Solution Reactions of HX Molecules ($X = \text{SH, Cl, Br}$) With
Dinuclear Palladium(I) Complexes Containing
Bis(diphenylphosphino)methane

by
Freddy A. Barnabas

B. Sc. (Chemistry) Madras University, India, 1975
M. Sc. (Chemistry) Madras University, India, 1977

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Department of Chemistry

The University of British Columbia
Vancouver, Canada

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Abstract

This thesis describes kinetic and spectroscopic studies on the reaction between Pd$_2$X$_2$(dpm)$_2$, 1 (X = Cl, a; Br, b; I, c; dpm = bis(diphenylphosphino)methane) and HX molecules (X = SH, Cl, Br) in solution. The reaction of 1 with hydrogen sulfide leads to the formation of the corresponding μ-sulfide, 2, and H$_2$ gas. Kinetic studies carried out in CH$_2$Cl$_2$ solutions over the temperature range 0 – 35°C reveal a first order dependence on both palladium dimer and hydrogen sulfide concentrations. The value of the bimolecular rate constant, $k_2$, is $1.71 \times 10^{-3}$ M$^{-1}$ s$^{-1}$ at 25°C, and the activation parameters for the reaction are $\Delta H^\ddagger = 55 \pm 5$ kJ mole$^{-1}$ and $\Delta S^\ddagger = -115 \pm 10$ J K$^{-1}$ mole$^{-1}$. Low temperature $^1$H and $^{31}$P{$^1$H} nmr spectroscopic investigations complement the kinetic studies, and show that the reaction proceeds via the formation of a hydride intermediate. The observations indicate that the reaction proceeds through oxidative-addition of H$_2$S across the metal–metal bond and the data are discussed in terms of the following reactions:

\[
\begin{align*}
\text{Pd}_2\text{X}_2(\text{dpm})_2 + \text{H}_2\text{S} & \rightleftharpoons \text{Pd}_2\text{X}_2(\text{dpm})_2(\text{H}_2\text{S}) \\
\text{I} & \\
\text{Pd}_2\text{X}_2(\text{dpm})_2(\text{H}_2\text{S}) & \rightleftharpoons \text{Pd}_2\text{X}_2(\text{dpm})_2(\text{H})(\text{SH}) \\
\text{Pd}_2\text{X}_2(\text{dpm})_2(\text{H})(\text{SH}) & \rightarrow \text{Pd}_2\text{X}_2(\text{dpm})_2(\mu\cdot\text{S}) + \text{H}_2 \end{align*}
\]

There is no direct evidence for the first reaction listed, however.

The analogous reactions between 1 and HX (X = Cl, Br) were studied with UV–visible, $^1$H and $^{31}$P{$^1$H} nmr spectroscopy. The reaction between
HCl and 1a in CH₂Cl₂ results in the 'direct' formation of Pd(II) monomer, PdCl₂(dpm), with no intermediates being seen. The corresponding reaction between the bromide, 1b and HBr, however, is seen to take place in several steps. Reaction with one mole of HBr results in the formation of a hydride intermediate; this then reacts with a second mole of HBr to form H₂ gas and a tetrabromo complex, Pd₂Br₄(dpm)₂, which subsequently fragments slowly to the Pd(II) monomer, PdBr₂(dpm). All the intermediate species involved in the bromide/HBr reaction were detected by UV-visible and low temperature ¹H and ³¹P{¹H} nmr spectroscopy.

An effective way of abstracting the bound μ-sulfide ligand in order to regenerate the palladium dimer, 1, has been demonstrated using reactions with dpm and with diphenyl; the abstraction by dpm results in formation of dpmS, the monosulfide of dpm, as the only sulfur-containing product. A new and as yet incompletely characterized system that catalytically desulfurizes H₂S was generated by having excess dpm present in the reaction between 1b and H₂S. This catalytic system transfers sulfur from H₂S to the bisphosphine dpm to form dpmS along with some uncharacterized palladium compounds.
Table of Contents

Abstract ii

Table of Contents iv

List of Figures viii

List of Tables xii

List of Abbreviations xiii

Acknowledgement xv

1 INTRODUCTION 1
  1.1 General introduction 1
  1.2 Transition metal/H₂S chemistry 4
  1.3 The chemistry of transition metal dpm dinuclear species 6
  1.4 Aim of work 9
  1.5 References 10

2 EXPERIMENTAL 17
  2.1 MATERIALS 17
    2.1.1 Solvents 17
    2.1.2 Gases 17
    2.1.3 Phosphines and other materials 18
    2.1.4 Palladium Compounds 19
      2.1.4.1 Pd(PhCN)₂Cl₂ 19
      2.1.4.2 Pd₂(dba)₃.CHCl₃ 20
2.1.4.3 Pd$_2$Cl$_2$(dpm)$_2$ ........................................ 20
2.1.4.4 Pd$_2$Br$_2$(dpm)$_2$ .......................................... 21
2.1.4.5 Pd$_2$I$_2$(dpm)$_2$.CH$_2$Cl$_2$ .............................. 21
2.1.4.6 Pd$_2$Cl$_2$(dpm)$_2$(μ-S) .................................... 22
2.1.4.7 Pd$_2$Br$_2$(dpm)$_2$(μ-S) .................................... 23
2.1.4.8 Pd$_2$I$_2$(dpm)$_2$(μ-S) .................................... 23
2.1.4.9 PdCl$_2$(dpm) .................................................. 24
2.1.4.10 PdBr$_2$(dpm) .................................................. 24

2.2 Instrumentation ..................................................... 25
2.3 Procedure for a typical kinetic run ............................... 26
2.4 Low temperature nmr experiments with Pd$_2$X$_2$(dpm)$_2$ and H$_2$S. 28
  2.4.1 Reaction of Pd$_2$Br$_2$(dpm)$_2$ with H$_2$S .................... 28
  2.4.2 Reaction of Pd$_2$I$_2$(dpm)$_2$ with H$_2$S .................... 28
2.5 Interaction of Pd$_2$Br$_2$(dpm)$_2$ with HX ........................ 29
  2.5.1 Room temperature reaction .................................... 29
  2.5.2 Low temperature reaction ..................................... 29
2.6 Sulfur abstraction reactions ...................................... 29
  2.6.1 Sulfur abstraction by dpm .................................... 29
  2.6.2 Desulfurization of H$_2$S ...................................... 30
2.7 Gas solubility measurements ...................................... 30
2.8 References .......................................................... 31

3 THE INTERACTION OF H$_2$S WITH Pd(I) DIMERS .................... 32
  3.1 The palladium(I) dpm dimer, Pd$_2$X$_2$(dpm)$_2$. ............... 32
  3.2 Reaction with D$_2$S .............................................. 33
  3.3 Kinetics and rate measurements .................................. 34
3.4 Spectroscopic detection of intermediates 45
  3.4.1 Reaction between Pd$_2$Br$_2$(dpm)$_2$ and H$_2$S 45
  3.4.2 Reaction between Pd$_2$I$_2$(dpm)$_2$ and H$_2$S 49
3.5 Discussion of kinetic and spectroscopic data 52
3.6 References 61

4 THE INTERACTION OF HX (X = Cl, Br) WITH Pd(I)
  DIMERS 64
  4.1 Introduction 64
  4.2 Stoichiometry of the reaction and product identification 67
    4.2.1 Reaction of Pd$_2$Cl$_2$(dpm)$_2$ with HCl at room temperature 67
    4.2.2 Reaction of Pd$_2$Br$_2$(dpm)$_2$ with HBr at room temperature 70
    4.2.3 Low temperature spectroscopic studies of the reaction
        between 1b and HBr 75
  4.3 Discussion 78
  4.4 References 83

5 SULFUR TRANSFER REACTIONS 84
  5.1 Introduction 84
  5.2 Sulfur abstraction reactions 87
    5.2.1 Sulfur abstraction by phosphines 87
    5.2.2 Sulfur abstraction by organics 88
  5.3 The desulfurization of H$_2$S 90
  5.4 References 94

6 GENERAL CONCLUSIONS 96
  6.1 Conclusions 96

vi
6.2 Recommendations for future work .......................... 97
List of Figures

2.1 Anaerobic spectral cell used for UV-visible spectroscopy. ...... 27
3.1 Visible absorption spectral changes of a CH₂Cl₂ solution of 
Pd₂Br₂(dpm)₂ upon addition of H₂S at 25°C. ......................... 35
3.2 Rate plot for the reaction between Pd₂Br₂(dpm)₂ (1.01 x 10⁻³
M) and H₂S (0.53 M) in CH₂Cl₂, at 25°C. ......................... 36
3.3 A rate plot analysed for first order Pd¹ dependence in CH₂Cl₂
at 25°C. ([Pd₂] = 1.01 x 10⁻³ M and [H₂S] = 0.53 M) .......... 37
3.4 Solubility of H₂S in CH₂Cl₂ at various pressures. ............. 40
3.5 Dependence of reaction rate on [Pd¹] in CH₂Cl₂ at 25°C...... 42
3.6 Dependence of reaction rate on [H₂S] at 1.01 x 10⁻³ M Pd¹ in
CH₂Cl₂ at 25°C. ......................................................... 43
3.7 Temperature dependence of the rate constant for the reaction
between 1b (at 1.01 x 10⁻³ M) and H₂S in CH₂Cl₂ ............... 44
3.8 The ¹H nmr spectra in CD₂Cl₂ solution for (A) -CH₂- region of
1b; (B) -CH₂- region of 1b + H₂S at -70°C and (C) hydride
region of 1b + H₂S at -70°C ............................................ 46
3.9 The ¹H nmr spectra in CD₂Cl₂ solution of (A) -CH₂- region
of 1b + H₂S warmed up to room temperature and (B) -CH₂-
region of 2b. .................................................................. 47
3.10 The ³¹P{¹H} nmr spectra in CD₂Cl₂ of 1b and H₂S ........... 48
3.11 The $^1$H nmr spectra in CD$_2$Cl$_2$ solution for (A) -CH$_2$- region of 1c; (B) -CH$_2$- region of 1c + H$_2$S kept at ~-74°C for 8 h and (C) -CH$_2$- region of 1c + H$_2$S kept at ~-74°C for 8 h then warmed up to ~-40°C.  

3.12 The $^1$H nmr spectra in CD$_2$Cl$_2$ solution of (A) 1c + H$_2$S kept at ~-74°C for 8 h (hydride and -SH region) and (B) 2c.  

3.13 The $^{31}$P{$^1$H} nmr spectra in CDCl$_3$ of (A) 1c at 20°C; (B) 1c + H$_2$S kept at ~-74°C for 8 h and (C) 1c + H$_2$S kept at ~-74°C for 8 h and then warmed up to ~-40°C.  

3.14 The $^{31}$P{$^1$H} nmr spectra in CDCl$_3$ of (A) 1c + H$_2$S kept at ~-74°C for 8 h and then warmed to room temperature and (B) authentic sample of 2c at 20°C.  

4.1 The $^{31}$P{$^1$H} nmr spectra of the reaction products of 1b and anhydrous HCl.  

4.2 The mechanistic pathway of the reaction between 1b and Br$_2$.  

4.3 The $^1$H nmr spectra (-CH$_2$- region) in CDCl$_3$ solution at 20°C of (A) 1a; (B) 1a + HCl(g) (~3:1) and (C) 1a + HCl(g) (1:2).  

4.4 The $^{31}$P{$^1$H} nmr spectra in CDCl$_3$ solution at 20°C of (A) 1a; (B) 1a + HCl(g) (~3:1) and (C) 1a + HCl(g) (1:2).  

4.5 The gas chromatograms of (A) the gaseous products evolved in the reaction of 1a + 2 HCl(g) in DMA; (B) the gaseous products evolved in the reaction of 1b + 2 HBr(g) in CH$_2$Cl$_2$ and (C) authentic dihydrogen gas.
4.6 Visible absorption spectrum of 1b upon addition of anhydrous HBr at 25°C, as a function of time. ................................. 72

4.7 The 1H nmr spectra (-CH$_2$- region) in CDCl$_3$ solution at 20°C of (A) 1b; (B) 1b + HBr(g) after 15 min; (C) 1b + HBr(g) after 6 h and (D) authentic sample of PdBr$_2$(dpm). .................. 73

4.8 The $^{31}$P{$^1$H} nmr spectra in CDCl$_3$ solution at 20°C of (A) 1b; (B) 1b + HBr(g) after 15 min; (C) 1b + HBr(g) after 6 h and (D) authentic sample of PdBr$_2$(dpm). .................. 74

4.9 The 1H nmr spectra (-CH$_2$- region) in CDCl$_3$ solution at -40°C of (A) 1b + HBr(g) (2:1); (B) 1b + HBr(g) (1:2) after ~15 min and (C) 1b + HBr(g) (1:2) after ~30 min. ............... 76

4.10 The 1H nmr spectra in CDCl$_3$ solution at -40°C of (A) 1b + HBr(g)(1:1), the high field region after ~ 2 min; (B) 1b + HBr(g) (1:2) after 60 min, -CH$_2$- region and (C) 1b + HBr(g) (1:2) after 6 h, -CH$_2$- region. .................. 77

4.11 The $^{31}$P{$^1$H} nmr spectra in CDCl$_3$ solution at -40°C of (A) 1b + HBr(g) (1:2) after ~15 min; (B) 1b + HBr(g) (1:5) after ~20 min and (C) 1b + HBr(g) (1:10) after ~25 min. .......... 79

5.1 The schematic representation of the regeneration of 1 from 2 by the oxidation of the $\mu$-sulfide to SO$_2$. .................. 86

5.2 The mechanistic pathway for the abstraction of sulfur by dpm from 2. ......................................................... 89

5.3 The $^{31}$P{$^1$H} nmr spectra of the reaction product of 1c and H$_2$S in the presence of 20-fold excess dpm. .................. 91
5.4 The $^{31}\text{P}^{1\text{H}}$ nmr spectra of the reaction product of 1b and H$_2$S in the presence of 20-fold excess dpm.
List of Tables

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>III-1</td>
<td>Solubility of H$_2$S in CH$_2$Cl$_2$ at various pressures at 25°C.</td>
<td>39</td>
</tr>
<tr>
<td>III-2</td>
<td>Dependence of reaction rate on [Pd$^+$] in CH$_2$Cl$_2$ at 25°C.</td>
<td>39</td>
</tr>
<tr>
<td>III-3</td>
<td>Dependence of reaction rate on [H$_2$S] at 1.01 x 10$^{-3}$ M Pd$_2^+$ in CH$_2$Cl$_2$ at 25°C.</td>
<td>41</td>
</tr>
<tr>
<td>III-4</td>
<td>Temperature dependence of the rate constant for the reaction between 1b and H$_2$S in CH$_2$Cl$_2$.</td>
<td>41</td>
</tr>
</tbody>
</table>
List of Abbreviations

The following list of abbreviations, most of which are commonly adopted in chemical literature, will be employed in this thesis.

br   broad
Cp   cyclopentadienyl, C₅H₅⁻
d    doublet
dba  dibenzylideneacetone, C₆H₅CH:CHC(0)CH:CHC₆H₅
dd   doublet of doublets
DMA  N,N'-dimethylacetamide, CH₃CON(CH₃)₂
dpm  bis(diphenylphosphino)methane, (C₆H₅)₂PCH₂P(C₆H₅)₂

dpmS  bis(diphenylphosphino)methane monosulfide,
      (thio(diphenyl)phosphinophosphinomethane),
      (C₆H₅)₂PCH₂P(S)(C₆H₅)₂
dpmS₂  bis(diphenylphosphino)methane disulfide, (bis(thio(diphenyl)phosphinomethane),
       (C₆H₅)₂P(S)CH₂P(S)(C₆H₅)₂
dpe  1,2-bis(diphenylphosphino)ethane, (C₆H₅)₂PCH₂CH₂P(C₆H₅)₂
i.r.  infra-red
J    coupling constant, Hz
m    multiplet

^{31}P{^1H}  proton broad-band decoupled phosphorus nmr
PPh₃  triphenylphosphine, (C₆H₅)₃P
PPh₃S  triphenylphosphine sulfide, (C₆H₅)₃P(S)
PPh₂Me  methyltriphenylphosphine, (C₆H₅)₂PMe
Pd₂  Pd₂X₂(dpm)₂
q  quintet  
s  singlet or second  
t  triplet  
UV  ultra-violet  
X  halide ligand, Cl, Br, or I  
δ  chemical shift, ppm  
ε  molar extinction coefficient or dielectric constant

Some of the compounds used during the course of this work have been referred to by numerical symbols in this thesis for the sake of brevity and simplicity. Following is the list of complexes corresponding to each such symbol:

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Formula</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pd$_2$X$_2$(dpm)$_2$</td>
<td><img src="image1.png" alt="Structure 1" /></td>
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<tr>
<td>1a</td>
<td>Pd$_2$Cl$_2$(dpm)$_2$</td>
<td></td>
</tr>
<tr>
<td>1b</td>
<td>Pd$_2$Br$_2$(dpm)$_2$</td>
<td></td>
</tr>
<tr>
<td>1c</td>
<td>Pd$_2$I$_2$(dpm)$_2$</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Pd$_2$X$_2$(μ-S)(dpm)$_2$</td>
<td><img src="image2.png" alt="Structure 2" /></td>
</tr>
<tr>
<td>2a</td>
<td>Pd$_2$Cl$_2$(μ-S)(dpm)$_2$</td>
<td></td>
</tr>
<tr>
<td>2b</td>
<td>Pd$_2$Br$_2$(μ-S)(dpm)$_2$</td>
<td></td>
</tr>
<tr>
<td>2c</td>
<td>Pd$_2$I$_2$(μ-S)(dpm)$_2$</td>
<td></td>
</tr>
<tr>
<td>3b</td>
<td>Pd$_2$Br$_2$(dpm)$_2$(H)(SH)</td>
<td><img src="image3.png" alt="Structure 3" /></td>
</tr>
<tr>
<td>3c</td>
<td>Pd$_2$I$_2$(dpm)$_2$(H)(SH)</td>
<td></td>
</tr>
<tr>
<td>4b</td>
<td>Pd$_2$Br$_2$(dpm)$_2$(H)(Br)</td>
<td><img src="image4.png" alt="Structure 4" /></td>
</tr>
<tr>
<td>5b</td>
<td>Pd$_2$Br$_4$(dpm)$_2$</td>
<td></td>
</tr>
<tr>
<td>6a</td>
<td>PdCl$_2$(dpm)</td>
<td></td>
</tr>
<tr>
<td>6b</td>
<td>PdBr$_2$(dpm)</td>
<td></td>
</tr>
</tbody>
</table>

![Pd$_2$Br$_2$(μ-S)(dpm)$_2$](image5.png)
Acknowledgements

I am most grateful to Professor B. R. James for his guidance and encouragement throughout the course of this work.

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The assistance and cooperation of various departmental services are gratefully acknowledged.
Chapter 1

INTRODUCTION

1.1 General introduction

Recent studies\(^1\) carried out in this laboratory to separate CO from gas mixtures using Pd(I) dimers of the type Pd\(_2\)X\(_2\)(dpm)\(_2\) (X = Cl, Br, I; dpm = Ph\(_2\)PCH\(_2\)PPh\(_2\)) led to the discovery of reaction 1.1, while testing the reactivity of the palladium complex toward H\(_2\)S, an impurity often present in such gas mixtures.

\[
Pd\(_2\)X\(_2\)(dpm)\(_2\) + H\(_2\)S \rightarrow Pd\(_2\)X\(_2\)(dpm)\(_2\)(\mu - S) + H\(_2\) \quad (1.1)
\]

\([X = Cl, Br, I]\)

For X = Cl and Br the reaction is quantitative and is the first of its kind in which hydrogen gas is generated from H\(_2\)S by a transition metal complex in solution.

Gaseous H\(_2\)S, a noxious pollutant, is produced as a result of both natural and man-made processes.\(^2\) Two main mechanisms account for the generation of the gas in the natural sources: bacterial reduction of sulfate, sulfur and organic sulfur compounds in plant and animal matter, and geochemical formation as in volcanic activity and thermal hot springs. These natural sources contribute an important part of atmospheric emission of H\(_2\)S (3 – 30 \(\mu g/m^3\)) that is part of the natural global sulfur cycle.
Though significant quantities of H$_2$S are generated in many industrial processes, most of it is consumed for the production of S and SO$_2$. Important production sources include petroleum refining operations, natural gas plants, petrochemical plants, coke oven plants and kraft pulp mills; H$_2$S is an occasional pollutant, and the main pollution sources are gas-well blow outs and pulp mills.$^2$

Though H$_2$S is as toxic as cyanide to most organisms, nature has evolved a few microbes, that depend on it for their survival.$^3$ For example, a class of bacteria known as 'sulfate reducers' produce H$_2$S by the reduction of sulfates in anoxic conditions. The generated H$_2$S is utilized in turn by other types of bacteria, and the subsequent oxidation results in elemental sulfur and sulfate. It is interesting to note that most of the world's native sulfur deposits are said to be formed as a result of bacterial action during the warm and sunny Permian and Jurasic periods ($\sim 2 \times 10^8$ years ago).

As a result of a geochemical reaction that takes place at a newly formed ocean floor, H$_2$S is generated.$^4$ When sulfate bearing sea water percolates and comes in contact with hot crustal rocks, iron present in the rock reduces the sulfate to H$_2$S gas. Thus the hot water, rising to the ocean floor through the so-called 'hydrothermal vents' or 'hot springs', is heavily charged with hydrogen sulfide. In the waters surrounding these vents, nature has evolved an ecosystem that solely depends on a bacterium that derives energy by oxidizing H$_2$S to sulfate. This unique, diversified, ecosystem apart from the bacterium includes giant worms, clams and crabs that tolerate the high concentration of H$_2$S and perhaps are the only higher organisms unaffected by H$_2$S.

The fossil fuels, petroleum, shale, oil bearing sands, coal and natural gas have varying amounts of sulfur depending on their origin. For example, in
petroleum the sulfur is mainly present as mercaptans (RSH), sulfides (RSR),
disulfides (RSSR) and sulfur heterocyclics. The presence of sulfur organics in
fossil fuels has the following implications:

(i) the refining of petroleum involves the catalytic cracking and catalytic
reforming processes that utilize transition metal catalysts. If sulfur or­
ganics are not removed prior to these processes, then the catalysts are
rendered ineffective by poisoning.

(ii) Combustion of sulfurous fossil fuels produces sulfur oxides (mainly SO₂)
that are not only corrosive to the machinery but if vented into the atmo­
sphere cause many environmental problems. It is interesting to note that
a substantially larger amount of SO₂ than it is utilized industrially is dis­
charged into the atmosphere. Acid rain, smog and other environmental
hazards result because of this discharge.

Thus sulfur removal is essential and is removed from petroleum by a process
called hydrodesulfurization(HDS), prior to the cracking and reforming. In
HDS processes, organic sulfur is removed as H₂S by reacting with H₂ gas in
the presence of sulfided Mo–Co or W–Ni oxide catalysts as in reactions 1.2 to
1.5.

\[
\begin{align*}
RSH + H_2 & \rightarrow RH + H_2S \\
RSR + 2H_2 & \rightarrow 2RH + H_2S \\
RSSR + 3H_2 & \rightarrow 2RH + 2H_2S \\
C_4H_4S(thiophene) + 2H_2 & \rightarrow CH_2 = CH - CH = CH_2 + H_2S
\end{align*}
\]

The resulting H₂S is either oxidized to elemental sulfur (as in Claus, Stretford,
Takahax, Giammarco-Vetrocok-sulfur and Konox processes) or converted to
CaSO₄. In the currently available technologies, the industrially expensive H₂ is lost and thus sulfur removal becomes an expensive process especially for petroleum crude with high sulfur content. However, the organic sulfur removal could become an industrially less expensive operation with little or no consumption of H₂, provided H₂ could be generated from H₂S by a catalytic process, perhaps one based on reaction 1.1. Such a process would be valuable, if not now, at least in the future, once currently usable petroleum reserves of low sulfur content become exhausted.

Thus the study of the interaction of H₂S with transition metal complexes, as in reaction 1.1, is of fundamental importance because of the biological, environmental and industrial importance of the gas. Further, the interesting reactivity pattern of H₂S, as exhibited in reaction 1.1, could lead to the development of an efficient catalytic system, perhaps a homogeneous one (the first of its kind) to desulfurize H₂S.

1.2 Transition metal/H₂S chemistry

Transition metals and sulfur have an 'affinity' for one another and readily form metal sulfides. This strong tendency to form metal sulfides can be readily seen in the Pearson's acid-base scale,⁸ where dⁿ- transition metal ions (with higher n values) and sulfide ions are both classified as 'soft' groups. The interaction of H₂S with transition metal complexes typically gives insoluble sulfides often polymeric in nature, but more interesting reactivity patterns are known. The first reported case of quantitative H₂ generation from H₂S by a transition metal complex was unearthed in this laboratory as noted in sec 1.1.¹⁰ This involved the insertion of S between the Pd–Pd metal-metal bond of Pd₂X₂(dpm)₂, X
= Cl, Br and I, to give a $\mu$-sulfide complex of the type $\text{Pd}_2X_2(\text{dpm})_2(\mu-S)$,

$$\text{Pd}_2X_2(\text{dpm})_2 + \text{H}_2\text{S} \rightarrow \text{Pd}_2X_2(\text{dpm})_2(\mu-S) + \text{H}_2$$ (1.6)

$$[X = \text{Cl}, \text{Br}, \text{I}]$$

Apart from this reaction, there is only one other system that generates $\text{H}_2$ quantitatively from $\text{H}_2\text{S}$.\(^9\)

$$2\text{Cp}^{\prime}\text{Zr}(\text{CO})_2 + 2\text{H}_2\text{S} \rightarrow [\text{Cp}^{\prime}\text{Zr}(\mu-S)]_2 + 2\text{H}_2 + 4\text{CO}$$ (1.7)

$$[\text{Cp}^{\prime} = \eta^5 - \text{C}_5\text{H}_5 \text{ or } \eta^5 - \text{C}_5\text{Me}_5]$$

The interaction of $\text{H}_2\text{S}$ with the ruthenium complexes $\text{RuH}_2(\text{PPh}_3)_4$,\(^10,11\) and $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$,\(^12\) results in $\text{H}_2$ production. The $\text{H}_2$ generated from the reaction of $\text{RuH}_2(\text{PPh}_3)_4$ and $\text{H}_2\text{S}$ is a consequence of the hydride content of the complex, and the net reaction, ignoring a labelling of the hydrogen atom, is the more usual oxidative addition of $\text{H}_2\text{S}$ via cleavage of the S−H bond.\(^11-13\)

$$\text{RuH}_2(\text{PPh}_3)_4 + \text{H}_2\text{S} \rightarrow \text{RuH}(\text{SH})(\text{PPh}_3)_3 + \text{H}_2 + \text{PPh}_3$$ (1.8)

The ruthenium complexes, $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$\(^12\) and $[\text{Ru(NH}_3)_6\text{(H}_2\text{S})]^{2+}$,\(^14\) reduce $\text{H}_2\text{S}$ to $\text{H}_2$ and $2\text{SH}^-$.

$$\text{Ru}(\text{CO})_2(\text{PPh}_3)_3 + \text{H}_2\text{S} \xrightarrow{\text{PPh}_3} \text{RuH}(\text{SH})(\text{CO})(\text{PPh}_3)_2$$

$$\xrightarrow{\text{H}_2\text{S}} \text{Ru}(\text{SH})_2(\text{CO})_2(\text{PPh}_3)_2 + \text{H}_2$$ (1.9)

$$2[\text{Ru(NH}_3)_6(\text{H}_2\text{S})]^{2+} \rightarrow 2[\text{Ru}(\text{SH})(\text{NH}_3)_6]^{2+} + \text{H}_2$$ (1.10)

The reaction was suggested tentatively because the precursor complex was not obtained in a pure state.\(^14\) The only other well characterised isolated $\text{H}_2\text{S}$ complex appears to be $\text{W}(\text{CO})_6(\text{H}_2\text{S})$,\(^15\) although $^1\text{H}$ nmr spectroscopic evidence
has been presented for the species Pt(PPh₃)₂(H₂S) en route to formation of more stable (hydrido)(mercapto) complex.⁶,¹⁷ Equation 6, analogous to Eqs 1 and 2, has been invoked for a solid state reaction to account for the filling of vacant anionic sites by sulfur in WS₂ lattices.⁸

\[ 2W^{3+} + H_2S \rightarrow 2W^{4+} + S^{2-} + H_2 \]  

(1.11)

1.3 The chemistry of transition metal dpm dinuclear species

The bisphosphine, bis(diphenylphosphino)methane (dpm), has proved to be a versatile ligand for linking two metals while allowing for considerable flexibility in the distance between the two metal ions involved. Though dinuclear metal complexes of dpm are known with one,¹⁹ two²⁰ or three²¹ bridging \( \mu \)-dpm ligands, two trans-\( \mu \)-dpm ligands are most common and these include homobimetallic Rh,²² Ir,²³ Pd,²⁴ Pt²⁵ and Mn²⁶ and heterobimetallic Pd/Pt,²⁷ Pd/Fe²⁸ and Pd/Mn²⁹ dinuclear complexes. Typically, these dinuclear complexes exhibit any one of three main structural types.

Firstly, a structure without either a metal–metal bond or other bridging groups between the two metal centers and the two metal ions are linked by two bridging dpm ligands. This structure is most common with Rh(I) dimers and is more elusive with other metals; R₇H₂(CO)₂Cl₂(dpm)₂³⁰ and Rh₇(MeNC)₄(dpm)₂³¹ are good examples of complexes having this structure, usually described as a face-to-face structure. Though face-to-face dinuclear complexes are known in the Pt(II) and Pd(II) systems, Pt₇(C≡CR)₄(dpm)₂ (R = Me, CF₃, Ph, 4-tolyt)³² and Pd₂Cl₂(CH₃)₂(dpm)₂,³³ those with other non–bridging, terminal ligands (i.e. X in M₂X₄(dpm)₂) rearrange rapidly to monomeric forms.³⁴
Secondly, a structure with no other bridging groups but with interaction between the metal centres is commonly adopted by both homo- and heterobimetallic complexes of dpm. The bond between the two metal centres is usually single for the majority of metals, but in certain Mo and Re systems multiple bonds are known. The singly metal-metal bonded derivatives, MM'X₂(dpm)₂ (M, M' = Pd, Pt; X = Cl) display high reactivity either by displacement of terminal chloride ligands by anionic or neutral ligands or by insertion of SnCl₂ into the metal-chloride bond. The displacement of the terminal chloride is effected by various ligands including Br⁻, I⁻, NCO⁻, NCS⁻, N₃⁻, NO₅⁻, this resulting in the alteration of the metal-metal bond strength. The change of bond strength is attributed to the trans-influence exerted by the terminal ligand. As a result, the reactivity of the metal-metal bond is altered and this is evident in most of the reactions in which the metal-metal bond is broken. However, in the reaction between CO and Pd₂X₂(dpm)₂ species (X = Cl, Br, I, NCO), the rate was governed by the Pd-CO bond strength rather than Pd-Pd bond energy. A number of unique chemical features have been observed as a result of the proximity of the two metal ions in the dpm complexes. Many of these complexes are able to co-ordinate (sometimes reversibly), in a bridging manner, atoms or small molecules such as H, S, Se, SO₂, SO₃, N₂, CO₂, CN⁻, NO₃⁻, CN⁻, RS⁻, R₂C=CR, N₂R⁺, and H₂. This type of co-ordination results in the third structural type that includes both A-frame structures with one bridging group, and double A-frame structures with two bridging groups. Both single and double atom bridges are known; CH₂, CO, SO₂ and PhN₂⁺ connect the metals centres via single atoms while CS₂ and R≡CR utilise two atoms. A metal-metal bond
may be present in complexes with either one and two bridging groups.

In dinuclear Pd complexes of the type Pd$_2$X$_2$(dpm)$_2$, a structure with a single metal–metal bond exists. However, in the analogous A-frame complexes with a single bridging group, the Pd–Pd bond is absent. The terminal, non-bridging ligands$^{24a}$ (i.e. X and X' in Pd$_2$XX'(dpm)$_2$) can be simple inorganic anions such as Cl$^-$, Br$^-$, I$^-$, NCS$^-$, N$_3^-$, NCO$^-$ or predominately non-ionic organic groups like C$_6$F$_5$, C$_6$Cl$_5$, or C$_6$H$_5$S.$^{24a}$ Complexes are also known with two different terminal ligands. In these mixed terminal ligand dimers, C$_6$Cl$_5$ or C$_6$F$_5$ is usually one of the ligands and the other terminal ligand is usually a simple inorganic anion mentioned above.

Both types of Pd$_2$ dimers with the same or mixed terminal ligands exhibit reactivity toward the insertion of small molecules. The reactivity is, however, altered considerably by changing the terminal ligands. For example, the CO insertion shows such a reactivity trend by changing ligands (Cl, Br, I, NCO), but the resulting $\mu$-CO complexes are isolable.$^{37}$ With C$_6$F$_5$ or C$_6$Cl$_5$ as one or both terminal ligands, CO inserts but the $\mu$-CO complex is non-isolable$^{36}$ and is observed only as a transient intermediate. The insertion of SO$_2$, on the other hand, results in the formation of stable $\mu$-SO$_2$ complexes$^{36}$ with X = C$_6$F$_5$ or C$_6$Cl$_5$; spontaneous loss of SO$_2$ occurs above 0°C when X = Cl, Br or I.$^{41a}$ Dinuclear complexes with related bisphosphine ligands such as (CH$_3$)$_2$PCH$_2$P(CH$_3$)$_2$ (dpm)$^{49}$ and Ph$_2$PCH(CH$_3$)PPh$_2$ (dpmMe)$^{42}$ generally exhibit reactivity toward the insertion of small molecules. In the case of Pd$_2$X$_2$(dpmMe)(dpm) species (X = Cl, Br, I, NCO), CO insertion, and S insertion from H$_2$S, take place, but with Pd$_2$X$_2$(dpmMe)$_2$ (X = Cl, Br, I, NCO) neither the insertion of CO or S occurs because of steric factors imposed by the additional methyl group.
1.4 Aim of work

The main objective of this thesis was to investigate in greater detail the kinetic and mechanistic aspects of reaction 1.1, the first of its kind to show full recovery of H₂ from H₂S. This study was aimed at answering some of the pertinent questions connected with reaction 1.1, such as the possible role of the acidic -CH₂- protons of dpm, the nature of attacking species, the nature of reaction intermediates, the reasons for the non-reactivity of other sulfur compounds (RSH and RSSR)⁴⁶ and the effect of solvent polarity (i.e. dielectric constant).

Further aims of the project were to study the reactivity of the Pd₂X₂(dpm)₂ dimers with analogous HX molecules (HCl, HBr and HI), and to find an effective way to remove the sulfur from the μ-S complex in order to regenerate the Pd dimer.
1.5 References


   (b) J. Edmond, *Oceanus*, (Summer 1982), p.22.


9. F. Bottomley, D. F. Drummond, G. O. Egharevba and P. S. White, 
organometallics, 5, 1620 (1986).


12. C. L. Lee, J. Chisholm, B. R. James, D. A. Nelson and M. A. Lilga, 


16. D. Morelli, A. Segre, R. Ugo, G. La Monica, S. Cenini, F. Conti and F. 

17. R. Ugo, G. La Monica, S. Cenini, and F. Conti J. Chem. Soc. (A), 522 
(1971).

Processes, McGraw-Hill, New York, 1979, Ch. 5.
19. See, for example,

20. See, for example,


22. See, for example:
   (b) C. Woodcock and R. Eisenberg, *Organometallics*, 1, 886 (1982).


24. (a) A. L. Balch, in *Catalytic Aspects of Metal Phosphine Complexes*,

25. See, for example,

26. See, for example,


35. See, for example,


Chapter 2

EXPERIMENTAL

2.1 MATERIALS

2.1.1 Solvents

Spectral or analytical grade solvents were obtained from MCB, BDH, Aldrich, Eastman, Fisher or Mallinckrodt Chemical Co.. Benzene, hexanes and toluene were refluxed with and distilled from sodium/benzophenone under an atmosphere of N₂. N,N'-Dimethylacetamide (DMA) was stirred over CaH₂ for 24 h prior to fractional distillation under vacuum, and subsequently stored in the dark. Methanol, ethanol, dichloromethane and acetone were distilled after refluxing with the appropriate drying agents (Mg/I₂ for methanol and ethanol, P₂O₅ for dichloromethane, and CaSO₄ for acetone). Acetonitrile was stored over molecular sieves (Fisher : Type 5A, Grade 522, 8-12 mesh) prior to use. Anhydrous diethyl ether and pentanes were used without further purification. All solvents were deoxygenated prior to use.

2.1.2 Gases

Purified argon (H.P.), nitrogen (U.S.P.) and hydrogen (U.S.P.) were obtained from Union Carbide Canada Ltd.. Hydrogen was passed through an Engelhard Deoxo catalytic hydrogen purifier to remove traces of oxygen. Hydrogen sulfide (C.P.), anhydrous hydrogen chloride and anhydrous hydrogen bromide were
obtained from Matheson Gas Co. All gases, except hydrogen, were used without further purification.

$D_2S$ was prepared by the action of $DCl/D_2O$ (10 mL) on $CaS$ (2 g). The resulting gas was first bubbled through $D_2O$ to remove any sulfur oxide impurities and $HCl$, and then dried over $CaCl_2$ and $P_2O_5$ prior to use.

### 2.1.3 Phosphines and other materials

Reagent grade triphenylphosphine, bis(diphenylphosphino)methane (dpm) and 1,3-(diphenylphosphino)propane (dpp) were supplied by Strem Chemicals Inc., while methyldiphenylphosphine was kindly made available by K.Bhangu of this department. All phosphines except dpp were used as such, without further purification, while dpp was crystallized from hot ethanol/hexane mixture under argon. The disulfide of dpm ($dpmS_2$) was prepared by refluxing a mixture of dpm (0.2 gm, 0.55 mmol) and elemental sulfur ($S_8$) (36 mg, 0.14 mmol) in deoxygenated toluene (25 mL) under argon atmosphere for 2 h. The white product which precipitated after the addition of ethanol (50 mL) was then filtered, washed with ethanol (2 x 10 mL) and dried. An attempt to prepare dpm monosulfide ($dpmS$) employing the above procedure, using one half the amount of elemental sulfur resulted in a mixture containing dpm (~20%), $dpmS$ (~60%) and $dpmS_2$ (~20%). The purity of all phosphines was checked by $^{31}P\{^1H\}$ nmr prior to use.

Benzonitrile (Aldrich), biphenyl (BDH), $CaS$ (Alfa Products) and $DCl/D_2O$ (35% (w/w) $DCl$) were used as such, without further purification. The ligand dibenzylideneacetone (dba) was prepared $^1$ by the condensation of acetone (1.45 g, 25 mmol) with benzaldehyde (5.3 g, 50 mmol) in a solution of sodium hydroxide in aqueous ethanol (90 mL); the yellow product was filtered, washed
with water (2 x 20 mL) and dried in vacuo. The crude product was recrystallized from hot ethyl acetate.

The adduct DMA.HCl\(^2\) was prepared by bubbling anhydrous HCl(g) into DMA(30 mL) to produce a copious white precipitate. The mixture was filtered under Ar, washed well with diethyl ether and vacuum dried. Recrystallization from acetone/diethyl ether afforded colourless, extremely hygroscopic crystals of DMA.HCl.

2.1.4 Palladium Compounds

The palladium, on loan by Johnson Matthey Ltd., was obtained as PdCl\(_2\). All synthetic reactions, unless specified otherwise, were carried out under an atmosphere of argon, employing Schlenk techniques.

2.1.4.1 Pd(PhCN)\(_2\)Cl\(_2\)

*Trans*-dichlorobis(benzonitrile)palladium(II).\(^3,4\)

Palladium(II) chloride, PdCl\(_2\) (2.0 g, 11.3 mmol) was suspended in benzonitrile (50 mL) and the mixture warmed to 100°C. After 20 minutes the greater part of palladium(II) chloride has dissolved to give a red solution. This red solution was filtered while still warm and the filtrate was poured into hexanes (300 mL). The light yellow product was filtered, washed with hexanes and vacuum dried.

Yield - 3.9 g(90%) calculated for \(C_{14}H_{16}N_2Cl_2Pd\); C : 43.84, H : 2.63. Found C : 44.01, H : 2.69%.
2.1.4.2 Pd$_2$(dba)$_3$.CHCl$_3$

Tris(dibenzyldieneacetone)dipalladium(0)-chloroform solvate.$^5$

Palladium chloride (1.05 g, 5.9 mmol) was added to hot (~50°C) methanol (150 mL), containing dibenzyldieneacetone (dba) (4.6 g, 19.6 mmol) and sodium acetate (3.9 g, 47.5 mmol). The mixture was stirred at 40°C to give a reddish-purple precipitate, cooled to complete the precipitation, filtered, and the solid then washed successively with water and acetone and dried in vacuo. The precipitate (3.39 g) was dissolved in hot chloroform (120 mL), and filtered to give a deep violet solution. The deep purple needles, which precipitated after the slow addition of diethyl ether (170 mL), were filtered, washed with diethyl ether and dried in vacuo.

Yield: 2.5 g (85%) calculated for $C_{52}H_{43}Cl_3O_3Pd_2$; C: 60.34, H: 4.19. Found C: 60.12, H: 4.10%.

2.1.4.3 Pd$_2$Cl$_2$(dpm)$_2$

Dichlorobis-$\mu$-[bis(diphenylphosphino)methane]dipalladium(I), $^6$ 1a

The title compound was prepared by a procedure slightly modified from that reported. Pd(PhCN)$_2$Cl$_2$ (0.41 g, 1.01 mmol), Pd$_2$(dba)$_3$.CHCl$_3$ (0.55 g, 0.53 mmol) and Ph$_2$PCH$_2$PPh$_2$ (0.82 g, 2.1 mmol) were refluxed in oxygen-free dichloromethane (50 mL), under a nitrogen atmosphere for 30 min. After being cooled, the resulting red solution was filtered to remove any insoluble materials, and filtrate reduced in volume to ~10 mL. The yellow-orange product, which precipitated after the addition of diethyl ether (25 mL), was then filtered, washed with acetone (2 x 10 mL) to remove any palladium(II) monomer, and dried in vacuo.
Yield - 1.0 g (90%) calculated for $C_{50}H_{44}P_4Cl_2Pd_2$; C : 57.05, H : 4.21. Found C : 57.45, H : 4.10%.

$^1H$ nmr $\delta_{^1H}^{10C} : 4.17$ ppm (-CH$_2$-, q, $J_{P-H} = 4$ Hz).

$^{31}P\{^1H\}$ nmr in CD$_2$Cl$_2$ showed a single peak at -3.46 ppm.

The spectroscopic data for this complex$^7$ and the others described in the following sections : Pd$_2$Br$_2$(dpm)$_2$, Pd$_2$I$_2$(dpm)$_2$, Pd$_2$Cl$_2$(dpm)$_2$(μ-S), Pd$_2$Br$_2$(dpm)$_2$(μ-S), Pd$_2$I$_2$(dpm)$_2$(μ-S), PdCl$_2$(dpm),$^{10,11}$ and PdBr$_2$(dpm),$^{10}$ agree with those reported in the literature.

2.1.4.4 Pd$_2$Br$_2$(dpm)$_2$

Dibromobis-μ-[bis(diphenylphosphino)methane]dipalladium(I), $^6$ 1b

To a solution of Pd$_2$Cl$_2$(dpm)$_2$ (0.23 g, 0.22 mmol) in dichloromethane (10 mL), a solution of NaBr (0.20 g, 2 mmol) in aqueous methanol (10 mL) was added. The resulting solution was filtered, and concentrated under vacuum until orange crystals were formed. Aqueous methanol was added to complete the precipitation and the product was filtered. Recrystallization from dichloromethane/aqueous methanol followed by vacuum drying yielded an orange-red crystalline product.

Yield - 2.35 g (95%) calculated for $C_{50}H_{44}P_4Br_2Pd_2$; C : 52.62, H : 3.89. Found C : 52.20, H : 3.80%.

$^1H$ nmr $\delta_{^1H}^{10C} : 4.26$ ppm (-CH$_2$-, q, $J_{P-H} = 4$ Hz).

$^{31}P\{^1H\}$ nmr in CDCl$_3$ showed a single peak at -5.5 ppm.

2.1.4.5 Pd$_2$I$_2$(dpm)$_2$.CH$_2$Cl$_2$

Diodobis-μ-[bis(diphenylphosphino)methane]dipalladium(I)dichloromethane solvate,$^6$ 1c
The complex was prepared using a procedure similar to that described for 
Pd$_2$Br$_2$(dpm)$_2$. To a solution of Pd$_2$Cl$_2$(dpm)$_2$ (0.23 g, 0.22 mmol) in dichloromethane (10 mL), a solution of NaI (0.15 g, 1 mmol) in aqueous methanol (10 mL) was added. The resulting solution was filtered and concentrated until brownish-violet crystals were formed. Aqueous methanol was added to complete the precipitation; the solid was filtered, washed with acetone (2 x 10 mL) and dried in vacuo.

Yield -0.27 g (92%) calculated for C$_{61}$H$_{46}$P$_4$Cl$_2$I$_2$Pd$_2$; C : 46.39, H : 3.51, I : 19.20. Found C : 46.70, H : 3.60, I : 19.11%.

$^1$H nmr $\delta^{29}$C$_{CDCl_3}$ : 4.23 ppm (-CH$_2$-, q, $J_P$-$H$ = 4 Hz).

$^{31}$P{$^1$H} nmr in CDCl$_3$ showed a single peak at -11.3 ppm.

2.1.4.6 Pd$_2$Cl$_2$(dpm)$_2$(μ-S)

Dichlorobis-μ-[bis(diphenylphosphino)methane]-μ-sulfidodipalladium-(II), $^6$22

Pd$_2$Cl$_2$(dpm)$_2$ (0.50 g, 0.48 mmol) was dissolved in dichloromethane (50 mL) and H$_2$S gas was bubbled through the solution for 20 min at 20°C; the colour changed from orange-red to brown with accompanying precipitation of brown solid that was completed by gradual addition of diethyl ether (50 mL). The product was filtered, washed successively with acetone (2 x 10 mL), diethyl ether (10 mL) and dried in vacuo.

Yield - 0.50 g (97%) calculated for C$_{60}$H$_{44}$P$_4$Cl$_2$SPd$_2$; C : 55.36, H : 4.09. Found C : 55.60, H : 4.27%.

$^1$H nmr $\delta^{29}$C$_{CDCl_3}$ : -CH$_2$-, 2.79 ppm ( dq, $J_H$-$H$ = 13 Hz, $J_P$-$H$ = 4 Hz),

4.70 ppm ( m, $J_H$-$H$ = 13 Hz, $J_P$-$H$ = 6 Hz).

$^{31}$P{$^1$H} nmr in CD$_2$Cl$_2$ showed a singlet at 5.50 ppm.
2.1.4.7 \( \text{Pd}_2\text{Br}_2(\text{dpm})_2(\mu-\text{S}) \)

Dibromobis-\( \mu-\)bis(diphenylphosphino)methane]-\( \mu-\)sulfidodipalladium(II), \( ^9 \)  

2b

\( \text{H}_2\text{S} \) (50 mL, 1 atm at 25°C) was injected into a Schlenk tube stoppered with a rubber septum, containing a solution of \( \text{Pd}_2\text{Br}_2(\text{dpm})_2 \) (0.50 g, 0.47 mmol), in oxygen-free dichloromethane (50 mL) and allowed to react for 3h; the colour changed from orange-red to brown with accompanying precipitation of brown product. The precipitation was completed by the addition of diethyl ether (50 mL); the solid was filtered, washed successively with acetone (2 x 10 mL), diethyl ether (10 mL) and dried in vacuo.

Yield - 0.51 g (98%) calculated for \( \text{C}_{50}\text{H}_{44}\text{P}_4\text{Br}_2\text{SPd}_2 \); C : 51.13, H : 3.78.

Found C : 51.41, H : 3.96%.

\( ^1\text{H} \text{nmr} \delta^{20\text{oC}}_{\text{CD}_2\text{Cl}_2} : -\text{CH}_2-, 2.85 \text{ ppm (dq, } J_{\text{H-H}} = 13 \text{ Hz, } J_{\text{P-H}} = 4 \text{ Hz), 4.80 ppm (m, } J_{\text{H-H}} = 13 \text{ Hz, } J_{\text{P-H}} = 6 \text{ Hz).}

\( ^{31}\text{P}\{^1\text{H}\} \text{nmr in CD}_2\text{Cl}_2 \text{ showed a singlet at 5.80 ppm.}

2.1.4.8 \( \text{Pd}_2\text{I}_2(\text{dpm})_2(\mu-\text{S}) \)

Diiodobis-\( \mu-\)bis(diphenylphosphino)methane]-\( \mu-\)sulfidodipalladium(II), \( ^9 \)  

2c

To a solution of \( \text{Pd}_2\text{Cl}_2(\text{dpm})_2(\mu-\text{S}) \) (0.25 g, 0.23 mmol), in oxygen-free dichloromethane (25 mL) a solution of NaI (0.30 g, 2 mmol) in aqueous methanol (10 mL) was added. The volume of the solution was reduced to \(~10 \text{ mL by rotovap to yield brown crystals that were collected, dissolved in dichloromethane (20 mL) and reprecipitated using methanol (50 mL). The precipitate was filtered, washed with methanol (2 x 10 mL) and dried in vacuo.}
Yield - 0.32 g (90%) calculated for \( C_{50}H_{44}P_4hSPd_2 \); C : 47.34, H : 3.50. Found C : 47.20, H : 3.46%.

\(^1H\) nmr \( \delta_{CDCl_3}^{296\circ}C \) : -CH\(_2\)-, 3.07 ppm (dq, \( J_{H-H} = 14 \) Hz, \( J_{P-H} = 3 \) Hz),

4.94 ppm (m, \( J_{H-H} = 14 \) Hz, \( J_{P-H} = 6 \) Hz).

\(^{31}P\{^1H\}\) nmr in CDCl\(_3\) showed a singlet at 5.77 ppm.

2.1.4.9 PdCl\(_2\)(dpm)

Dichloro[bis(diphenylphosphino)methane]palladium(II), \(^{10,11}6a\)

To a dichloromethane (10 mL) solution of dpm (0.30 g, 0.78 mmol), a solution of Pd(PhCN)\(_2\)Cl\(_2\) (0.30 g, 0.77 mmol) in dichloromethane (10 mL) was added with stirring. The stirring continued for 2h and diethyl ether (50 mL) was added to the yellow solution, which afforded a pale yellow solid. The solid was filtered, and after reprecipitation twice from dichloromethane/diethyl ether, washed with diethyl ether, and dried in vacuo.

Yield - 0.35 g (80%) calculated for \( C_{25}H_{22}P_2Cl_2SPd \); C : 53.46, H : 3.95. Found C : 53.14, H : 3.90%.

\(^1H\) nmr \( \delta_{CDCl_3}^{296\circ}C \) : 4.28 ppm (-CH\(_2\)-, t, \( J_{P-H} = 10.8 \) Hz).

\(^{31}P\{^1H\}\) nmr in CDCl\(_3\) showed a singlet at -54 ppm.

2.1.4.10 PdBr\(_2\)(dpm)

Dibromo[bis(diphenylphosphino)methane]palladium(II), \(^{10}6b\)

To a dichloromethane solution (10 mL) of PdCl\(_2\)(dpm) (0.25 g, 0.45 mmol), a solution of NaBr (0.20 g, 2 mmol) in aqueous methanol (10 mL) was added. The resulting solution was filtered, and the volume of the solution reduced
to ~5 mL in a rotovap. Aqueous methanol (25 mL) was added to complete the precipitation of the yellow solid. Recrystallization from dichloromethane/methanol, followed by vacuum drying, yielded a yellow product.

Yield - 0.23 g (79%) calculated for $C_{25}H_{22}P_2Br_2SPd$; C: 46.15, H: 3.41. Found C: 46.00, H: 3.63%.

$^1H$ nmr $\delta_{CDCl_3}^{20^\circ C}$: 4.32 ppm (-CH$_2$-, t, $J_{P-H} = 10.5$ Hz).

$^{31}P\{^1H\}$ nmr in CDCl$_3$ showed a singlet at -55.8 ppm.

### 2.2 Instrumentation

Infrared spectra were recorded on a Nicolet DX FT-IR spectrometer, as Nujol mulls between CsI plates or as KBr pellets. UV-visible spectra were recorded on a Perkin-Elmer 552A spectrophotometer with thermostated cell compartments using anaerobic spectral cells of path length 1.0 or 0.1 cm (Fig 2.1).

$^1H$ nmr spectra were recorded on Bruker WP-80, Varian XL-300 or Bruker WH-400 spectrometers, with tetramethylsilane (TMS) at $\delta$ 0.0 ppm as standard. $^{31}P\{^1H\}$ nmr spectra were recorded on a Varian XL-300 (121.4 MHz) or a Bruker WP-80 (32.3 MHz). The reference for the $^{31}P\{^1H\}$ nmr spectra was the signal for triphenylphosphine at -6 ppm (relative to 85% $H_3PO_4$). Chemical shifts are positive in the direction of decreasing field and are reported relative to 85% $H_3PO_4$. All spectrometers were operating in the Fourier transform mode and were equipped with variable temperature control. All samples were sealed under argon, unless otherwise specified.

Gas chromatographic analyses were performed on a temperature programmable Hewlett Packard 5890A instrument equipped with a thermal conductivity detector (TCD). A packed molecular sieve column was used with helium
as a carrier gas.

Mass spectra were recorded on a mass spectrometer (AE1MS9) by the mass spectrometry services of this department.

Elemental analyses were carried out by P. Borda of this department.

2.3 Procedure for a typical kinetic run

The kinetics of reaction between the Pd\textsuperscript{II} complex and H\textsubscript{2}S were monitored spectrophotometrically, under anaerobic conditions by using cells shown in Fig 2.1. In a typical experiment where P\textsubscript{H\textsubscript{2}S} was 1 atm, the study was carried out as follows: a weighed amount of complex was placed in the quartz side of the cell which was then evacuated and then filled with H\textsubscript{2}S gas. A slow stream of H\textsubscript{2}S gas was then allowed to flow while a saturated solution of H\textsubscript{2}S (25°C, 1 atm) in dichloromethane (10 mL) was pipetted into the side-arm flask. The solid and the solvent then were mixed and shaken until a homogeneous solution was obtained. The cell was placed in a thermostated cell compartment and the change in optical density was monitored at a fixed wavelength. The cell was agitated periodically to maintain the "physical equilibrium" of the solution (i.e. to avoid any diffusion problems).

For kinetic runs requiring P\textsubscript{H\textsubscript{2}S} values different from 1 atm a slightly modified procedure was adopted. A weighed amount of solid complex was placed in the cell whilst an appropriate volume of solvent was pipetted into the flask. The solvent was degassed by employing a freeze and thaw static vacuum technique. The solid and the solvent were then mixed and shaken until a homogeneous solution was obtained. The cell was placed in the thermostated cell compartment to allow the solution temperature to equilibrate; when this was
Figure 2.1: Anaerobic spectral cell used for UV–visible spectroscopy.
achieved, an appropriate amount of H₂S gas or a solution of H₂S in the solvent was injected into the cell with the aid of a gas-tight syringe, the experiment then carried out as described above.

2.4 Low temperature nmr experiments with Pd₂X₂(dpm)₂ and H₂S.

2.4.1 Reaction of Pd₂Br₂(dpm)₂ with H₂S

A CD₂Cl₂ (0.6 mL) solution of Pd₂Br₂(dpm)₂, 1b, (5 mg) in a 5 mm nmr tube, stoppered with rubber septum, was degassed employing a freeze and thaw static vacuum technique, and ¹H and ³¹P{¹H} nmr spectra were run at -78°C. The sample was then removed from the probe, and H₂S (5 mL, 1 atm, at 25°C) was injected into the cold tube with a gas-tight syringe. The H₂S gas condensed inside the tube (b.p. -65°C) and the liquid interface (CD₂Cl₂ solution of 1b and liquid H₂S) turned green. The nmr tube was shaken, replaced into the -78°C probe, and ¹H and ³¹P{¹H} spectra were run first at -78°C and then at higher temperatures.

2.4.2 Reaction of Pd₂I₂(dpm)₂ with H₂S

A CD₂Cl₂ (2.5 mL) solution of 1c (20 mg) in a Schlenk tube (10 mL volume) was degassed three times employing the freeze and thaw static vacuum technique. A large excess of H₂S (~50 mL, 1 atm, 25°C) was then administered into the Schlenk tube, which was then cooled to -74°C in a low-temperature slush bath (solid CO₂/ethanol), and the system allowed to react for several hours (8 - 20 h). The initially brownish-red solution of 1c, which turned green over this period, was transferred (at -74°C) to an nmr tube with the aid of a cannula, and ¹H and ³¹P{¹H} nmr spectra were then run at different
temperatures, from -74 to 20°C.

2.5 Interaction of Pd₂Br₂(dpm)₂ with HX

2.5.1 Room temperature reaction

A solution of 1b (3 mg) in oxygen-free CDCl₃ (5 mL) or C₆D₆, in a small Schlenk tube (5 mL), was degassed three times by the freeze and thaw static vacuum technique. On addition of anhydrous hydrogen bromide gas (50 μL, 1 atm, 25°C) from a gas-tight syringe, the orange-red solution of 1b turned green. UV-visible and ¹H and ³¹P{¹H} nmr spectra were run immediately after the addition of HBr gas, and after several hours when the solution had become pale yellow.

2.5.2 Low temperature reaction

The reaction between the CDCl₃ solution of 1b and HBr was carried out at low temperature (−40°C) in a nmr tube, stoppered with a rubber septum. The solution was first degassed several times by employing the freeze and thaw technique, then cooled in a low temperature bath (−40°C), and then anhydrous HBr gas was injected into the nmr tube in small increments; after each addition, the ¹H and ³¹P{¹H} nmr spectra were run at −40°C.

2.6 Sulfur abstraction reactions

2.6.1 Sulfur abstraction by dpm

In a typical experiment, an equimolar mixture of 2b or 2c and dpm (5 x 10⁻² mmol) in dichloromethane solution (10 mL) were stirred under Ar for 4-10
h at room temperature. The solvent was then pumped off and the solid left behind was characterized by $^1\text{H}$ and $^{31}\text{P}$\{$^1\text{H}$\} nmr spectra (see section 5.2.1).

2.6.2 Desulfurization of H$_2$S

The reaction between the complex 2 and H$_2$S was carried out in the presence of dpm. The molar ratios of Pd$_2$ to dpm were varied from 1:1 to 1:200 in several experiments, always keeping the H$_2$S concentration in large excess. A solution of 2b or 2c (3 mg) and a large excess of dpm (100 mg) in dichloromethane solution (25 mL) were stirred with excess H$_2$S (50 mL, 1 atm, 25°C) at room temperature for 4-6 h. The resulting solid was isolated by pumping off the solvent and characterized by $^1\text{H}$ and $^{31}\text{P}$\{$^1\text{H}$\} nmr spectra (see section 5.3).

2.7 Gas solubility measurements

The solubility of H$_2$S in dichloromethane at specific pressures at 25°C was determined using $^1\text{H}$ nmr spectroscopy. In a typical experiment, a known volume of CD$_2$Cl$_2$ solution containing either benzene (3 µL) or acetonitrile (5 µL) was taken in an nmr tube sealed with a rubber septum. The CD$_2$Cl$_2$ solution was degassed employing the freeze and thaw static vacuum technique. An appropriate volume of H$_2$S gas was injected into the nmr tube, which was then shaken well to attain physical equilibrium; the $^1\text{H}$ nmr spectrum was run at 25°C after allowing the solution temperature to equilibrate. From the integral peak intensities, using the benzene or acetonitrile peaks as standard, the H$_2$S solubility was readily measured. H$_2$S solubility was measured directly at various temperatures for the solution initially saturated with H$_2$S at room temperature and at 1 atm.
2.8 References


31


Chapter 3

THE INTERACTION OF $\text{H}_2\text{S}$ WITH Pd(I) DIMERS

3.1 The palladium(I) dpm dimer, Pd$_2$X$_2$(dpm)$_2$.

The palladium(I) diphenylphosphinomethane dimers, Pd$_2$X$_2$(dpm)$_2$, [X = Cl (1a), Br (1b), I (1c); dpm = Ph$_2$PCH$_2$PPh$_2$], first reported by Colton et al.,$^1$ contain an unusually reactive metal-metal bond. The crystal structure of Pd$_2$Br$_2$(dpm)$_2$, 1b, reveals that the two palladium atoms are connected by a metal-metal bond, of length 2.669 Å.$^2$ The coordinating geometries about each metal are approximately square planar, but the two coordination planes (Pd, P, P, Br) are twisted about the Br–Pd–Pd–Br axis which results in a dihedral angle of $39^\circ$ between the planes.

In solutions 1 undergoes addition of a number of small molecules, including S, RNC,$^{3,4}$ SO$_2$,$^{3,7}$ CS$_2$,$^8$ CO,$^{2,5,6,8}$ and activated acetylenes.$^{10}$ Addition of these molecules involves their insertion into the Pd–Pd bond, which breaks, the Pd, Pd separation increasing by $\sim$0.5 Å.

The insertion of sulfur into the Pd–Pd bond results in the formation of so-called A-frame complexes, Pd$_2$X$_2$(dpm)$_2$(μ-S), 2. Elemental sulfur and organic episulfides effect the conversion of 1 to 2. Recent studies$^4$ in this laboratory have unearthed reaction (3.1), which occurs quantitatively in solution at ambient conditions for X = Cl or Br.

$$\text{Pd}_2\text{X}_2(\text{dpm})_2 + \text{H}_2\text{S} \rightarrow \text{Pd}_2\text{X}_2(\text{dpm})_2(\mu - \text{S}) + \text{H}_2 \quad (3.1)$$
This reaction is of considerable interest because it generates dihydrogen quantitatively from the environmentally hazardous and common industrial by-product H\textsubscript{2}S. So it was decided to investigate the kinetic and mechanistic aspects of this reaction in detail. The results of these studies are discussed in the following sections.

3.2 Reaction with D\textsubscript{2}S

A solution of 1a (25 mg) in oxygen-free CH\textsubscript{2}Cl\textsubscript{2} in a 10 mL Schlenk tube under vacuum was allowed to react with D\textsubscript{2}S (4 mL, 1 atm, 25°C). The red-orange solution of 1a turned brown with accompanying precipitation of 2a. The solution was stirred for 30 min to complete the reaction. The possible gaseous products evolved (H\textsubscript{2}, HD, D\textsubscript{2}) were identified as follows: the contents of the Schlenk flask were cooled at liquid-N\textsubscript{2} temperature (to freeze CH\textsubscript{2}Cl\textsubscript{2} and D\textsubscript{2}S), and the mass spectrum of a sample of the gaseous phase was run at low mass range (0-10). The spectrum revealed the presence of only D\textsubscript{2}.

The brown precipitate of 2a was isolated after the addition of ether (5 mL) to complete the precipitation. The isolated solid was dissolved in CD\textsubscript{2}Cl\textsubscript{2} and the \textsuperscript{1}H nmr spectrum was run. The integral intensities of the -CH\textsubscript{2}- proton peaks (4 H) and those of the phenyl proton peaks (40 H) were compared and found to be in a 1:10 ratio, reconfirming that there was no deuterium exchange between D\textsubscript{2}S and the -CH\textsubscript{2}- protons of 1a in CH\textsubscript{2}Cl\textsubscript{2} solution during the reaction conditions. Thus the H\textsubscript{2} formed via the reaction (3.1) comes exclusively from the H\textsubscript{2}S reactant.
3.3 Kinetics and rate measurements

A dichloromethane solution of $1b$ is yellow-orange with the following electronic absorptions:

<table>
<thead>
<tr>
<th>$\lambda$ (nm)</th>
<th>$\epsilon$ (M$^{-1}$cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>428</td>
<td>10,600</td>
</tr>
<tr>
<td>364</td>
<td>17,500</td>
</tr>
<tr>
<td>301</td>
<td>23,100</td>
</tr>
</tbody>
</table>

while the dichloromethane solution of $\text{Pd}_2\text{Br}_2(\text{dpm})_2(\mu-\text{S})$, $2b$, is pale yellow with visible absorption bands at 473 nm (1200 M$^{-1}$cm$^{-1}$) and 348 nm (15200 M$^{-1}$cm$^{-1}$). When a dichloromethane solution of $1b$ reacts with hydrogen sulfide, the visible absorption bands at 428 and 364 nm decrease in intensity while the 473 and 348 nm bands of $2b$ grow in intensity, as shown in Fig 3.1.

Anaerobic spectral cells with path lengths of either 1.0 or 0.1 cm were used to monitor the reaction between complex $1b$ and $\text{H}_2\text{S}$ by observing the disappearance of the 428 nm band in a UV-visible spectrometer with a well thermostatted cell compartment. All rates were measured under pseudo-first order conditions in that the concentration of $\text{H}_2\text{S}$ was at least 100 times greater than that of complex $1b$. The reactions were monitored for up to $2\frac{1}{2} - 3$ half-lives. A typical rate plot and a plot of the data, which analysed for first order in $\text{Pd}_2$ dependence, are shown in Figs 3.2 and 3.3. The rates were measured at palladium concentrations ranging from $8.41 \times 10^{-5}$ to $2.23 \times 10^{-3}$ M, at different $\text{H}_2\text{S}$ concentrations ($7.1 \times 10^{-2}$ to $5.3 \times 10^{-1}$ M) and at different temperatures (0-35°C). Only one parameter at a time was varied.

The dependences of the rate on palladium concentration and hydrogen sulfide concentration were studied at 25°C, in dichloromethane. The solubility
Figure 3.1: Visible absorption spectral changes of a dichloromethane solution of Pd$_2$Br$_2$(dpm)$_2$ upon addition of H$_2$S at 25°C.
Figure 3.2: Rate plot for the reaction between Pd\(_2\)Br\(_2\)(dpm)\(_2\) (1.01 \times 10^{-3} \text{ M})
and H\(_2\)S (0.53 M) in CH\(_2\)Cl\(_2\), at 25°C.
Figure 3.3: A rate plot analysed for first order Pd\(_2\) dependence in CH\(_2\)Cl\(_2\) at 25°C. ([Pd\(_2\)] = 1.01 \times 10^{-3} \text{ M} \text{ and } [\text{H}_2\text{S}] = 0.53 \text{ M}).
of $H_2S$ in $CH_2Cl_2$ at 25°C at various $H_2S$ pressures was determined using the procedure described in section 2.4, and found to obey Henry’s law at least up to about 1 atm of $H_2S$ pressure (Table III-1, Fig 3.4). Further, the solubility of $H_2S$ was calculated to be $1.14 \text{ M atm}^{-1}$ or $1.5 \times 10^{-3}$ M torr$^{-1}$. The kinetic data for the 1b and $H_2S$ reaction are summarized in Tables III-2 and III-3, and Figs. 3.5 and 3.6. The reaction is first order in both $[Pd_2]$ and in $H_2S$; $k_{obs}$ is the pseudo-first order rate constant determined in the presence of excess $[H_2S]$, and equals $k_2[H_2S]$, where $k_2$ is the true bimolecular, second-order rate constant for the reaction. The temperature dependence of the rates over the range 0-35°C was investigated at a single palladium concentration (Table III-4). The plot of $ln(k_2/T)$ vs. $1/T$ yields a reasonably good straight line (Fig. 3.7). Values of $\Delta H^\ddagger = 55 \pm 5 \text{ kJ mole}^{-1}$ and $\Delta S^\ddagger = -115 \pm 10 \text{ J K}^{-1} \text{ mole}^{-1}$ were calculated from the slope and intercept, respectively.

Attempts were made to investigate the effect of the added bromide and phosphine on the reaction rate. With these ligands, however, reaction 1.1 took a completely different course; reaction of 1b with $H_2S$ in the presence of a five-fold excess of tetraethylammonium bromide ($NEt_4^+ Br^-$) resulted in the formation of 2b in only $\sim 70\%$, and several other products were evidenced by $^{31}P\{^1H\}$ nmr and UV-visible spectroscopy, especially an unidentified species with $\delta_P = 22.2 \text{ ppm}$. A five-fold excess of dpm rendered a catalytic system for the removal of $H_2$ from $H_2S$, and resulted in the formation of dpm monosulfide along with other palladium compounds (See Ch.5).
Table III-1: Solubility of H₂S in CH₂Cl₂ at various pressures at 25°C.

| P<sub>H₂S</sub>, atm | | | [H₂S]<sub>CH₂Cl₂</sub>, M |
|---------------------|---|---|
| 0.16                | | 0.20 |
| 0.22                | | 0.25 |
| 0.33                | | 0.38 |
| 0.43                | | 0.50 |
| 0.46                | | 0.55 |
| 0.50                | | 0.56 |
| 0.54                | | 0.62 |
| 0.58                | | 0.67 |
| 0.59                | | 0.69 |
| 0.67                | | 0.74 |
| 0.78                | | 0.91 |

Table III-2: Dependence of reaction rate on [Pd<sub>2</sub>] at 0.53 M [H₂S] in CH₂Cl₂ at 25°C.

<table>
<thead>
<tr>
<th>[Pd&lt;sub&gt;2&lt;/sub&gt;]/10⁻⁴, M</th>
<th>k&lt;sub&gt;obs&lt;/sub&gt;/10⁻⁴, s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.84</td>
<td>8.91</td>
</tr>
<tr>
<td>1.81</td>
<td>9.05</td>
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<tr>
<td>3.37</td>
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<td>4.42</td>
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<tr>
<td>7.45</td>
<td>8.62</td>
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<td>8.09</td>
<td>9.07</td>
</tr>
<tr>
<td>10.0</td>
<td>8.84</td>
</tr>
<tr>
<td>22.3</td>
<td>8.73</td>
</tr>
</tbody>
</table>
Figure 3.4: Solubility of H$_2$S in CH$_2$Cl$_2$ at various pressures.
Table III-3: Dependence of reaction rate on [H₂S] at 1.01 x 10⁻³ M Pd²⁺ in CH₂Cl₂ at 25°C.

<table>
<thead>
<tr>
<th>[H₂S]/10⁻¹, M</th>
<th>k_{obs}/10⁻⁴, s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.70</td>
<td>1.18</td>
</tr>
<tr>
<td>1.3</td>
<td>2.24</td>
</tr>
<tr>
<td>1.4</td>
<td>2.80</td>
</tr>
<tr>
<td>1.8</td>
<td>3.01</td>
</tr>
<tr>
<td>2.1</td>
<td>3.85</td>
</tr>
<tr>
<td>2.5</td>
<td>4.01</td>
</tr>
<tr>
<td>2.7</td>
<td>4.47</td>
</tr>
<tr>
<td>2.8</td>
<td>4.90</td>
</tr>
<tr>
<td>3.2</td>
<td>5.25</td>
</tr>
<tr>
<td>5.3</td>
<td>8.90</td>
</tr>
</tbody>
</table>

Table III-4: Temperature dependence of the rate constant for the reaction between 1b (at 1.01 x 10⁻³ M) and H₂S in CH₂Cl₂.

<table>
<thead>
<tr>
<th>Temp.K</th>
<th>[H₂S]⁺ M</th>
<th>k₂/10⁻⁴, M⁻¹s⁻¹</th>
<th>T⁻¹/10⁻³, K⁻¹</th>
<th>ln(k₂/T)/10⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>273</td>
<td>0.50</td>
<td>1.59</td>
<td>3.66</td>
<td>-1.44</td>
</tr>
<tr>
<td>279</td>
<td>0.51</td>
<td>3.61</td>
<td>3.58</td>
<td>-1.36</td>
</tr>
<tr>
<td>288</td>
<td>0.52</td>
<td>6.53</td>
<td>3.47</td>
<td>-1.30</td>
</tr>
<tr>
<td>298</td>
<td>0.53</td>
<td>17.1</td>
<td>3.36</td>
<td>-1.21</td>
</tr>
<tr>
<td>303</td>
<td>0.54</td>
<td>20.1</td>
<td>3.30</td>
<td>-1.19</td>
</tr>
<tr>
<td>308</td>
<td>0.55</td>
<td>25.5</td>
<td>3.25</td>
<td>-1.17</td>
</tr>
</tbody>
</table>

*: solubility measured directly by ¹H nmr experiments.
Figure 3.5: Dependence of reaction rate on $[\text{Pd}^2]$ at 0.53 M $[\text{H}_2\text{S}]$ in CH$_2$Cl$_2$ at 25°C.
Figure 3.6: Dependence of reaction rate on $[\text{H}_2\text{S}]$ at $1.01 \times 10^{-3}$ M Pd$_2$ in CH$_2$Cl$_2$ at 25°C.
Figure 3.7: The temperature dependence of the rate constant for the reaction between 1b (at 1.01 x 10^{-3} M) and H_2S in CH_2Cl_2.
3.4 Spectroscopic detection of intermediates.

3.4.1 Reaction between Pd$_2$Br$_2$(dpm)$_2$ and H$_2$S.

The low temperature (−78°C) $^1$H nmr spectrum of 1b in CD$_2$Cl$_2$ shows the characteristic -CH$_2$- proton signal of dpm (δ = 4.26 ppm, q, $J_{P-H} = 4$ Hz) along with that of phenyl proton signals (δ between 7 and 8 ppm), which are less informative. The nmr spectra of the 1b solution after the addition of H$_2$S showed, in addition to the H$_2$S signal (0.9 ppm), two additional sets of peaks (in the -CH$_2$- region δ = 3.4 ppm, δ = 3.6 ppm, both broad, 4H, and in the Pd-H region (δ = −8.45 ppm, t, $J_{P-H} = 18$ Hz, 1H) attributed to the formation of a new species in a small amount (~10%), and presumed to be a metal hydride (Figs. 3.8 A - C). Spectra recorded at higher temperatures showed a decrease in the intensity of both sets of peaks up to −65°C, with the gradual formation of Pd$_2$Br$_2$(dpm)$_2$(μ-S), 2b, as evidenced by the appearance of peaks in the -CH$_2$- region (δ = 2.85 ppm, $J_{H-H} = 13$ Hz, $J_{P-H} = 4$ Hz, δ = 4.8 ppm, $J_{H-H} = 13$ Hz, $J_{P-H} = 6$ Hz) (Figs. 3.9 A & B). At temperatures above −65°C, only signals due to 1b and 2b were observed.

Comparison of the $^{31}$P{¹H} nmr spectrum of 1b, and that of 1b with H$_2$S, at −78°C in CD$_2$Cl$_2$ showed the formation of the intermediate hydride. The spectrum of 1b with H$_2$S had at least four new unresolved broad peaks (δ ~ 5, 8, 19 and 23 ppm) in addition to the single sharp peak of 1b at −5.5 ppm (Fig. 3.9). Similar to the $^1$H nmr spectra, the spectrum run at higher temperatures showed a decrease in intensity of the unresolved broad peaks, with the appearance of a new peak (5.8 ppm), that of Pd$_2$Br$_2$(dpm)$_2$(μ-S). At −65°C and above, the nmr spectra showed the presence of only 1b and 2b.
Figure 3.8: The $^1$H nmr spectra in CD$_2$Cl$_2$ solution for (A) -CH$_2$- region of 1b; (B) -CH$_2$- region of 1b + H$_2$S at -70°C and (C) hydride region of 1b + H$_2$S at -70°C.
Figure 3.9: The $^1$H nmr spectra in CD$_2$Cl$_2$ solution of (A) -CH$_2$- region of $1b$ + H$_2$S warmed up to room temperature and (B) -CH$_2$- region of $2b$. 
Figure 3.10: The $^{31}$P{¹H} nmr spectra in CD$_2$Cl$_2$ of 1b and H$_2$S.
These observations, to be discussed later (Section 3.5) are explained by:

(i) oxidative addition $H_2S$ to $Pd_2Br_2$(dpm)$_2$, 1b, to form a Pd(H)(SH) intermediate, observable at temperatures below $-65^\circ$C, and (ii) the formation of $Pd_2Br_2$(dpm)$_2$(μ-S), 2b, from the hydride intermediate at temperatures above $\sim -78^\circ$C.

$$Pd_2Br_2(dpm)_2 + H_2S \rightarrow Pd_2Br_2(dpm)_2(H)(SH)$$

1b \hspace{2cm} 3b

$$Pd_2Br_2(dpm)_2(H)(SH) + \rightarrow Pd_2Br_2(dpm)_2(\mu - S) + H_2$$

(3.2)

3b \hspace{2cm} 2b

3.4.2 Reaction between $Pd_2I_2$(dpm)$_2$ and $H_2S$.

Compared to the $^1H$ nmr spectrum of the complex $Pd_2I_2$(dpm)$_2$, 1c, in CD$_2$Cl$_2$, recorded at $\sim -78^\circ$C, the spectrum of the mixture of 1c and $H_2S$ in CD$_2$Cl$_2$ showed additional peaks in the $-CH_2-$ region ($\delta = 5.02$ ppm, br singlet, 4H) and in the Pd-H region ($\delta = -6.05$ ppm, br singlet, 1H) in addition to the $H_2S$ peak ($\delta = 0.93$ ppm, br ), again indicating the formation of an intermediate hydride (Fig. 3.11 A – C). The spectra recorded at higher temperatures ($> -70^\circ$C) showed a general decrease in the intensity of both the 5.02 and -6.05 ppm peaks along with the appearance of a new set of peaks ($\delta$ 3.07 and 4.97 ppm), which are due to the $-CH_2-$ protons of $Pd_2I_2$(dpm)$_2$(μ-S), 2c (Fig. 3.12 A & B). The room temperature spectrum showed the presence of only the Pd$_2$ dimer, 1c, and the μ-sulfide, 2c.

The $^{31}P\{^1H\}$ spectrum of the hydride intermediate, which was recorded at $-74^\circ$C in CD$_2$Cl$_2$ solutions and more conveniently in neat $H_2S$ liquid containing a small amount of CDCl$_3$, showed two broad peaks ($-2.7, -6.7$ ppm) in
Figure 3.11: The $^1$H nmr spectra in CD$_2$Cl$_2$ solution for (A) -CH$_2$- region of 1c; (B) -CH$_2$- region of 1c + H$_2$S kept at ~74°C for 8 h and (C) -CH$_2$- region of 1c + H$_2$S kept at ~-74°C for 8 h then warmed up to -40°C.
Figure 3.12: The $^1$H nmr spectra in CD$_2$Cl$_2$ solution of (A) 1c + H$_2$S kept at ~-74°C for 8 h (hydride and -SH region) and (B) 2c.
addition to a broadened singlet of 1c (-11.3 ppm) (Fig. 3.13 A & B). However, as the temperature was increased, the $^{31}P\{^1H\}$ spectrum of the intermediate underwent two changes. Firstly, increasing amounts of the intermediate decomposed to form the $\mu$-sulfide, 2c, as evidenced from the decrease in the intensity of the intermediate's peaks, along with the appearance of the $\mu$-sulfide peak at 5.7 ppm. Secondly, the two peaks of the intermediate coalesced to form a single peak at $-4.0$ ppm near the vicinity of $-40^{\circ}C$ (Fig. 3.13 C). As in case of the $^1H$ nmr spectra the room temperature spectrum showed the presence of only 1c and 2c (Fig. 3.14 A & B).

These observations are explained in terms of the same general processes shown above in equation (3.2) for the corresponding bromide system (see section 3.4.1).

3.5 Discussion of kinetic and spectroscopic data

The first-order dependence of rate on both $[Pd^1]$ and $[H_2S]$ can be explained by either of the following mechanisms:

(a)

$$Pd_2X_2(dpm)_2 + H_2S \xrightleftharpoons[k_1^{-1}]{k_1} Pd_2X_2(dpm)_2(H)(SH) \quad (3.3)$$

1

$$Pd_2X_2(dpm)_2(H)(SH) + k_2 \rightarrow Pd_2X_2(dpm)_2(\mu - S) + H_2 \quad (3.4)$$

2

where $k_1$, $k^{-1}$ and $k_2$ are the rate constants of the individual steps as written.

Application of the steady state treatment to the intermediate, $Pd_2X_2(dpm)_2(H)(SH)$,
Figure 3.13: The $^{31}\text{P}^1\text{H}$ nmr spectra in CDCl$_3$ of (A) 1c at 20°C; (B) 1c + H$_2$S kept at $\sim$-74°C for 8 h and (C) 1c + H$_2$S kept at $\sim$-74°C for 8 h and then warmed up to -40°C. (Similar data are obtained in CD$_2$Cl$_2$.)
Figure 3.14: The $^{31}$P{$^1$H} nmr spectra in CDCl$_3$ of (A) 1e + H$_2$S kept at $\sim$-74°C for 8 h and then warmed to room temperature and (B) authentic sample of 2e at 20°C. (Similar data are obtained in CD$_2$Cl$_2$.)
3 gives the following rate law.

\[
\text{Rate} = \frac{-d[Pd^1_2]}{dt} = \frac{d[Pd_2(\mu - S)]}{dt} = \frac{k_1k_2[Pd^1_2][H_2S]}{k_{-1} + k_2}
\]

That is,

\[
\text{Rate} = k'[Pd^1_2][H_2S]
\]

where

\[
k' = \frac{k_1k_2}{k_{-1} + k_2}
\]

If \( k_2 \gg k_{-1} \), the rate simplifies to \( k_1[Pd^1_2][H_2S] \), meaning that the reaction 3.3 is rate determining. If \( k_{-1} \gg k_2 \), the rate expression becomes \( k_1k_2/k_{-1}[Pd^1_2][H_2S] \) or \( Kk_2[Pd^1_2][H_2S] \) where \( K \) is now the equilibrium constant \((k_1/k_{-1})\) for reaction 3.3, and reaction 3.4 is rate determining. The more complete expression for a rapid pre-equilibrium (eq 3.3) followed by a rate determining \( k_2 \) step is

\[
\text{Rate} = \frac{k_2K[Pd^1_2]r[H_2S]}{1 + K[H_2S]}
\]

where the \( T \) subscript implies total \( Pd^1_2 \). The strictly first order dependence on \( H_2S \) requires that up to \( [H_2S] = 5.3 \times 10^{-1} \text{ M} \) (Fig 3.4), at 25°C, \( K[H_2S] \ll 1 \), and that \( 3b \) is not detectable at the conditions where the \( H_2S \) dependence was measured.

(b) An extra step with accompanying kinetic/equilibrium parameters is involved if the first step in the reaction sequence is formation of an \( H_2S \) adduct:

\[
Pd_2X_2(dpm)_2 + H_2S \xrightleftharpoons[k_{-a}]{k_a} Pd_2X_2(dpm)_2(H_2S) \quad (3.5)
\]

\[
Pd_2X_2(dpm)_2(H_2S) \xrightleftharpoons[k_{-b}]{k_b} Pd_2X_2(dpm)_2(H)(SH) \quad (3.6)
\]

55
\[ Pd_2X_2(dpm)_2(H)(SH) + \xrightarrow{k_2} Pd_2X_2(dpm)_2(\mu - S) + H_2 \quad (3.7) \]

Consistency with the observed kinetic dependences requires one of the following:

(i) the \( k_a \) step is slow and rate determining; rate = \( k_a [Pd_2^1][H_2S] \).

(ii) \( k_b \) governs the rate determining step, following a rapid \( K_a \) pre-equilibrium \( (k_a/k_{-a}) \) with \( Pd_2(H_2S) \) being undetectable; rate = \( k_b K_a [Pd_2^1][H_2S] \).

(iii) the \( k_2 \) step is rate determining, the two pre-equilibria \( (k_a/k_{-a} \text{ and } k_b/k_{-b}) \) now again generating undetectable amounts of \( Pd_2(H_2S) \) and \( Pd_2X_2(dpm)_2(H)(SH) \); rate = \( k_2 K_a K_b [Pd_2^1][H_2S] \).

The simple kinetics measured do not distinguish between the mechanisms of reactions 3.3 and 3.4, and that outlined in 3.5 to 3.7. Nevertheless, further insight into the process, along with information about a reaction intermediate, is gained from the low temperature nmr experiments. The oxidative-addition of \( H_2S \) across the metal-metal bond of 1 would presumably lead to a hydride intermediate of the type 3, with terminal hydride and terminal SH.

\[ \text{3 (} X = \text{Cl, } a; \text{ Br, } b; \text{ I, } c \text{)} \]
Such oxidative-addition type reactions to the Pd$_2$X$_2$(dpm)$_2$ complexes, in which the metal-metal bond acts as a nucleophile, are well established. In the H$_2$S/Pd$_2$Br$_2$(dpm)$_2$ reactions, a hydride intermediate thought to be (3b) is formed at 78°C quite rapidly in a liquid H$_2$S interface region and this species rapidly decomposes ($t_\frac{1}{2} < 30$ s) to form 2b at temperatures above ~65°C. Thus at 0-35°C, the rate determining step will not be decomposition of 3b, (i.e. the $k_2$ steps of the mechanisms discussed). The rate determining step could be the formation of the hydride 3b (or the H$_2$S adduct), and this would be consistent with the non-detection of 3b at ambient conditions. It then seems surprising, however, that 3b is detected at low temperatures. Its formation could presumably result because of one or both of the following factors:

(i) the H$_2$S addition at low temperatures (below the H$_2$S liquefaction temperature) produces a very high localized concentration of H$_2$S.

(ii) optimum temperature conditions prevail so that the oxidative-addition takes place (perhaps because of high H$_2$S concentration), while decomposition of the hydride is slowed down sufficiently to build up the concentration of 3b.

It was initially thought that the presence of liquid H$_2$S might increase the dielectric constant of the medium, and rates of oxidative-addition of polar molecules are typically enhanced in more polar media. However, dielectric constant data for CH$_2$Cl$_2$ and liquid H$_2$S at ~65°C give $\epsilon$ values of 15 and 9, respectively, and thus the changes in dielectric constant are unlikely to be important. Two qualitative observations support the rationale presented above in (i) and (ii). When liquid H$_2$S comes in contact with solid 1b at ~78°C a green solution is produced, presumably because of the formation of 3b; based
on nmr data, the green solution subsequently yields 2b on warming. Secondly, warming an nmr tube containing successively frozen layers of a solution of 1b and H₂S (liquid N₂ temperature) generates a green colour in the upper part of the liquid but only in a very narrow temperature range (between ~−70 and −60°C).

The hydride ¹H nmr signal (δ = −8.9 ppm, triplet, Jₚ₋ₜ = 18 Hz) is characteristic of a terminal Pd-H hydride cis to a phosphine ligand.¹⁴ The non-observation of the δ(Pd-SH) ¹H nmr signal (typically at δ between 1.5 and −1.5 ppm)¹⁵ could be attributed to two possible factors:

(i) the burial of the S-H resonance under the large, broad H₂S signal (~0.9 ppm), because the intermediate 3b is generated only under high H₂S concentration.

(ii) the S-H proton, which will certainly be acidic¹⁶ may undergo rapid exchange with H₂S protons thus producing a broad resonance not detected under the experimental conditions.

Additional structural information could not be obtained from the ³¹P{¹H} nmr spectrum as it was of poor quality (Fig 3.9) because of the low concentration of 3b (~10%). However, the solutions of 3b should generate a AA' BB' type ³¹P{¹H} nmr which typically is seen as a pattern centred at four major resonances,¹⁷ and the observed unresolved peaks could result from such a spectrum. The hydride intermediate for the analogous Pd₂I₂(dpm)₂/H₂S system is slow in forming (~8 h at ~−78°C) but could be obtained at a much higher concentration (≥50%); the hydride 3c is much more stable than 3b but rapidly decomposes at temperatures above −30°C. This further indicates that the oxidative-addition is the rate determining step.
It should be noted that formation of a possible \( \text{H}_2\text{S}\)-adduct (i.e. the \( K_a \) equilibrium in reaction 3.5) is expected to be favoured at lower temperatures, because solution reactions of this type must be entropically unfavourable and therefore exothermic if they are to occur at all. Thus \( K_a \) would be favoured at lower temperatures. However, the \(^1\text{H} \) nmr data show the presence of an intermediate hydride and not \( \text{H}_2\text{S} \) complex formation; \( J_{P-H} \) for three-bond coupling within an \( \text{Pd-SH}_2 \) would be much less than the observed 18 Hz which is typical for \( 2J_{P-H} \) values with hydride cis to phosphorus.\(^{14}\)

The activation parameters (\( \Delta H^1 = 55 \text{ KJ}, \Delta S^1 = -115 \text{ J K}^{-1} \)) are quite typical of those observed for oxidative addition reactions at one metal centre,\(^{18-20}\) but there are not any useful, comparable data for dinuclear systems. For the present \( \text{Pd}_2^1 \rightarrow \text{Pd}_2^0 \), formation of a species such as \( 3b \) necessitates breaking the \( \text{Pd-Pd} \) bond but the electronic promotional energy\(^{18-20}\) is now only for a single electron at \( \text{Pd} \) centre and will be less than that required for 2e-oxidative addition at one 'comparable' metal centre; the other factors contributing to \( \Delta H^1 \) are breaking of an \( \text{S-H} \) bond and formation of the \( \text{Pd-H} \) and \( \text{Pd-SH} \) bonds. Overall, the activation parameter for oxidative addition process for the same molecule at one or two metal centres may turn out to be similar. It is not clear from the present study if \( \Delta H^1 \) and \( \Delta S^1 \) refer to \( k_1 \) (eqn. 3.3), \( k_a \) or \( k_4K_a \) (eqn. 3.5 & 3.6). Corresponding ambiguities arise in oxidative addition of \( \text{H}_2 \) to give a dihydrogen species, now that \( \eta^2-\text{H}_2 \) complexes as possible intermediates have been recognized.\(^{21}\) Of note, the reaction of \( 1b \) with \( \text{CO} \) to give \( \text{Pd}_2\text{Br}_2(\text{dpm})_2(\mu-\text{CO}) \) in dimethylacetamide solution, with \( \Delta H^1 = 15 \text{ KJ}, \Delta S^1 = -121 \text{ J K}^{-1} \), \(^9\) is some 10 times faster than \( \text{H}_2\text{S} \) reaction in \( \text{CH}_2\text{Cl}_2 \) at comparable temperatures, and the difference is reflected entirely in the \( \Delta H^1 \) values; presumably, the higher value for the \( \text{H}_2\text{S} \) system results from energy
required to break an S-H bond.

It would be particularly useful to have activation parameters for the other halide systems; unfortunately the iodide system is photosensitive, but at 25°C the H₂S reaction is about 10 times slower than for the bromide. The reactivity trend of 1 toward H₂S (X = Cl > Br > I) is opposite to that normally encountered for oxidative addition of gas molecules to a single metal centre, where more basic auxiliary ligands promote reactions. Within 1, the Pd-Pd bond strength is expected to increase in the order I < Br < Cl, the reverse of the trans effect of the halides, and thus the reactivity trend is not dominated by differences in the metal-metal bond strength. Reactivity of 1 toward CO in terms of equilibrium constants is also Cl > Br > I, and this is governed by the off-rates that decrease in the reverse order (I > Br > Cl), the on-rates being essentially the same; it has been suggested that the strength of metal-carbonyl bond in the product (I < Br < Cl) governs the reactivity trend. Such could be the case in the H₂S systems, if the k₋₁ step of the mechanism outlined in eqns. 3.3 and 3.4, or the k₋ₙ step of the mechanism given in eqn. 3.5, case (ii), become increasingly important (i.e. these rate constants increase in the order k_Cl < k_Br < k_I).
3.6 References


15. See, for example:


22. (a) D. Sallin *Private Communication.*


Chapter 4

THE INTERACTION OF HX (X = Cl, Br) WITH Pd(I) DIMERS

4.1 Introduction

The interaction between anhydrous HCl gas and Pd(I) dimer, Pd$_2$Br$_2$(dpm)$_2$ 1b, was discovered accidentally, while testing for the effect of HX impurities present in D$_2$S gas (section 3.2.) on its reaction with 1b. The yellowish-orange chloroform or dichloromethane solutions of 1b turned dark green on exposure to anhydrous HCl gas, en route to the formation of the pale yellow Pd(II) monomeric species Pd(dpm)X$_2$ (X = halide), at ambient conditions. Approximately 2 mole equivalents of anhydrous HCl per mole equivalent of Pd$_2^+$ complex were required for the complete conversion of Pd$_2^+$ dimer to a Pd(II) monomer, as evidenced by nmr spectroscopy. The green intermediate, initially formed, subsequently broke down to the pale yellow Pd(II) complexes of the type Pd(dpm)X$_2$, in a slow reaction ($t_\frac{1}{2} \sim 30$ min). The final Pd(II) products comprised a mixture of Pd(dpm)Cl$_2$, Pd(dpm)Br$_2$ and Pd(dpm)ClBr (Fig 4.1).

The oxidative addition of X$_2$ (X = Cl, Br, I) to Pd$_2$X$_2$(dpm)$_2$ had been studied by Balch et al.$^1$ The reaction proceeded through the oxidative addition of X$_2$ across the metal-metal bond, resulting in a green tetrahalo intermediate, which was detected at low temperatures before the subsequent break-down to
Figure 4.1: The $^{31}$P{¹H} nmr spectra in CDCl$_3$ of the reaction products of 1b and anhydrous HCl; the AB pattern $J_{PP} = 60$ Hz is assigned to Pd(dpm)(Cl)(Br). The $\delta$ values for Pd(dpm)Cl$_2$ and Pd(dpm)Br$_2$ are shifted slightly to those given in sections 2.1.4.9 and 2.1.4.10 because of the presence of HCl.

Pd(II) monomers (eq 4.1, Fig 4.2).

$$Pd_2X_2(dpm)_2 + X_2 \rightarrow 2PdX_2(dpm)$$

(4.1)

As the HX reaction with the Pd(I) dimers seemed to take a similar route, it was decided to investigate the reaction in more detail to unravel the mechanistic pathway of the HX additions.
Figure 4.2: The mechanistic pathway of the reaction between 1b and Br₂.
(Adapted from ref. 1).
4.2 Stoichiometry of the reaction and product identification

4.2.1 Reaction of Pd₂Cl₂(dpm)₂ with HCl at room temperature

The Pd(І) complex 1a reacted with 2 mole equivalents of HCl, or with the adduct DMA.HCl² in DMA, resulting in formation of Pd(dpm)Cl₂ and H₂.

\[ \text{Pd₂Cl₂}(\text{dpm})₂ + 2\text{HCl} \rightarrow 2\text{PdCl₂}(\text{dpm}) + \text{H₂} \]  (4.2)

The reaction was monitored in DMA as well as in CH₂Cl₂ by UV-visible, and \(^1\text{H}\) and \(^{31}\text{P}\{^1\text{H}\}\) nmr spectroscopy. The nmr spectra are presented in Figs. 4.3 and 4.4 along with that of an authentic sample of Pd(dpm)Cl₂, which was prepared from Pd(PhCN)₂Cl₂ (section 2.1.4.9.).

Both \(^1\text{H}\) and \(^{31}\text{P}\{^1\text{H}\}\) nmr data for 1a in CDCl₃ indicated the disappearance of the 1a signals (\(^1\text{H}\), -CH₂- protons, \(\delta = 4.17\) ppm, q, \(J_{\text{P-H}} = 4\) Hz; \(^{31}\text{P}\{^1\text{H}\}\), singlet, \(-3.46\) ppm), and the appearance of the signals of Pd(dpm)Cl₂, (\(^1\text{H}\), \(\delta = 4.28\) ppm, t, \(J_{\text{P-H}} = 10\) Hz; \(^{31}\text{P}\{^1\text{H}\}\), \(-55.2\) ppm) on gradual additions of HCl gas. When the Pd₂ dimer to HCl ratio was 1:2 mole equivalents, the 1a signals were completely lost. The rapid interaction \(t_\frac{1}{2} < 30\) s of anhydrous HCl(g) with 1a in CH₂Cl₂ or CHCl₃ solutions at room temperature resulted in the appearance (UV-visible spectra) of a new band at 320 nm at the expense of the 416 and 347 nm bands of 1a. A similar reaction was observed in DMA solutions between 1a and DMA.HCl but at a much slower rate \(t_\frac{1}{2} \sim 45\) min.

The gaseous product, dihydrogen, was detected and identified by gas chromatography by comparison with authentic H₂ gas. A packed molecular sieve
Figure 4.3: The $^1$H nmr spectra (-CH$_2$- region) in CDCl$_3$ solution at 20°C of (A) 1a; (B) 1a + HCl(g) (~3:1) and (C) 1a + HCl(g) (1:2).
Figure 4.4: The $^{31}\text{P}^{1\text{H}}$ nmr spectra in CDCl$_3$ solution at 20°C of (A) $\text{I}_a$; (B) $\text{I}_a + \text{HCl(g)}$ (3:1) and (C) $\text{I}_a + \text{HCl(g)}$ (1:2).
column was used in a Hewlett Packard 5890A instrument equipped with a thermal conductivity detector (TCD); a retention time of 1.05 min was measured for the gaseous product and authentic H₂ (Fig 4.5). An attempt to detect reaction intermediates at low temperature (−78°C), akin to Cl₂ addition to 1a₁ (cf. Fig 4.2), was not successful.

4.2.2 Reaction of Pd₂Br₂(dpm)₂ with HBr at room temperature

As summarised in section 4.1 and shown in section 4.2.1, the chloroform and dichloromethane solutions of 1a or 1b required ~2 mole equivalents of HX per mole of palladium complex for reaction. This is readily rationalized in terms of (i) oxidative-addition of a mole of, for example, HBr to 1b leading to a palladium hydride product, 4b:

\[
Pd₂Br₂(dpm)₂ + 2HBr \rightarrow Pd₂Br₂(dpm)₂(H)(Br)
\] (4.3)

\[
1b \quad 4b
\]

(ii) the reaction of 4b with a second mole of HBr leading to a tetrabromopalladium(II) product, 5b, and hydrogen (H₂):

\[
Pd₂Br₂(dpm)₂(H)(Br) + HBr \rightarrow Pd₂Br₄(dpm)₂ + H₂
\] (4.4)

\[
4b \quad 5b
\]

and (iii) the break-down of 5b to the monomeric Pd(II) species:

\[
Pd₂Br₄(dpm)₂ \rightarrow 2PdBr₂(dpm)
\] (4.5)

\[
5b \quad 6b
\]

Evidence for the pathways of reactions (4.3) - (4.5) was obtained from the
Figure 4.5: The gas chromatograms of (A) the gaseous products evolved in the reaction of $1\alpha + 2\text{ HCl(g)}$ in DMA; (B) the gaseous products evolved in the reaction of $1\beta + 2\text{ HBr(g)}$ in $\text{CH}_2\text{Cl}_2$ and (C) authentic dihydrogen gas.
Pd$_2$Br$_2$(dpm)$_2$/HBr system. The reaction of 1b with HBr in CDCl$_3$ was monitored by $^1$H nmr, $^{31}$P{$^1$H} nmr and UV-visible spectroscopy (Fig 4.6).

![Figure 4.6: Visible absorption spectrum of dichloromethane solution of Pd$_2$Br$_2$(dpm)$_2$ upon addition of anhydrous HBr at 25°C, as a function of time; the Pd$_2$Br$_2$(dpm)$_2$(A$_{max}$ = 364, 428 nm) 'instantly' gives Pd$_2$Br$_4$(dpm)$_2$(A$_{max}$ = 360, 600 nm) that slowly converts to PdBr$_2$(dpm)(A$_{max}$ = 338, 380 nm).](image)

nmr spectra at 20°C are presented in figures 4.7 and 4.8, along with the spectrum of an authentic sample of PdBr$_2$(dpm), 6b, which was prepared from PdCl$_2$(dpm) (see section 2.1.4.10). In the $^1$H nmr spectrum, two sets of peaks, a singlet ($\delta$ = 4.63 ppm) and a triplet ($\delta$ = 4.31 ppm, $J_{P-H}$ = 10 Hz) appeared in the -CH$_2$- proton region, immediately on addition of anhydrous hydrogen bromide gas to 1b in solution; the signal due to the -CH$_2$- proton of the dpm of 1b ($\delta$ = 4.26 ppm, q, $J_{P-H}$ = 4 Hz) had disappeared. The singlet at 4.63
Figure 4.7: The $^1$H nmr spectra (-CH$_2$- region) in CDCl$_3$ solution at 20°C of (A) 1b; (B) 1b + HBr(g) after 15 min.; (C) 1b + HBr(g) after 6 h and (D) authentic sample of PdBr$_2$(dpm).
Figure 4.8: The $^{31}$P{"H} nmr spectra in CDCl$_3$ solution at 20°C of (A) 1b; (B) 1b + HBr(g) after 15 min.; (C) 1b + HBr(g) after 6 h and (D) authentic sample of PdBr$_2$(dpm).
ppm then lost its intensity slowly ($t_{1/2} \sim 30$ min), while the triplet grew in
intensity as the reaction proceeded. A singlet appeared at $\delta = 5.2$ ppm in the
$^{31}P\{^1H\}$ spectrum nmr along with a low intensity singlet at $-56.9$ ppm. The
high field singlet ($\delta = -56.9$ ppm) grew in intensity as the reaction proceeded.
The $^1H$ and $^{31}P\{^1H\}$ nmr spectra (Figs. 4.7 C, D, 4.8 C & D) show that the
identity of the final palladium product is PdBr$_2$(dpm).

The $^1H$ ($\delta = 4.63$ ppm) and $^{31}P\{^1H\}$ nmr data along with absence of
high field resonance in the hydride region show that the intermediate is 5b
rather than 4b. Both the $^1H$ and $^{31}P\{^1H\}$ nmr data are in good agreement
with those of 5b observed by Balch et al.,$^1$ on reacting 1b with Br$_2$ in CDCl$_3$
solution at $-40^\circ$C ($^1H: \delta = 4.6$ ppm and $^{31}P\{^1H\}: \delta = 4.90$ ppm).

The gaseous product dihydrogen formed during the reaction was detected
as described in section 4.2.1 for the 1a/HCl reaction (Fig 4.5).

4.2.3 Low temperature spectroscopic studies of the reaction be­
tween 1b and HBr.

A low temperature titration between a CDCl$_3$ solution of 1b and anhydrous
HBr gas was carried out at $-40^\circ$C, and the changes monitored with $^1H$ and
$^{31}P\{^1H\}$ nmr spectroscopy, (section 2.5.2.). Addition of up to 1 mole equiva­
 lent of anhydrous HBr to 1b in solution resulted in the formation of a new
species, a green hydride intermediate with $^1H$ nmr signals at $\delta = 4.60$ ppm (br,
s, 4 H) and at $\delta = -8.9$ ppm (br, s, 1 H) (Figs 4.9 A & 4.10 A). Further addition
of HBr gas resulted in the depletion of the hydride intermediate, as evidenced
by the decrease in the intensity of hydride intermediate's $^1H$ nmr signals, with
concomitant formation of the tetrabromo intermediate, Pd$_2$Br$_4$(dpm)$_2$.
Figure 4.9: The $^1$H nmr spectra (-CH$_2$- region) in CDCl$_3$ solution at $-40^\circ$C of (A) 1b + HBr(g) (2:1); (B) 1b + HBr(g) (1:2) after ~15 min and (C) 1b + HBr(g) (1:2) after ~30 min.
Figure 4.10: The $^1$H nmr spectra in CDCl$_3$ solution at $-40^\circ$C of (A) 1b + HBr(g)(1:1), the high field region after $\sim$ 2 min; (B) 1b + HBr(g) (1:2) after 60 min, -CH$_2$- region and (C) 1b + HBr(g) (1:2) after 6 h, -CH$_2$- region.
The tetrabromo intermediate slowly broke down at low temperature to Pd(II) monomer or more rapidly if the solution was warmed up to room temperature.

The \( ^{31}P\{^1H\} \) nmr spectrum of a solution of \( 1b \) containing 2 mole equivalents of HBr (analogous to Fig 4.9 B) had signals at \( \delta_P = -55.6 \) ppm (sharp, s) and at \( \delta_P = 6.2 \) ppm (br, s) (Fig 4.11 A). The high field signal corresponds to that of PdBr\( _2 \)(dpm) (see section 2.1.4.10). The low field signal is not easily assigned but could arise from the time averaging of various signals (for example, Pd\( _2 \)Br\( _4 \)(dpm)\( _2 \) and Pd\( _2 \)Br\( _2 \)(dpm)\( _2 \)(H)(Br) species.) Further, in the presence of excess HBr, the \( \delta_P = 6.2 \) ppm peak shifted to the low field side and is seen as a multiplet, while the corresponding shift in the high field signal was negligible (Fig 4.11 B & C).

### 4.3 Discussion

The HBr/\( 1b \) reaction proceeds stepwise and the changes taking place at the low temperatures are depicted as follows:

\[
Pd_2Br_2(dpm)_2 + HBr \overset{fast}{\rightarrow} Pd_2Br_2(dpm)_2(H)(Br) \quad (4.6)
\]

\( 1b \), yellow orange

\[
Pd_2Br_2(dpm)_2(H)(Br) + HBr \overset{fast}{\rightarrow} Pd_2Br_4(dpm)_2 + H_2 \quad (4.7)
\]

\( 4b \), green

\[
Pd_2Br_4(dpm)_2 \overset{slow}{\rightarrow} 2PdB_2(dpm) \quad (4.8)
\]

\( 5b \), green

\( 6b \), pale yellow
Figure 4.11: The $^{31}$P{$^1$H} nmr spectra in CDCl$_3$ solution at $-40^\circ$C of (A) $\mathbf{1b}$ + HBr(g) (1:2) after $\sim$15 min; (B) $\mathbf{1b}$ + HBr(g) (1:5) after $\sim$20 min and (C) $\mathbf{1b}$ + HBr(g) (1:10) after $\sim$25 min. $\mathbf{1b}$ + HBr(g) (2:1) after $\sim$15 min, the $^{31}$P{$^1$H} nmr spectra in CDCl$_3$ shows peaks at $-55.6$ ppm (sharp, s) and $5.4$ ppm (br, s).
The first mole of HBr oxidatively adds across the Pd, Pd bond, and leads to the formation a transient palladium hydride intermediate observable at low temperatures (−40°C) by nmr spectroscopy. Such a hydride intermediate could have any one or more of the following structures:

(i) A face-to-face bridged structure as observed in the Rh(I) dimers Rh₂(dpm)₂-(CO)₂Cl₂,² and Rh₂(dam)₂(CO)₂Cl₂,³ and in the Pd(II) dimers Pd₂(dpm)₂-Cl₂(CH₃)₂,⁴ Pd₂Cl₄[Bu₂P(CH₂)₇PBu₂]₂,⁵,⁶ and Pd₂Cl₄[Bu₂P(CH₂)₁₀PBu₂]₂.⁵,⁶

(ii) A μ-hydrido μ-bromo bridged structure commonly observed in doubly bridged dimers⁷.

(iii) A dimer having a A-frame structure, with a hydrido bridge, as found
in many Pt and Pd dimers with dpm as the bridging ligand. $[\text{Pt}_2(\text{dpm})_2]\text{Cl}_2(\text{H})]^+$, $[\text{Pt}_2(\text{dpm})_2\text{Me}_2(\text{H})]^+$, $[\text{Pt}_2(\text{dpm})_2\text{Me}_2(\text{H})]^+$, $[\text{Pd}_2(\text{dpm})_2\text{Me}_2(\text{H})]^+$ are examples of cationic complexes exhibiting A-frame structures with bridging hydride.

![Diagram of A-frame structure](image)

The observed $^1\text{H}$ (broad -CH$_2$ signal and hydride signal) and $^{31}\text{P}[^1\text{H}]$ (broad singlet) nmr spectra of 4b can be accounted for by any one of the above structures or by two or more of the structures in equilibrium with each other.

The reaction of the second mole of HBr with the hydride intermediate leads to the generation of H$_2$ gas along with formation of a tetrabromide intermediate. The presence of a sharp singlet in both the $^1\text{H}$ and $^{31}\text{P}[^1\text{H}]$ nmr spectra indicates a more symmetric structure presumably with equivalent phosphorus atoms and methylene protons. A face-to-face bridged structure, a dibromo bridged structure, or a $\mu$-bromo bridged A-frame structure with rapidly exchanging methylene protons, would give the observed $^1\text{H}$ and $^{31}\text{P}[^1\text{H}]$ nmr spectra. The subsequent break down of the tetrabromo intermediate, 5b, to Pd(II) monomer, 6b, is a much slower process ($t_j \sim 30$ min at $20^\circ\text{C}$) than that of the corresponding iodide species, Pd$_2$I$_4$(dpm)$_2$ ($t_j = 6$ min at $15^\circ\text{C}$). The breakdown of 5b, if it exibits the face-to-face dimer structure, would proceed simply through the scission of Pd–P bonds. Of interest, the complexes of
the type Pd$_2$Cl$_4$[Bu$_4$P(CH$_2$)$_n$PBu$_4$]$_2$ (n = 7, 10), in which the Pd centers are well separated by the long methylene chains of the bridging bisphosphine ligands, are found to be indefinitely stable in solution; obviously, in these cases, the formation of a halide bridge between the metal centers is not possible and this indicates that the formation of a halogen bridge between the metal atoms is a prerequisite for the scission of a Pd-P bond. Thus the breakdown of 5b is likely to take place through the structures (ii) and/or (iii).

If the reaction between 1a and HCl proceeds through the above mechanism, then at low temperatures the reaction would generate the transient intermediates Pd$_2$Cl$_2$(dpm)$_2$(H)(Cl) and Pd$_2$Cl$_4$(dpm)$_2$, analogous to the 1b system. The tetrachloro intermediate has been observed in the oxidative addition of Cl$_2$ to 1a at low temperatures (−40°C) in CH$_2$Cl$_2$ solutions. Failure to detect any intermediate in the present work even at −78°C indicates that the HCl/1a reaction proceeds either through a mechanistic pathway in which Pd$_2$Cl$_4$(dpm)$_2$ is not formed or, more likely, the tetrachloro species is formed but its subsequent breakdown to the monomer is fast (perhaps catalysed by HCl) and no longer rate determining as in the reaction between 1a and Cl$_2$. 

82
4.4 References


7. See, for example:


5.1 Introduction

The key factor in transforming the stoichiometric reaction 3.1 into some useful type of catalytic process lies in the successful regeneration of 1, by the removal of the bound $\mu_2$-sulfide ligand. In principle, numerous strategies could be applied (scheme 5.1) for the sulfur removal, because $\mu_2$-sulfur exhibits both nucleophilic and electrophilic nature in transition metal complexes.$^1$–$^5$

\[
Pd_2 + H_2S \quad \rightarrow \quad Pd_2S + H_2 \quad \cdots \cdots \cdots (3.1)
\]

\[
\begin{array}{c}
Pd_2S \quad \xrightarrow{hv} \quad Pd_2 + S \\
\xrightarrow{[O]} \quad Pd_2SO_2 \quad \xrightarrow{E/N} \quad Pd_2 + ES/NS \\
\end{array}
\]

\[
Pd_2 = Pd_2X_2(dpm)_2, \quad 1, \quad X = Cl(a), Br(b), I(c);
\]
\[
Pd_2S = Pd_2X_2(dpm)_2(\mu-S), \quad 2a - 2c; \quad Pd_2SO_2 = Pd_2X_2(dpm)_2(\mu-SO_2);
\]
\[
[O] = oxidizing agent such as m-Cl-C_6H_4C(O)O_2H;
\]
\[
N = nucleophilic S acceptor and E = electrophilic S acceptor.
\]

\textbf{Scheme 5.1}
Successful regeneration of 1 could lead to a catalytic process that would desulfurize H₂S and generate dihydrogen gas.

The interaction between SO₂ and 1 leads to the formation of the known A-frame complex Pd₂X₂(dpm)₂(μ-SO₂), which loses SO₂ reversibly⁶ and thus has a much weaker Pd-S bond than that of 2; oxidation of 2 thus presented a plausible pathway to regenerate 1, and this was accomplished using peracids,⁷ but the SO₂ co-product in the net catalytic reaction (equation 5.1) makes the process relatively unattractive.

\[ H₂S + 2RC(O)O₂H \rightarrow H₂ + SO₂ + 2RCO₂H \] (5.1)

Photolysis of 2 has been considered⁸ to lead to the possible regeneration of 1 along with elemental sulfur, which would precipitate out in solvents like dibutylphthalate of low sulfur solubility. Finally μ₂-S could perhaps be abstracted by transferring it to a sulfur-accepting moiety. Both electrophilic (H⁺, R⁺) and nucleophilic (PR₃, PAr₃, CN⁻) reagents offer possibilities.

Of the above methods outlined for the sulfur removal, the oxidation with peracids is the only successful route utilized so far for the regeneration of 1. The oxidation of the μ₂-sulfide proceeded through the formation of an μ-SO₂ isolable intermediate, which was subsequently oxidized to the μ-SO₂ complex, which in turn lost SO₂ spontaneously at room temperature to yield 1 (Fig 5.1). Some attempts to dislodge the μ₂-sulfide by 'non-oxidative' routes (i.e. to sulfur oxides) are discussed in the following sections.
Figure 5.1: The schematic representation of the regeneration of 1 from 2 by the oxidation of the μ-sulfide to SO₂.
5.2 Sulfur abstraction reactions

5.2.1 Sulfur abstraction by phosphines

Co-ordinated sulfur atoms are effectively removed as SPPh$_3$, by reacting with PPh$_3$. Attempts to regenerate 1a by reacting 2a with excess PPh$_3$ were unsuccessful; a slow reaction in CH$_2$Cl$_2$ at 40°C destroyed much of the 2a but 1a was never recovered in more than 20% yield. In the present work both 2b and 2c showed inertness toward $\mu_2$-sulfide abstraction by PPh$_3$, and indeed could be recovered back unchanged in good yields (>90%). In an attempt to abstract the $\mu_2$-sulfide ligand, the bisphosphines dpm and dpe and the monophosphine PPh$_2$Me were also tried.

The reaction between 2b or 2c and dpm in CH$_2$Cl$_2$ at 20°C generated 1b in ~75% yield or 1c quantitatively after ~6 h stirring. Interestingly, in each case (eq 5.2), dpm monosulfide (nmr : $^1$H, $\delta = 3.32$ ppm, dd, $J_{P-H} = 1$ Hz, $J_{P(S)-H} = 12.8$ Hz ; and $^{31}P\{^1H\}$ $\delta = -28$ ppm, d, ; $40$ ppm, d, $J_{P-P} = 76$ Hz) was the only phosphorus-sulfur compound formed and the nmr data are in excellent agreement with literature data.$^{11}$

$$Pd_2X_2(dpm)_2(\mu - S) + dpm \rightarrow Pd_2X_2(dpm)_2 + dpmS \quad (5.2)$$

The reactions between 2b or 2c with dpe or PPh$_2$Me were, like the PPh$_3$ reactions, unsuccessful for the regeneration of 1b or 1c, respectively. In the dpe case, 1b or 1c was generated in ~50% yield along with numerous(from $^1$H & $^{31}P\{^1H\}$), as yet unidentified, Pd complexes. The PPh$_2$Me reaction did not regenerate any 1b or 1c, but much of the respective 2b or 2c was destroyed, presumably by the break down of the Pd$_2^1$ and $\mu$-sulfide dimers.
The inability of PPh$_3$ to mobilize sulfur from 2b/2c indicates that either 2b/2c is thermodynamically stable with respect to the formation of 1b/1c and SPPh$_3$, or else the reaction is thermodynamically favourable but kinetically difficult. The facile formation of dpm monosulfide in reaction (5.2) indicates that the PPh$_3$ reaction does not take place because of kinetic reasons. The specific transfer of sulfur to one phosphorus atom of the dpm (dpm disulfide formation was facile in a reaction between dpmS and elemental sulfur(S$_8$), and in a dpm reaction with sulfur (1:1), along with some dpmS) suggests that the reaction may involve a dangling (monodentate) dpm intermediate, with perhaps the binding of dpm at one end being necessary during the sulfur transfer. Further, such a dangling dpm ligand would severely weaken the Pd-S bond because the $\mu$-sulfide would now be trans to two ligands (Br and the P atom of the added dpm) with different trans-influences.$^{12}$ The reaction may proceed through the following plausible mechanism, as shown in Figure 5.2; the bromine at the Pd metal being attacked could alternatively dissociate, and then finally reassociate, as bromide. Further, preliminary kinetic investigations$^{13}$ carried out subsequent to this work, indicate that the reaction between 2c and dpm is well behaved, as evidenced from UV-visible spectroscopy and shows a first order dependence on both [Pd$_2$] and [dpm] in accordance with the proposed mechanism if the first step is rate-determining.

5.2.2 Sulfur abstraction by organics

The successful abstraction of $\mu_2$-sulfide by dpm signalled searches for other ways of abstracting the bound sulfur from 2, because the abstraction of $\mu_2$-sulfide by dpm is unlikely to be unique. Benzo thiophene and dibenzo thiophene derivatives are quite inert toward hydrodesulfurization (i.e. removal of sulfur
Figure 5.2: The proposed mechanistic pathway for the abstraction of sulfur by bis(diphenylphosphino)methane from $\text{2}$. 
as \( \text{H}_2\text{S} \), indicating a stable carbon-sulfur framework. Thus, sulfur abstraction from \( \text{2} \) was considered likely to occur if it led to the formation of benzothiophene or dibenzothiophene derivatives, and so biphenyl and styrene were judged to be likely molecules for abstraction of the bound \( \mu \)-sulfide from \( \text{2} \).

The reaction between \( \text{2c} \) and styrene was unsuccessful, however, for the sulfur abstraction. With diphenyl a small amount (~15%) of \( \text{1c} \) was regenerated from \( \text{2c} \) at room temperature in 2 h. A much higher conversion (~45%) was effected in refluxing toluene in 2 h. From the \( ^{31}\text{P}\{^{1}\text{H}\} \) spectrum, the reaction appeared to be clean, showing the presence of only \( \text{1c} \) and \( \text{2c} \). The organic sulfur product formed remains to be identified.

5.3 The desulfurization of \( \text{H}_2\text{S} \)

As discussed in section 5.1, the coupling of reaction 3.1 and reaction 5.2 should yield a process which catalytically desulfurizes \( \text{H}_2\text{S} \) and result in the generation of \( \text{H}_2 \) and \( \text{dpmS} \), eq 5.3.

\[
\text{H}_2\text{S} + \text{dpm} \rightarrow \text{H}_2 + \text{dpmS}
\] (5.3)

Such proved to be the case. In a blank reaction containing no Pd complexes, dpm was recovered quantitatively, unchanged after reacting with \( \text{H}_2\text{S} \) (excess) in \( \text{CH}_2\text{Cl}_2 \) at 25°C even after 2 days. However, in the presence of a small amount of \( \text{1(b or c)} \) (Pd_2 : dpm = 1 : 200, \( \text{CH}_2\text{Cl}_2 \), 25°C, 8h) dpm was catalytically converted to dpmS, indicating the generation of an efficient catalytic system for desulfurization of \( \text{H}_2\text{S} \) (Figs. 5.3 and 5.4). Of interest, on closer examination, the desulfurization of \( \text{H}_2\text{S} \) perhaps proceeds through a route different from the one predicted by the coupling of the reactions 3.1 and 5.2. Catalysis via these reactions should generate (finally or during the catalysis)
Figure 5.3: The $^{31}P\{^1H\}$ nmr spectra in CDCl$_3$ solution at 20°C of (A) the reaction product of $1c$ and H$_2$S in the presence of 20 fold excess dpm after 2 h; (B) the expanded region of (A) between -5 and 36 ppm.
Figure 5.4: The $^{31}\text{P}\{^1\text{H}\}$ nmr spectra in CDCl$_3$ solution at 20°C of (A) the reaction product of 1b and H$_2$S in the presence of 20-fold excess dpm after 2 h, the dpm signal had completely disappeared after 8 h. (B) the expanded region of (A)
either 1(b or c) in the system if dpm was in excess, or 2(b or c) if H$_2$S was in excess. However, in desulfurization reactions catalyzed by 1 species neither 1 nor 2 was detected. Instead, a few unidentified palladium products, presumably dpmS substituted derivatives of 1 and/or 2, were detected in the $^{31}P\{^1H\}$ nmr spectra (Figs. 5.3B and 5.4B).
5.4 References


8. B. R. James, *Personal Communication*.


Chapter 6

GENERAL CONCLUSIONS

6.1 Conclusions

The analysis of kinetic data for the reaction between Pd$_2$Br$_2$(dpm)$_2$, 1b and H$_2$S is consistent with, and can be accounted for, by either of mechanisms (a) (Eqs. 3.3 and 3.4) and (b) (Eqs. 3.5 - 3.7). The first order dependence on both Pd$^2_2$ complex and H$_2$S does not distinguish between the two mechanisms. The detection of a transient hydride intermediate at low temperatures shows that the reaction proceeds through the oxidative addition of H$_2$S across the metal-metal bond. Further, the rapid decomposition of the hydride intermediate at ambient conditions indicates that the formation of the hydride (or the H$_2$S adduct in Eq 3.5) is the rate determining step. Obviously, more extensive kinetic studies on related systems, especially for complexes of the same metal, are necessary before any conclusion regarding the generality of any mechanism can be reached for H$_2$S reactivity toward dimers.

Low temperature nmr experiments show that the reaction between HBr and 1b proceeds stepwise. The oxidative addition of the first mole of HBr results in the formation of a hydride intermediate; this then reacts with the second mole of HBr to form dihydrogen and a tetrabromo complex, Pd$_2$Br$_4$(dpm)$_2$, which subsequently fragments slowly to the Pd(II) monomer, PdBr$_2$(dpm).

The bound $\mu$-sulfide ligand was effectively abstracted from the A-frame
complex, Pd$_2$X$_2$(dpm)$_2$(μ-S), by dpm to generate the Pd(I) dimer, Pd$_2$X$_2$(dpm)$_2$, along with dpm monosulfide as the only sulfur-containing co-product. It was also demonstrated that the sulfur could be transferred to an organic moiety such as biphenyl. Apart from these systems with stoichiometric sulfur transfer, an effective catalytic system was unearthed. Catalytic desulfurization of H$_2$S was effected in the presence of Pd$_2$X$_2$(dpm)$_2$ and excess dpm along with the formation of dpmS as the only sulfur-containing product.

6.2 Recommendations for future work

Further studies should be pursued to distinguish between the proposed mechanisms (a) and (b). This could be accomplished by utilizing Pd(I) dpm complexes with different auxiliary ligands (i.e. varying X in Pd$_2$X$_2$(dpm)$_2$) as well as other dinuclear complexes of transition metals. So far, there are no kinetic models available for the reactions between H$_2$S and dinuclear metal complexes that generate dihydrogen gas. There is little doubt that future investigations in these areas would lead to the improvement of the present system as well as to new systems for the generation of dihydrogen. Understanding the kinetic and the mechanistic aspects of the reaction that leads to the desulfurization of H$_2$S by Pd$_2$X$_2$(dpm)$_2$ could lead to the utilization of an economically more viable sulfur acceptor moiety instead of the bisphosphine dpm. Also the synthetic potential of this reaction to transfer sulfur to specific sites should be explored in greater detail.