$ $\sim 5 \%$ of an unidentified byproduct was observed.

Branched (26a): light yellow oil; 15\% ethyl acetate/petroleum ether used as eluant for flash chromatography. ${ }^{1} \mathrm{H} \quad \mathrm{NMR}\left(\mathrm{CDCl}_{3}, \quad 300 \mathrm{MHz}\right): \delta 7.55-7.52(\mathrm{~m}, \quad 2 \mathrm{H})$, $7.41-7.37(\mathrm{~m}, 3 \mathrm{H}), 5.61(\mathrm{~s}, 1 \mathrm{H}), 5.55(\mathrm{~s}, 1 \mathrm{H}), 3.11(\mathrm{q}, 2 \mathrm{H}, J=9.6 \mathrm{~Hz}) .{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CDCl}_{3}, 100 \mathrm{MHz}\right): \delta 142.2,137.8,128.9,128.6,127.7,117.3,34.6$. HRMS (EI) $\mathrm{m} / \mathrm{z}$ calcd for $\mathrm{C}_{10} \mathrm{H}_{9} \mathrm{SF}_{3}$ : 218.0377; found: 218.0373 .

E-linear (26b): Characterization matches previously reported data. ${ }^{80}$

Z-linear (26c): light yellow oil; 10\% ethyl acetate/petroleum ether used as eluant for flash chromatography. ${ }^{1} \mathrm{H} \mathrm{NMR}\left(\mathrm{CDCl}_{3}, 400 \mathrm{MHz}\right): \delta 7.46-7.29(\mathrm{~m}, 5 \mathrm{H}), 6.53(\mathrm{~d}, 1 \mathrm{H}, J=$ $10.7 \mathrm{~Hz}), 6.19(\mathrm{~d}, 1 \mathrm{H}, J=10.7 \mathrm{~Hz}), 3.33(\mathrm{q}, 2 \mathrm{H}, J=10.7 \mathrm{~Hz}) .{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\} \operatorname{NMR}\left(\mathrm{CDCl}_{3}\right.$, 100 MHz ): $\delta 136.4,136.2,132.1,128.9,128.6,128.2,127.6,37.7$. HRMS (EI) $\mathrm{m} / \mathrm{z}$ calcd for $\mathrm{C}_{10} \mathrm{H}_{9} \mathrm{SF}_{3}$ : 218.0377 ; found: 218.0384 .

${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}, 300 \mathrm{MHz}\right)$ spectrum of compound $\mathbf{2 6 a}$ at 298 K

${ }^{13} \mathrm{C}\left\{{ }^{\prime} \mathrm{H}\right\} \mathrm{NMR}\left(\mathrm{CDCl}_{3}, 100 \mathrm{MHz}\right)$ spectrum of compound 26a at 298 K

Compound 26c observed in situ as mixture with 26b


## Reaction of Cyclopentylthiol (15) and Phenylacetylene (17)


$\mathrm{Tp} * \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}(12 \mathrm{mg}, 0.013 \mathrm{mmol})$ was weighed out using a spatula into a 20 mL vial. 1,3,5-Trimethoxybenzene, ( $24 \mathrm{mg}, 0.14 \mathrm{mmol}, 360 \mu \mathrm{~L}$ of a 0.40 M stock solution in a $1: 1$ DCE:toluene mixture) was added via micropipette. To this solution, cyclopentylthiol (51 $\mu \mathrm{L}, 0.48 \mathrm{mmol}$ ) and phenylacetylene ( $47 \mu \mathrm{~L}, 0.43 \mathrm{mmol}$ ) were added sequentially via micropipette. After stirring for 2 hours at room temperature, the reaction was concentrated and the residue dissolved in $\mathrm{CDCl}_{3} .{ }^{1} \mathrm{H}$ NMR analysis indicated the formation of the branched (27a) isomer in 78\% yield.

Table 3.13. Hydrothiolation of cyclopentylthiol with phenylacetylene catalyzed by complexes 1,5 and 6

| Entry | Complex | Time | Ratio | Yield |
| :---: | :---: | :---: | :---: | :---: |
| 1 | $\mathrm{Tp} \mathrm{Rh}_{\left(\mathrm{PPh}_{3}\right)_{2}}$ | 2 h | 27a | 78\% |
| 2 | $\mathrm{Tp}{ }^{\mathrm{Me}} \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}$ | 2 h | 27a | 16\% |
| 3 | $\mathrm{Tp}{ }^{\mathrm{Ph}} \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}$ | 2 h | 27a | 54\% a, b |

[^4]Branched (27a): Characterization matches previously reported data. ${ }^{8 m}$

## Reaction of Phenoxyethane Thiol (13) and 4-Ethynylanisole (18)


$\mathrm{Tp}{ }^{*} \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}(0.005 \mathrm{mmol}, 44 \mu \mathrm{~L}$ of a 0.12 M stock solution in a $1: 1$ DCE:toluene mixture) was added to a 5 mL vial via micropipette. 1,3,5-Trimethoxybenzene, ( 8 mg , $0.05 \mathrm{mmol}, 81 \mu \mathrm{~L}$ of a 0.62 M stock solution in a 1:1 DCE:toluene mixture) was added via micropipette. To this solution, phenoxyethane thiol ( $23 \mu \mathrm{~L}, 0.165 \mathrm{mmol}$ ) and 4ethynylanisole ( $20 \mu \mathrm{~L}, 0.15 \mathrm{mmol}$ ) were added sequentially via micropipette. After stirring for 2 hours at room temperature, the reaction was concentrated and the residue dissolved in $\mathrm{CDCl}_{3}$. ${ }^{1} \mathrm{H}$ NMR analysis indicated the formation of the branched (28a) isomer in $>95 \%$ yield.

Table 3.14. Hydrothiolation of phenoxyethanethiol with 4-ethynylanisole catalyzed by complexes 1 and 4-7

| Entry | Complex | Time | Ratio | Yield |
| :---: | :---: | :---: | :---: | :---: |
| 1 | $\mathrm{Tp} \mathrm{Rh}_{\left(\mathrm{PPh}_{3}\right)_{2}}$ | 2 h | 28a | >95\% |
| 2 | $\mathrm{TpRh}\left(\mathrm{PPh}_{3}\right)_{2}$ | 24 h | $\begin{gathered} \text { 28a : 28c } \\ (1: 1) \end{gathered}$ | 14\% |
| 3 | $\mathrm{Tp}{ }^{\mathrm{Me}} \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}$ | 2 h | 28a | 49\% |
| 4 | $\mathrm{Tp}{ }^{\mathrm{Ph}} \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}$ | 2 h | 28a | >95\% |
| 5 | $\mathrm{Tp}{ }^{\mathrm{Ph}, \mathrm{Me}} \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}$ | 2 h | 28a | >95\% |

Branched (28a): Characterization matches previously reported data. ${ }^{8 m}$

## Reaction of Cyclopentylthiol (15) and 4-Ethynylanisole (18)


$\mathrm{Tp}{ }^{*} \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}(9 \mathrm{mg}, 0.01 \mathrm{mmol})$ was weighed out using a spatula into a 5 mL vial. $1,3,5-$ Trimethoxybenzene, ( $17 \mathrm{mg}, 0.10 \mathrm{mmol}$ ) was added using a spatula and $250 \mu \mathrm{~L}$ 1:1 DCE:toluene was added via micropipette. To this solution, cyclopentylthiol ( $36 \mu \mathrm{~L}, 0.34$ mmol) and 4-ethynylanisole ( $40 \mu \mathrm{~L}, 0.31 \mathrm{mmol}$ ) were added sequentially via micropipette. After stirring for 2 hours at room temperature, the reaction was concentrated and the residue dissolved in $\mathrm{CDCl}_{3} .{ }^{1} \mathrm{H}$ NMR analysis indicated the formation of the branched (29a) isomer in $61 \%$ yield. An additional $10 \%$ yield of an unidentified product was also observed.

Table 3.15. Hydrothiolation of cyclopentylthiol with 4-ethynylanisole catalyzed by complexes 1 and 4-7

| Entry | Complex | Time | Ratio | Yield ${ }^{\text {a }}$ |
| :---: | :---: | :---: | :---: | :---: |
| 1 | $\mathrm{Tp} \mathrm{Rh}^{\left(P P h_{3}\right)_{2}}$ | 2 h | 29a | 61\% |
| 2 | $\mathrm{TpRh}\left(\mathrm{PPh}_{3}\right)_{2}$ | 24 h | - | no rxn |
| 3 | $\mathrm{Tp}{ }^{\mathrm{Me}} \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}$ | 2 h | 29a | 62\% |
| 4 | $\mathrm{Tp}^{\mathrm{Ph}} \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}$ | 2 h | 29a | 73\% |
| 5 | $\mathrm{Tp}{ }^{\mathrm{Ph}, \mathrm{Me}} \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}$ | 2 h | 29a | 75\% |

[^5]Branched (29a): orange oil; 10\% ethyl acetate/petroleum ether used as eluant for flash chromatography. ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}, 300 \mathrm{MHz}\right): \delta 7.59(\mathrm{~d}, 2 \mathrm{H}, J=9.0 \mathrm{~Hz}), 6.95(\mathrm{~d}, 2 \mathrm{H}, J$ $=9.0 \mathrm{~Hz}), 5.50(\mathrm{~s}, 1 \mathrm{H}), 5.26(\mathrm{~s}, 1 \mathrm{H}), 3.87(\mathrm{~s}, 3 \mathrm{H}), 3.45-3.42(\mathrm{~m}, 1 \mathrm{H}), 2.16-2.02(\mathrm{~m}, 2 \mathrm{H})$, $1.80-1.59(\mathrm{~m}, 6 \mathrm{H}) .{ }^{13} \mathrm{C}\left\{{ }^{\mathrm{I}} \mathrm{H}\right\} \operatorname{NMR}\left(\mathrm{CDCl}_{3}, 75 \mathrm{MHz}\right): \delta 159.9,145.4,132.7,129.2$, $128.5,125.5,113.8,110.6,55.4,44.2,33.3,25.2$. HRMS (EI) $\mathrm{m} / \mathrm{z}$ calcd for $\mathrm{C}_{14} \mathrm{H}_{18} \mathrm{OS}$ : 234.1078; found: 234.1074.



## Reaction of Benzenethiol (16) and Phenylacetylene (17)


$\mathrm{TpRh}\left(\mathrm{PPh}_{3}\right)_{2}(8 \mathrm{mg}, 0.01 \mathrm{mmol})$ was weighed out using a spatula into a 5 mL vial. $1,3,5-$ Trimethoxybenzene, ( $17 \mathrm{mg}, 0.10 \mathrm{mmol}$ ) was added using a spatula and $250 \mu \mathrm{~L} 1: 1$ DCE:toluene was added via micropipette. To this solution, benzenethiol ( $35 \mu \mathrm{~L}, 0.34$ mmol) and phenylacetylene ( $34 \mu \mathrm{~L}, 0.31 \mathrm{mmol}$ ) were added sequentially via micropipette. After stirring for 2 hours at room temperature, the reaction was concentrated and the residue dissolved in $\mathrm{CDCl}_{3} .{ }^{1} \mathrm{H}$ NMR analysis indicated the formation of the $E$-linear ( $\mathbf{3 0 b}$ ) and $Z$-linear (30c) isomers in a $1.5: 1$ ratio in $60 \%$ combined yield.

Table 3.16. Hydrothiolation of benzenethiol with phenylacetylene catalyzed by complexes 1 and 4

| Entry | Complex | Time | Ratio | Yield |
| :---: | :---: | :---: | :---: | :---: |
| 1 | $\operatorname{Tp*Rh}\left(\mathrm{PPh}_{3}\right)_{2}$ | 2 h | 30 a | $84 \% \mathrm{a}, \mathrm{b}$ |
| 2 | $\operatorname{TpRh}\left(\mathrm{PPh}_{3}\right)_{2}$ | 24 h | $30 \mathrm{~b}: 30 \mathrm{c}$ <br> $(1.5: 1)$ | $60 \%$ |

${ }^{a}$ This experiment was performed by C. Cao, see ref $8 \mathrm{~m} .{ }^{\text {b }}$ Isolated yield.

Branched (30a): Characterization from previously reported data. ${ }^{8 m}$
$E$-linear (30b): Characterization matches previously reported data. ${ }^{8 h}$
Z-linear (30c): Characterization matches previously reported data. ${ }^{8 h}$

## Reaction of Benzylthiol (10) and 1-Octyne (19)


$\mathrm{Tp} * \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}(17 \mathrm{mg}, 0.018 \mathrm{mmol})$ was weighed out using a spatula into a 20 mL vial. 1,3,5-Trimethoxybenzene, $(30 \mathrm{mg}, 0.18 \mathrm{mmol}, 408 \mu \mathrm{~L}$ of a 0.44 M stock solution in a $1: 1$ DCE:toluene mixture) was added via micropipette. To this solution, benzylthiol ( $70 \mu \mathrm{~L}$, $0.59 \mathrm{mmol})$ and 1 -octyne ( $80 \mu \mathrm{~L}, 0.54 \mathrm{mmol}$ ) were added sequentially via micropipette. After stirring for 2 hours at room temperature, the reaction was concentrated and the residue dissolved in $\mathrm{CDCl}_{3} .{ }^{1} \mathrm{H}$ NMR analysis indicated the formation of the branched (31a) isomer in $>95 \%$ yield.

Table 3.17. Hydrothiolation of benylthiol with 1-octyne catalyzed by complexes 1 and 57

| Entry | Complex | Time | Ratio | Yield |
| :---: | :---: | :---: | :---: | :---: |
| 1 | $\mathrm{Tp}{ }^{*} \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}$ | 2 h | 31a | >95\% |
| 2 | $T p^{\text {Me }} \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}$ | 2 h | 31a | $<5 \%$ |
| 3 | $\mathrm{Tp}{ }^{\mathrm{Ph}} \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}$ | 2 h | 31a | 71\% |
| 4 | $\mathrm{Tp}{ }^{\mathrm{Ph}, \mathrm{Me} \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}}$ | 2 h | 31a | >95\% |

Branched (31a): Characterization matches previously reported data. ${ }^{8 m}$

## Reaction of Butyl 3-Mercaptopropionate (14) and Trimethylsilylacetylene (21)


$\mathrm{Tp}{ }^{*} \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}(9 \mathrm{mg}, 0.01 \mathrm{mmol})$ was weighed out using a spatula into a 5 mL vial. $1,3,5-$ Trimethoxybenzene, ( $17 \mathrm{mg}, 0.10 \mathrm{mmol}$ ) was added using a spatula and $250 \mu \mathrm{~L} 1: 1$ DCE:toluene was added via micropipette. To this solution, butyl 3-mercaptopropionate ( $55 \mu \mathrm{~L}, 0.34 \mathrm{mmol}$ ) and trimethylsilylacetylene ( $44 \mu \mathrm{~L}, 0.31 \mathrm{mmol}$ ) were added sequentially via micropipette. After stirring for 2 hours at room temperature, the reaction was concentrated and the residue dissolved in $\mathrm{CDCl}_{3} .{ }^{1} \mathrm{H}$ NMR analysis indicated the formation of the branched (32a) isomer in $74 \%$ yield. An additional $10 \%$ yield of an unidentified product was also observed.

Table 3.18. Hydrothiolation of butyl 3-mercaptopropionate with 4-ethynylanisole catalyzed by complexes $\mathbf{1}$ and 5-7

| Entry | Complex | Time | Ratio | Yield ${ }^{\text {a }}$ |
| :---: | :---: | :---: | :---: | :---: |
| 1 | Tp *h $\left(\mathrm{PPh}_{3}\right)_{2}$ | 2 h | 32a | 74\% |
| 2 | $\mathrm{Tp}{ }^{\mathrm{Me}} \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}$ | 2 h | 32a | <5\% |
| 3 | $\mathrm{Tph} \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}$ | 2 h | 32a | 18\% |
| 4 | $T p^{\mathrm{Ph}, \mathrm{Me}} \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}$ | 2 h | 32a | 40\% |

[^6]Branched (32a): clear, colorless oil. ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}, 400 \mathrm{MHz}\right): \delta 5.49(\mathrm{~s}, 1 \mathrm{H}), 5.40(\mathrm{~s}$,
$1 \mathrm{H}), 4.13(\mathrm{t}, 2 \mathrm{H}, J=6.6 \mathrm{~Hz}), 3.04(\mathrm{t}, 2 \mathrm{H}, J=7.3 \mathrm{~Hz}), 2.66(\mathrm{t}, 2 \mathrm{H}, J=7.3 \mathrm{~Hz}), 1.64(\mathrm{qn}$, $2 \mathrm{H}, J=6.6 \mathrm{~Hz}), 1.40(\mathrm{sx}, 2 \mathrm{H}, J=7.3 \mathrm{~Hz}), 0.96(\mathrm{t}, 3 \mathrm{H}, J=7.3 \mathrm{~Hz}), 0.19(\mathrm{~s}, 9 \mathrm{H})$. HRMS (EI) $\mathrm{m} / \mathrm{z}$ calcd for $\mathrm{C}_{12} \mathrm{H}_{24} \mathrm{SO}_{2} \mathrm{Si}: 260.1266$; found: 260.1265 .


## Reaction of Benzylthiol (10) and Ethylpropiolate (22)


$\mathrm{Tp} * \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}$ ( $39 \mathrm{mg}, 0.03 \mathrm{mmol}$ ) was weighed out using a spatula into a 5 mL vial. Next, $840 \mu \mathrm{~L}$ of a 1:1 DCE:toluene mixture was added via micropipette. To this solution, benzylthiol ( $136 \mu \mathrm{~L}, 1.15 \mathrm{mmol}$ ) and ethylpropiolate $(106 \mu \mathrm{~L}, 1.05 \mathrm{mmol})$ were added sequentially via micropipette. After stirring for 48 hours at room temperature, the reaction was concentrated and the residue dissolved in $\mathrm{CDCl}_{3}$. ${ }^{\mathrm{I}} \mathrm{H}$ NMR analysis indicated the formation of the $E$-linear (33b) and $Z$-linear (33c) isomers in a $2.5: 1$ ratio in $59 \%$ combined conversion relative to the benzylthiol starting material.

Table 3.19. Hydrothiolation of benzylthiol with ethylpropiolate catalyzed by complexes 1 and 4

| Entry | Complex | Time | Ratio | Yield |
| :---: | :---: | :---: | :---: | :---: |
| 1 | $T p^{*} R\left(\mathrm{PPh}_{3}\right)_{2}$ | 24 h | $33 \mathrm{~b}: 33 \mathrm{c}$ <br> $(2.5: 1)$ | $59 \% \mathrm{a}$ |
| 2 | $\mathrm{TpRh}\left(\mathrm{PPh}_{3}\right)_{2}$ | 24 h | $33 \mathrm{~b}: 33 \mathrm{c}$ <br> $(1: 2.5)$ | $67 \%$ |

[^7]E-linear (33b): clear oil; 10\% ethyl acetate/petroleum ether used as eluant for flash chromatography. ${ }^{1} \mathrm{H} \mathrm{NMR}\left(\mathrm{CDCl}_{3}, 300 \mathrm{MHz}\right): \delta 7.65(\mathrm{~d}, 1 \mathrm{H}, J=15.0 \mathrm{~Hz})$,
$7.29-7.11(\mathrm{~m}, 5 \mathrm{H}), 5.76(\mathrm{~d}, 1 \mathrm{H}, J=15.0 \mathrm{~Hz}), 4.11(\mathrm{q}, 2 \mathrm{H}, J=7.0 \mathrm{~Hz}), 3.94(\mathrm{~s}, 2 \mathrm{H})$, $1.22(\mathrm{t}, 2 \mathrm{H}, J=7.0 \mathrm{~Hz}) .{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(\mathrm{CDCl}_{3}, 75 \mathrm{MHz}\right): \delta 165.3,146.1,135.7,129.3$, 128.7, 127.9, 114.6, 60.4, 36.7, 14.5. HRMS (EI) $\mathrm{m} / \mathrm{z}$ calcd for $\mathrm{C}_{12} \mathrm{H}_{14} \mathrm{O}_{2} \mathrm{~S}: 222.3068$; found: 222.0715 .

Z-linear (33c): clear oil; 10\% ethyl acetate/petroleum ether used as eluant for flash chromatography. ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}, 300 \mathrm{MHz}\right): \delta 7.27-7.11(\mathrm{~m}, 5 \mathrm{H}), 6.97(\mathrm{~d}, 1 \mathrm{H}, J=$ $10.2 \mathrm{~Hz}), 5.76(\mathrm{~d}, 1 \mathrm{H}, J=10.2 \mathrm{~Hz}), 3.65(\mathrm{q}, 2 \mathrm{H}, J=7.7 \mathrm{~Hz}), 3.87(\mathrm{~s}, 2 \mathrm{H}), 1.69(\mathrm{t}, 2 \mathrm{H}, J=$ $7.7 \mathrm{~Hz}) .{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(\mathrm{CDCl}_{3}, 75 \mathrm{MHz}\right): \delta 148.6,138.8,137.3,129.1,128.5,127.6$, 113.8, 62.1, 39.6, 14.4. HRMS (EI) $\mathrm{m} / \mathrm{z}$ calcd for $\mathrm{C}_{12} \mathrm{H}_{14} \mathrm{O}_{2} \mathrm{~S}$ : 222.3068; found: 222.0715 .



Compound 33c observed in situ as mixture with 33b



## Reaction of Cyclopentylthiol (15) and 1-Ethynylcyclohexene (23)


$\mathrm{Tp}^{*} \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}(10 \mathrm{mg}, 0.01 \mathrm{mmol})$ was weighed out using a spatula into a 5 mL vial. 1,3,5-Trimethoxybenzene, ( $17 \mathrm{mg}, 0.10 \mathrm{mmol}$ ) was added using a spatula and $250 \mu \mathrm{~L} 1: 1$ DCE:toluene was added via micropipette. To this solution, cyclopentylthiol ( $37 \mu \mathrm{~L}, 0.34$ mmol ) and 1-ethynylcyclohexene ( $36 \mu \mathrm{~L}, 0.31 \mathrm{mmol}$ ) were added sequentially via micropipette. After stirring for 3 hours at room temperature, the reaction was concentrated and the residue dissolved in $\mathrm{CDCl}_{3}$. ${ }^{1} \mathrm{H}$ NMR analysis indicated the formation of the branched (34a) isomer in $56 \%$ yield. An additional $5 \%$ yield of an unidentified product was also observed.

Table 3.20. Hydrothiolation of cyclopentylthiol with 1-ethynylcyclohexene catalyzed by complexes 1 and 4-7

| Entry | Complex | Time | Ratio | Yield |
| :---: | :---: | :---: | :---: | :---: |
| 1 | $\mathrm{Tp} \mathrm{Rh}^{\left(\mathrm{PPh}_{3}\right)_{2}}$ | 3 h | 34a | 56\% ${ }^{\text {a }}$ |
| 2 | $\mathrm{TpRh}\left(\mathrm{PPh}_{3}\right)_{2}$ | 24 h | - | no rxn |
| 3 | $\mathrm{Tp}{ }^{\mathrm{Me}} \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}$ | 2 h | 34a | 48\% |
| 4 | $\mathrm{Tp}{ }^{\mathrm{Ph}} \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}$ | 3 h | 34a | 60\% |
| 5 | $T p^{\mathrm{Ph}, \mathrm{Me}} \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}$ | 3 h | 34a | $80 \%{ }^{\text {a }}$ |

[^8]Branched (34a): light yellow oil; 5\% ethyl acetate/petroleum ether used as eluant for flash chromatography. ${ }^{1} \mathrm{H} \operatorname{NMR}\left(\mathrm{CDCl}_{3}, 300 \mathrm{MHz}\right): \delta 6.31-6.20(\mathrm{~m}, 1 \mathrm{H}), 5.29(\mathrm{~s}, 1 \mathrm{H})$, $4.99(\mathrm{~s}, 1 \mathrm{H}), 3.35-3.40(\mathrm{~m}, 1 \mathrm{H}), 2.25-2.23(\mathrm{~m}, 2 \mathrm{H}), 2.16-2.15(\mathrm{~m}, 2 \mathrm{H}), 2.02-1.99(\mathrm{~m}$, $2 \mathrm{H}), 1.76-1.66(\mathrm{~m}, 10 \mathrm{H}) .{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(\mathrm{CDCl}_{3}, 75 \mathrm{MHz}\right): \delta 162.5,128.1,109.1,93.9$, 56.3, 51.4, 44.6, 34.1, 26.0, 25.7, 23.9. HRMS (EI) $\mathrm{m} / \mathrm{z}$ calcd for $\mathrm{C}_{13} \mathrm{H}_{20} \mathrm{~S}: 208.1286$; found: 208.1279 .

${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}, 300 \mathrm{MHz}\right)$ spectrum of compound 34a at 298 K


$\mathrm{Tp}^{*} \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}(0.005 \mathrm{mmol}, 44 \mu \mathrm{~L}$ of a 0.12 M stock solution in a $1: 1 \mathrm{DCE}$ :toluene mixture) was added to a 5 mL vial. $1,3,5$-Trimethoxybenzene, ( $8 \mathrm{mg}, 0.05 \mathrm{mmol}, 81 \mu \mathrm{~L}$ of a 0.62 M stock solution in a $1: 1 \mathrm{DCE}$ :toluene mixture) was added via micropipette. To this solution, benzene thiol ( $19 \mu \mathrm{~L}, 0.165 \mathrm{mmol}$ ) and 1-phenyl-1-propyne ( $19 \mu \mathrm{~L}, 0.15$ mmol ) were added sequentially via micropipette. After stirring for 2 hours at room temperature, the reaction was concentrated and the residue dissolved in $\mathrm{CDCl}_{3}$. ${ }^{1} \mathrm{H}$ NMR analysis indicated the formation of the branched (35a) and $E$-linear (35b) isomers in a 1:3.5 ratio in $70 \%$ combined yield.

Table 3.21. Hydrothiolation of benzylthiol with 1-phenyl-1-propyne catalyzed by complexes 1 and 5-7

| Entry | Complex | Time | Ratio | Yield |
| :---: | :---: | :---: | :---: | :---: |
| 1 | $\mathrm{Tp} \mathrm{Rh}^{\left(\mathrm{PPh}_{3}\right)_{2}}$ | 4 h | $\begin{gathered} 35 a: 35 b \\ (1: 3.5) \end{gathered}$ | 70\% |
| 2 | $\mathrm{Tp}{ }^{\mathrm{Me}} \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}$ | 1 h | - | no rxn |
| 3 | $\mathrm{Tp}{ }^{\mathrm{Ph}} \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}$ | 1 h | $\begin{gathered} 35 a: 35 b \\ (1: 1) \end{gathered}$ | 11\% |
| 4 | $\mathrm{Tp}{ }^{\mathrm{Ph}, \mathrm{Me} \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}}$ | 1 h | $\begin{gathered} 35 a: 35 b \\ (1: 1) \end{gathered}$ | 24\% |

35a: Characterization matches previously reported data. ${ }^{8 m}$
35b: Characterization matches previously reported data. ${ }^{8 \mathrm{~m}}$

## Reaction of Benzylthiol (10) and tert-Butylacetylene (20)


$\operatorname{BpRh}\left(\mathrm{PPh}_{3}\right)_{2}(12 \mathrm{mg}, 0.016 \mathrm{mmol})$ was weighed out using a spatula into a 20 mL vial. Next, 3.0 mL of a 1:1 DCE:toluene mixture was added via micropipette. To this solution, benzylthiol ( $65 \mu \mathrm{~L}, 0.55 \mathrm{mmol}$ ) and tert-butylacetylene ( $62 \mu \mathrm{~L}, 0.50 \mathrm{mmol}$ ) were added sequentially via micropipette. After stirring for 24 hours at room temperature, the reaction was concentrated and the residue dissolved in $\mathrm{CDCl}_{3}$. ${ }^{1} \mathrm{H}$ NMR analysis indicated the formation of the branched (36a) and $E$-linear ( $\mathbf{3 6 b}$ ) isomers in a $1: 2$ ratio in $35 \%$ combined conversion relative to the benzylthiol starting material.

Table 3.22. Hydrothiolation of benzylthiol with tert-butylacetylene catalyzed by complexes 2 and 3

| Entry | Complex | Time | Ratio | Yield ${ }^{\text {a }}$ |
| :---: | :---: | :---: | :---: | :---: |
| 1 | $\mathrm{BpRh}\left(\mathrm{PPh}_{3}\right)_{2}$ | 24 h | $36 \mathrm{a}: \mathbf{3 6 b}$ <br> $(1: 2)$ <br> $26 a$ | $35 \%$ |
| $\mathrm{Bp}^{*} \mathrm{Rh}_{\left(\mathrm{PPh}_{3}\right)_{2}}$ | 4 h | 36 a | $28 \% \mathrm{~b}$ |  |

${ }^{a}$ Percent yield with respect to remaining thiol. ${ }^{\text {b }}$ Solvent $=$ DCE.

Branched (36a): Characterization matches previously reported data. ${ }^{8 m}$ E-linear (36b): Characterization matches previously reported data. ${ }^{58}$

## Reaction of Benylthiol (10) and 1-Ethynylcyclohexene (23)


$\mathrm{BpRh}\left(\mathrm{PPh}_{3}\right)_{2}(7 \mathrm{mg}, 0.009 \mathrm{mmol})$ was weighed out using a spatula into a 20 mL vial. Next, 1.5 mL of a 1:1 DCE:toluene mixture was added via micropipette. To this solution, benzylthiol ( $33 \mu \mathrm{~L}, 0.28 \mathrm{mmol}$ ) and 1-ethynylcyclohexene ( $29 \mu \mathrm{~L}, 0.25 \mathrm{mmol}$ ) were added sequentially via micropipette. After stirring for 48 hours at room temperature, the reaction was concentrated and the residue dissolved in $\mathrm{CDCl}_{3}$. ${ }^{1} \mathrm{H} \mathrm{NMR}$ analysis indicated the formation of the branched (37a) and $E$-linear ( $\mathbf{3 7 b}$ ) isomers in a $1: 3$ ratio in $54 \%$ combined conversion relative to the benzylthiol starting material.

Table 3.23. Hydrothiolation of benzylthiol with 1-ethynylcyclohexene catalyzed by complexes 2 and 3

| Entry | Complex | Time | Ratio | Yield ${ }^{\text {a }}$ |
| :---: | :---: | :---: | :---: | :---: |
| 1 | $B p R h\left(\mathrm{PPh}_{3}\right)_{2}$ | 48 h | $37 \mathrm{a}: 37 \mathrm{~b}$ <br> $(1: 3)$ | $54 \%$ |
| 2 | $\mathrm{Bp}^{* R h}\left(\mathrm{PPh}_{3}\right)_{2}$ | 24 h | $37 \mathrm{a}: 37 \mathrm{~b}$ <br> $(7.5: 1)$ | $53 \%{ }^{\mathrm{b}}$ |

${ }^{a}$ Percent conversion with respect to remaining thiol. ${ }^{b}$ Solvent $=$ DCE.

Branched (37a): Characterization matches previously reported data. ${ }^{8 m}$
$E$-linear (37b): Characterization matches previously reported data. ${ }^{80}$

## Reaction of Propane Thiol (12) and Phenylacetylene (17)


$\mathrm{BpRh}\left(\mathrm{PPh}_{3}\right)_{2}(0.03 \mathrm{mmol}, 600 \mu \mathrm{~L}$ of a 0.05 M stock solution in a $1: 1 \mathrm{DCE}$ :toluene mixture) was added to a 5 mL vial. $1,3,5$-Trimethoxybenzene, ( $56 \mathrm{mg}, 0.33 \mathrm{mmol}, 200$ $\mu \mathrm{L}$ of a 1.6 M stock solution in a 1:1 DCE:toluene mixture) was added via micropipette. To this solution, propane thiol $(100 \mu \mathrm{~L}, 1.1 \mathrm{mmol})$ and phenylacetylene $(110 \mu \mathrm{~L}, 1.1$ mmol) were added sequentially via micropipette. After stirring for 48 hours at room temperature, the reaction was concentrated and the residue dissolved in $\mathrm{CDCl}_{3} .{ }^{1} \mathrm{H} \mathrm{NMR}$ analysis indicated the formation of the branched (38a) and $E$-linear ( $\mathbf{3 8 b}$ ) isomers in a $1: 1$ ratio in 6\% combined yield.

Branched (38a): Characterization matches previously reported data. ${ }^{8 m}$

E-linear (38b): ${ }^{1} \mathrm{H} \mathrm{NMR}\left(\mathrm{CDCl}_{3}, 300 \mathrm{MHz}\right): \delta 7.39-7.21(\mathrm{~m}), 6.78(\mathrm{~d}, 1 \mathrm{H}, J=15.5 \mathrm{~Hz})$, $6.53(\mathrm{~d}, 1 \mathrm{H}, J=15.5 \mathrm{~Hz}), 2.80(\mathrm{t}, 2 \mathrm{H}, J=7.3 \mathrm{~Hz}), 1.80-1.61(\mathrm{~m}), 0.83(\mathrm{t}, 3 \mathrm{H}, J=7.3$ Hz ).

## Chapter 4 - Summary, Conclusions and Future Work

### 4.1 Summary

This thesis covers two areas: the solution and solid state structures of rhodium pyrazolylborate complexes and their utility in catalytic alkyne hydrothiolation. Pyrazolylborate complexes were chosen as they are easily manipulated and have versatility with respect to substitution on and the number of pyrazolyl rings attached to the boron. As well, their highly electron-rich nature made them good candidates for the use in hydrothiolation reactions with alkyl thiols.

A series of bis- and tris(pyrazolyl)borate complexes (1-7) were synthesized and structurally characterized. These include bis(pyrazolyl)borate complexes $\mathrm{Bp} * \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}$ (2) and $\mathrm{BpRh}\left(\mathrm{PPh}_{3}\right)_{2}$ (3) and tris(pyrazolyl)borate complexes $\mathrm{Tp} \mathrm{Rh}_{\left(\mathrm{PPh}_{3}\right)_{2} \text { (1), }}$, $\mathrm{TpRh}\left(\mathrm{PPh}_{3}\right)_{2}$ (4), $\mathrm{Tp}^{\mathrm{Me}} \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}$ (5), $\mathrm{Tp}^{\mathrm{Ph}} \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}$ (6) and $\mathrm{Tp}^{\mathrm{Ph}, \mathrm{Me}} \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}$ (7). These were all synthesized by modified literature methods with higher yields than have previously been reported. The crystals used to obtain X-ray structures of known complexes 2 and 4 and new complexes 5-7 were obtained by layering a saturated solution of each complex in toluene with hexanes and leaving the resulting biphasic solution at $-35^{\circ} \mathrm{C}$ for approximately one week.

Tris(pyrazolyl)borate complexes have been cited in the literature as adopting certain structural geometries based on the solvent system as well as the substitution around the pyrazolyl rings. ${ }^{13,14,28 \mathrm{a}}$ The solid state structures of the complexes appear to be in agreement with the previously reported literature data. Complexes $\mathbf{1 , 5}$ and 7, which have
substituents in the 5-position, are all in form $\mathbf{B}$, where the third uncoordinated pyrazolyl ring is located overtop of the rhodium atom. Complexes 4 and $\mathbf{6}$, which lack substitution in the 5 -positon, favor form $\mathbf{A}$, where the third uncoordinated pyrazolyl ring is rotated away from the rhodium centre.

All seven complexes were tested in a series of hydrothiolation reactions. Common reactivity trends were found with respect to substitution and number of pyrazolyl rings on the boron. The methyl substituted bis(pyrazolyl)borate complex $\mathbf{2}$ gave better regioselecitvity than complex 3, which lacked substitution on the pyrazolyl rings. The majority of tris(pyrazolyl)borate complexes (1, 6 and 7 ) were superior with respect to yield and regioselectivity in comparison to the bis(pyrazolyl)borate complexes (2 and 3). Tris(pyrazolyl)borate complexes with substitution on all pyrazolyl rings at both the 3and 5-positions (1 and 7) were superior with respect to yield and regioselectivity to those with substitution only at the 3-position (5 and 6). Tris(pyrazolyl)borate complex 4, which lacked substitution on the pyrazolyl rings, favored the Z-linear isomer and therefore possibly goes through a different mechanism. Consequently, the ability to adopt a $\kappa^{3}$ coordinated intermediate during the postulated catalytic cycle and substitution at both the 3- and 5-positions of the pyrazolyl rings seems to be important for the regioselectivity and yields of hydrothiolation reactions. It is also interesting to note that all seven complexes catalyzed alkyne hydrothiolation reactions using alkyl thiols.

### 4.2 Future Work

In this thesis, work concerning the synthesis, structure and hydrothiolation activity of rhodium pyrazolylborate complexes has been presented. Additional studies are expected to reveal greater insight into the catalytic activity. Mechanistic investigations are currently being studied within our group. This will presumably provide evidence as to whether tris(pyrazolyl)borate complexes go through the postulated $\kappa^{3}$-coordinated intermediate and explain how the substitution on the pyrazolyl rings affects the rate, yield and selectivity of the reaction. Additionally, the identity of the byproduct should be determined. Using the mechanistic information along with the byproduct identity, perhaps conditions can be found that minimize the formation of this compound. Furthermore, the scope of the hydrothiolation reaction can be expanded to include more examples of aryl thiols and as well as a variety of functionalized substrates.

The rhodium pyrazolylborate complexes have been shown to decompose after prolonged reaction times as shown in the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectra. Complex 7, in particular, produced a thermal decomposition product that was presumably irreversible because it remained upon cooling back to room temperature. This product showed a rhodium hydride peak in the ${ }^{1} \mathrm{H}$ NMR spectrum. Therefore, the identity of the decomposition products should be investigated and compared to the known orthometallation product. ${ }^{28 \mathrm{j}}$

Electron withdrawing (ie. nitro, cyano, halo etc.) or electron donating (hydroxy, methoxy) substituents can be added to the 3-, 4- or 5-positions on the pyrazolyl rings. The catalytic activity of complexes containing pyrazolyl rings with these electron withdrawing or electron donating substituents can then be studied. Furthermore, other ligand systems such as monoanionic tridentate phosphine ligands or
tris(pyrazolyl)methane ligands can be synthesized. These ligands can be used to form rhodium complexes and their catalytic activity tested in hydrothiolation reactions.

Although hydrothiolation reactions are a starting point to test the ability of rhodium pyrazolylborate complexes as effective catalysts other reactions can also be examined. For example, activation of $\mathrm{H}-\mathrm{X}$ bonds $(\mathrm{X}=$ heteroatom $)$ can be investigated. Our group has demonstrated the use of $\mathrm{Tp} * \mathrm{Rh}\left(\mathrm{PPh}_{3}\right)_{2}$ in $\mathrm{P}-\mathrm{H}$ bond activation reactions and are currently studying $\mathrm{O}-\mathrm{H}$ bond activation reactions.

Using alkyne hydrothiolation reactions we have the potential to produce vinyl sulfide products that are not commercially available or readily synthesized by other means. This is an important advance as vinyl sulfides are precursors to many functionalized molecules and can be used as synthetic intermediates as described in Chapter 1.

There are a variety of directions available for continuing studies in this area of research. From mechanistic investigations to substrate scope, ligand design and H-X bond activation reactions. Some of these directions are currently being investigated within our research group and others have potential as future studies. As we have shown pyrazolylborates are a diverse set of compounds in which their full capabilities are yet to be explored.

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Appendix I: X-ray Crystallographic Data for Bp $\mathbf{R h}^{\left(\mathbf{P P h}_{3}\right)_{2}(\mathbf{2})}$


Configuration represented in Chapter 2


Configuration including all atoms
Figure 1. ORTEP diagrams of complex 2. Thermal ellipsoids are drawn at the $50 \%$ probability level. Hydrogen atoms, except for the B-H hydrogens, and phenyl groups of $\mathrm{PPh}_{3}$ (in configuration represented in Chapter 2) are excluded for clarity.

## A. Crystal Data

Empirical Formula
Formula Weight
Crystal Color, Habit
Crystal Dimensions
Crystal System
Lattice Type
Lattice Parameters

Space Group
Z value
Dealc
F000
$\mu(\operatorname{MoK} \alpha)$

## B. Intensity Measurements

Diffractometer
Radiation
Data Images
Detector Position
$2 \theta_{\text {max }}$
No. of Reflections Measured

Corrections

## C. Structure Solution and Refinement

Structure Solution
Refinement
Function Minimized
Least Squares Weights
Anomalous Dispersion
No. Observations ( $\mathrm{I}>0.00 \sigma(\mathrm{I})$ )
No. Variables
Reflection/Parameter Ratio
Residuals (refined on $\mathrm{F}^{2}$, all data): R1; wR2
$\mathrm{C}_{52.5} \mathrm{H}_{57} \mathrm{BN}_{4} \mathrm{P}_{2} \mathrm{Rh}$
919.68
orange, prism
$0.25 \times 0.25 \times 0.40 \mathrm{~mm}$
monoclinic
primitive
$\mathrm{a}=11.168(1) \AA \quad \alpha=90.0^{\circ}$
$\mathrm{b}=17.004(2) \AA \quad \beta=98.470(6)^{\circ} \mathrm{o}$
$\mathrm{c}=24.853(2) \AA \quad \gamma=90.0^{\circ}$
$\mathrm{V}=4667.9(8) \AA^{3}$
$P 21 / c$ (\#14)
4
$1.309 \mathrm{~g} / \mathrm{cm}^{3}$
1920.00
$4.74 \mathrm{~cm}^{-1}$

Bruker X8 APEX II
$\operatorname{MoK} \alpha(\lambda=0.71073 \AA)$
graphite monochromated
1322 exposures @ 10.0 seconds
36.00 mm
$56.4^{\circ}$
Total: 50326
Unique: $11268\left(\mathrm{R}_{\text {int }}=0.052\right)$
Absorption ( $\mathrm{T}_{\text {min }}=0.802$,
$\mathrm{T}_{\text {max }}=0.888$ ); Lorentz-polarization

## Direct Methods (SIR97)

Full-matrix least-squares on $\mathrm{F}^{2}$
$\Sigma \mathrm{w}\left(\mathrm{Fo}^{2}-\mathrm{Fc}^{2}\right)^{2}$
$\mathrm{w}=1 /\left(\sigma^{2}\left(\mathrm{Fo}^{2}\right)+(0.0403 \mathrm{P})^{2}+3.468 \mathrm{P}\right)$
All non-hydrogen atoms
11268
573
19.66
$0.061 ; 0.098$

| Goodness of Fit Indicator | 1.02 |
| :--- | :--- |
| No. Observations (I>2.00 (I)) | 8528 |
| Residuals (refined on F): R1; wR2 | $0.039 ; 0.087$ |
| Max Shift/Error in Final Cycle | 0.00 |
| Maximum peak in Final Diff. Map | $0.47 \mathrm{e}^{-} / \AA^{3}$ |
| Minimum peak in Final Diff. Map | $-0.44 \mathrm{e}^{-} / \AA^{3}$ |

Table 1. Atomic Coordinates ( $\times 10^{4}$ ) and Equivalent Isotropic Displacement Parameters ( $\AA \times 10^{3}$ )

| Atom | X | Y | Z | Ueq |
| :--- | :--- | :--- | :--- | :--- |
| C1 | $-1026(2)$ | $1740(2)$ | $2262(1)$ | $22(1)$ |
| C7 | $801(2)$ | $965(1)$ | $2956(1)$ | $20(1)$ |
| C13 | $960(2)$ | $2642(2)$ | $2732(1)$ | $22(1)$ |
| C19 | $2169(2)$ | $2394(2)$ | $4100(1)$ | $23(1)$ |
| C25 | $621(2)$ | $2186(2)$ | $4883(1)$ | $22(1)$ |
| C31 | $542(2)$ | $3628(1)$ | $4235(1)$ | $22(1)$ |
| C37 | $-2211(3)$ | $3109(2)$ | $4792(1)$ | $31(1)$ |
| C38 | $-2354(2)$ | $2244(2)$ | $4718(1)$ | $24(1)$ |
| C39 | $-2866(2)$ | $1713(2)$ | $5044(1)$ | $29(1)$ |
| C40 | $-2860(2)$ | $996(2)$ | $4789(1)$ | $27(1)$ |
| C41 | $-3306(3)$ | $213(2)$ | $4952(1)$ | $38(1)$ |
| C42 | $-3374(3)$ | $2809(2)$ | $2614(1)$ | $36(1)$ |
| C43 | $-3543(2)$ | $2013(2)$ | $2846(1)$ | $26(1)$ |
| C44 | $-4529(3)$ | $1510(2)$ | $2753(1)$ | $34(1)$ |
| C45 | $-4236(2)$ | $861(2)$ | $3073(1)$ | $30(1)$ |
| C46 | $-4974(3)$ | $151(2)$ | $3159(1)$ | $49(1)$ |
| B1 | $-2368(3)$ | $532(2)$ | $3832(1)$ | $26(1)$ |
| N1 | $-2028(2)$ | $1869(1)$ | $4291(1)$ | $20(1)$ |
| N2 | $-2365(2)$ | $1091(1)$ | $4332(1)$ | $23(1)$ |
| N3 | $-3110(2)$ | $971(1)$ | $3349(1)$ | $24(1)$ |
| N4 | $-2684(2)$ | $1684(1)$ | $3204(1)$ | $21(1)$ |
| P1 | $-63(1)$ | $1891(1)$ | $2923(1)$ | $18(1)$ |
| P2 | $573(1)$ | $2551(1)$ | $4183(1)$ | $18(1)$ |
| Rh1 | $-1027(1)$ | $2053(1)$ | $3635(1)$ | $17(1)$ |
| H1B | $-2810(20)$ | $-18(15)$ | $3915(10)$ | $20(7)$ |
| H2B | $-1420(20)$ | $409(16)$ | $3723(10)$ | $27(7)$ |
|  |  |  |  |  |

Table 2. Bond Lengths ( $\AA$ )

| Atoms | Length | Atoms | Length |
| :--- | :--- | :--- | :--- |
| C1-P1 | $1.842(2)$ | C43-C44 | $1.387(4)$ |
| C7-P1 | $1.842(2)$ | C44-C45 | $1.373(4)$ |
| C13-P1 | $1.822(3)$ | C45-N3 | $1.353(3)$ |
| C19-P2 | $1.844(3)$ | C45-C46 | $1.495(4)$ |
| C25-P2 | $1.840(3)$ | B1-N3 | $1.547(4)$ |
| C31-P2 | $1.837(3)$ | B1-N2 | $1.564(4)$ |
| C37-C38 | $1.487(4)$ | B1-H1B | $1.09(3)$ |
| C38-N1 | $1.333(3)$ | B1-H2B | $1.16(3)$ |
| C38-C39 | $1.392(4)$ | N1-N2 | $1.384(3)$ |
| C39-C40 | $1.374(4)$ | N1-Rh1 | $2.132(2)$ |
| C40-N2 | $1.342(3)$ | N3-N4 | $1.369(3)$ |
| C40-C41 | $1.498(4)$ | N4-Rh1 | $2.092(2)$ |
| C42-C43 | $1.494(4)$ | P1-Rh1 | $2.2202(7)$ |
| C43-N4 | $1.332(3)$ | P2-Rh1 | $2.2468(7)$ |

Table 3. Bond Angles ( ${ }^{\circ}$ )

| Atoms | Angle |
| :--- | :--- |
| N1-C38-C39 | $109.7(2)$ |
| N1-C38-C37 | $122.3(2)$ |
| C39-C38-C37 | $128.0(2)$ |
| C40-C39-C38 | $106.0(2)$ |
| N2-C40-C39 | $108.3(2)$ |
| N2-C40-C41 | $122.0(3)$ |
| C39-C40-C41 | $129.7(3)$ |
| N4-C43-C44 | $109.2(2)$ |
| N4-C43-C42 | $121.3(2)$ |
| C44-C43-C42 | $129.5(3)$ |
| C45-C44-C43 | $106.4(2)$ |
| N3-C45-C44 | $107.9(2)$ |
| N3-C45-C46 | $122.0(3)$ |
| C44-C45-C46 | $130.0(3)$ |
| N3-B1-N2 | $105.2(2)$ |
| N3-B1-H1B | $110.8(13)$ |
| N2-B1-H1B | $108.5(13)$ |
| N3-B1-H2B | $108.2(13)$ |
| N2-B1-H2B | $113.7(13)$ |
| H1B-B1-H2B | $110.3(19)$ |
| C38-N1-N2 | $106.8(2)$ |
| C38-N1-Rh1 | $140.67(18)$ |
| N2-N1-Rh1 | $112.11(15)$ |
| C40-N2-N1 | $109.1(2)$ |
| C40-N2-B1 | $130.3(2)$ |


| Atoms | Angle |
| :--- | :--- |
| N1-N2-B1 | $119.4(2)$ |
| C45-N3-N4 | $108.8(2)$ |
| C45-N3-B1 | $132.7(2)$ |
| N4-N3-B1 | $117.6(2)$ |
| C43-N4-N3 | $107.6(2)$ |
| C43-N4-Rh1 | $135.31(18)$ |
| N3-N4-Rh1 | $116.56(15)$ |
| C13-P1-C7 | $105.46(12)$ |
| C13-P1-C1 | $99.93(11)$ |
| C7-P1-C1 | $98.90(11)$ |
| C13-P1-Rh1 | $121.05(8)$ |
| C7-P1-Rh1 | $112.49(8)$ |
| C1-P1-Rh1 | $116.06(8)$ |
| C31-P2-C25 | $105.53(11)$ |
| C31-P2-C19 | $100.43(12)$ |
| C25-P2-C19 | $99.36(12)$ |
| C31-P2-Rh1 | $113.37(8)$ |
| C25-P2-Rh1 | $110.88(8)$ |
| C19-P2-Rh1 | $124.97(8)$ |
| N4-Rh1-N1 | $79.84(8)$ |
| N4-Rh1-P1 | $92.93(6)$ |
| N1-Rh1-P1 | $164.16(6)$ |
| N4-Rh1-P2 | $170.88(6)$ |
| N1-Rh1-P2 | $92.91(6)$ |
| P1-Rh1-P2 | $95.43(3)$ |

Table 4. Anisotropic Displacement Parameters $\left(\AA \times 10^{3}\right)$

| Atom | $\mathrm{U}^{11}$ | $\mathrm{U}^{22}$ | $\mathrm{U}^{33}$ | $\mathrm{U}^{23}$ | $\mathrm{U}^{13}$ | $\mathrm{U}^{12}$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| C1 | $21(1)$ | $27(1)$ | $17(1)$ | $-4(1)$ | $4(1)$ | $3(1)$ |
| C7 | $17(1)$ | $20(1)$ | $22(1)$ | $-2(1)$ | $2(1)$ | $-1(1)$ |
| C13 | $25(1)$ | $24(1)$ | $18(1)$ | $2(1)$ | $2(1)$ | $-2(1)$ |
| C19 | $18(1)$ | $29(1)$ | $21(1)$ | $-5(1)$ | $0(1)$ | $-3(1)$ |
| C25 | $19(1)$ | $28(1)$ | $20(1)$ | $1(1)$ | $3(1)$ | $1(1)$ |
| C31 | $26(1)$ | $21(1)$ | $21(1)$ | $0(1)$ | $5(1)$ | $-2(1)$ |
| C37 | $34(2)$ | $32(2)$ | $28(1)$ | $-6(1)$ | $10(1)$ | $2(1)$ |
| C38 | $18(1)$ | $32(1)$ | $21(1)$ | $-4(1)$ | $3(1)$ | $-1(1)$ |
| C39 | $25(1)$ | $43(2)$ | $20(1)$ | $1(1)$ | $6(1)$ | $-3(1)$ |
| C40 | $21(1)$ | $37(2)$ | $24(1)$ | $8(1)$ | $5(1)$ | $-4(1)$ |
| C41 | $39(2)$ | $40(2)$ | $38(2)$ | $13(1)$ | $13(1)$ | $-7(1)$ |
| C42 | $32(2)$ | $38(2)$ | $37(2)$ | $8(1)$ | $2(1)$ | $8(1)$ |
| C43 | $21(1)$ | $35(1)$ | $22(1)$ | $-2(1)$ | $5(1)$ | $3(1)$ |
| C44 | $20(1)$ | $51(2)$ | $28(1)$ | $-2(1)$ | $-1(1)$ | $1(1)$ |
| C45 | $21(1)$ | $40(2)$ | $31(1)$ | $-10(1)$ | $6(1)$ | $-8(1)$ |
| C46 | $33(2)$ | $55(2)$ | $58(2)$ | $-8(2)$ | $5(2)$ | $-21(2)$ |
| B1 | $26(2)$ | $21(1)$ | $32(2)$ | $1(1)$ | $6(1)$ | $-2(1)$ |
| N1 | $19(1)$ | $23(1)$ | $20(1)$ | $0(1)$ | $4(1)$ | $-3(1)$ |
| N2 | $24(1)$ | $24(1)$ | $23(1)$ | $2(1)$ | $5(1)$ | $-3(1)$ |
| N3 | $22(1)$ | $25(1)$ | $25(1)$ | $-4(1)$ | $5(1)$ | $-6(1)$ |
| N4 | $20(1)$ | $24(1)$ | $19(1)$ | $-1(1)$ | $2(1)$ | $-3(1)$ |
| P1 | $19(1)$ | $19(1)$ | $17(1)$ | $1(1)$ | $3(1)$ | $0(1)$ |
| P2 | $19(1)$ | $19(1)$ | $18(1)$ | $0(1)$ | $2(1)$ | $-1(1)$ |
| Rh1 | $17(1)$ | $17(1)$ | $16(1)$ | $0(1)$ | $3(1)$ | $-1(1)$ |

Table 5. Torsional Angles ( ${ }^{\circ}$ )

| Atoms | Angle |
| :--- | :--- |
| N1-C38-C39-C40 | $-1.2(3)$ |
| C37-C38-C39-C40 | $176.2(3)$ |
| C38-C39-C40-N2 | $0.2(3)$ |
| C38-C39-C40-C41 | $-179.5(3)$ |
| N4-C43-C44-C45 | $0.5(3)$ |
| C42-C43-C44-C45 | $-178.9(3)$ |
| C43-C44-C45-N3 | $-0.2(3)$ |
| C43-C44-C45-C46 | $176.6(3)$ |
| C39-C38-N1-N2 | $1.8(3)$ |
| C37-C38-N1-N2 | $-175.8(2)$ |
| C39-C38-N1-Rh1 | $-169.9(2)$ |
| C37-C38-N1-Rh1 | $12.5(4)$ |
| C39-C40-N2-N1 | $0.9(3)$ |
| C41-C40-N2-N1 | $-179.4(2)$ |


| Atoms | Angle |
| :--- | :--- |
| C2-C1-P1-C7 | $60.0(2)$ |
| C6-C1-P1-Rh1 | $118.7(2)$ |
| C2-C1-P1-Rh1 | $-60.5(2)$ |
| C36-C31-P2-C25 | $-119.4(2)$ |
| C32-C31-P2-C25 | $62.2(3)$ |
| C36-C31-P2-C19 | $137.7(2)$ |
| C32-C31-P2-C19 | $-40.7(2)$ |
| C36-C31-P2-Rh1 | $2.1(2)$ |
| C32-C31-P2-Rh1 | $-176.3(2)$ |
| C30-C25-P2-C31 | $-16.4(3)$ |
| C26-C25-P2-C31 | $165.8(2)$ |
| C30-C25-P2-C19 | $87.3(2)$ |
| C26-C25-P2-C19 | $-90.5(2)$ |
| C30-C25-P2-Rh1 | $-139.5(2)$ |

Table 5. Torsional Angles ( ${ }^{\circ}$ )...continued

C39-C40-N2-B1
C41-C40-N2-B1
C38-N1-N2-C40
Rh1-N1-N2-C40
C38-N1-N2-B1
Rh1-N1-N2-B1
N3-B1-N2-C40
N3-B1-N2-N1
C44-C45-N3-N4
C46-C45-N3-N4
C44-C45-N3-B1
C46-C45-N3-B1
N2-B1-N3-C45
N2-B1-N3-N4
C44-C43-N4-N3
C42-C43-N4-N3
C44-C43-N4-Rh1
C42-C43-N4-Rh1
C45-N3-N4-C43
B1-N3-N4-C43
C45-N3-N4-Rh1
B1-N3-N4-Rh1
C14-C13-P1-C7
C18-C13-P1-C7
C14-C13-P1-C1
C18-C13-P1-C1
C14-C13-P1-Rh1
C18-C13-P1-Rh1
C12-C7-P1-C13
C8-C7-P1-C13
C12-C7-P1-C1
C8-C7-P1-C1
C12-C7-P1-Rh1
C8-C7-P1-Rh1
C6-C1-P1-C13
C2-C1-P1-C13
C6-C1-P1-C7
-165.8(3)
13.9(4)
-1.7(3)
172.64(16)
166.7(2)
-19.0(3)
114.4(3)
-51.2(3)
$-0.2(3)$
-177.3(3)
168.4(3)
-8.8(5)
-106.5(3)
61.3(3)
$-0.6(3)$
$178.8(2)$
-171.93(19)
7.5(4)
0.5(3)
-170.0(2)
173.70(16)
3.2(3)
10.8(3)
-173.28(19)
-91.4(2)
84.5(2)
139.9(2)
-44.3(2)
120.3(2)
-64.8(2)
-136.7(2)
38.1(2)
-13.6(2)
161.24(19)
-13.2(3)
167.5(2)
-120.8(2)

C26-C25-P2-Rh1
42.7(2)
147.2(2)
-33.4(2)
39.4(2)
-141.2(2)
-84.4(2)
95.0(2)
114.9(3)
-55.89(17)
-79.3(2)
109.91(16)
77.1(5)
-93.6(4)
-125.5(3)
63.08(16)
170.69(19)
-0.7(3)
48.9(3)
-122.49(15)
133.82(11)
-100.30(10)
12.58(11)
-164.0(2)
-38.1(2)
74.8(2)
-42.53(10)
83.35(9)
-163.77(9)
-56.4(4)
62.1(4)
-179(19)
-93.46(10)
25.03(10)
143.67(12)
100.02(9)
-141.49(9)
-22.85(11)

## Appendix II: X-ray Crystallographic Data for $\mathbf{T p R h}\left(\mathbf{P P h}_{3}\right)_{2}(4)$



Configuration represented in Chapter 2


Configuration including all atoms
Figure 1. ORTEP diagrams of complex 4. Thermal ellipsoids are drawn at the $50 \%$ probability level. Hydrogen atoms, except for the B-H hydrogen, and phenyl groups of $\mathrm{PPh}_{3}$ (in configuration represented in Chapter 2) are excluded for clarity.

## A. Crystal Data

Empirical Formula
Formula Weight
Crystal Color, Habit
Crystal Dimensions
Crystal System
Lattice Type
Lattice Parameters

Space Group
$Z$ value
Dcalc
F000
$\mu(\operatorname{MoK} \alpha)$

## B. Intensity Measurements

Diffractometer
Radiation
Data Images
Detector Position
$2 \theta_{\text {max }}$
No. of Reflections Measured

Corrections

## C. Structure Solution and Refinement

Structure Solution
Refinement
Function Minimized
Least Squares Weights

Anomalous Dispersion
No. Observations (I>0.00 $\sigma(\mathrm{I})$ )
No. Variables
Reflection/Parameter Ratio
$\mathrm{C}_{52} \mathrm{H}_{48} \mathrm{BN}_{6} \mathrm{P}_{2} \mathrm{RhFeP}$
932.62
red, irregular
0.20 X 0.20 X 0.10 mm
triclinic
primitive
$\mathrm{a}=12.2490(9) \AA \alpha=112.004(3)^{\circ} \mathrm{o}$
$\mathrm{b}=13.637(1) \AA \quad \beta=98.051(3)^{\circ}$
$\mathrm{c}=14.971(1) \AA \quad \gamma=90.387(3)^{\circ}$
$\mathrm{V}=2291.0(3) \AA^{3}$
P-1 (\#2)
2
$1.352 \mathrm{~g} / \mathrm{cm}^{3}$
964.00
$4.86 \mathrm{~cm}^{-1}$

Bruker X8 APEX
$\operatorname{MoKa}(\lambda=0.71073 \AA)$
graphite monochromated
3504 exposures @ 5.0 seconds
38.01 mm
$55.8^{\circ}$
Total: 77370
Unique: $10812\left(\mathrm{R}_{\text {int }}=0.042\right)$
Absorption ( $\mathrm{T}_{\text {min }}=0.858$,
$\mathrm{T}_{\text {max }}=0.953$ ); Lorentz-polarization

Direct Methods (SIR97)
Full-matrix least-squares on $\mathrm{F}^{2}$
$\Sigma \mathrm{w}\left(\mathrm{Fo}^{2}-\mathrm{Fc}^{2}\right)^{2}$
$\mathrm{w}=1 /\left(\sigma^{2}\left(\mathrm{Fo}^{2}\right)+(0.0287 \mathrm{P})\right.$
$2+0.3727 \mathrm{P})$
All non-hydrogen atoms
10812
603
17.93

| Residuals (refined on $\mathrm{F}^{2}$, all data): R1; wR2 | $0.036 ; 0.064$ |
| :--- | :--- |
| Goodness of Fit Indicator | 1.11 |
| No. Observations (I>2.00 $\sigma(\mathrm{I})$ ) | 9032 |
| Residuals (refined on F): R1; wR2 | $0.027 ; 0.063$ |
| Max Shift/Error in Final Cycle | 0.00 |
| Maximum peak in Final Diff. Map | $0.37 \mathrm{e}^{-/} \AA^{3}$ |
| Minimum peak in Final Diff. Map | $-0.35 \mathrm{e}^{-} / \AA^{3}$ |

Table 1. Atomic Coordinates ( $\times 10^{4}$ ) and Equivalent Isotropic Displacement Parameters ( $\AA \times 10^{3}$ )

| Atom | X | Y | Z | Ueq |
| :--- | :--- | :--- | :--- | :--- |
| C1 | $1746(1)$ | $1039(1)$ | $3272(1)$ | $19(1)$ |
| C7 | $2385(1)$ | $3099(1)$ | $3637(1)$ | $20(1)$ |
| C13 | $2279(1)$ | $1426(1)$ | $1632(1)$ | $20(1)$ |
| C19 | $1584(1)$ | $3717(1)$ | $1421(1)$ | $21(1)$ |
| C25 | $-2(1)$ | $4976(1)$ | $2488(1)$ | $22(1)$ |
| C31 | $-693(1)$ | $3350(1)$ | $599(1)$ | $21(1)$ |
| C37 | $-2709(1)$ | $2902(1)$ | $1611(1)$ | $29(1)$ |
| C38 | $-3739(1)$ | $2984(2)$ | $1915(1)$ | $33(1)$ |
| C39 | $-3580(1)$ | $2757(1)$ | $2747(1)$ | $28(1)$ |
| C40 | $-666(1)$ | $-62(1)$ | $2110(1)$ | $25(1)$ |
| C41 | $-1297(2)$ | $-648(1)$ | $2461(1)$ | $31(1)$ |
| C42 | $-1840(1)$ | $98(1)$ | $3128(1)$ | $29(1)$ |
| C43 | $-4142(2)$ | $1787(2)$ | $4931(2)$ | $42(1)$ |
| C44 | $-3522(2)$ | $2570(2)$ | $5734(2)$ | $44(1)$ |
| C45 | $-2609(2)$ | $2798(2)$ | $5391(1)$ | $34(1)$ |
| B1 | $-1913(2)$ | $2192(2)$ | $3727(1)$ | $22(1)$ |
| N1 | $-1959(1)$ | $2646(1)$ | $2216(1)$ | $22(1)$ |
| N2 | $-2513(1)$ | $2556(1)$ | $2922(1)$ | $21(1)$ |
| N3 | $-1535(1)$ | $1065(1)$ | $3169(1)$ | $22(1)$ |
| N4 | $-806(1)$ | $979(1)$ | $2535(1)$ | $20(1)$ |
| N5 | $-2700(1)$ | $2174(1)$ | $4427(1)$ | $27(1)$ |
| N6 | $-3663(1)$ | $1534(1)$ | $4132(1)$ | $36(1)$ |
| P1 | $1521(1)$ | $1999(1)$ | $2668(1)$ | $17(1)$ |
| P2 | $210(1)$ | $3583(1)$ | $1766(1)$ | $18(1)$ |
| R41 | $-236(1)$ | $2316(1)$ | $2303(1)$ | $17(1)$ |
| H1 | $-1176(12)$ | $2756(12)$ | $4143(11)$ | $12(4)$ |

Table 2. Bond Lengths ( $\AA$ )

| Atoms | Length |
| :--- | :--- |
| C1-P1 | $1.8521(15)$ |
| C7-P1 | $1.8422(16)$ |
| C13-P1 | $1.8397(16)$ |
| C19-P2 | $1.8553(16)$ |
| C25-P2 | $1.8414(16)$ |
| C31-P2 | $1.8474(16)$ |
| C37-N1 | $1.340(2)$ |
| C37-C38 | $1.392(2)$ |
| C38-C39 | $1.381(2)$ |
| C39-N2 | $1.347(2)$ |
| C40-N4 | $1.343(2)$ |
| C40-C41 | $1.390(2)$ |
| C41-C42 | $1.381(3)$ |
| C42-N3 | $1.346(2)$ |
| C43-N6 | $1.335(2)$ |


| Atoms | Length |
| :--- | :--- |
| C43-C44 | $1.391(3)$ |
| C44-C45 | $1.374(3)$ |
| C45-N5 | $1.361(2)$ |
| B1-N5 | $1.526(2)$ |
| B1-N3 | $1.558(2)$ |
| B1-N2 | $1.564(2)$ |
| B1-H1 | $1.126(15)$ |
| N1-N2 | $1.3741(18)$ |
| N1-Rh1 | $2.1575(13)$ |
| N3-N4 | $1.3661(18)$ |
| N4-Rh1 | $2.1111(13)$ |
| N5-N6 | $1.378(2)$ |
| P1-Rh1 | $2.2299(4)$ |
| P2-Rh1 | $2.2558(4)$ |

Table 3. Bond Angles ( ${ }^{\circ}$ )

| Atoms | Angle |
| :--- | :--- |
| N1-C37-C38 | $110.89(15)$ |
| C39-C38-C37 | $104.87(15)$ |
| N2-C39-C38 | $108.56(15)$ |
| N4-C40-C41 | $110.92(15)$ |
| C42-C41-C40 | $104.62(15)$ |
| N3-C42-C41 | $108.63(16)$ |
| N6-C43-C44 | $112.14(19)$ |
| C45-C44-C43 | $104.74(18)$ |
| N5-C45-C44 | $108.09(19)$ |
| N5-B1-N3 | $111.70(14)$ |
| N5-B1-N2 | $110.16(13)$ |
| N3-B1-N2 | $105.52(13)$ |
| N5-B1-H1 | $109.6(8)$ |
| N3-B1-H1 | $110.5(8)$ |
| N2-B1-H1 | $109.3(8)$ |
| C37-N1-N2 | $105.97(13)$ |
| C37-N1-Rh1 | $136.79(11)$ |
| N2-N1-Rh1 | $117.20(9)$ |
| C39-N2-N1 | $109.72(13)$ |
| C39-N2-B1 | $129.64(14)$ |
| N1-N2-B1 | $120.52(12)$ |
| C42-N3-N4 | $109.90(13)$ |
| C42-N3-B1 | $132.53(14)$ |
| N4-N3-B1 | $117.41(13)$ |
| C40-N4-N3 | $105.92(13)$ |


| Atoms | Angle |
| :--- | :--- |
| C40-N4-Rh1 | $132.63(11)$ |
| N3-N4-Rh1 | $121.24(9)$ |
| C45-N5-N6 | $110.12(15)$ |
| C45-N5-B1 | $126.85(16)$ |
| N6-N5-B1 | $122.94(14)$ |
| C43-N6-N5 | $104.91(16)$ |
| C13-P1-C7 | $109.05(7)$ |
| C13-P1-C1 | $101.25(7)$ |
| C7-P1-C1 | $95.69(7)$ |
| C13-P1-Rh1 | $116.17(5)$ |
| C7-P1-Rh1 | $116.23(5)$ |
| C1-P1-Rh1 | $115.72(5)$ |
| C25-P2-C31 | $102.16(7)$ |
| C25-P2-C19 | $100.96(7)$ |
| C31-P2-C19 | $100.48(7)$ |
| C25-P2-Rh1 | $119.22(6)$ |
| C31-P2-Rh1 | $108.34(5)$ |
| C19-P2-Rh1 | $122.50(5)$ |
| N4-Rh1-N1 | $83.37(5)$ |
| N4-Rh1-P1 | $91.52(3)$ |
| N1-Rh1-P1 | $169.58(4)$ |
| N4-Rh1-P2 | $169.18(4)$ |
| N1-Rh1-P2 | $92.98(4)$. |
| P1-Rh1-P2 | $93.605(15)$ |
|  |  |

Table 4. Anisotropic Displacement Parameters $\left(\AA \times 10^{3}\right)$

| Atom | $\mathrm{U}^{11}$ | $\mathrm{U}^{22}$ | $\mathrm{U}^{33}$ | $\mathrm{U}^{23}$ | $\mathrm{U}^{13}$ | $\mathrm{U}^{12}$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| C1 | $20(1)$ | $16(1)$ | $19(1)$ | $8(1)$ | $-1(1)$ | $1(1)$ |
| C7 | $23(1)$ | $19(1)$ | $22(1)$ | $12(1)$ | $3(1)$ | $1(1)$ |
| C13 | $23(1)$ | $20(1)$ | $23(1)$ | $13(1)$ | $7(1)$ | $8(1)$ |
| C19 | $22(1)$ | $20(1)$ | $27(1)$ | $15(1)$ | $8(1)$ | $6(1)$ |
| C25 | $23(1)$ | $21(1)$ | $24(1)$ | $11(1)$ | $4(1)$ | $6(1)$ |
| C31 | $21(1)$ | $25(1)$ | $22(1)$ | $14(1)$ | $6(1)$ | $2(1)$ |
| C37 | $22(1)$ | $38(1)$ | $36(1)$ | $25(1)$ | $4(1)$ | $5(1)$ |
| C38 | $19(1)$ | $46(1)$ | $45(1)$ | $30(1)$ | $3(1)$ | $7(1)$ |
| C39 | $19(1)$ | $31(1)$ | $36(1)$ | $15(1)$ | $9(1)$ | $5(1)$ |
| C40 | $27(1)$ | $22(1)$ | $28(1)$ | $10(1)$ | $5(1)$ | $5(1)$ |
| C41 | $37(1)$ | $20(1)$ | $39(1)$ | $14(1)$ | $6(1)$ | $2(1)$ |
| C42 | $29(1)$ | $29(1)$ | $37(1)$ | $21(1)$ | $7(1)$ | $-1(1)$ |
| C43 | $37(1)$ | $54(1)$ | $58(1)$ | $40(1)$ | $26(1)$ | $21(1)$ |
| C44 | $60(1)$ | $47(1)$ | $42(1)$ | $30(1)$ | $32(1)$ | $33(1)$ |
| C45 | $49(1)$ | $30(1)$ | $29(1)$ | $16(1)$ | $12(1)$ | $18(1)$ |
| B1 | $23(1)$ | $23(1)$ | $23(1)$ | $11(1)$ | $4(1)$ | $3(1)$ |
| N1 | $20(1)$ | $25(1)$ | $26(1)$ | $14(1)$ | $5(1)$ | $4(1)$ |
| N2 | $18(1)$ | $22(1)$ | $24(1)$ | $11(1)$ | $5(1)$ | $3(1)$ |
| N3 | $21(1)$ | $22(1)$ | $26(1)$ | $13(1)$ | $5(1)$ | $3(1)$ |
| N4 | $19(1)$ | $20(1)$ | $24(1)$ | $10(1)$ | $5(1)$ | $4(1)$ |
| N5 | $28(1)$ | $31(1)$ | $28(1)$ | $16(1)$ | $9(1)$ | $7(1)$ |
| N6 | $28(1)$ | $46(1)$ | $43(1)$ | $27(1)$ | $12(1)$ | $4(1)$ |
| P1 | $17(1)$ | $17(1)$ | $20(1)$ | $9(1)$ | $3(1)$ | $3(1)$ |
| P2 | $19(1)$ | $19(1)$ | $21(1)$ | $11(1)$ | $5(1)$ | $4(1)$ |
| Rh1 | $15(1)$ | $18(1)$ | $21(1)$ | $11(1)$ | $3(1)$ | $3(1)$ |

Table 5. Torsional Angles ( ${ }^{\circ}$ )

| Atoms | Angle | Atoms | Angle |
| :--- | :--- | :--- | :--- |
| N1-C37-C38-C39 | $-0.2(2)$ | C6-C1-P1-C7 | $-97.13(14)$ |
| C37-C38-C39-N2 | $0.2(2)$ | C2-C1-P1-C7 | $78.10(13)$ |
| N4-C40-C41-C42 | $0.23(19)$ | C6-C1-P1-Rh1 | $140.12(12)$ |
| C40-C41-C42-N3 | $-0.45(19)$ | C2-C1-P1-Rh1 | $-44.65(13)$ |
| N6-C43-C44-C45 | $-0.1(2)$ | C26-C25-P2-C31 | $107.90(14)$ |
| C43-C44-C45-N5 | $0.2(2)$ | C30-C25-P2-C31 | $-68.45(14)$ |
| C38-C37-N1-N2 | $0.2(2)$ | C26-C25-P2-C19 | $-148.73(13)$ |
| C38-C37-N1-Rh1 | $177.75(13)$ | C30-C25-P2-C19 | $34.92(14)$ |
| C38-C39-N2-N1 | $-0.05(19)$ | C26-C25-P2-Rh1 | $-11.39(15)$ |
| C38-C39-N2-B1 | $-175.80(16)$ | C30-C25-P2-Rh1 | $172.26(11)$ |
| C37-N1-N2-C39 | $-0.10(18)$ | C36-C31-P2-C25 | $-170.89(13)$ |
| Rh1-N1-N2-C39 | $-178.21(11)$ | C32-C31-P2-C25 | $5.42(16)$ |
| C37-N1-N2-B1 | $176.10(14)$ | C36-C31-P2-C19 | $85.36(14)$ |
| Rh1-N1-N2-B1 | $-2.00(18)$ | C32-C31-P2-C19 | $-98.33(15)$ |
| N5-B1-N2-C39 | $-5.5(2)$ | C36-C31-P2-Rh1 | $-44.20(14)$ |
| N3-B1-N2-C39 | $115.21(18)$ | C32-C31-P2-Rh1 | $132.10(13)$ |
| N5-B1-N2-N1 | $179.14(13)$ | C24-C19-P2-C25 | $-135.95(13)$ |
| N3-B1-N2-N1 | $-60.15(18)$ | C20-C19-P2-C25 | $44.53(14)$ |
| C41-C42-N3-N4 | $0.52(18)$ | C24-C19-P2-C31 | $-31.24(14)$ |
| C41-C42-N3-B1 | $175.71(16)$ | C20-C19-P2-C31 | $149.24(13)$ |
| N5-B1-N3-C42 | $6.6(2)$ | C24-C19-P2-Rh1 | $88.58(13)$ |
| N2-B1-N3-C42 | $-113.13(18)$ | C20-C19-P2-Rh1 | $-90.94(13)$ |
| N5-B1-N3-N4 | $-178.52(12)$ | C40-N4-Rh1-N1 | $128.30(14)$ |
| N2-B1-N3-N4 | $61.78(17)$ | N3-N4-Rh1-N1 | $-45.59(11)$ |
| C41-C40-N4-N3 | $0.07(18)$ | C40-N4-Rh1-P1 | $-60.81(14)$ |
| C41-C40-N4-Rh1 | $-174.50(11)$ | N3-N4-Rh1-P1 | $125.30(10)$ |
| C42-N3-N4-C40 | $-0.36(17)$ | C40-N4-Rh1-P2 | $57.5(3)$ |
| B1-N3-N4-C40 | $-176.37(13)$ | N3-N4-Rh1-P2 | $-116.38(18)$ |
| C42-N3-N4-Rh1 | $174.97(10)$ | C37-N1-Rh1-N4 | $-131.17(17)$ |
| B1-N3-N4-Rh1 | $-1.04(17)$ | N2-N1-Rh1-N4 | $46.16(11)$ |
| C44-C45-N5-N6 | $-0.20(19)$ | C37-N1-Rh1-P1 | $167.77(15)$ |
| C44-C45-N5-B1 | $176.43(15)$ | N2-N1-Rh1-P1 | $-14.9(3)$ |
| N3-B1-N5-C45 | $128.26(16)$ | C37-N1-Rh1-P2 | $38.61(17)$ |
| N2-B1-N5-C45 | $-114.82(17)$ | N2-N1-Rh1-P2 | $-144.06(10)$ |
| N3-B1-N5-N6 | C13-P1-Rh1-N4 | $104.30(7)$ |  |
|  |  |  |  |


| Table 5. Torsional Angles $\left({ }^{\circ}\right) \ldots$ continued |  |  |  |
| :--- | :--- | :--- | :--- |
| N2-B1-N5-N6 | $61.42(19)$ | C7-P1-Rh1-N4 | $-125.35(7)$ |
| C44-C43-N6-N5 | $0.0(2)$ | C1-P1-Rh1-N4 | $-14.25(7)$ |
| C45-N5-N6-C43 | $0.14(18)$ | C13-P1-Rh1-N1 | $164.7(2)$ |
| B1-N5-N6-C43 | $-176.66(15)$ | C7-P1-Rh1-N1 | $-64.9(2)$ |
| C14-C13-P1-C7 | $7.27(16)$ | C1-P1-Rh1-N1 | $46.2(2)$ |
| C18-C13-P1-C7 | $-175.87(11)$ | C13-P1-Rh1-P2 | $-66.18(6)$ |
| C14-C13-P1-C1 | $-92.85(15)$ | C7-P1-Rh1-P2 | $64.17(6)$ |
| C18-C13-P1-C1 | $84.01(12)$ | C1-P1-Rh1-P2 | $175.28(6)$ |
| C14-C13-P1-Rh1 | $140.94(13)$ | C25-P2-Rh1-N4 | $132.11(19)$ |
| C18-C13-P1-Rh1 | $-42.20(13)$ | C31-P2-Rh1-N4 | $16.0(2)$ |
| C12-C7-P1-C13 | $-51.03(15)$ | C19-P2-Rh1-N4 | $-100.0(2)$ |
| C8-C7-P1-C13 | $138.76(12)$ | C25-P2-Rh1-N1 | $62.17(7)$ |
| C12-C7-P1-C1 | $52.96(15)$ | C31-P2-Rh1-N1 | $-53.90(7)$ |
| C8-C7-P1-C1 | $-117.25(13)$ | C19-P2-Rh1-N1 | $-169.91(7)$ |
| C12-C7-P1-Rh1 | $175.33(12)$ | C25-P2-Rh1-P1 | $-109.75(6)$ |
| C6-C1-P1-C13 | $13.62(15)$ | C31-P2-Rh1-P1 | $134.17(5)$ |
| C2-C1-P1-C13 | $-171.15(12)$ | C19-P2-Rh1-P1 | $18.17(6)$ |

Appendix III: X-ray Crystallographic Data for $\mathbf{T p}{ }^{\mathrm{Me}} \mathbf{R h}\left(\mathbf{P P h}_{3}\right)_{2}\left(\mathbf{5}^{*}\right)$


## Configuration represented in Chapter 2



Configuration including all atoms
Figure 1. ORTEP diagrams of complex 5*. Thermal ellipsoids are drawn at the $50 \%$ probability level. Hydrogen atoms, except for the B-H hydrogen, and phenyl groups of $\mathrm{PPh}_{3}$ (in configuration represented in Chapter 2) are excluded for clarity.

## A. Crystal Data

Empirical Formula
Formula Weight
Crystal Color, Habit
Crystal Dimensions
Crystal System
Lattice Type
Lattice Parameters

Space Group
$Z$ value
D calc
F000
$\mu(\operatorname{MoK} \alpha)$

## B. Intensity Measurements

Diffractometer
Radiation

Data Images
Detector Position
$2 \theta_{\text {max }}$
No. of Reflections Measured

Corrections

## C. Structure Solution and Refinement

## Structure Solution

Refinement
Function Minimized
Least Squares Weights
Anomalous Dispersion
No. Observations ( $\mathrm{I}>0.00 \sigma(\mathrm{I})$ )
No. Variables
Reflection/Parameter Ratio
$\mathrm{C}_{48} \mathrm{H}_{46} \mathrm{BN}_{6} \mathrm{P}_{2} \mathrm{Rh}$
882.57
orange, prism
$0.10 \times 0.15 \times 0.15 \mathrm{~mm}$
triclinic
primitive
$\mathbf{a}=11.2313(7) \AA \quad \alpha=83.741(3)^{\circ}$
$\mathrm{b}=12.5804(7) \AA \quad \beta=73.336(3)^{\circ}$
$\mathrm{c}=16.992(1) \AA \quad \gamma=65.135(2)^{\circ}$
$\mathrm{V}=2086.6(2) \AA^{3}$
P-1 (\#2)
2
$1.405 \mathrm{~g} / \mathrm{cm}^{3}$
912.00
$5.29 \mathrm{~cm}^{-1}$

Bruker X8 APEX II
$\operatorname{MoK} \alpha(\lambda=0.71073 \AA)$
graphite monochromated
1814 exposures @ 10.0 seconds
36.00 mm
$50.2^{\circ}$
Total: 32934
Unique: $7377\left(\mathrm{R}_{\mathrm{int}}=0.042\right)$
Absorption ( $\mathrm{T}_{\text {min }}=0.883$, $\mathrm{T}_{\text {max }}=0.945$ ); Lorentz-polarization

Direct Methods (SIR97)
Full-matrix least-squares on $\mathrm{F}^{2}$
$\Sigma \mathrm{w}\left(\mathrm{Fo}^{2}-\mathrm{Fc}^{2}\right)^{2}$
$\mathrm{w}=1 /\left(\sigma^{2}\left(\mathrm{Fo}^{2}\right)+(0.0228 \mathrm{P})^{2}\right.$
+2.0617 P )
All non-hydrogen atoms
7377
.530
13.92

| Residuals (refined on $\mathrm{F}^{2}$, all data): R1; wR2 | $0.040 ; 0.072$ |
| :--- | :--- |
| Goodness of Fit Indicator | 1.07 |
| No. Observations (I>2.00 $\sigma(\mathrm{I})$ ) | 6335 |
| Residuals (refined on F): R1; wR2 | $0.037 ; 0.086$ |
| Max Shift/Error in Final Cycle | 0.00 |
| Maximum peak in Final Diff. Map | $0.38 \mathrm{e}^{-/} / \AA^{3}$ |
| Minimum peak in Final Diff. Map | $-0.31 \mathrm{e}^{-} / \AA^{3}$ |

Table 1. Atomic Coordinates ( $\times 10^{4}$ ) and Equivalent Isotropic Displacement Parameters ( $\AA \times 10^{3}$ )

| Atom | X | Y | Z | Ueq |
| :--- | :--- | :--- | :--- | :--- |
| C1 | $7416(3)$ | $2969(2)$ | $1947(2)$ | $20(1)$ |
| C7 | $5658(3)$ | $2947(2)$ | $3527(2)$ | $21(1)$ |
| C13 | $4936(3)$ | $4986(2)$ | $2451(2)$ | $22(1)$ |
| C19 | $2262(3)$ | $4007(2)$ | $3794(2)$ | $23(1)$ |
| C25 | $1520(3)$ | $4297(2)$ | $2261(2)$ | $23(1)$ |
| C31 | $1699(3)$ | $2260(2)$ | $3267(2)$ | $23(1)$ |
| C37 | $3215(3)$ | $987(2)$ | $1506(2)$ | $23(1)$ |
| C38 | $3492(3)$ | $-46(2)$ | $1129(2)$ | $26(1)$ |
| C39 | $4872(3)$ | $-680(2)$ | $996(2)$ | $22(1)$ |
| C40 | $5731(3)$ | $-1874(2)$ | $610(2)$ | $31(1)$ |
| C41 | $8320(3)$ | $496(2)$ | $189(2)$ | $22(1)$ |
| C42 | $8128(3)$ | $1573(2)$ | $-150(2)$ | $23(1)$ |
| C43 | $6901(3)$ | $2352(2)$ | $344(2)$ | $20(1)$ |
| C44 | $6134(3)$ | $3629(2)$ | $224(2)$ | $27(1)$ |
| C45 | $6111(3)$ | $-817(2)$ | $2834(2)$ | $26(1)$ |
| C46 | $6752(3)$ | $-1209(2)$ | $3452(2)$ | $31(1)$ |
| C47 | $8037(3)$ | $-1201(2)$ | $3119(2)$ | $31(1)$ |
| C48 | $9184(4)$ | $-1540(3)$ | $3509(2)$ | $47(1)$ |
| B1 | $6872(3)$ | $-377(3)$ | $1281(2)$ | $22(1)$ |
| N1 | $4343(2)$ | $1010(2)$ | $1601(1)$ | $20(1)$ |
| N2 | $5383(2)$ | $-48(2)$ | $1280(1)$ | $20(1)$ |
| N3 | $7278(2)$ | $612(2)$ | $860(1)$ | $19(1)$ |
| N4 | $6403(2)$ | $1771(2)$ | $964(1)$ | $17(1)$ |
| N5 | $6973(2)$ | $-589(2)$ | $2174(1)$ | $22(1)$ |
| N6 | $8190(2)$ | $-839(2)$ | $2340(2)$ | $27(1)$ |
| P1 | $5589(1)$ | $3378(1)$ | $2462(1)$ | $18(1)$ |
| P2 | $2619(1)$ | $3201(1)$ | $2847(1)$ | $19(1)$ |
| Rh1 | $4721(1)$ | $2352(1)$ | $1983(1)$ | $16(1)$ |
| H1 | $7520(20)$ | $-1190(20)$ | $908(15)$ | $17(7)$ |
|  |  |  |  |  |


| Table 2. Bond Lengths $(\boldsymbol{\AA})$ |  |  |  |
| :--- | :--- | :--- | :--- |
| Atoms | Length | Atoms | Length |
| C1-P1 | $1.849(3)$ | C45-N5 | $1.349(3)$ |
| C7-P1 | $1.847(3)$ | C45-C46 | $1.374(4)$ |
| C13-P1 | $1.838(3)$ | C46-C47 | $1.396(4)$ |
| C19-P2 | $1.850(3)$ | C47-N6 | $1.338(4)$ |
| C25-P2 | $1.841(3)$ | C47-C48 | $1.499(4)$ |
| C31-P2 | $1.844(3)$ | P1-Rh1 | $2.2404(7)$ |
| C37-N1 | $1.335(3)$ | P2-Rh1 | $2.2585(7)$ |
| C37-C38 | $1.386(4)$ | Rh1-N4 | $2.084(2)$ |
| C38-C39 | $1.374(4)$ | Rh1-N1 | $2.110(2)$ |
| C39-N2 | $1.349(3)$ | B1-N3 | $1.538(4)$ |
| C39-C40 | $1.500(4)$ | B1-N5 | $1.539(4)$ |
| C41-N3 | $1.349(3)$ | B1-N2 | $1.544(4)$ |
| C41-C42 | $1.368(4)$ | B1-H1 | $1.11(2)$ |
| C42-C43 | $1.394(4)$ | N1-N2 | $1.386(3)$ |
| C43-N4 | $1.340(3)$ | N3-N4 | $1.369(3)$ |
| C43-C44 | $1.494(4)$ | N5-N6 | $1.373(3)$ |

Table 3. Bond Angles $\left(^{\circ}\right.$ )

| Atoms | Angle | Atoms | Angle |
| :--- | :--- | :--- | :--- |
| N1-C37-C38 | $111.5(2)$ | N4-Rh1-P1 | $91.69(6)$ |
| C39-C38-C37 | $105.1(2)$ | N1-Rh1-P1 | $164.93(6)$ |
| N2-C39-C38 | $108.4(2)$ | N4-Rh1-P2 | $165.68(6)$ |
| N2-C39-C40 | $123.2(2)$ | N1-Rh1-P2 | $94.27(6)$ |
| C38-C39-C40 | $128.4(3)$ | P1-Rh1-P2 | $94.66(3)$ |
| N3-C41-C42 | $109.1(2)$ | N3-B1-N5 | $113.8(2)$ |
| C41-C42-C43 | $105.3(2)$ | N3-B1-N2 | $107.9(2)$ |
| N4-C43-C42 | $109.6(2)$ | N5-B1-N2 | $108.5(2)$ |
| N4-C43-C44 | $121.5(2)$ | N3-B1-H1 | $108.4(13)$ |
| C42-C43-C44 | $128.7(2)$ | N5-B1-H1 | $110.2(13)$ |
| N5-C45-C46 | $108.3(3)$ | N2-B1-H1 | $107.8(13)$ |
| C45-C46-C47 | $104.9(3)$ | C37-N1-N2 | $105.3(2)$ |
| N6-C47-C46 | $111.1(3)$ | C37-N1-Rh1 | $131.98(18)$ |
| N6-C47-C48 | $119.8(3)$ | N2-N1-Rh1 | $122.20(16)$ |
| C46-C47-C48 | $129.1(3)$ | C39-N2-N1 | $109.6(2)$ |
| C13-P1-C7 | $106.00(12)$ | C39-N2-B1 | $128.6(2)$ |
| C13-P1-C1 | $100.94(12)$ | N1-N2-B1 | $121.8(2)$ |
| C7-P1-C1 | $100.67(12)$ | C41-N3-N4 | $108.7(2)$ |
| C13-P1-Rh1 | $124.13(9)$ | C41-N3-B1 | $126.0(2)$ |
| C7-P1-Rh1 | $109.76(9)$ | N4-N3-B1 | $122.8(2)$ |
| C1-P1-Rh1 | $112.62(8)$ | C43-N4-N3 | $107.2(2)$ |
| C25-P2-C31 | $103.12(12)$ | C43-N4-Rh1 | $131.59(17)$ |
| C25-P2-C19 | $103.44(12)$ | N3-N4-Rh1 | $121.12(16)$ |
| C31-P2-C19 | $99.58(12)$ | C45-N5-N6 | $110.2(2)$ |
| C25-P2-Rh1 | $107.65(9)$ | C45-N5-B1 | $128.6(2)$ |
| C31-P2-Rh1 | $117.27(9)$ | N6-N5-B1 | $119.6(2)$ |
| C19-P2-Rh1 | $123.35(9)$ | C47-N6-N5 | $105.4(2)$ |
| N4-Rh1-N1 | $82.46(8)$ |  |  |

Table 4. Anisotropic Displacement Parameters $\left(\AA \times 10^{3}\right)$

| Atom | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| C1 | $21(1)$ | $26(2)$ | $18(1)$ | $-4(1)$ | $-5(1)$ | $-12(1)$ |
| C7 | $18(1)$ | $23(1)$ | $19(1)$ | $-3(1)$ | $-1(1)$ | $-7(1)$ |
| C13 | $26(1)$ | $15(1)$ | $22(2)$ | $-2(1)$ | $1(1)$ | $-10(1)$ |
| C19 | $15(1)$ | $26(2)$ | $21(2)$ | $-4(1)$ | $2(1)$ | $-7(1)$ |
| C25 | $20(1)$ | $20(1)$ | $28(2)$ | $1(1)$ | $-5(1)$ | $-8(1)$ |
| C31 | $23(1)$ | $24(1)$ | $19(2)$ | $-2(1)$ | $0(1)$ | $-10(1)$ |
| C37 | $18(1)$ | $29(2)$ | $24(2)$ | $1(1)$ | $-8(1)$ | $-10(1)$ |
| C38 | $26(2)$ | $34(2)$ | $26(2)$ | $-1(1)$ | $-9(1)$ | $-18(1)$ |
| C39 | $30(2)$ | $25(2)$ | $17(1)$ | $2(1)$ | $-6(1)$ | $-18(1)$ |
| C40 | $36(2)$ | $27(2)$ | $33(2)$ | $-8(1)$ | $-4(1)$ | $-18(1)$ |
| C41 | $16(1)$ | $29(2)$ | $20(2)$ | $-7(1)$ | $-3(1)$ | $-8(1)$ |
| C42 | $19(1)$ | $32(2)$ | $20(2)$ | $-3(1)$ | $0(1)$ | $-13(1)$ |
| C43 | $23(1)$ | $27(2)$ | $15(1)$ | $0(1)$ | $-7(1)$ | $-13(1)$ |
| C44 | $30(2)$ | $25(2)$ | $25(2)$ | $4(1)$ | $-7(1)$ | $-11(1)$ |
| C45 | $27(2)$ | $19(1)$ | $33(2)$ | $1(1)$ | $-6(1)$ | $-11(1)$ |
| C46 | $44(2)$ | $20(2)$ | $29(2)$ | $5(1)$ | $-12(1)$ | $-13(1)$ |
| C47 | $42(2)$ | $19(2)$ | $36(2)$ | $4(1)$ | $-20(1)$ | $-10(1)$ |
| C48 | $55(2)$ | $43(2)$ | $53(2)$ | $11(2)$ | $-36(2)$ | $-18(2)$ |
| B1 | $19(2)$ | $19(2)$ | $27(2)$ | $-2(1)$ | $-6(1)$ | $-7(1)$ |
| N1 | $20(1)$ | $17(1)$ | $21(1)$ | $-3(1)$ | $-4(1)$ | $-6(1)$ |
| N2 | $19(1)$ | $18(1)$ | $22(1)$ | $-3(1)$ | $-4(1)$ | $-8(1)$ |
| N3 | $15(1)$ | $17(1)$ | $23(1)$ | $-3(1)$ | $-6(1)$ | $-5(1)$ |
| N4 | $15(1)$ | $18(1)$ | $20(1)$ | $-3(1)$ | $-4(1)$ | $-7(1)$ |
| N5 | $23(1)$ | $18(1)$ | $30(1)$ | $2(1)$ | $-10(1)$ | $-9(1)$ |
| N6 | $26(1)$ | $23(1)$ | $36(2)$ | $4(1)$ | $-15(1)$ | $-9(1)$ |
| P1 | $19(1)$ | $16(1)$ | $19(1)$ | $-1(1)$ | $-3(1)$ | $-8(1)$ |
| P2 | $16(1)$ | $19(1)$ | $20(1)$ | $0(1)$ | $-2(1)$ | $-5(1)$ |
| Rh1 | $14(1)$ | $15(1)$ | $18(1)$ | $-2(1)$ | $-3(1)$ | $-5(1)$ |
|  |  |  |  |  | -10 |  |

Table 5. Torsional Angles ( ${ }^{\circ}$ )

| Atoms | Angle |
| :---: | :---: |
| N1-C37-C38-C39 | 0.4(3) |
| C37-C38-C39-N2 | -0.1(3) |
| C37-C38-C39-C40 | 179.6(3) |
| N3-C41-C42-C43 | -0.9(3) |
| C41-C42-C43-N4 | 1.8(3) |
| C41-C42-C43-C44 | -174.5(3) |
| N5-C45-C46-C47 | -0.1(3) |
| C45-C46-C47-N6 | -0.7(3) |
| C45-C46-C47-C48 | 180.0(3) |
| C14-C13-P1-C7 | -130.5(2) |
| C18-C13-P1-C7 | 51.5(3) |
| C14-C13-P1-C1 | 124.9(2) |
| C18-C13-P1-C1 | -53.0(3) |
| C14-C13-P1-Rh1 | -2.3(3) |
| C18-C13-P1-Rh1 | 179.78(19) |
| C8-C7-P1-C13 | 169.0(2) |
| C12-C7-P1-C13 | -12.5(3) |
| C8-C7-P1-C1 | -86.2(2) |
| C12-C7-P1-C1 | 92.2(3) |
| C8-C7-P1-Rh1 | 32.7(2) |
| C12-C7-P1-Rh1 | -148.8(2) |
| C2-C1-P1-C13 | -17.1(3) |
| C6-C1-P1-C13 | 168.6(2) |
| C2-C1-P1-C7 | -125.8(2) |
| C6-C1-P1-C7 | 59.9(2) |
| C2-C1-P1-Rh1 | 117.3(2) |
| C6-C1-P1-Rh1 | -57.0(2) |
| C26-C25-P2-C31 | -110.8(2) |
| C30-C25-P2-C31 | 70.5(3) |
| C26-C25-P2-C19 | 145.8(2) |
| C30-C25-P2-C19 | -32.9(3) |
| C26-C25-P2-Rh1 | 13.8(2) |
| C30-C25-P2-Rh1 | -164.9(2) |
| C36-C31-P2-C25 | 169.0(2) |
| C32-C31-P2-C25 | -12.0(3) |
| C36-C31-P2-C19 | -84.7(2) |
| C32-C31-P2-C19 | 94.3(2) |
| C36-C31-P2-Rh1 | 50.9(2) |
| C32-C31-P2-Rh1 | -130.1(2) |
| C24-C19-P2-C25 | -33.1(3) |
| C20-C19-P2-C25 | 151.0(2) |
| C24-C19-P2-C31 | -139.2(2) |


| Atoms | Angle |
| :---: | :---: |
| C25-P2-Rh1-N1 | -90.04(11) |
| C31-P2-Rh1-N1 | 25.57(12) |
| C19-P2-Rh1-N1 | 149.86(12) |
| C25-P2-Rh1-P1 | 102.11(9) |
| C31-P2-Rh1-P1 | -142.28(10) |
| C19-P2-Rh1-P1 | -17.99(11) |
| C38-C37-N1-N2 | -0.5(3) |
| C38-C37-N1-Rh1 | 171.44(19) |
| N4-Rh1-N1-C37 | -133.5(2) |
| P1-Rh1-N1-C37 | 158.70(19) |
| P2-Rh1-N1-C37 | 32.5(2) |
| N4-Rh1-N1-N2 | 37.31(18) |
| P1-Rh1-N1-N2 | -30.5(4) |
| P2-Rh1-N1-N2 | -156.71(18) |
| C38-C39-N2-N1 | -0.2(3) |
| C40-C39-N2-N1 | -179.9(2) |
| C38-C39-N2-B1 | 179.4(3) |
| C40-C39-N2-B1 | -0.3(4) |
| C37-N1-N2-C39 | 0.4(3) |
| Rh1-N1-N2-C39 | -172.51(17) |
| C37-N1-N2-B1 | -179.3(2) |
| Rh1-N1-N2-B1 | 7.8(3) |
| N3-B1-N2-C39 | 126.1(3) |
| N5-B1-N2-C39 | -110.2(3) |
| N3-B1-N2-N1 | -54.3(3) |
| N5-B1-N2-N1 | 69.4(3) |
| C42-C41-N3-N4 | -0.3(3) |
| C42-C41-N3-B1 | 161.9(2) |
| N5-B1-N3-C41 | 118.0(3) |
| N2-B1-N3-C41 | -121.5(3) |
| N5-B1-N3-N4 | -82.2(3) |
| N2-B1-N3-N4 | 38.3(3) |
| C42-C43-N4-N3 | -1.9(3) |
| C44-C43-N4-N3 | 174.7(2) |
| C42-C43-N4-Rh1 | 174.45(18) |
| C44-C43-N4-Rh1 | -8.9(4) |
| C41-N3-N4-C43 | 1.4(3) |
| B1-N3-N4-C43 | -161.5(2) |
| C41-N3-N4-Rh1 | -175.48(16) |
| B1-N3-N4-Rh1 | 21.7(3) |
| N1-Rh1-N4-C43 | 131.7(2) |
| P1-Rh1-N4-C43 | -62.2(2) |

Table 5. Torsional Angles ( ${ }^{\circ}$ )...continued C20-C19-P2-C31
C24-C19-P2-Rh1
C20-C19-P2-Rh1
C13-P1-Rh1-N4
C7-P1-Rh1-N4
C1-P1-Rh1-N4
C13-P1-Rh1-N1
C7-P1-Rh1-N1
C1-P1-Rh1-N1
C13-P1-Rh1-P2
C7-P1-Rh1-P2
C1-P1-Rh1-P2
C25-P2-Rh1-N4
C31-P2-Rh1-N4
C19-P2-Rh1-N4
44.9(2)
88.9(2)
-87.0(2)
107.70(12)
-125.62(10)
-14.36(11)
174.4(2)
$-58.9(3)$
52.4(3)
-59.44(11)
67.23(9)
178.50(9)
-13.9(3)
101.7(3)
-134.0(3)

P2-Rh1-N4-C43
54.1(4)

N1-Rh1-N4-N3
-52.29(17)
P1-Rh1-N4-N3
113.77(17)

P2-Rh1-N4-N3
-129.9(2)
C46-C45-N5-N6
C46-C45-N5-B1
0.8(3)

N3-B1-N5-C45
N2-B1-N5-C45
N3-B1-N5-N6
N2-B1-N5-N6
C46-C47-N6-N5
C48-C47-N6-N5
C45-N5-N6-C47
B1-N5-N6-C47
166.2(2)
139.1(3)
19.0(4)
-56.6(3)
-176.8(2)
1.1(3)
-179.5(3)
-1.2(3)
-168.1(2)

## Appendix IV: X-ray Crystallographic Data for $\mathbf{T p}{ }^{\mathbf{P h}} \mathbf{R h}\left(\mathbf{P P h}_{3}\right)_{2}(\mathbf{6})$



## Configuration represented in Chapter 2



Configuration including all atoms

Figure 1. ORTEP diagrams of complex 6. Thermal ellipsoids are drawn at the $50 \%$ probability level. Hydrogen atoms, except for the B-H hydrogen, and phenyl groups of $\mathrm{PPh}_{3}$ are excluded for clarity.

## A. Crystal Data

Empirical Formula
Formula Weight
Crystal Color, Habit
Crystal Dimensions
Crystal System
Lattice Type
Lattice Parameters

Space Group
$Z$ value
Dcalc
F000
$\mu(\mathrm{MoK} \alpha)$

## B. Intensity Measurements

Diffractometer
Radiation

Data Images
Detector Position
$2 \theta_{\text {max }}$
No. of Reflections Measured

Corrections

## C. Structure Solution and Refinement

Structure Solution
Refinement
Function Minimized
Least Squares Weights
Anomalous Dispersion
No. Observations (I>0.00 $\sigma(\mathrm{I})$ )
No. Variables
Reflection/Parameter Ratio
Residuals (refined on $\mathrm{F}^{2}$, all data): R1; wR2
$\mathrm{C}_{68} \mathrm{H}_{64} \mathrm{BN}_{6} \mathrm{P}_{2} \mathrm{Rh}$
1140.91
orange, irregular
0.035 X $0.10 \times 0.20 \mathrm{~mm}$
monoclinic
primitive
$a=17.4909(9) \AA \alpha=90.0^{\circ}$
$\mathrm{b}=18.524(1) \AA \quad \beta=107.914(5)^{\circ} \mathrm{o}$
$\mathrm{c}=18.517(1) \AA \quad \gamma=90.0^{\circ}$
$\mathrm{V}=5708.7(5) \AA^{3}$
$P 21 / n$ (\#14)
4
$1.327 \mathrm{~g} / \mathrm{cm}^{3}$
2376.00
$4.03 \mathrm{~cm}^{-1}$

Bruker X8 APEX II
$\operatorname{MoK} \alpha(\lambda=0.71073 \AA)$
graphite monochromated
1220 exposures @ 9.0 seconds
36.00 mm
$56.0^{\circ}$
Total: 60965
Unique: $13758\left(\mathrm{R}_{\mathrm{int}}=0.044\right)$
Absorption ( $\mathrm{T}_{\text {min }}=0.839$,
$\mathrm{T}_{\text {max }}=0.986$ ); Lorentz-polarization

## Direct Methods (SIR97)

Full-matrix least-squares on $\mathrm{F}^{2}$
$\Sigma \mathrm{w}\left(\mathrm{Fo}^{2}-\mathrm{Fc}^{2}\right)^{2}$
$\mathrm{w}=1 /\left(\sigma^{2}\left(\mathrm{Fo}^{2}\right)+(0.0396 \mathrm{P})^{2}+4.037 \mathrm{P}\right)$
All non-hydrogen atoms
13758
701
19.63
0.053; 0.093

Goodness of Fit Indicator
1.02

No. Observations ( $\mathrm{I}>2.00 \sigma(\mathrm{I})$ )
Residuals (refined on F): R1; wR2
Max Shift/Error in Final Cycle
Maximum peak in Final Diff. Map
Minimum peak in Final Diff. Map

10811
$0.037 ; 0.085$
0.00
$0.82 \mathrm{e}^{-/} / \AA^{3}$
$-0.55 \mathrm{e}^{-/} / \AA^{3}$

Table 1. Atomic Coordinates ( $\times 10^{4}$ ) and Equivalent Isotropic Displacement Parameters ( $\AA \times 10^{3}$ )

| Atom | X | Y | Z | Ueq |
| :--- | :--- | :--- | :--- | :--- |
| C1 | $5586(1)$ | $1262(1)$ | $8085(1)$ | $19(1)$ |
| C7 | $5152(1)$ | $1713(1)$ | $6555(1)$ | $21(1)$ |
| C13 | $4903(1)$ | $2618(1)$ | $7774(1)$ | $18(1)$ |
| C19 | $3205(1)$ | $2880(1)$ | $6092(1)$ | $25(1)$ |
| C25 | $1827(1)$ | $2087(1)$ | $6053(1)$ | $22(1)$ |
| C31 | $2903(1)$ | $1559(1)$ | $5260(1)$ | $22(1)$ |
| C37 | $1751(1)$ | $558(1)$ | $6903(1)$ | $23(1)$ |
| C38 | $1152(1)$ | $624(1)$ | $7251(2)$ | $30(1)$ |
| C39 | $1498(1)$ | $1000(1)$ | $7907(2)$ | $27(1)$ |
| C40 | $4334(1)$ | $15(1)$ | $8402(1)$ | $22(1)$ |
| C41 | $4295(2)$ | $-181(2)$ | $9120(1)$ | $31(1)$ |
| C42 | $3838(2)$ | $335(2)$ | $9311(1)$ | $30(1)$ |
| C43 | $2350(1)$ | $1412(1)$ | $10283(1)$ | $25(1)$ |
| C44 | $2750(2)$ | $2077(2)$ | $10396(2)$ | $32(1)$ |
| C45 | $2999(2)$ | $2164(1)$ | $9771(2)$ | $30(1)$ |
| C46 | $1765(1)$ | $95(1)$ | $6265(1)$ | $24(1)$ |
| C47 | $1169(2)$ | $108(1)$ | $5567(2)$ | $32(1)$ |
| C48 | $1188(2)$ | $-382(2)$ | $5009(2)$ | $42(1)$ |
| C49 | $1792(2)$ | $-877(2)$ | $5133(2)$ | $43(1)$ |
| C50 | $2389(2)$ | $-901(2)$ | $5823(2)$ | $36(1)$ |
| C51 | $2374(1)$ | $-417(1)$ | $6387(2)$ | $29(1)$ |
| C52 | $4720(1)$ | $-386(1)$ | $7929(1)$ | $24(1)$ |
| C53 | $4475(2)$ | $-315(1)$ | $7146(1)$ | $27(1)$ |
| C54 | $4830(2)$ | $-720(2)$ | $6709(2)$ | $39(1)$ |
| C55 | $5427(2)$ | $-1206(2)$ | $7043(2)$ | $47(1)$ |
| C56 | $5674(2)$ | $-1282(2)$ | $7822(2)$ | $46(1)$ |
| C57 | $5329(2)$ | $-877(2)$ | $8260(2)$ | $35(1)$ |
| C58 | $1932(1)$ | $1051(1)$ | $10760(1)$ | $25(1)$ |
| C59 | $2060(2)$ | $1262(2)$ | $11511(1)$ | $32(1)$ |
| C60 | $1649(2)$ | $937(2)$ | $11949(2)$ | $38(1)$ |
| C61 | $1113(2)$ | $391(2)$ | $11659(2)$ | $41(1)$ |
| C62 | $986(2)$ | $167(2)$ | $10917(2)$ | $39(1)$ |
|  |  |  |  |  |

Table 1. Atomic Coordinates...continued

| C63 | $1392(2)$ | $500(2)$ | $10474(2)$ | $32(1)$ |
| :--- | :--- | :--- | :--- | :--- |
| B1 | $2988(2)$ | $1441(2)$ | $8602(2)$ | $24(1)$ |
| N2 | $2259(1)$ | $1157(1)$ | $7948(1)$ | $23(1)$ |
| N1 | $2413(1)$ | $898(1)$ | $7318(1)$ | $20(1)$ |
| N5 | $2761(1)$ | $1588(1)$ | $9316(1)$ | $25(1)$ |
| N6 | $2357(1)$ | $1115(1)$ | $9629(1)$ | $26(1)$ |
| N3 | $3621(1)$ | $826(1)$ | $8750(1)$ | $21(1)$ |
| N4 | $3927(1)$ | $632(1)$ | $8185(1)$ | $19(1)$ |
| P1 | $4757(1)$ | $1708(1)$ | $7365(1)$ | $17(1)$ |
| P2 | $2894(1)$ | $1941(1)$ | $6170(1)$ | $19(1)$ |
| Rh1 | $3519(1)$ | $1272(1)$ | $7206(1)$ | $16(1)$ |
| H1B | $3264(14)$ | $1922(13)$ | $8464(13)$ | $19(6)$ |

Table 2. Bond Lengths ( $\AA$ )

| Atoms | Length |
| :--- | :--- |
| C1-P1 | $1.838(2)$ |
| C7-P1 | $1.833(2)$ |
| C13-P1 | $1.833(2)$ |
| C19-P2 | $1.843(2)$ |
| C25-P2 | $1.831(2)$ |
| C31-P2 | $1.832(2)$ |
| C37-N1 | $1.335(3)$ |
| C37-C38 | $1.394(3)$ |
| C37-C46 | $1.466(3)$ |
| C38-C39 | $1.370(4)$ |
| C39-N2 | $1.343(3)$ |
| C40-N4 | $1.341(3)$ |
| C40-C41 | $1.400(3)$ |
| C40-C52 | $1.462(3)$ |
| C41-C42 | $1.362(4)$ |
| C42-N3 | $1.345(3)$ |
| C43-N6 | $1.332(3)$ |
| C43-C44 | $1.400(4)$ |
| C43-C58 | $1.470(3)$ |
| C44-C45 | $1.366(4)$ |
| C45-N5 | $1.344(3)$ |
| C46-C47 | $1.388(3)$ |
| C46-C51 | $1.392(3)$ |
| C47-C48 | $1.383(4)$ |
| C48-C49 | $1.365(4)$ |


| Atoms | Length |
| :--- | :--- |
| C49-C50 | $1.379(4)$ |
| C50-C51 | $1.382(4)$ |
| C52-C53 | $1.387(3)$ |
| C52-C57 | $1.390(3)$ |
| C53-C54 | $1.382(3)$ |
| C54-C55 | $1.374(4)$ |
| C55-C56 | $1.379(5)$ |
| C56-C57 | $1.374(4)$ |
| C58-C63 | $1.381(4)$ |
| C58-C59 | $1.395(3)$ |
| C59-C60 | $1.376(4)$ |
| C60-C61 | $1.372(4)$ |
| C61-C62 | $1.385(4)$ |
| C62-C63 | $1.385(4)$ |
| B1-N5 | $1.518(3)$ |
| B1-N3 | $1.553(3)$ |
| B1-N2 | $1.555(3)$ |
| B1-H1B | $1.08(2)$ |
| N2-N1 | $1.363(3)$ |
| N1-Rh1 | $2.1240(18)$ |
| N5-N6 | $1.362(3)$ |
| N3-N4 | $1.361(2)$ |
| N4-Rh1 | $2.1000(18)$ |
| P1-Rh1 | $2.2429(6)$ |
| P2-Rh1 | $2.2618(6)$ |

## Table 3. Bond Angles ( ${ }^{\circ}$ )

| Atoms | Angle |
| :---: | :---: |
| N1-C37-C38 | 109.6(2) |
| N1-C37-C46 | 120.9(2) |
| C38-C37-C46 | 128.7(2) |
| C39-C38-C37 | 105.4(2) |
| N2-C39-C38 | 108.7(2) |
| N4-C40-C41 | 109.2(2) |
| N4-C40-C52 | 123.6(2) |
| C41-C40-C52 | 127.1(2) |
| C42-C41-C40 | 105.6(2) |
| N3-C42-C41 | 108.8(2) |
| N6-C43-C44 | 110.9(2) |
| N6-C43-C58 | 120.2(2) |
| C44-C43-C58 | 128.9(2) |
| C45-C44-C43 | 104.6(2) |
| N5-C45-C44 | 108.5(2) |
| C47-C46-C51 | 118.7(2) |
| C47-C46-C37 | 123.1(2) |
| C51-C46-C37 | 118.0(2) |
| C48-C47-C46 | 120.0(3) |
| C49-C48-C47 | 120.7(3) |
| C48-C49-C50 | 120.2(3) |
| C49-C50-C51 | 119.6(3) |
| C50-C51-C46 | 120.7(2) |
| C53-C52-C57 | 118.2(2) |
| C53-C52-C40 | 121.7(2) |
| C57-C52-C40 | 120.0(2) |
| C54-C53-C52 | 120.6(2) |
| C55-C54-C53 | 120.6(3) |
| C54-C55-C56 | 119.2(3) |
| C57-C56-C55 | 120.6(3) |
| C56-C57-C52 | 120.8(3) |
| C63-C58-C59 | 118.0(2) |
| C63-C58-C43 | 120.9(2) |
| C59-C58-C43 | 121.1(2) |
| C60-C59-C58 | 120.9(3) |
| C61-C60-C59 | 120.6(3) |
| C60-C61-C62 | 119.4(3) |
| C61-C62-C63 | 119.9(3) |
| C58-C63-C62 | 121.1(3) |
| N5-B1-N3 | 110.0(2) |


| Atoms | Angle |
| :---: | :---: |
| N5-B1-N2 | 111.6(2) |
| N3-B1-N2 | 104.97(19) |
| N5-B1-H1B | 108.3(13) |
| N3-B1-H1B | 107.4(12) |
| N2-B1-H1B | 114.4(13) |
| C39-N2-N1 | 109.26(19) |
| C39-N2-B1 | 132.7(2) |
| N1-N2-B1 | 117.08(18) |
| C37-N1-N2 | 107.05(18) |
| C37-N1-Rh1 | 138.84(16) |
| N2-N1-Rh1 | 113.28(14) |
| C45-N5-N6 | 110.3(2) |
| C45-N5-B1 | 125.0(2) |
| N6-N5-B1 | 124.4(2) |
| C43-N6-N5 | 105.7(2) |
| C42-N3-N4 | 109.35(19) |
| C42-N3-B1 | 130.3(2) |
| N4-N3-B1 | 119.14(18) |
| C40-N4-N3 | 107.03(18) |
| C40-N4-Rh1 | 138.44(16) |
| N3-N4-Rh1 | 113.85(14) |
| C13-P1-C7 | 107.10(10) |
| C13-P1-C1 | 97.75(10) |
| C7-P1-C1 | 100.58(10) |
| C13-P1-Rh1 | 113.06(7) |
| C7-P1-Rh1 | 119.04(7) |
| C1-P1-Rh1 | 116.60(7) |
| C25-P2-C31 | 104.17(11) |
| C25-P2-C19 | 99.55(11) |
| C31-P2-C19 | 101.89(11) |
| C25-P2-Rh1 | 113.04(8) |
| C31-P2-Rh1 | 115.42(8) |
| C19-P2-Rh1 | 120.40(7) |
| N4-Rh1-N1 | 78.98(7) |
| N4-Rh1-P1 | 91.82(5) |
| N1-Rh1-P1 | 167.28(5) |
| N4-Rh1-P2 | 171.38(5) |
| N1-Rh1-P2 | 92.54(5) |
| P1-Rh1-P2 | 96.32(2) |

Table 4. Anisotropic Displacement Parameters ( $\AA \times 10^{3}$ )

| Atom | $U^{11}$ | $\mathrm{U}^{22}$ | $U^{33}$ | $\mathrm{U}^{23}$ | $U^{13}$ | $U^{12}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| C1 | 18(1) | 18(1) | 21(1) | 3(1) | 6(1) | -2(1) |
| C7 | 22(1) | 24(1) | 19(1) | -1(1) | 9(1) | -1(1) |
| C13 | 22(1) | 17(1) | 15(1) | $0(1)$ | 6(1) | -1(1) |
| C19 | 29(1) | 22(1) | 19(1) | 5(1) | -2(1) | -4(1) |
| C25 | 23(1) | 19(1) | 23(1) | 4(1) | 6(1) | 1(1) |
| C31 | 21(1) | 28(1) | 18(1) | -2(1) | 6(1) | -6(1) |
| C37 | 21(1) | 21(1) | 26(1) | 4(1) | 7(1) | -1(1) |
| C38 | 21(1) | 31(1) | 39(2) | 1(1) | 12(1) | -4(1) |
| C39 | 23(1) | 28(1) | 35(1) | 2(1) | 16(1) | 1(1) |
| C40 | 21(1) | 22(1) | 24(1) | 5(1) | 7(1) | $0(1)$ |
| C41 | 36(1) | 32(2) | 26(1) | 12(1) | 11(1) | 8(1) |
| C42 | 35(1) | 38(2) | 20(1) | $9(1)$ | 12(1) | 3(1) |
| C43 | 27(1) | 27(1) | 23(1) | $0(1)$ | 11(1) | 7(1) |
| C44 | 39(1) | 32(2) | 28(1) | -10(1) | 15(1) | -2(1) |
| C45 | 36(1) | 24(1) | 35(1) | -4(1) | 16(1) | -2(1) |
| C46 | 26(1) | 20(1) | 28(1) | 2(1) | 10(1) | -7(1) |
| C47 | 35(1) | 24(1) | 34(1) | 4(1) | 4(1) | -2(1) |
| C48 | 55(2) | 32(2) | 30(2) | -2(1) | 1(1) | -7(1) |
| C49 | 71(2) | 23(2) | 35(2) | -6(1) | 19(2) | -7(1) |
| C50 | 41(2) | 25(1) | 45(2) | -2(1) | 17(1) | -2(1) |
| C51 | 27(1) | 26(1) | 33(1) | 1(1) | 8(1) | -4(1) |
| C52 | 21(1) | 19(1) | 33(1) | 2(1) | 11(1) | -1(1) |
| C53 | 31(1) | 22(1) | 32(1) | -1(1) | 14(1) | -1(1) |
| C54 | 52(2) | 32(2) | 41(2) | -6(1) | 27(1) | -1(1) |
| C55 | 51(2) | 32(2) | 72(2) | -6(2) | 40(2) | 5(1) |
| C56 | 35(2) | 35(2) | 72(2) | 6(2) | 24(2) | 13(1) |
| C57 | 28(1) | 32(2) | 45(2) | 8(1) | 11(1) | 4(1) |
| C58 | 29(1) | 26(1) | 24(1) | 4(1) | 13(1) | 11(1) |
| C59 | 35(1) | 37(2) | 24(1) | -1(1) | 11(1) | 12(1) |
| C60 | 42(2) | 51(2) | 25(1) | 7(1) | 18(1) | 19(1) |
| C61 | 41(2) | 51(2) | 38(2) | 19(1) | 23(1) | 13(1) |
| C62 | 37(2) | 41(2) | 43(2) | 7(1) | 17(1) | 1(1) |
| B1 | 28(1) | 24(2) | 23(1) | $0(1)$ | 11(1) | -1(1) |
| N2 | 24(1) | 24(1) | 23(1) | 2(1) | 11(1) | 1(1) |
| N1 | 21(1) | 21(1) | 19(1) | 1(1) | 8(1) | -1(1) |
| N5 | 32(1) | 22(1) | 24(1) | -1(1) | 14(1) | $0(1)$ |
| N6 | 35(1) | 24(1) | 25(1) | -1(1) | 16(1) | -1(1) |
| N3 | 24(1) | 24(1) | 17(1) | 1(1) | 9(1) | $0(1)$ |
| N4 | 20(1) | 21(1) | 17(1) | 1(1) | 7(1) | $0(1)$ |
| P1 | 18(1) | 17(1) | 16(1) | -1(1) | 6(1) | $0(1)$ |
| P2 | 20(1) | 19(1) | 16(1) | 1(1) | 4(1) | -2(1) |
| Rh1 | 17(1) | 16(1) | 15(1) | 1(1) | 6(1) | -1(1) |

Table 5. Torsional Angles ( ${ }^{\circ}$ )

| Atoms | Angle |
| :---: | :---: |
| N1-C37-C38-C39 | -2.1(3) |
| C46-C37-C38-C39 | 167.4(2) |
| C37-C38-C39-N2 | 0.6(3) |
| N4-C40-C41-C42 | 1.2(3) |
| C52-C40-C41-C42 | -176.5(2) |
| C40-C41-C42-N3 | -1.1(3) |
| N6-C43-C44-C45 | 0.0(3) |
| C58-C43-C44-C45 | -177.7(2) |
| C43-C44-C45-N5 | 0.1(3) |
| N1-C37-C46-C47 | -136.0(2) |
| C38-C37-C46-C47 | 55.6(4) |
| N1-C37-C46-C51 | 49.0(3) |
| C38-C37-C46-C51 | -119.5(3) |
| C51-C46-C47-C48 | 0.0(4) |
| C37-C46-C47-C48 | -175.0(2) |
| C46-C47-C48-C49 | -0.5(4) |
| C47-C48-C49-C50 | 0.7(5) |
| C48-C49-C50-C51 | -0.3(4) |
| C49-C50-C51-C46 | -0.3(4) |
| C47-C46-C51-C50 | 0.4(4) |
| C37-C46-C51-C50 | 175.7(2) |
| N4-C40-C52-C53 | -23.1(4) |
| C41-C40-C52-C53 | 154.3(3) |
| N4-C40-C52-C57 | 159.5(2) |
| C41-C40-C52-C57 | -23.1(4) |
| C57-C52-C53-C54 | -0.2(4) |
| C40-C52-C53-C54 | -177.6(2) |
| C52-C53-C54-C55 | 0.7(4) |
| C53-C54-C55-C56 | -0.6(4) |
| C54-C55-C56-C57 | 0.1(5) |
| C55-C56-C57-C52 | 0.4(4) |
| C53-C52-C57-C56 | -0.4(4) |
| C40-C52-C57-C56 | 177.1(2) |
| N6-C43-C58-C63 | -15.1(3) |
| C44-C43-C58-C63 | 162.4(3) |
| N6-C43-C58-C59 | 165.9(2) |
| C44-C43-C58-C59 | -16.6(4) |
| C63-C58-C59-C60 | -1.0(4) |
| C43-C58-C59-C60 | 178.1(2) |
| C58-C59-C60-C61 | 0.9(4) |
| C59-C60-C61-C62 | 0.0(4) |
| C60-C61-C62-C63 | -0.7(4) |


| Atoms | Angle |
| :---: | :---: |
| C41-C40-N4-N3 | -0.8(3) |
| C52-C40-N4-N3 | 176.9(2) |
| C41-C40-N4-Rh1 | -170.32(18) |
| C52-C40-N4-Rh1 | 7.5(4) |
| C42-N3-N4-C40 | 0.2(2) |
| B1-N3-N4-C40 | -168.6(2) |
| C42-N3-N4-Rh1 | 172.55(16) |
| B1-N3-N4-Rh1 | 3.8(2) |
| C14-C13-P1-C7 | 126.22(18) |
| C18-C13-P1-C7 | -60.8(2) |
| C14-C13-P1-C1 | -130.14(18) |
| C18-C13-P1-C1 | 42.8(2) |
| C14-C13-P1-Rh1 | -6.8(2) |
| C18-C13-P1-Rh1 | 166.13(17) |
| C8-C7-P1-C13 | -164.83(18) |
| C12-C7-P1-C13 | 15.2(2) |
| C8-C7-P1-C1 | 93.6(2) |
| C12-C7-P1-C1 | -86.4(2) |
| C8-C7-P1-Rh1 | -35.1(2) |
| C12-C7-P1-Rh1 | 144.91(19) |
| C6-C1-P1-C13 | -129.3(2) |
| C2-C1-P1-C13 | 48.1(2) |
| C6-C1-P1-C7 | -20.2(2) |
| C2-C1-P1-C7 | 157.17(19) |
| C6-C1-P1-Rh1 | 110.06(19) |
| C2-C1-P1-Rh1 | -72.61(19) |
| C26-C25-P2-C31 | -9.0(2) |
| C30-C25-P2-C31 | 175.45(19) |
| C26-C25-P2-C19 | 95.9(2) |
| C30-C25-P2-C19 | -79.6(2) |
| C26-C25-P2-Rh1 | -135.10(19) |
| C30-C25-P2-Rh1 | 49.4(2) |
| C32-C31-P2-C25 | -101.60(19) |
| C36-C31-P2-C25 | 80.3(2) |
| C32-C31-P2-C19 | 155.22(19) |
| C36-C31-P2-C19 | -22.9(2) |
| C32-C31-P2-Rh1 | 22.9(2) |
| C36-C31-P2-Rh1 | -155.19(18) |
| C20-C19-P2-C25 | 29.8(2) |
| C24-C19-P2-C25 | -156.00(19) |
| C20-C19-P2-C31 | 136.6(2) |
| C24-C19-P2-C31 | -49.2(2) |

Table 5. Torsional Angles ( ${ }^{\circ}$ )...continued

C59-C58-C63-C62
C43-C58-C63-C62
C61-C62-C63-C58
C38-C39-N2-N1
C38-C39-N2-B1
N5-B1-N2-C39
N3-B1-N2-C39
N5-B1-N2-N1
N3-B1-N2-N1
C38-C37-N1-N2
C46-C37-N1-N2
C38-C37-N1-Rh1
C46-C37-N1-Rh1
C39-N2-N1-C37
B1-N2-N1-C37
C39-N2-N1-Rh1
B1-N2-N1-Rh1
C44-C45-N5-N6
C44-C45-N5-B1
N3-B1-N5-C45
N2-B1-N5-C45
N3-B1-N5-N6
N2-B1-N5-N6
C44-C43-N6-N5
C58-C43-N6-N5
C45-N5-N6-C43
B1-N5-N6-C43
C41-C42-N3-N4
C41-C42-N3-B1
N5-B1-N3-C42
N2-B1-N3-C42
N5-B1-N3-N4
N2-B1-N3-N4
0.2(4)
-178.8(2)
$0.6(4)$
1.0(3)
-167.2(2)
-2.5(4)
116.7(3)
-169.96(19)
-50.8(3)
2.7(3)
-167.8(2)
-165.57(19)
24.0(4)
-2.3(3)
168.0(2)
169.30(16)
-20.4(2)
-0.1(3)
-173.7(2)
105.7(3)
-138.2(2)
-67.0(3)
49.1(3)
-0.1(3)
177.8(2)
0.1(3)
173.7(2)
$0.6(3)$
167.7(2)
16.5(4)
-103.7(3)
-177.46(18)
62.3(2)

C20-C19-P2-Rh1 -94.2(2)
C24-C19-P2-Rh1 80.0(2)
C40-N4-Rh1-N1 112.6(2)
N3-N4-Rh1-N1 -56.39(14)
C40-N4-Rh1-P1 -76.3(2)
N3-N4-Rh1-P1 114.76(14)
C40-N4-Rh1-P2 123.1(3)
N3-N4-Rh1-P2 -45.9(4)
C37-N1-Rh1-N4 -125.8(2)
N2-N1-Rh1-N4 66.39(15)
C37-N1-Rh1-P1 -170.11(18)
N2-N1-Rh1-P1 22.1(4)
C37-N1-Rh1-P2 55.7(2)
N2-N1-Rh1-P2 -112.04(14)
C13-P1-Rh1-N4 -101.43(9)
C7-P1-Rh1-N4 131.56(10)
C1-P1-Rh1-N4 10.71(10)
C13-P1-Rh1-N1 -58.2(3)
C7-P1-Rh1-N1 174.8(3)
C1-P1-Rh1-N1 54.0(3)
C13-P1-Rh1-P2 75.70(8)
C7-P1-Rh1-P2 -51.31(9)
C1-P1-Rh1-P2 -172.16(9)
C25-P2-Rh1-N4 5.9(4)
C31-P2-Rh1-N4 -113.9(4)
C19-P2-Rh1-N4 123.2(4)
C25-P2-Rh1-N1 16.28(10)
C31-P2-Rh1-N1
-103.51(10)
133.57(11)
-154.57(9)
85.64(8)
-37.28(10)

## Appendix V: X-ray Crystallographic Data for $\mathbf{T p}{ }^{\mathbf{P h}, \mathrm{Me}} \mathbf{R h}\left(\mathbf{P P h}_{3}\right)_{2}(7)$



Configuration represented in Chapter 2


Configuration including all atoms
Figure 1. ORTEP diagrams of complex 7. Thermal ellipsoids are drawn at the $50 \%$ probability level. Hydrogen atoms, except for the B-H hydrogen, and phenyl groups of $\mathrm{PPh}_{3}$ are excluded for clarity.

## A. Crystal Data

Empirical Formula
Formula Weight
Crystal Color, Habit
Crystal Dimensions
Crystal System
Lattice Type
Lattice Parameters

Space Group
$Z$ value
Dcalc
F000
$\mu(\operatorname{MoK} \alpha)$

## B. Intensity Measurements

Diffractometer
Radiation
Data Images
Detector Position
$2 \theta_{\text {max }}$
No. of Reflections Measured

Corrections

## C. Structure Solution and Refinement

Structure Solution
Refinement
Function Minimized
Least Squares Weights
Anomalous Dispersion
No. Observations ( $\mathrm{I}>0.00 \sigma(\mathrm{I})$ )
No. Variables
Reflection/Parameter Ratio
$\mathrm{C}_{72} \mathrm{H}_{72} \mathrm{BN}_{6} \mathrm{P}_{2} \mathrm{Rh}$
1197.02
red, irregular
0.05 X 0.12 X 0.25 mm
monoclinic
primitive
$\mathrm{a}=14.9000(5) \AA \quad \alpha=90.0^{\circ}$
$\mathrm{b}=14.8303(5) \AA \quad \beta=92.260(2)^{\circ} \mathrm{o}$
$\mathrm{c}=29.460(1) \AA \quad \gamma=90.0^{\circ}$
$\mathrm{V}=6504.8(4) \AA^{3}$
P21/n(\#14)
4
$1.222 \mathrm{~g} / \mathrm{cm}^{3}$
2504.00
$3.57 \mathrm{~cm}^{-1}$

Bruker X8 APEX II
$\operatorname{MoK} \alpha(\lambda=0.71073 \AA)$
graphite monochromated
1138 exposures @ 30.0 seconds
36.00 mm
$50.1^{\circ}$
Total: 49830
Unique: $11499\left(\mathrm{R}_{\text {int }}=0.052\right)$
Absorption ( $\mathrm{T}_{\text {min }}=0.842$,
$\mathrm{T}_{\text {max }}=0.982$ ); Lorentz-polarization

Direct Methods (SIR97)
Full-matrix least-squares on $\mathrm{F}^{2}$
$\Sigma \mathrm{w}\left(\mathrm{Fo}^{2}-\mathrm{Fc}^{2}\right)^{2}$
$\mathrm{w}=1 /\left(\sigma^{2}\left(\mathrm{Fo}^{2}\right)+(0.0474 \mathrm{P})^{2}\right.$
+0.0000 P )
All non-hydrogen atoms
11499
692
16.62

| Residuals (refined on F2, all data): R1; wR2 | $0.058 ; 0.090$ |
| :--- | :--- |
| Goodness of Fit Indicator | 0.99 |
| No. Observations (I>2.00 $\sigma(\mathrm{I})$ ) | 8482 |
| Residuals (refined on F): R1; wR2 | $0.037 ; 0.084$ |
| Max Shift/Error in Final Cycle | 0.00 |
| Maximum peak in Final Diff. Map | $0.46 \mathrm{e}^{-/} / \AA^{3}$ |
| Minimum peak in Final Diff. Map | $-0.31 \mathrm{e}^{-} / \AA^{3}$ |

Table 1. Atomic Coordinates ( $\times 10^{4}$ ) and Equivalent Isotropic Displacement Parameters ( $\AA \times 10^{\mathbf{3}}$ )

| Atom | X | Y | Z | Ueq |
| :--- | :--- | :--- | :--- | :--- |
| C1 | $5415(2)$ | $2035(2)$ | $2536(1)$ | $26(1)$ |
| C7 | $3900(2)$ | $3147(2)$ | $2327(1)$ | $24(1)$ |
| C13 | $3998(2)$ | $2042(2)$ | $3134(1)$ | $24(1)$ |
| C19 | $3892(2)$ | $3620(2)$ | $4054(1)$ | $22(1)$ |
| C25 | $3031(2)$ | $4541(2)$ | $3278(1)$ | $22(1)$ |
| C31 | $4272(2)$ | $5407(2)$ | $3905(1)$ | $22(1)$ |
| C37 | $5408(2)$ | $6513(2)$ | $3063(1)$ | $30(1)$ |
| C38 | $5225(2)$ | $7428(2)$ | $3129(1)$ | $39(1)$ |
| C39 | $4668(2)$ | $7886(2)$ | $2825(1)$ | $52(1)$ |
| C40 | $4270(2)$ | $7456(2)$ | $2455(1)$ | $52(1)$ |
| C41 | $4450(2)$ | $6560(2)$ | $2385(1)$ | $46(1)$ |
| C42 | $5011(2)$ | $6091(2)$ | $2685(1)$ | $35(1)$ |
| C43 | $6040(2)$ | $6041(2)$ | $3377(1)$ | $27(1)$ |
| C44 | $6746(2)$ | $6427(2)$ | $3634(1)$ | $32(1)$ |
| C45 | $7218(2)$ | $5740(2)$ | $3828(1)$ | $33(1)$ |
| C46 | $8066(2)$ | $5809(2)$ | $4121(1)$ | $44(1)$ |
| C47 | $6577(2)$ | $3863(2)$ | $2052(1)$ | $31(1)$ |
| C48 | $6304(2)$ | $4740(2)$ | $1958(1)$ | $37(1)$ |
| C49 | $5982(2)$ | $4982(2)$ | $1532(1)$ | $49(1)$ |
| C50 | $5919(3)$ | $4343(3)$ | $1192(1)$ | $62(1)$ |
| C51 | $6187(3)$ | $3466(3)$ | $1280(1)$ | $61(1)$ |
| C52 | $6522(2)$ | $3227(2)$ | $1705(1)$ | $43(1)$ |
| C53 | $7006(2)$ | $3635(2)$ | $2497(1)$ | $29(1)$ |
| C54 | $7857(2)$ | $3275(2)$ | $2575(1)$ | $37(1)$ |
| C55 | $8012(2)$ | $3288(2)$ | $3035(1)$ | $35(1)$ |
| C56 | $8819(2)$ | $2975(3)$ | $3312(1)$ | $55(1)$ |
| C57 | $6372(2)$ | $941(2)$ | $4191(1)$ | $33(1)$ |
| C58 | $6590(2)$ | $465(2)$ | $3807(1)$ | $40(1)$ |
| C59 | $6447(2)$ | $-449(2)$ | $3771(1)$ | $50(1)$ |
| C60 | $6075(2)$ | $-915(2)$ | $4120(1)$ | $51(1)$ |
| C61 | $5852(2)$ | $-463(2)$ | $4506(1)$ | $53(1)$ |
| C62 | $6005(2)$ | $458(2)$ | $4547(1)$ | $46(1)$ |
|  |  |  |  |  |

Table 1. Atomic Coordinates...continued

| C63 | $6532(2)$ | $1916(2)$ | $4234(1)$ | $32(1)$ |
| :--- | :--- | :--- | :--- | :--- |
| C64 | $6577(2)$ | $2442(2)$ | $4632(1)$ | $37(1)$ |
| C65 | $6753(2)$ | $3306(2)$ | $4488(1)$ | $34(1)$ |
| C66 | $6938(2)$ | $4126(2)$ | $4771(1)$ | $43(1)$ |
| B1 | $7236(2)$ | $3994(2)$ | $3722(1)$ | $30(1)$ |
| N1 | $6067(1)$ | $5140(1)$ | $3432(1)$ | $23(1)$ |
| N2 | $6808(1)$ | $4949(2)$ | $3709(1)$ | $26(1)$ |
| N3 | $7283(1)$ | $3642(2)$ | $3230(1)$ | $28(1)$ |
| N4 | $6636(1)$ | $3840(1)$ | $2895(1)$ | $25(1)$ |
| N5 | $6785(2)$ | $3290(2)$ | $4029(1)$ | $29(1)$ |
| N6 | $6659(2)$ | $2426(2)$ | $3868(1)$ | $30(1)$ |
| P1 | $4671(1)$ | $2844(1)$ | $2806(1)$ | $22(1)$ |
| P2 | $4133(1)$ | $4363(1)$ | $3575(1)$ | $20(1)$ |
| Rh1 | $5336(1)$ | $4041(1)$ | $3161(1)$ | $20(1)$ |
| H1 | $7923(18)$ | $4055(17)$ | $3870(8)$ | $34(8)$ |

Table 2. Bond Lengths ( $\AA$ )

| Atoms | Length |
| :--- | :--- |
| C1-P1 | $1.837(3)$ |
| C7-P1 | $1.839(3)$ |
| C13-P1 | $1.852(3)$ |
| C19-P2 | $1.839(3)$ |
| C25-P2 | $1.849(3)$ |
| C31-P2 | $1.837(3)$ |
| C37-C42 | $1.388(4)$ |
| C37-C38 | $1.399(4)$ |
| C37-C43 | $1.471(4)$ |
| C38-C39 | $1.377(4)$ |
| C39-C40 | $1.375(5)$ |
| C40-C41 | $1.373(5)$ |
| C41-C42 | $1.381(4)$ |
| C43-N1 | $1.346(3)$ |
| C43-C44 | $1.396(4)$ |
| C44-C45 | $1.352(4)$ |
| C45-N2 | $1.362(3)$ |
| C45-C46 | $1.504(4)$ |
| C47-C48 | $1.387(4)$ |
| C47-C52 | $1.391(4)$ |
| C47-C53 | $1.475(4)$ |
| C48-C49 | $1.374(4)$ |
| C49-C50 | $1.379(5)$ |
| C50-C51 | $1.382(5)$ |
| C51-C52 | $1.377(4)$ |
| C53-N4 | $1.350(3)$ |


| Atoms | Length |
| :--- | :--- |
| C54-C55 | $1.366(4)$ |
| C55-N3 | $1.354(3)$ |
| C55-C56 | $1.500(4)$ |
| C57-C58 | $1.383(4)$ |
| C57-C62 | $1.397(4)$ |
| C57-C63 | $1.471(4)$ |
| C58-C59 | $1.376(4)$ |
| C59-C60 | $1.375(4)$ |
| C60-C61 | $1.372(5)$ |
| C61-C62 | $1.389(4)$ |
| C63-N6 | $1.337(3)$ |
| C63-C64 | $1.405(4)$ |
| C64-C65 | $1.378(4)$ |
| C65-N5 | $1.355(3)$ |
| C65-C66 | $1.494(4)$ |
| B1-N3 | $1.545(4)$ |
| B1-N5 | $1.551(4)$ |
| B1-N2 | $1.554(4)$ |
| B1-H1 | $1.10(3)$ |
| N1-N2 | $1.377(3)$ |
| N1-Rh1 | $2.100(2)$ |
| N3-N4 | $1.383(3)$ |
| N4-Rh1 | $2.140(2)$ |
| N5-N6 | $1.377(3)$ |
| P1-Rh1 | $2.2683(7)$ |
| P2-Rh1 | $2.2572(7)$ |
|  |  |

Table 3. Bond Angles ( ${ }^{\circ}$ )

| Atoms | Angle |
| :---: | :---: |
| C42-C37-C38 | 118.0(3) |
| C42-C37-C43 | 122.1(3) |
| C38-C37-C43 | 119.8(3) |
| C39-C38-C37 | 120.2(3) |
| C40-C39-C38 | 121.1(3) |
| C41-C40-C39 | 119.2(3) |
| C40-C41-C42 | 120.4(3) |
| C41-C42-C37 | 121.0(3) |
| N1-C43-C44 | 108.9(2) |
| N1-C43-C37 | 124.3(2) |
| C44-C43-C37 | 126.6(3) |
| C45-C44-C43 | 106.8(3) |
| C44-C45-N2 | 108.6(2) |
| C44-C45-C46 | 127.0(3) |
| N2-C45-C46 | 124.3(3) |
| C48-C47-C52 | 118.7(3) |
| C48-C47-C53 | 120.4(3) |
| C52-C47-C53 | 120.6(3) |
| C49-C48-C47 | 121.1(3) |
| C48-C49-C50 | 119.7(3) |
| C49-C50-C51 | 120.0(3) |
| C52-C51-C50 | 120.3(3) |
| C51-C52-C47 | 120.2(3) |
| N4-C53-C54 | 110.1(2) |
| N4-C53-C47 | 122.9(2) |
| C54-C53-C47 | 126.6(3) |
| C55-C54-C53 | 106.1(3) |
| N3-C55-C54 | 108.5(3) |
| N3-C55-C56 | 121.9(3) |
| C58-C57-C62 | 117.6(3) |
| C58-C57-C63 | 122.0(3) |
| C62-C57-C63 | 120.4(3) |
| C59-C58-C57 | 121.7(3) |
| C60-C59-C58 | 120.2(3) |
| C61-C60-C59 | 119.5(3) |
| C60-C61-C62 | 120.5(3) |
| C61-C62-C57 | 120.5(3) |
| N6-C63-C64 | 110.8(3) |
| N6-C63-C57 | 120.9(3) |
| C64-C63-C57 | 128.3(3) |
| C65-C64-C63 | 105.3(3) |
| N5-C65-C64 | 107.7(3) |


| Atoms | Angle |
| :---: | :---: |
| N5-C65-C66 | 123.9(3) |
| C64-C65-C66 | 128.3(3) |
| N3-B1-N5 | 110.9(2) |
| N3-B1-N2 | 108.6(2) |
| N5-B1-N2 | 116.2(2) |
| N3-B1-H1 | 108.9(14) |
| N5-B1-H1 | 104.0(14) |
| N2-B1-H1 | 108.0(14) |
| C43-N1-N2 | 107.1(2) |
| C43-N1-Rh1 | 135.38(17) |
| N2-N1-Rh1 | 117.27(16) |
| C45-N2-N1 | 108.5(2) |
| C45-N2-B1 | 126.8(2) |
| N1-N2-B1 | 121.3(2) |
| C55-N3-N4 | 109.2(2) |
| C55-N3-B1 | 126.5(2) |
| N4-N3-B1 | 122.7(2) |
| C53-N4-N3 | 106.0(2) |
| C53-N4-Rh1 | 139.10(19) |
| N3-N4-Rh1 | 112.63(15) |
| C65-N5-N6 | 110.5(2) |
| C65-N5-B1 | 127.1(2) |
| N6-N5-B1 | 118.8(2) |
| C63-N6-N5 | 105.7(2) |
| C1-P1-C7 | 101.33(12) |
| C1-P1-C13 | 98.93(12) |
| C7-P1-C13 | 102.87(12) |
| C1-P1-Rh1 | 116.79(9) |
| C7-P1-Rh1 | 114.23(9) |
| C13-P1-Rh1 | 119.87(8) |
| C31-P2-C19 | 96.84(11) |
| C31-P2-C25 | 102.10(12) |
| C19-P2-C25 | 104.62(12) |
| C31-P2-Rh1 | 112.89(8) |
| C19-P2-Rh1 | 118.12(9) |
| C25-P2-Rh1 | 118.98(8) |
| N1-Rh1-N4 | 77.49 (8) |
| N1-Rh1-P2 | 92.42(6) |
| N4-Rh1-P2 | 167.66(6) |
| N1-Rh1-P1 | 173.25(6) |
| N4-Rh1-P1 | 96.18(6) |
| P2-Rh1-P1 | 94.15(3) |

Table 4. Anisotropic Displacement Parameters $\left(\AA \times 10^{3}\right)$

| Atom | $\mathrm{U}^{11}$ | $\mathrm{U}^{22}$ | $U^{33}$ | $U^{23}$ | $\mathrm{U}^{13}$ | $U^{12}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| C1 | 32(2) | 18(2) | 28(1) | 1(1) | 11(1) | 1(1) |
| C7 | 30(2) | 19(2) | 24(1) | -4(1) | 1(1) | 1(1) |
| C13 | 30(2) | 19(2) | 22(1) | -5(1) | 4(1) | -7(1) |
| C19 | 24(1) | 20(2) | 23(1) | -3(1) | -1(1) | -6(1) |
| C25 | 23(1) | 18(2) | 25(1) | -8(1) | 1(1) | 3(1) |
| C31 | 25(1) | 20(2) | 22(1) | -3(1) | 8(1) | -3(1) |
| C37 | 25(2) | 23(2) | 45(2) | 3(1) | 14(1) | -5(1) |
| C38 | 44(2) | 20(2) | 55(2) | 2(2) | 17(2) | 1(2) |
| C39 | 50(2) | 22(2) | 86(3) | 15(2) | 27(2) | 10(2) |
| C40 | 38(2) | 44(2) | 75(3) | 31(2) | 8(2) | 6(2) |
| C41 | 39(2) | 42(2) | 57(2) | 22(2) | -2(2) | -4(2) |
| C42 | 32(2) | 25(2) | 47(2) | 8(1) | 6(1) | -4(1) |
| C43 | 28(2) | 20(2) | 34(2) | -4(1) | 10(1) | -3(1) |
| C44 | 32(2) | 25(2) | 40(2) | -8(1) | 9(1) | -9(1) |
| C45 | 28(2) | 36(2) | 34(2) | -7(1) | 5(1) | -13(1) |
| C46 | 37(2) | 50(2) | 46(2) | -9(2) | 1(1) | -18(2) |
| C47 | 29(2) | 33(2) | 33(2) | -1(1) | 13(1) | -7(1) |
| C48 | 32(2) | 36(2) | 44(2) | 2(2) | 5(1) | -7(2) |
| C49 | 49(2) | 49(2) | 49(2) | 16(2) | 3(2) | -6(2) |
| C50 | 67(3) | 82(3) | 35(2) | 13(2) | -2(2) | -7(2) |
| C51 | 73(3) | 74(3) | 37(2) | -10(2) | 8(2) | -11(2) |
| C52 | 51(2) | 40(2) | 40(2) | -5(2) | 15(2) | -5(2) |
| C53 | 29(2) | 22(2) | 37(2) | -1(1) | 11(1) | -4(1) |
| C54 | 36(2) | 35(2) | 43(2) | 1(1) | 19(1) | 3(2) |
| C55 | 28(2) | 31(2) | 48(2) | 6(1) | 9(1) | 5(1) |
| C56 | 35(2) | 71(3) | 61(2) | 6(2) | 10(2) | 22(2) |
| C57 | 36(2) | 30(2) | 33(2) | 8(1) | 2(1) | 7(2) |
| C58 | 50(2) | 33(2) | 37(2) | 9(1) | 9(2) | 5(2) |
| C59 | 71(3) | 34(2) | 44(2) | 0 (2) | 13(2) | 6(2) |
| C60 | 72(3) | 27(2) | 56(2) | 8(2) | 7(2) | 3(2) |
| C61 | 70(3) | 39(2) | 51(2) | 19(2) | 19(2) | 4(2) |
| C62 | 62(2) | 38(2) | 40(2) | 8(2) | 12(2) | 10(2) |
| C63 | 32(2) | 31(2) | 32(2) | 5(1) | 3(1) | 11(1) |
| C64 | 43(2) | 38(2) | 29(2) | 3(1) | 3(1) | 7(2) |
| C65 | 36(2) | 34(2) | 30(2) | -1(1) | -1(1) | 8(1) |
| C66 | 50(2) | 43(2) | 35(2) | -2(2) | -1(1) | -4(2) |
| B1 | 24(2) | 31(2) | 36(2) | 2(2) | -1(1) | -2(2) |
| N1 | 18(1) | 23(1) | 29(1) | -1(1) | 2(1) | -1(1) |
| N2 | 20(1) | 28(1) | 31(1) | -3(1) | 2(1) | -4(1) |
| N3 | 21(1) | 28(1) | 35(1) | 3(1) | 6(1) | 4(1) |
| N4 | 23(1) | 21(1) | 31(1) | -1(1) | 8(1) | -1(1) |
| N5 | 29(1) | 29(1) | 30(1) | 1(1) | -1(1) | 2(1) |


| Table 4. | Anisotropic | Displacement Parameters $\left(\begin{array}{l}\AA \\ \mathbf{x ~ 1 0} \\ \mathbf{3} \\ \mathbf{3}\end{array}\right) \ldots$ continued |  |  |  |  |
| :--- | :---: | :---: | :---: | :---: | :---: | :--- |
| N6 | $32(1)$ | $28(1)$ | $31(1)$ | $3(1)$ | $2(1)$ | $4(1)$ |
| P1 | $23(1)$ | $17(1)$ | $25(1)$ | $-2(1)$ | $4(1)$ | $-1(1)$ |
| P2 | $20(1)$ | $18(1)$ | $23(1)$ | $-2(1)$ | $1(1)$ | $0(1)$ |
| Rh1 | $19(1)$ | $16(1)$ | $25(1)$ | $-2(1)$ | $3(1)$ | $-1(1)$ |

Table 5. Torsional Angles ( ${ }^{\circ}$ )

| Atoms | Angle | Atoms | Angle |
| :--- | :--- | :--- | :--- |
| C42-C37-C38-C39 | $-0.1(4)$ | B1-N3-N4-Rh1 | $-29.7(3)$ |
| C43-C37-C38-C39 | $176.8(3)$ | C64-C65-N5-N6 | $-1.7(3)$ |
| C37-C38-C39-C40 | $1.0(5)$ | C66-C65-N5-N6 | $174.9(3)$ |
| C38-C39-C40-C41 | $-1.5(5)$ | C64-C65-N5-B1 | $-159.8(3)$ |
| C39-C40-C41-C42 | $1.2(5)$ | C66-C65-N5-B1 | $16.9(4)$ |
| C40-C41-C42-C37 | $-0.4(5)$ | N3-B1-N5-C65 | $169.1(2)$ |
| C38-C37-C42-C41 | $-0.2(4)$ | N2-B1-N5-C65 | $-66.2(4)$ |
| C43-C37-C42-C41 | $-177.0(3)$ | N3-B1-N5-N6 | $12.7(3)$ |
| C42-C37-C43-N1 | $-23.9(4)$ | N2-B1-N5-N6 | $137.3(2)$ |
| C38-C37-C43-N1 | $159.3(3)$ | C64-C63-N6-N5 | $-0.2(3)$ |
| C42-C37-C43-C44 | $150.6(3)$ | C57-C63-N6-N5 | $179.9(2)$ |
| C38-C37-C43-C44 | $-26.3(4)$ | C65-N5-N6-C63 | $1.2(3)$ |
| N1-C43-C44-C45 | $2.7(3)$ | B1-N5-N6-C63 | $161.3(2)$ |
| C37-C43-C44-C45 | $-172.5(3)$ | C2-C1-P1-C7 | $165.4(2)$ |
| C43-C44-C45-N2 | $-2.0(3)$ | C6-C1-P1-C7 | $-19.7(3)$ |
| C43-C44-C45-C46 | $177.1(3)$ | C2-C1-P1-C13 | $-89.5(2)$ |
| C52-C47-C48-C49 | $0.2(4)$ | C6-C1-P1-C13 | $85.4(2)$ |
| C53-C47-C48-C49 | $173.8(3)$ | C2-C1-P1-Rh1 | $40.6(2)$ |
| C47-C48-C49-C50 | $0.7(5)$ | C6-C1-P1-Rh1 | $-144.5(2)$ |
| C48-C49-C50-C51 | $-0.6(6)$ | C12-C7-P1-C1 | $85.8(2)$ |
| C49-C50-C51-C52 | $-0.4(6)$ | C8-C7-P1-C1 | $-90.9(2)$ |
| C50-C51-C52-C47 | $1.3(5)$ | C12-C7-P1-C13 | $-16.2(3)$ |
| C48-C47-C52-C51 | $-1.2(5)$ | C8-C7-P1-C13 | $167.1(2)$ |
| C53-C47-C52-C51 | $-174.7(3)$ | C12-C7-P1-Rh1 | $-147.7(2)$ |
| C48-C47-C53-N4 | $52.7(4)$ | C8-C7-P1-Rh1 | $35.6(2)$ |
| C52-C47-C53-N4 | $-133.8(3)$ | C14-C13-P1-C1 | $33.1(2)$ |
| C48-C47-C53-C54 | $-120.4(3)$ | C18-C13-P1-C1 | $-151.6(2)$ |
| C52-C47-C53-C54 | $53.0(4)$ | C14-C13-P1-C7 | $137.0(2)$ |
| N4-C53-C54-C55 | $-1.7(3)$ | C18-C13-P1-C7 | $-47.7(2)$ |
| C47-C53-C54-C55 | $172.2(3)$ | C14-C13-P1-Rh1 | $-95.0(2)$ |
| C53-C54-C55-N3 | $0.0(3)$ | C18-C13-P1-Rh1 | $80.4(2)$ |
| C53-C54-C55-C56 | $179.4(3)$ | C32-C31-P2-C19 | $-127.2(2)$ |
| C62-C57-C58-C59 | $0.6(5)$ | C36-C31-P2-C19 | $54.5(2)$ |
| C63-C57-C58-C59 | $179.4(3)$ | C32-C31-P2-C25 | $-20.6(3)$ |
| C57-C58-C59-C60 | $0.2(5)$ | C36-C31-P2-C25 | $161.1(2)$ |
| C58-C59-C60-C61 | $-0.3(5)$ | C32-C31-P2-Rh1 | $108.3(2)$ |
|  |  |  |  |

Table 5. Torsional Angles $\left({ }^{\circ}\right)$...continued C59-C60-C61-C62 C60-C61-C62-C57 C58-C57-C62-C61 C63-C57-C62-C61 C58-C57-C63-N6
C62-C57-C63-N6
C58-C57-C63-C64
C62-C57-C63-C64
N6-C63-C64-C65
C57-C63-C64-C65
C63-C64-C65-N5
C63-C64-C65-C66
C44-C43-N1-N2
C37-C43-N1-N2
C44-C43-N1-Rh1
C37-C43-N1-Rh1
C44-C45-N2-N1
C46-C45-N2-N1
C44-C45-N2-B1
C46-C45-N2-B1
C43-N1-N2-C45
Rh1-N1-N2-C45
C43-N1-N2-B1
Rh1-N1-N2-B1
N3-B1-N2-C45
N5-B1-N2-C45
N3-B1-N2-N1
N5-B1-N2-N1
C54-C55-N3-N4
C56-C55-N3-N4
C54-C55-N3-B1
C56-C55-N3-B1
N5-B1-N3-C55
N2-B1-N3-C55
N5-B1-N3-N4
N2-B1-N3-N4
C54-C53-N4-N3
C47-C53-N4-N3
C54-C53-N4-Rh1
C47-C53-N4-Rh1
C55-N3-N4-C53
B1-N3-N4-C53
C55-N3-N4-Rh1
-0.5(6)
$1.4(5)$
-1.4(5)
179.8(3)
18.6(4)
-162.7(3)
-161.3(3)
17.4(5)
-0.8(3)
179.1(3)
1.5(3)
-174.9(3)
-2.3(3)
173.0(2)
-176.47(19)
-1.2(4)
0.6(3)
-178.5(3)
159.9(3)
-19.2(4)
1.1(3)
176.49(17)
-159.6(2)
15.8(3)
-113.6(3)
120.6(3)
43.3(3)
-82.5(3)
1.6(3)
-177.9(3)
-164.5(3)
16.0(5)
-101.3(3)
129.9(3)
94.3(3)
-34.5(3)
2.6(3)
-171.5(2)
-157.6(2)
28.2(4)
-2.6(3)
164.2(2)
163.53(18)

C36-C31-P2-Rh1
C20-C19-P2-C31
C24-C19-P2-C31
C20-C19-P2-C25
C24-C19-P2-C25
C20-C19-P2-Rh1
C24-C19-P2-Rh1
C30-C25-P2-C31
C26-C25-P2-C31
C30-C25-P2-C19
C26-C25-P2-C19
C30-C25-P2-Rh1
C26-C25-P2-Rh1
C43-N1-Rh1-N4
N2-N1-Rh1-N4
C43-N1-Rh1-P2
N2-N1-Rh1-P2
C43-N1-Rh1-P1
N2-N1-Rh1-P1
C53-N4-Rh1-N1
N3-N4-Rh1-N1
C53-N4-Rh1-P2
N3-N4-Rh1-P2
C53-N4-Rh1-P1
N3-N4-Rh1-P1
C31-P2-Rh1-N1
C19-P2-Rh1-N1
C25-P2-Rh1-N1
C31-P2-Rh1-N4
C19-P2-Rh1-N4
C25-P2-Rh1-N4
C31-P2-Rh1-P1
C19-P2-Rh1-P1
C25-P2-Rh1-P1
C1-P1-Rh1-N1
C7-P1-Rh1-N1
C13-P1-Rh1-N1
C1-P1-Rh1-N4
C7-P1-Rh1-N4
C13-P1-Rh1-N4
C1-P1-Rh1-P2
C7-P1-Rh1-P2
C13-P1-Rh1-P2
-70.0(2)
-127.6(2)
50.0(2)
128.0(2)
-54.4(2)
-7.0(2)
170.58(18)
91.2(2)
-88.8(3)
-168.3(2)
11.7(3)
-33.8(2)
146.2(2)
113.3(3)
-60.41(17)
-73.9(2)
112.42(16)
92.7(6)
-81.0(5)
-134.1(3)
66.49(16)
-169.8(2)
30.8(4)
43.5(3)
-115.90(16)
4.18(11)
-107.68(10)
123.78(11)
38.9(3)
-72.9(3)
158.6(3)
-174.25(9)
73.90(9)
-54.64(10)
31.8(5)
-86.2(5)
151.2(5)
11.54(11)
-106.41(11)
130.91(12)
-161.71(10)
80.35(10)
-42.33(11)


[^0]:    ${ }^{\text {a }}$ Isolated yields. ${ }^{\mathrm{b}}$ See ref $22 .{ }^{\mathrm{c}}$ See ref 28 i. ${ }^{\mathrm{d}}$ See ref 28 b . ${ }^{\mathrm{e}}$ See ref 28 c .
    ${ }^{\mathrm{i}}$ Toluene used as solvent in place of THF.

[^1]:    ${ }^{31} \mathrm{P}\left\{{ }^{\mathrm{l}} \mathrm{H}\right\}$ NMR $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}, 162 \mathrm{MHz}\right)$ spectrum of complexes $\mathbf{5}$ and $\mathbf{5}^{*}$ at 188 K

[^2]:    ${ }^{\text {a }}$ Yields based on ${ }^{1} \mathrm{H}$ NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. ${ }^{\text {b }}$ Percent conversion with respect to remaining thiol.

[^3]:    ${ }^{\text {a }}$ Yields based on ${ }^{1} \mathrm{H}$ NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. ${ }^{\text {b }}$ An additional $\sim 5-20 \%$ of an unidentified byproduct was observed. ${ }^{\text {c }}$ An additional $\sim 5 \%$ of the $E$-linear phenylacetylene dimer was observed.

[^4]:    ${ }^{\text {a }}$ An additional $9 \%$ yield of an unidentified byproduct was observed. ${ }^{\mathrm{b}}$ Solvent $=$ $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ : $d_{8}$-toluene (1:1).

[^5]:    ${ }^{\text {a }} \mathrm{An}$ additional 5-20\% yield of an unidentified byproduct was observed.

[^6]:    ${ }^{a}$ An additional 5-20\% yield of an unidentified byproduct was observed.

[^7]:    ${ }^{a}$ Percent conversion with respect to remaining thiol.

[^8]:    ${ }^{\text {a }}$ An additional $\sim 5-10 \%$ yield of an unidentified byproduct was observed.

