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# SYNTHESIS, CHARACTERIZATION AND COMPLEXATION OF MIXED IMINO-CHALCOGENIDE BISPHOSPHINES

BY ©

VIVIAN JANET MOZOL

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfilment
of the requirements for the degree of Master of Science

DEPARTMENT OF CHEMISTRY

EDMONTON, ALBERTA

SPRING 1993

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ISBN 0-315-82133-7

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DEGREE: MASTER OF SCIENCE

YEAR THIS DEGREE GRANTED: 1993

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FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled Synthesis, Characterization and Complexation of Mixed Imino-Chalcogenide Bisphosphines submitted by Vivian Janet Mozol in partial fulfilment of the requirements for the degree of Master of Science.

Dr. R. G. Cavell

Dr. J. Takats

Dr. P. Sporns

March 23rd, 1993

*For my parents and Rob.*

## ABSTRACT

A series of ligands with the general formula $Ph_2P(X)C_nH_mP(NR)Ph_2$ (X = O, S, Se; R = tfbn, T; $C_nH_m = CH_2$, $CH(CH_3)$, *cis*-CHCH, $CH_2CH_2$, 1,2-$C_6H_4$) has been synthesized. The coordination chemistry of the ligands where $C_nH_m = CH_2$, with the metals Pt, Pd and Rh was investigated.

The reaction of the Pt and Pd chloro bridged dimers $[MCl(\mu\text{-}Cl)(PEt_3)]_2$ with neutral $Ph_2P(X)CH_2P(Ntfbn)Ph_2$ (X = S, Se) ligands and $NaClO_4$ generated the six-membered cationic {-X,N} chelate complexes $[(Ph_2P(X)CH_2P(Ntfbn)Ph_2\{\text{-}X,N\})M(PEt_3)Cl][ClO_4]$ (M = Pt, Pd). Treatment of the Pt chelate complexes with NaH or reaction of the deprotonated ligands, $[Ph_2P(X)CHP(Ntfbn)Ph_2]^-$, with the Pt and Pd dimers generated the four-membered neutral {-X,C} metallacyclic complexes $(Ph_2P(X)CHP(Ntfbn)Ph_2\{\text{-}X,C\})M(PEt_3)Cl$ (M = Pt, Pd). Nuclear magnetic resonance data and x-ray structures of the Pt {-S,N} and {-S,C} complexes showed that in both cases only one isomer is formed, in which the Cl is located *trans* to the chalcogen atom. Reaction of the neutral {-S,C} Pt metallacycle with $HBF_4$ resulted in protonation of the imino nitrogen and formation of a cationic {-S,C} metallacycle that possessed a free aminophosphonium group. Recrystallization of the cationic {-S,C} metallacycle resulted in the formation of the six-membered cationic {-S,N} chelate and is believed to occur *via* proton transfer from the nitrogen to the dppm carbon backbone.

The reaction of $Ph_2P(S)CH_2P(Ntfbn)Ph_2$ with $[Rh(L)L'Cl]_2$ (L = CO, L' = Cl; LL' = cod) both in the absence and presence of $NaClO_4$ generated the monodentate neutral complex $(Ph_2P(S)CH_2P(Ntfbn)Ph_2\{\text{-}X\})Rh(L)L'Cl$. The reaction of $[Ph_2P(S)CHP(Ntfbn)Ph_2][K]$ with $[Rh(cod)Cl]_2$ generated the {-S,C} metallacycle, $Ph_2P(S)CHP(Ntfbn)Ph_2\{\text{-}S,C\})Rh(cod)$. The $^{31}P\{^1H\}$ NMR spectra indicated that fluxional processes were occurring in solution. It is postulated that the dynamic

exchange in solution involves the interconversion between four and five coordinate Rh(I) metal complexes.

The reaction of the Pt and Pd dimers with neutral $Ph_2P(Se)CH_2P(NT)Ph_2$ in the presence of $NaClO_4$ generated a mixture of the six-membered cationic {-Se,N} chelate complex $[(Ph_2P(Se)CH_2P(NT)Ph_2\{-Se,N\})M(PEt_3)Cl][ClO_4]$ and the four-membered cationic {-Se,C} metallacycle $[(Ph_2P(Se)CHP(N(H)T)Ph_2\{-Se,N\})M(PEt_3)Cl][ClO_4]$. The {-Se,C} to {-Se,N} ratios were 90:10 and 60:40, for the Pt and Pd dimers, respectively.

The reaction of $[Pt(PEt_3)Cl_2]_2$ with $Ph_2P(Se)CH_2P(NT)Ph_2$ generated the six-membered cationic {-Se,N} ring complex $[(Ph_2P(Se)CH_2P(NT)Ph_2\{-Se,N\})Pt(PEt_3)Cl][Cl]$ which during recrystallization hydrolyzed to $[(Ph_2P(Se)CH_2P(NH)Ph_2\{-Se,N\})Pt(PEt_3)Cl][Cl]$

# ACKNOWLEDGEMENTS

There are many people at the University of Alberta who I would like to thank for the emotional support or academic assistance they afforded me during my degree and I apologize that due to economy of space, I can mention only a few: Dr. M.S. Balakrishna, Paul Collins, Jackie Jorgensen, Dr. Kal Mahadev, Mike Mikoluk, Dr. Robert Reed and the members of the Takats research group.

I would like to thank Dr. D.E. Berry and Dr. K.R. Dixon of the Univeristy of Victoria; Victoria, B.C for providing me with some of their reference material.

I would also like to acknowledge members of various analytical departments at the University of Alberta for their assistance in learning how to use required instrumentation or their time spent running various tests for me: Andrew Jodhan from Mass Spectral Services; Darlene Mahlow and Andrea Dunn of Microanalytical Services; Cerdy Aarts, Glen Bigam, Tom Brisbane, Dr. T. Nakashima and Lai Kong of NMR Services and Dr. B. Santarsiero and Dr. R. McDonald of the Structure Determination Laboratory.

A special thanks goes to Dr. Robert Hilts (University of Calgary; Calgary, Alta) for his valuable discussions and taking the time to read over my thesis.

Finally I would like to thank my supervisor Dr. R.G. Cavell, since without the opportunity to work for him and his financial support over the last three months, this thesis would never have been written.

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# LIST OF ABBREVIATIONS

| | |
|---|---|
| [illegible]n | *para*-tetrafluorobenzonitrile (*p*-$C_6F_4CN$) |
| T | trimethylsilyl ($SiMe_3$) |
| cod | cyclooctadiene ($C_8H_{12}$) |
| nbd | norbornadiene ($C_7H_8$) |
| dppm | bis(diphenylphosphino)methane ($Ph_2PCH_2PPh_2$) |
| dppmO | mono-oxide of dppm |
| dppmS | mono-sulfide of dppm |
| dppmSe | mono-selenide of dppm |
| THF | tetrahydrofuran ($C_4H_8O$) |
| LDA | lithium diisopropylamide ($^iPr_2NLi$) |

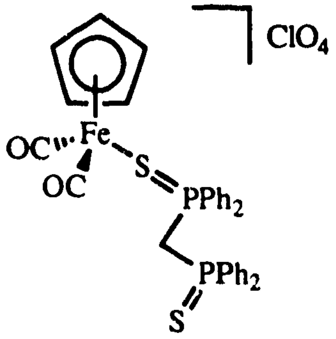
# CHAPTER 1

# INTRODUCTION

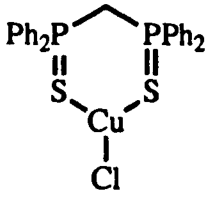
## 1.1 Bisphosphine Dichalcogenides

Bisphosphine dichalcogenides, $[R_2P(X)CH_nP(Y)R'_2]^{(n-2)}$ (X, Y = O, S, Se; n = 0, 1, 2; R, R' = alkyl, aryl), which are an extremely versatile class of inorganic ligands, have been known since the early 1970's. It was not until the 1980's, however, that the coordination chemistry of these compounds was investigated with any zeal. The recent interest in these ligands stems from their apparently unparalleled ability to bind to both late and early transition metals via several different coordination modes. The neutral dichalcogenides coordinate to metal centres using one or both of their chalcogen atoms, thus giving rise to monodentate,[1] bidentate,[2-15] tridentate,[16] and bridging[8,17] complexes. The deprotonated monoanionic ligands, on the other hand, exhibit bidentate {-X,X} (X = S),[9,18,19] bidentate {-X,C} (X = S, Se),[9,17,20] bidentate {-X,C} coupled with monodentate {-X} chelation[17,21] and M-C sigma bonding coupled with {-X,X} chelation (X = O) to Li or Na.[9,22] The doubly deprotonated dianionic ligand, $[Ph_2P(S)CP(S)Ph_2]^{2-}$, has been observed coordinated to platinum in a diplatinum species, $(Ph_2P(S)CP(S)Ph_2\{-S,C;S,C\})(Pt(MeOcod))_2$.[18] The ligand in this complex bridges the two platinum metals and is {-C,S} chelated to each platinum. An example of each of these coordination modes is shown below:

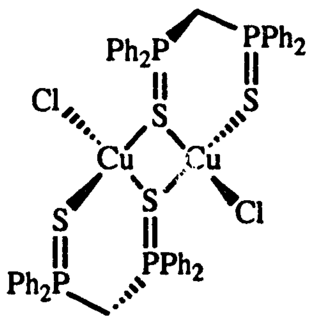
**Monodentate sulfur coordination by a neutral ligand[1]**



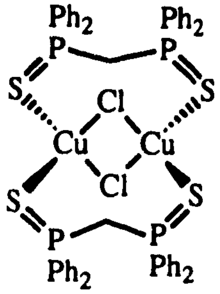
**Bidentate sulfur coordination by a neutral ligand[8,16]**



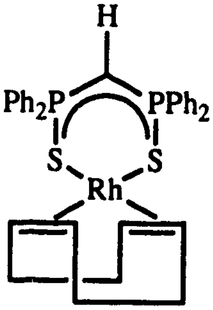
**Tridentate $\mu$-S, $\eta^2$-S,S coordination by a neutral ligand[16]**



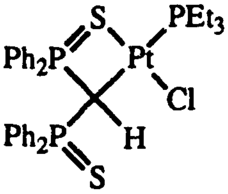
**Bridging $\mu$-S,S, $\eta^1$-S coordination by a neutral ligand**[16]



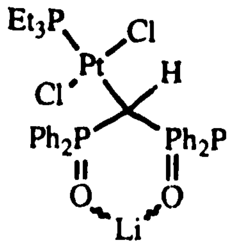
**Bidentate sulfur coordination by an anionic ligand**[19]



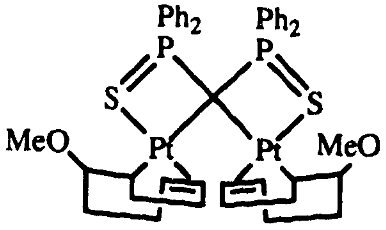
**M-C bonding and monodentate sulfur coordination by an anionic ligand**[20]



**Monodentate carbon coordination and bidentate oxygen chelation by an anionic ligand[22]**



**Tetradentate carbon and sulfur coordination by the dianionic ligand[18]**



The bisphosphine dichalcogenide ligands have been characterized by their P=O/P=S/P=Se bands in their IR spectra (approximately 1100, 600 and 500 cm$^{-1}$ respectively); however, assignments are not definitive, especially for P=Se, due mainly to the large number of medium to strong absorption bands that the parent phosphine exhibits in these regions. More effective identification is made through the use of the signals for the methylene carbon and protons in the $^1$H and $^{13}$C{$^1$H} NMR spectra (around δ 4 and δ 40 ppm, respectively) and by their $^{31}$P NMR chemical shifts (δ 25-35 ppm vs $H_3PO_4$). In the case of the selenide ligands there is also the added advantage of $^{77}$Se satellites and $^{77}$Se NMR chemical shift data. A crystal structure has been reported for dppmSe$_2$,[23,24] but to date dppmO$_2$ and dppmS$_2$ have not been crystallographically characterized. There is, however, structural information available for the closely related trisphosphinesulphide ligand, $(Ph_2P(S))_3CH$.[25] In particular

P=S bond lengths were found to be *ca.* 1.944 Å and the average of the PCP bond angles was 115°.

Upon complexation, there is a marked decrease in the frequencies assigned to the $\nu$(P=X) bands with respect to those found in the free ligands reflecting the use of a lone pair of electrons in the bonding to the metal centre which causes the P=X bond to lengthen.

There is a general trend towards shielding of the phosphorus resonances for the S and Se ligands and a deshielding of the phosphorus resonance for the O ligand upon attachment to a metal. In unsymmetrical bisphosphine dichalcogenides ($[Ph_2P(X)CH_nP(Y)Ph_2]^{n-2}$ X = Y = S, Se, O; n = 1, 2) $^2J_{PP}$ is seen to decrease upon metal complexation. For a few of the metal complexes of the dichalcogens, $[Ph_2P(X)CH_nP(X)Ph_2]^{n-2}$ (X = O, S; n = 1, 2) the $^{31}P\{^1H\}$ NMR spectra show exchange between the two P=X groups. It is believed that the lability exhibited in the M-X bonding of these complexes demonstrates their potential use in promoting catalysis at metal centres. Examples of such complexes are $(Ph_2P(S)CHP(S)Ph_2\{\text{-}C,S\})Pt(PEt_3)Cl$[20] and $(Ph_2(O)CH_2P(O)Ph_2)ZnCl_2$.[12] This lability has not been observed for analogous metal complexes containing $Ph_2(Se)CH_2P(Se)Ph_2$, due to the propensity of dppmSe$_2$ to lose a Se atom upon complexation.[15]

The chemical shifts for the methylene or methine carbons and protons in the $^{13}C\{^1H\}$ and $^1H$ NMR spectra also experience deshielding upon metal complexation. Structures have been determined for a number of these complexes.[7,8,16,18-22] Of relevance to this work are the {-X,X} and {-X,C} bonding modes (X = O, S, Se). In general, the geometry about the phosphorus atoms and the carbon interposed between the two phosphorus atoms is tetrahedral while the coordination around the metal centres is square planar. The {-X,X} chelates form six-membered rings which adopt a twist-boat conformation. The Rh complex containing the neutral $Ph_2P(S)CH_2P(S)Ph_2$ ligand is shown below:[7]

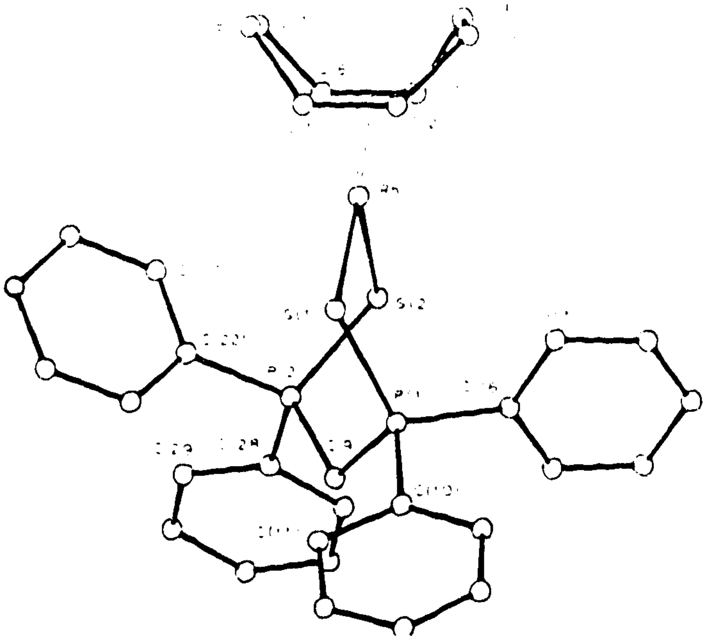


**Figure 1.1**

**The molecular structure of the cationic portion of $[Ph_2P(S)CH_2P(S)Ph_2\{-S,S\})Rh(cod)][ClO_4]$, hydrogens have been omitted for clarity [Reference 7]**

P=S bond lengths are slightly lengthened (1.994(6) and 2.001(6) Å) relative to those observed for P=S in the free ligand, $(Ph_2P(S))_3CH$ (1.944 Å).[25] From the atomic coordinates and cell parameters a PCP bond angle of 114.6° is calculated. We can also refer to the crystal structure of $[(Ph_2P(S)CH_2P(S)(NEt_2)_2\{-S,S\})Pd(PEt_3)Cl][BF_4]$, which appears in the M.Sc. thesis of A.J. Phillips.[26] The dichalcogenide ligand in this complex, bears a close resemblance to $dppmS_2$ but it has different substituents on each phosphorus atom, thereby making it unsymmetrical. Compared with the structure for $[Ph_2P(S)CH_2P(S)Ph_2\{-S,S\})Rh(cod)]^+$, the average P=S bond length is similar

(2.018(7) and 1.978(6) Å), the chelate ring again adopts a distorted boat conformation and a PCP bond angle of 112.9(9)° was found.

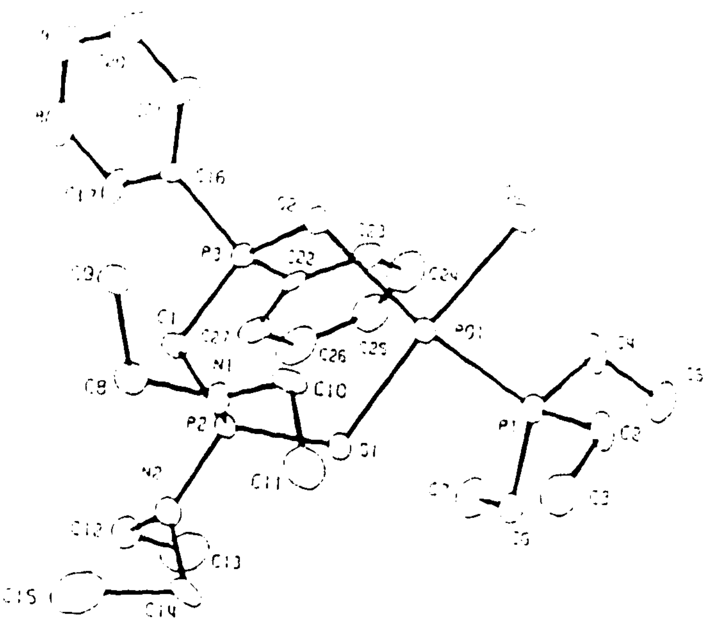


**Figure 1.2**

**The molecular structure of the cationic portion of $[(Ph_2P(S)CH_2P(S)(NEt_2)_2\{\text{-}S,S\})Pd(PEt_3)Cl][BF_4]$, hydrogens have been omitted for clarity [Reference 26]**

The {-X,C} metallacycles are four-membered rings that adopt a butterfly conformation. Shown below is the crystal structure of the platinum complex $(Ph_2P(S)CHP(S)Ph_2\{\text{-}S,C\})Pt(PEt_3)Cl$.[20]

**Figure 1.3**

**Molecular structure of $(Ph_2P(S)CHP(S)Ph_2\{-S,C\})Pt(PEt_3)Cl$, hydrogens have been omitted for clarity [Reference 20]**

The coordinated $P(S)Ph_2$ group contains an elongated P-S bond (2.014(5)Å), whereas the noncoordinated P-S bond length (1.936(4) Å) remains close to that of a free P=S (1.944Å).[25] The P-C bond length in the ring (1.821(12)Å) indicates a normal P-C single bond. The Pt-S bond length (2.390(4) Å), one of the longest known for Pt(II), foreshadows the facile exchange of 'free' and coordinated $P(S)Ph_2$ groups in solution.

Neutral Rh and Ir complexes containing the $[Ph_2P(S)CHP(S)Ph_2]^-$ ligand are accessible *via* the treatment of $[M(\mu\text{-}Cl)(cod)]_2$ with $[Ph_2P(S)CHP(S)Ph_2][Li]$, or by the reaction of $[M(\mu\text{-}Cl)(cod)]_2$ with $Ph_2P(S)CH_2P(S)Ph_2$ followed by deprotonation of the resultant cationic {-S,S} chelate with NaH.[19]

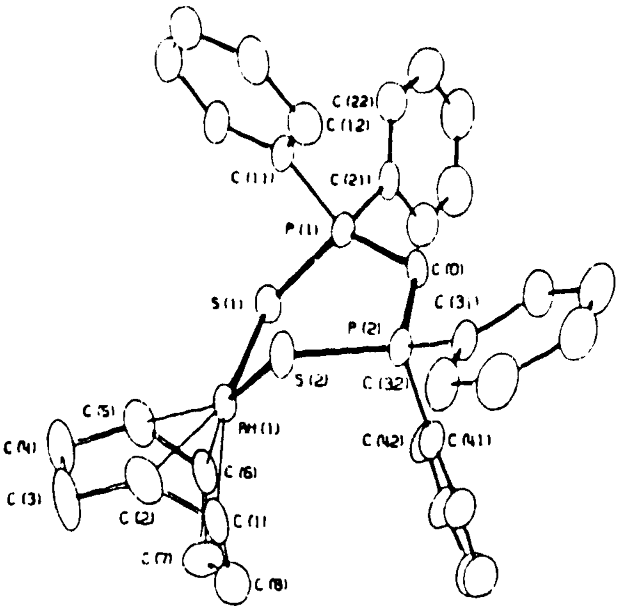


**Figure 1.4**

**The molecular structure of $(Ph_2P(S)CHP(S)Ph_2\{\text{-}S,S\})Rh(cod)$, hydrogens have been omitted for clarity [Reference 19]**

The structures of both the Rh and Ir complexes contain puckered six-membered rings possessing distorted boat conformations. The relatively long P-S bonds (2.016(4)-2.055(4) Å) and the contracted P-C bonds (1.705(11)-1.722(11) Å) and the opening of the PCP bond angles (120.8(3)-120.6(6) Å) in the deprotonated disulfide ligand are indicative of substantial delocalization of π-electron density over the five non-metal atoms of the chelate ring. They are also indicative of increased s character at the central carbon atom.

Metal complexes containing the doubly deprotonated ligand, $[Ph_2P(S)CP(S)Ph_2]^{2-}$, have also recently been reported in the literature. For example, the decomposition of $[(Ph_2P(S)CHP(S)Ph_2\{\text{-}S,S\})Pt(MeOcod)]$ in $CHCl_3$ affords the diplatinum complex $[(\mu\text{-}Ph_2P(S)CP(S)Ph_2\{\text{-}C,S;\text{-}C,S\})Pt_2(MeOcod)_2]$ which contains the $[Ph_2P(S)CP(S)Ph_2]^{2-}$ dianion.[18]

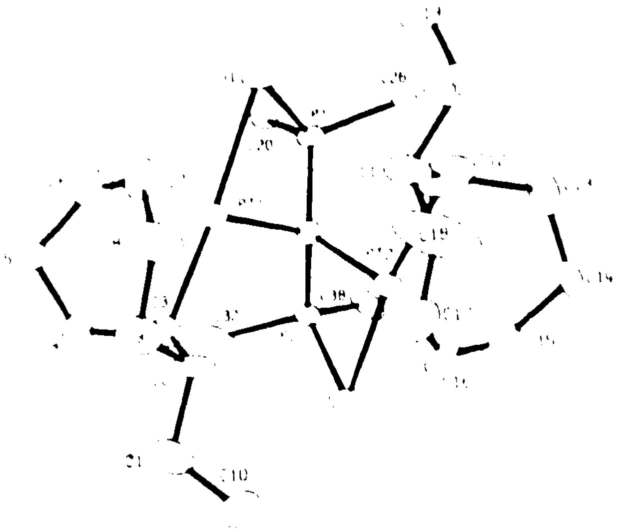


**Figure 1.5**

**The molecular structure of ($\mu$-$Ph_2P(S)CP(S)Ph_2\{$-C,S;-C,S$\})Pt_2(MeOcod)_2$, hydrogens have been omitted for clarity [Reference 18]**

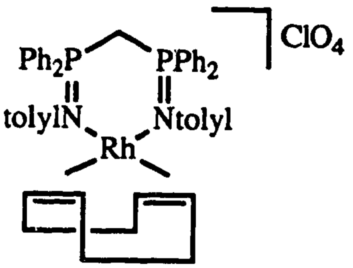
The central carbon atom of the $[Ph_2P(S)CP(S)Ph_2]^{2-}$ ligand forms a bridge between the two Pt metal centres. Square planar coordination about each metal is then completed by Pt-S bonding via the attachment of one $P(S)Ph_2$ group. What is particularly interesting in this complex is that it possesses a methylene bridge unsupported by a metal-metal bond.

## 1.2 Bisphosphinimines

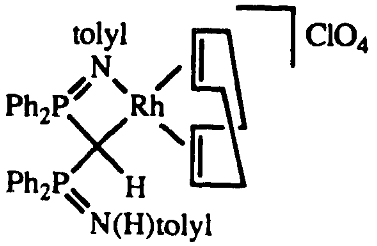
The preparation and study of the bisphosphinimines, $Ph_2P(NR)CH_2P(NR)Ph_2$, was a logical extension of the work done on the related bisphosphine dichalcogenides in the 1970's. The bis-silyliminophosphine derived from dppm was prepared in 1974 by Appel and Ruppert.[27,28] Early investigations into the chemistry of these ligands did not include the transition metals. It wasn't until the late 1980's that the group 8B transition-metal chemistry of these[29,30] and related ligands, $Ph_2P(NR)CH_2P(NR)Ph_2$ (R = p-$C_6H_4Me$, p-$C_6H_4OMe$, p-$C_6H_4NO_2$) was explored.[31-34] These ligands are characterized by strong P=N bands in the IR spectrum in the range 1345-1280 $cm^{-1}$. An interesting feature of these ligands is that the methylene protons are often kinetically labile. This is demonstrated by the disappearance of the C<u>H</u>$_2$ resonance in the $^1H$ NMR spectrum due to deuterium exchange with the solvent. Crystal structures[31,32] show that in general, the geometry of the phosphorus atoms is essentially tetrahedral. P=N bond lengths for the P=N-Ar unit typically range from 1.580(4)-1.566(2) Å. The angle at the bridging carbon is *ca.* 115°. The P-N-aryl bonding is planar suggesting that delocalization exists between the arene and P=N. Indeed, N-C bonds are shorter (1.390(2)-1.372(5) Å) than those observed for $sp^3$-$sp^3$ hybridized N-C single bonds but are of the same order of magnitude as the N-C bond in diazaphenanthrene,[35] which corroborates such delocalization. P-C bond lengths, however, for the PCP backbone range from 1.828(2)-1.819(4) Å indicating that there is not extensive delocalization over the PCP backbone. The plane containing one of the phenyl groups on phosphorus is coincident with the plane containing the aryl substituent on nitrogen and is attributed to steric repulsion within the molecule.

Much like the bisphosphine dichalcogenides, these ligands exhibit a wide variety of coordination modes.

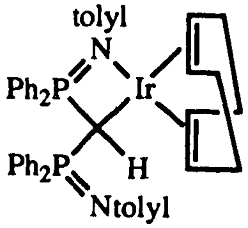
**Bidentate {-N,N} coordination by the neutral ligand[31,34]**



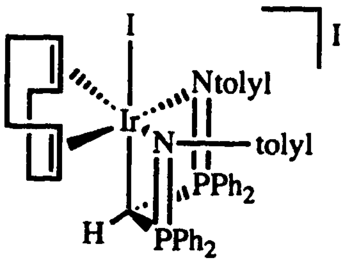
**Bidentate {-N,C} coordination by the neutral ligand[31,34]**



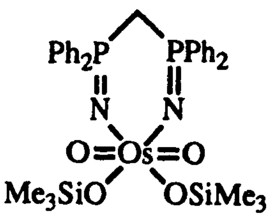
**Bidentate {-N,C} coordination by the anionic ligand[31,33]**



**Tridentate {-N,N,C} coordination by the anionic ligand[31]**



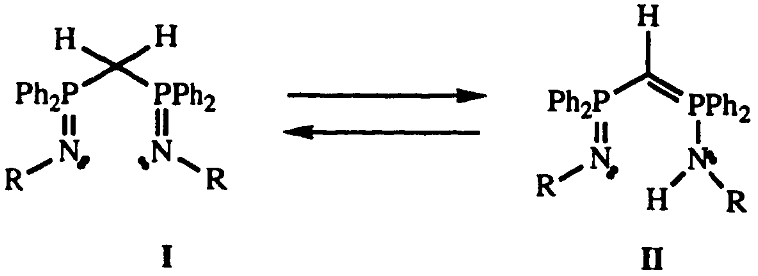
**Bidentate M-N sigma bonding[29]**



Of primary interest to this thesis are the {-N,N} and {-N,C} bonding modes.

The {-N,N} and {-N,C} bonded cationic complexes were obtained as a mixture through the reaction of the phosphinimine ligands with $[ML_2Cl]_2$ (M = Rh: $L_2$ = cod, nbd, L = CO; M = Ir: $L_2$ = cod).[31,34] Adoption of one mode over the other is apparently dependent upon the substitution at the imino nitrogen, type of metal complex and reaction conditions. The {-C,N} coordination mode could be seen as arising from complexation of **II**, which is one of two tautomeric forms that can be drawn for these types of bisphosphinimines (Scheme I).

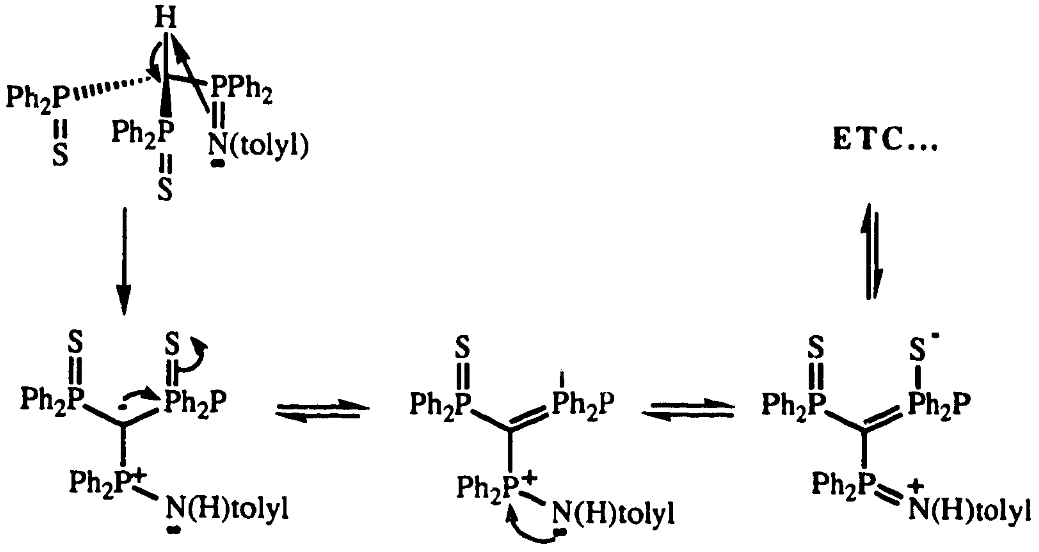
**Scheme I**



This tautomeric equilibrium may also provide a mechanism for the observed facile exchange of hydrogen and deuterium in the $CH_2$ backbones. However, variable temperature NMR studies conducted by Imhoff *et al*[31,34] seem to suggest that the tautomeric equilibrium lies almost completely to the left hand side.

It is worth noting at this point, however, that in a related mixed imino/dichalcogenide trisphosphine, $[Ph_2P(S)]_2[Ph_2P(N(H)tolyl)]CH$, the transfer of the hydrogen from the methine carbon to the imino nitrogen can be observed ($^1H$ NMR 213K: $\delta$ N(H)R 10.18 ppm, $^2J_{PH}$ 19.1 Hz) and the ligand is believed to exist as a mesomerically stabilized zwitterion (Scheme II).[36]

**Scheme II**



Upon coordination of the bisphosphinimines, the IR ν(P=N) bands shift to lower frequencies (1230-1280 $cm^{-1}$) consistent with the donation of the lone pair of the nitrogen to the metal centre. The chemical shift for the phosphorus atoms in the metal complexes are significantly deshielded relative to the signals for the free ligand (ca. $\Delta\delta$ 30 ppm). The imino phosphorus atoms generally appear upfield (*ca.* 5-8 ppm) of phosphorus centres with amino groups (i.e. P-NR vs $P\text{-}N(H)R^+$) The observed coupling between the inequivalent phosphorus atoms in the {-C,N} bonded complexes is rather small (4.4-4.9 Hz). The methylene hydrogens are deshielded slightly (δ 3.8-5.4) and the hydrogen of the aminophosphorane can be found very far downfield (δ 8.6-11.9) Both coordination modes have been structurally characterized with $[Rh(cod)]^+$ as the metal fragment and *para*-tolyl as the substituent on the imino nitrogen.[31,34]

The structure of the {-N,N} bonded chelate complex was found to consist of a discrete cation/anion pair.

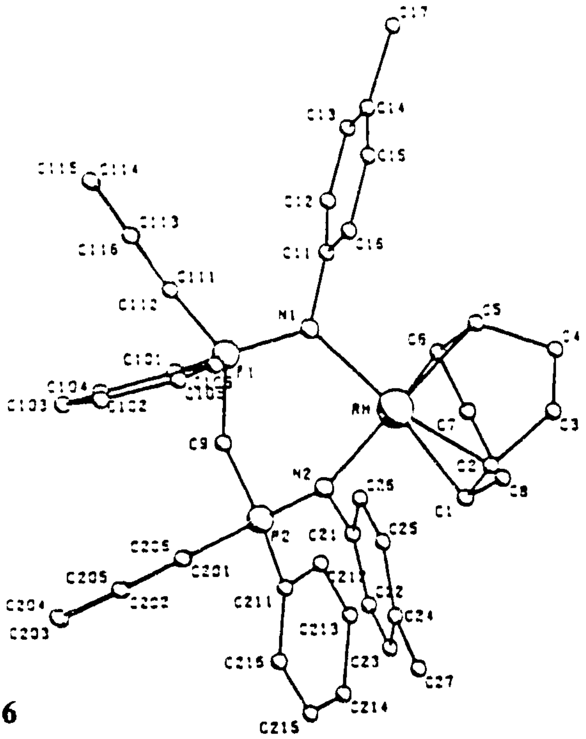


**Figure 1.6**

**The molecular structure of the cationic portion of $[(Ph_2P(Ntolyl)CH_2P(Ntolyl)Ph_2\{-N,N\})Rh(cod)][PF_6]$, hydrogens have been omitted for clarity [Reference 31,34]**

The cation shown above contains the homodifunctional ligand attached to the metal by two imino nitrogen atoms and displays distorted square planar coordination geometry about rhodium. The Rh-N bond distances of 2.144(9) and 2.17(1) Å are comparable to the Rh-N bond length in the monophosphine complex (2.142(3) Å), $(Et_3P(Ntolyl)\{-N\})Rh(cod)Cl$.[31] The P=N bonds, 1.59(1) and 1.61(1) Å, are elongated with respect to those in the uncoordinated ligand (1.568(2) and 1.566(2) Å). The six-membered metallacycle has an overall distorted boat conformation. The P-N-Ar planarity is lost upon chelation, indicating the electron pair from nitrogen is involved in the delocalization similar to that proposed for the free ligand.

The {-N,C} bonded complex also consists of a discrete cation/anion pair but this time the cation contains a puckered four-membered Rh-N-P-C metallacycle.

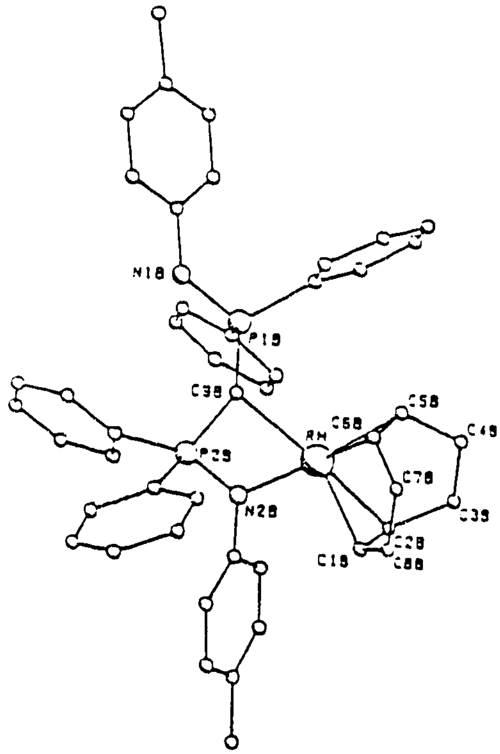


**Figure 1.7**

**The molecular structure of the cationic portion of $[(Ph_2P(Ntolyl)CHP(N(H)tolyl)Ph_2\{\text{-}N,C\})Rh(cod)][PF_6]$, hydrogens have been omitted for clarity [Reference 31]**

The P=N bond length of the coordinated imino group is quite long, 1.613(8) Å. The Rh-N bond length is 2.081(8) Å. The quaternized aminophosphonium entity is pointing away from the metal atom; its P=N bond length (1.658 Å) has been lengthened with respect to both the free ligand and the coordinated imino group, presumably due to the attachment of the migrated proton to nitrogen.

Neutral {-N,C} bonded complexes can be produced using three different routes;[31,33] (i) Reaction of the dimeric complexes $[ML_2Cl]_2$ (M = Rh, L = CO, $L_2$ = cod, nbd; M = Ir, $L_2$ = cod) with two equivalents of the appropriate deprotonated bisphosphinimine ligand, $Ph_2P(NR)CHP(NR)Ph_2$ (R = tolyl, p-$C_6H_4NO_2$), (ii) Direct reaction between the bisphosphinimine ligand $Ph_2P(Ntolyl)CH_2P(Ntolyl)Ph_2$ and $[Rh(cod)OMe]_2$ and (iii) Substitution of cod for CO in the {-N,C} bonded complex $(Ph_2P(NR)CHP(NR)Ph_2\{-N,C\})Ir(cod)$ (R = tolyl, $p\text{-}C_6H_4NO_2$) by treatment with CO gas. All of these complexes are four-membered metallacycles.

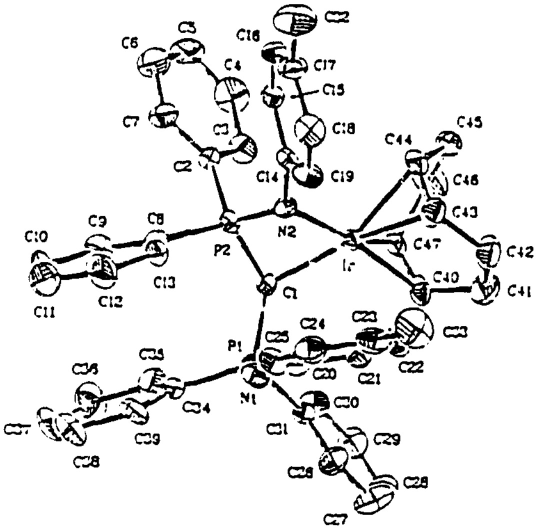


**Figure 1.8**

**The molecular structure of $(Ph_2P(Ntolyl)CHP(Ntolyl)Ph_2\{-N,C\})Ir(cod)$, hydrogens have been omitted for clarity [References 31, 33]**

The pendant $Ph_2P{=}NR$ group in $(Ph_2P(NR)CHP(NR)Ph_2\{-N,C\})Ir(cod)$ (R = tolyl) points towards the metal centre, but the large separation between the nitrogen and Ir atom suggests that if there is any bonding between these atoms it is at best very weak (N(1)-Ir = 3.84(1) Å). The $^{31}P\{^1H\}$ NMR spectrum for $(Ph_2P(NR)CHP(NR)Ph_2\{-N,C\})Ir(cod)$ (R = tolyl) contains a broad singlet which remains virtually unchanged down to -100°C. The facile averaging of the two phosphorus environments in this molecule has been ascribed to a dynamic intramolecular phosphorus exchange which passes through a {-C,N,N} bonded five-coordinate intermediate. Coupling between rhodium and phosphorus was not resolved for the neutral {-N,C} coordinated Rh and Ir complexes. In the IR spectra bands at lower wave numbers (1279-1304 $cm^{-1}$) were attributed to ν(P=N) of the coordinated phosphinimine while stretches at higher wave numbers (1313-1366 $cm^{-1}$), were assigned to the uncoordinated phosphinimine moiety.

## 1.3 Mixed Imino-Chalcogenide Bisphosphines

As stated earlier, the unusual rotation about M-X and M-C bonds, seen for the cationic {-X,X} bonded chelate complexes and neutral {-X,C} bonded metallacycles, indicate that such ligands may be useful for catalysis. The facile exchange in the methylene protons of bisphosphinimine derivatives of dppm leads to a rich coordination chemistry and the functional group bonded to nitrogen allows the chemist to change the electronic and steric nature of the free or complexed ligands upon demand. Unfortunately the cationic {-N,C} bonded metal complexes do not exhibit the unusual fluxional behaviour observed for their bisphosphine dichalcogenide analogs, probably due to the presence of the H on the free aminophosphonium group. This assumption is supported by the observation that the neutral {-N,C} bonded complexes are fluxional in solution.

The body of work described in this thesis explores the chemistry of mixed bisphosphine imino-chalcogenides, $Ph_2P(X)C_nH_mP(NR)Ph_2$, with the hope that such ligands might possess features both similar to and simultaneously different from their bis imino and bis chalcogenide analogues. The labile nature of P=X/P=N bonding to a metal centre, of course, increases the probability that these ligand types might be effective catalysts. Indeed, one might expect that such lability will be favoured when bonding hard chalcogen/nitrogen atoms to soft group 8B transition-metal centres.

### 1.3.1 Attachment of NR to Phosphorus

Adding an imino moiety to a phosphorous centre can be achieved by several different methods, for example: (i) A tertiary phosphine can be reacted with an organic azide (i.e. the Staudinger reaction).[37] (ii) A phosphorous (V) dihalogenide can be reacted with an amine (i.e. the Kirsanov reaction).[38] (iii) Diethyl azodicarboxylate can be used to couple a phosphine with an amine.[39,40] (iv) An aminophosphonium salt can be deprotonated and then reacted with the appropriate alkylhalide.[41]

(i)

$$R_3P + R'N_3 \longrightarrow R_3P{=}NR' + N_2$$

(ii)

$$R_3PX_2 + R'NH_2 \longrightarrow R_3P{=}NR' + 2\,HX$$

(iii)

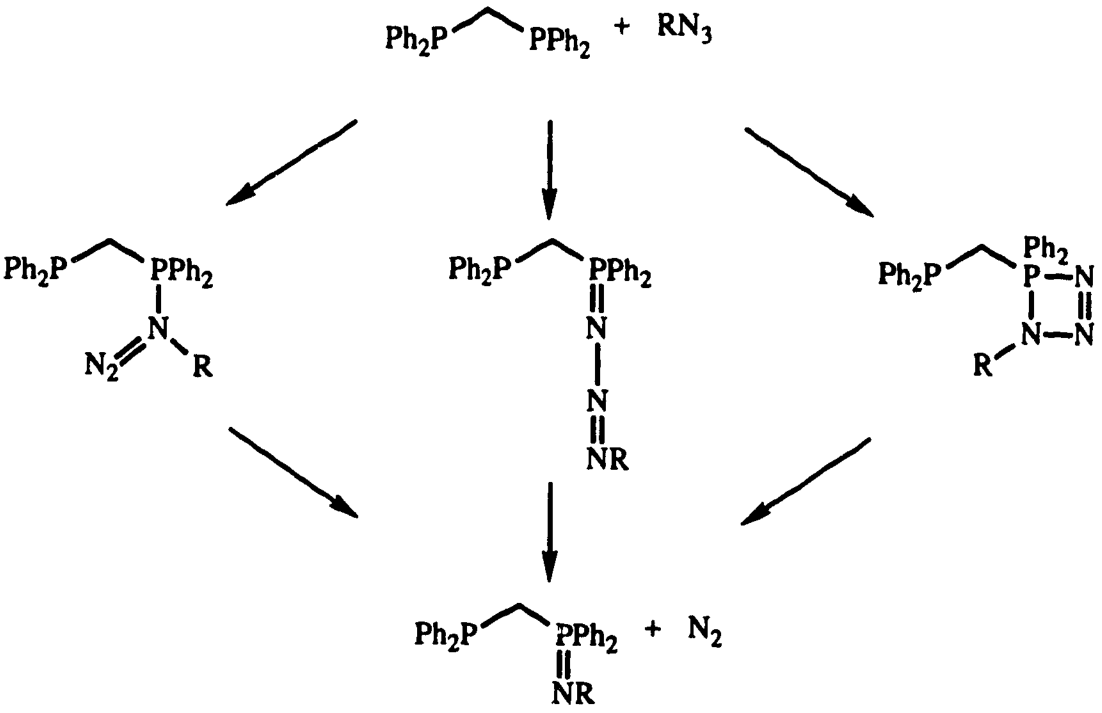
$$R_3P + R'NH_2 \xrightarrow{EtOC(O)N_2C(O)OEt} R_3P{=}NR' + EtOC(O)NH\text{-}NHC(O)OEt$$

(iv)

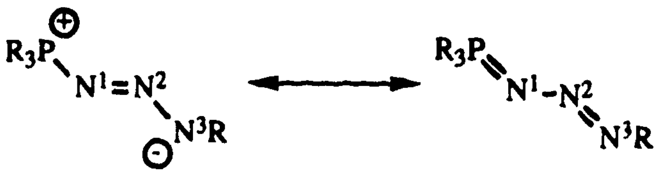
$$[R_3PNH_2]X + 2\,R''Li \xrightarrow[-\,LiX]{-\,2R''H} R_3P{=}NLi \xrightarrow{R'X} R_3P{=}NR' + LiX$$

For this work the preferred method of introducing the imino moiety proved to be the Staudinger reaction. Depending on the azide used the reaction conditions varied from refluxing a neat mixture of azide and phosphine (>130°C; $N_3T$), to the low temperature (-78°C; $N_3$tfbn) addition of the azide to a methylene chloride solution of the phosphine.

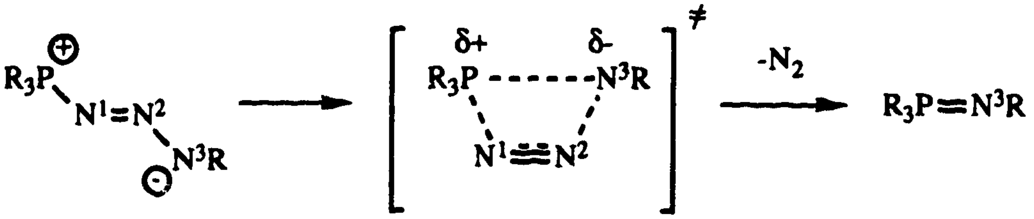
This is in keeping with the finding that the Staudinger reaction is accelerated by the presence of acceptor groups on the azide.[42] Mechanistic studies of this reaction have shown that the α-nitrogen of the azide is retained in the phosphinimine.[43,44] To explain the final product, three phosphazide intermediates have been proposed having branched[45,46], linear[47] and cyclic[48] structures:



The linear form has been generally accepted as the favoured structure for phosphazides in view of chemical spectroscopic and kinetic data;[49] the cyclic and branched forms, however, seemed to provide better models for the expulsion of $N_2$ to yield the phosphinimines. Recently further insight into the mechanism was provided by x-ray analysis of germane phosphazide and metal phosphazides.[50] These studies showed that the structures are indeed acyclic, as predicted, and that the terminal nitrogen is attached to a P(III) centre. The $PN_3C$ linkage is nearly planar and $N^1$-$N^2$ exhibits partial double bond character.



For a series of such linkages a reduction of the $N^1$-$N^2$ bond order results in a reduction in thermal stability. It is assumed, therefore, that the expulsion of $N_2$ occurs though rotation about the $N^1$-$N^2$ bond (ie. the transition state intermediate is expected to be the aforementioned cyclic form).



## 1.3.2 Oxidation of Phosphorus by Chalcogens

In general, chalcogen oxidation of a phosphorus centre is accomplished by either refluxing a mixture of the phosphine and elemental chalcogen (S, Se) in toluene (Equation (i)) or by adding hydrogen peroxide dropwise to the phosphine in acetonitrile at room temperature (Equation (ii)).[51] However, use of these routes, to prepare the mono-oxide and mono-sulfide of dppm, results in very poor yields. A preferred method of synthesis is to combine the appropriate molecular fragments, one possessing a phosphorus (V) chalcogen the other a phosphorus (III) centre (Equation (iii)).[52]

**Equation (i)**

$$R_3P + X \xrightarrow{\text{Toluene}} R_3P(X)$$

(X = S, Se)

**Equation (ii)**

$$R_3P + H_2O_2 \xrightarrow{CH_3CN} R_3P(O)$$

**Equation (iii)**

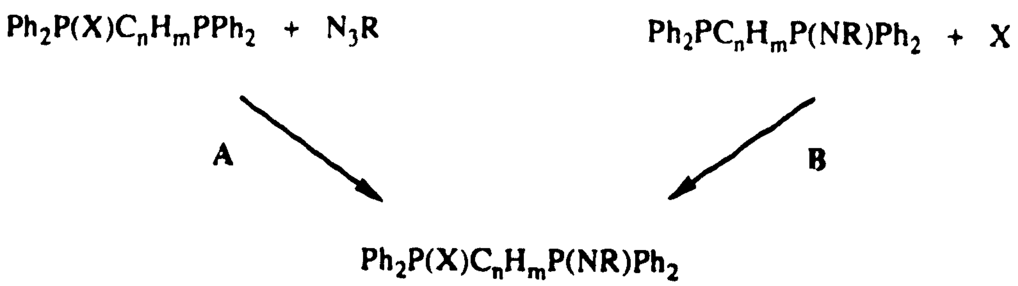
$$Ph_3P(X) + MeLi \xrightarrow[\text{- PhH}]{\text{THF}} Ph_2P(X)CH_2Li \xrightarrow[\text{-LiCl}]{Ph_2PCl} Ph_2P(X)CH_2PPh_2$$

(X = O, S)

The methods (i) and (iii) were utilized to give the novel series of the imino-chalcogenide bisphosphines described in this thesis.

### 1.3.3 Synthesis of Imino-Chalcogenide Bisphosphines

Armed with the knowledge of how to add both chalcogen and imino groups to phosphorus centres, it becomes apparent that there are two possible direct routes to the formation of mixed imino-chalcogenide bisphosphines: the imino functionality can be introduced to a bisphosphine mono-chalcogenide or the chalcogen can be added to the desired mono-imino bisphosphine (vide infra).



(X = O, S, Se; n = 1 or 2; m = 2 or 4; R = tfbn, T)

For this work both of the synthetic approaches shown above were utilized. Route A was employed in those cases where the NR group in the starting mono-imino bisphosphine was prone to substitution by the chalcogen in refluxing toluene. Conversely, route B was used if the chalcogen was easily supplanted by the azide. As we shall see route A proved to be the most reliable method for preparing high yields of the desired imino-chalcogenide bisphosphines.

# CHAPTER 2

# THE MIXED IMINO-CHALCOGENIDE LIGANDS, $Ph_2P(X)C_nH_mP(Ntfbn)Ph_2$ ($X= O, S, Se$; $CnHm = CH_2$, $CH(CH_3)$, *cis*-CHCH, $CH_2CH_2$, 1,2-$C_6H_4$)

## 2.1 Synthesis

Ligands with $C_nH_m = CH_2$ were used for this study since there is much data available for the homologously oxidized analogs, the bisphosphine dichalcogenides and bisphosphinimines.[1,6-24,27-34,51-55] The dppm bisphosphine chalcogenides and bisphosphinimine ligands have been shown to prefer coordination modes involving chelation. To date there are only two examples in which a bisphosphine dichalcogenide, $Ph_2P(S)CH_2P(S)Ph_2$, bridges two metal centres,[16,17] and there are no known examples of a bridging bisphosphinimine ligand. Ligands with $C_nH_m$ = $CH(CH_3)$, *cis*-CHCH, $CH_2CH_2$, 1,2-$C_6H_4$ linkages between the phosphorus atoms, however, could be excellent candidates for bridging two metal centres. They were used to study the effect of the backbone on the formation or stability of the mixed imino-chalcogenide bisphosphines. The tetrafluorobenzonitrile azide was chosen as it seems to produce a most stable phosphinimine moiety. However. as will be seen later, such stability was not achieved without a significant disadvantage. The increased electron-withdrawing ability of tfbn rendered the imino nitrogen less basic and therefore less prone to attach to a metal centre.

Route A, the addition of the azide to a monochalcogenide, was chosen as the method for preparing these imino-chalcogenide bisphosphines. The yield limiting step proved to be the preparation of the mono-chalcogenide. The mono-sulfides and selenides of the desired bisphosphines were introduced by refluxing a mixture of the phosphine with elemental chalcogen (S, Se) in toluene, the exception being dppmS and dppmO.

DppmS and dppmO were prepared using the method of Grim *et al* [52] which involves reaction of $Ph_3P(S)$ with MeLi followed by treatment of the resulting $LiCH_2P(S)Ph_2$ salt with $Ph_2PCl$. The oxidation of the second phosphorus centre involved the dropwise addition of azide to a cooled (-78°C) dichloromethane solution of the chalcogen oxidized bisphosphine. It was comforting to see the formation and decomposition of the bright yellow phosphazide intermediate during the course of the reaction. This was also accomplished by performing *in situ* $^{31}P$ NMR experiments following the addition of azide to the desired phosphine. The intermediate for these species could be isolated if both addition of azide and subsequent removal of solvent was carried out at -78°C.

The new ligands are not soluble in low polarity solvents (hexane, ether), but are rather soluble in halogenated solvents, THF, benzene, and acetonitrile. The ligands are stable both to air and moisture as solids and in solution. Some change in colour is noted upon prolonged exposure to light but this does not seem to affect the bulk of the sample.

### 2.1.1 IR data

Most noticeable in the IR spectra (KBr) (Tables 2.1-2.2; pp. 54-55) is the intense $\nu(P{=}N)$ band, which appears between 1506-1519 $cm^{-1}$. Although these absorptions are different from the literature values for known bisphosphinimine ligands, the lower $\nu(P{=}N)$ agrees with the observation that electron-donating substituents on nitrogen cause hypsochromic shifts.[49,56,57] The position of the band is not greatly affected by the introduction of the chalcogen atom, for example in the dppm series, $\nu(P{=}N)$ for $Ph_2P(Ntfbn)CH_2P(Ntfbn)Ph_2$ is 1514 $cm^{-1}$ and for $Ph_2P(X)CH_2P(Ntfbn)Ph_2$ (X = O, S, Se), 1511, 1510 and 1509 $cm^{-1}$.

Though ν(CN) is quite weak, it is clearly evident in the spectra at circa 2230 $cm^{-1}$. The effect that the introduction of a chalcogen atom has on this band is variable; referring to the dppm series, the largest perturbation is seen with the S atom. For example, ν(CN) for $Ph_2P(Ntfbn)CH_2P(Ntfbn)Ph_2$ is found at 2230 $cm^{-1}$ while for the imino chalcogens $Ph_2P(X)CH_2P(Ntfbn)Ph_2$ (X = O, S, Se), the CN stretch is observed at 2233, 2218 and 2229 $cm^{-1}$, respectively. When interpreting infrared data,however, such a small variation makes any analysis inconclusive.

The other diagnostic band observed for these ligands is of course the P=X stretch (X = O, S, Se). This band is not as well defined as the ν(P=N) band but could nevertheless be identified for $C_nH_m = CH_2$ by comparison with the spectrum of $Ph_2P(Ntfbn)CH_2P(Ntfbn)Ph_2$. They are assigned as follows: ν(P=O) 1213, ν(P=S) 780 $cm^{-1}$ and ν(P=Se) 520 $cm^{-1}$. The values of ν(P=O) and ν(P=S) are higher and that of ν(P=Se) is lower than those previously observed for the analogous bisphosphine dichalcogenides ($Ph_2P(X)CH_2P(X)Ph_2$, ν(P=O) 1195 and ν(P=S) 628 $cm^{-1}$; ν(P=Se) 531).[6,12,51] Again, ν(P=S) experiences the largest shift. It is possible that a third row anomaly may be responsible but placement of ν(P=S) is generally not consistent within related groups of P=S compounds, therefore, these results can not be readily interpreted.

The ν(P=N) and ν(CN) bands are affected by changing the nature of the hydrocarbon chain between the phosphorus atoms. Such an observation was not possible for the ν(P=S) band due to its uncertain assignment.

Comparing $PCH_2P$ to $PCH(CH_3)P$ we see a shift of ν(P=N) and ν(CN) to higher frequencies (1510 to 1519 and 2218 to 2231 $cm^{-1}$, respectively) indicating a strengthening of these bonds. This is due to the replacement of H by the more electron releasing $CH_3$ group.

Progressing through the series of $PCH_2CH_2P$, PCHCHP and $PC_6H_4P$ ligands there is essentially no change in the ν(P=N) frequency (1506, 1507 and 1507 $cm^{-1}$, respectively) but there is a change in ν(CN) (2232, 2227 and 2224 cm$^{-1}$). the value of ν(CN) decreases as the s character of the carbon atom in the backbone decreases and as the electron density throughout the backbone is increased.

### 2.1.2 Multinuclear NMR Data

The $^{31}P\{^{1}H\}$ spectra of the ligands contain two resonances for the chemically different phosphorus atoms (chemical shift and coupling data found in Tables 2.3-2.4). The resonance for the phosphorus bound to the chalcogen is split into a doublet displaying coupling to the imino phosphorus. The resonance for the imino phosphorus atom appears as a doublet of triplets displaying coupling to the chalcogen phosphorus and coupling to the *ortho*-fluorines of the tfbn group. For the selenium derivatives there is the added benefit of $^{77}Se$ satellites on either side of one of the phosphorus resonances clearly labelling the chalcogen bonded phosphorus. The above information allows us to place the imino phosphorus downfield from the chalcogen phosphorus. A typical spectrum is shown in Figure 2.1.

If we consider just the dppm derivatives we can examine the effect that the introduction of a chalcogen atom has on the $^{31}P\{^{1}H\}$ chemical shifts (Table 2.4). The chalcogen phosphorus experiences increased deshielding in the order Se, O and S (δ 20.63, 21.84 and 32.22 ppm, respectively). The reason for this particular sequence is uncertain. The imino phosphorus experiences increased deshielding in the order S, Se and O (δ 5.50, 5.57 and 7.15 ppm, respectively) which can be be loosely correlated with the electronegativity of X (2.5, 2.4 and 3.5 respectively).

The coupling between the phosphorus atoms is seen to decrease in the order O, S, Se (11.9, 9.5, 8.8 Hz, respectively). The coupling between the imino phosphorus and the *ortho* fluorines on the tfbn group alters slightly with the introduction of the chalcogens in the order Se, O and S (6.1, 5.6, 5.2 Hz). It is risky, however, to arrive at any conclusions from these trends since these are relatively minute changes in coupling.

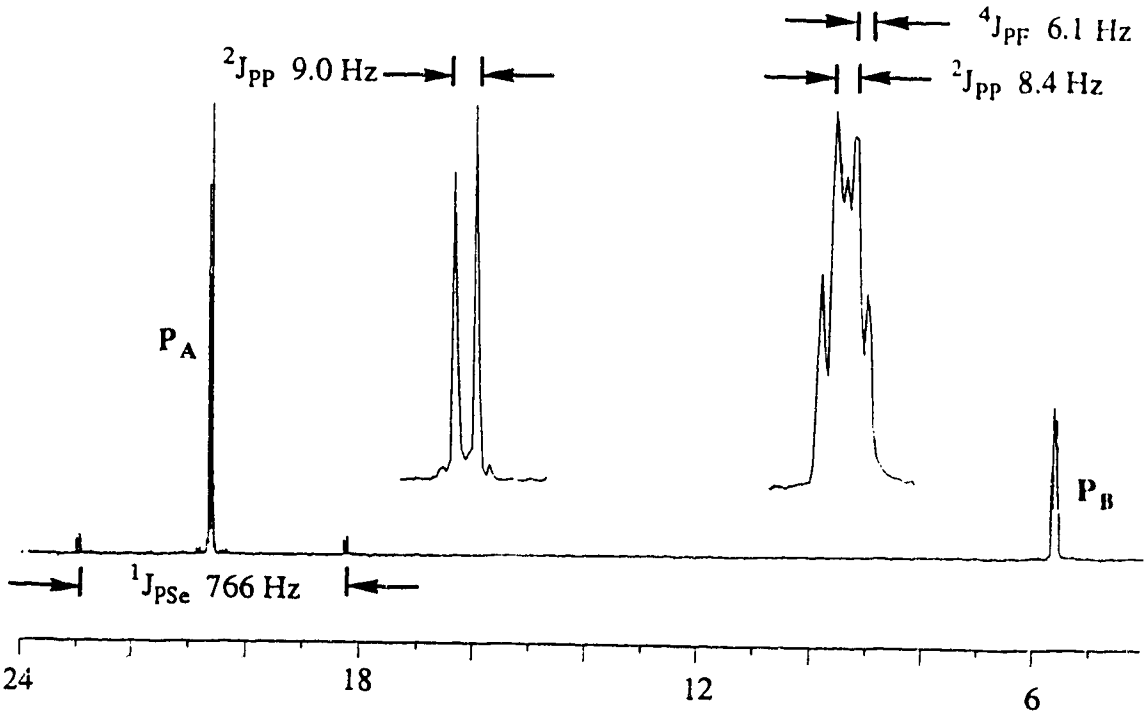


**Figure 2.1**

**$^{31}P\{^1H\}$ NMR spectrum of $Ph_2(Se)P_ACH_2P_B(Ntfbn)Ph_2$ in $CD_2Cl_2$**

There is a marked effect on the $^{31}P\{^1H\}$ chemical shifts upon changing the backbone (Table 2.3). As for the IR data we must consider the PCP and PCCP backbones separately. Two-bond phosphorus-phosphorus coupling is known to be quite different from three-bond coupling.[58] Indeed, looking at $PCH_2P$ and $PCH_2CH_2P$ we see $^3J_{PP}$ (56.7 Hz) is markedly increased over $^2J_{PP}$ (9.5 Hz) and with the change in coupling comes a change in chemical shifts ($\underline{P}$(S) δ 32.22, $\underline{P}$(N) 5.5

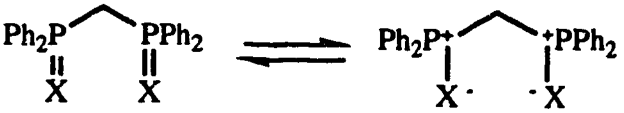
ppm, P(S) δ 44.31, P(N) 17.22 ppm, respectively) associated with a change in shielding.

When one of the methylene hydrogens of the P**C**$H_2$P carbon is replaced by an electron donating methyl group there is an increase in shielding of the P(N) resonance and a small deshielding of the P(S) resonance. This may be related to the fact that the highly electron withdrawing tfbn substituent on the nitrogen may cause the extra electron density supplied to the backbone to be directed to the imino phosphorus atom.

In general, for the series $PCH_2CH_2P$, PCHCHP and $PC_6H_4P$ we see that changing the hybridization of the carbon atoms in the backbone as well as changing the electron donating ability of substituents on these carbons has the effect of increasing the P(S) shielding, deshielding P(N) and decreasing $^3J_{PP}$.

$^{13}C\{^1H\}$ NMR data (Table 2.6) were most useful for the characterization of the dppm ligands, more specifically, the resonance for the methylene carbon in the dppm backbone provided valuable information about the mode of coordination for the ligand. These carbons appear as a doublet of doublets between δ 33 and δ 35 ppm, due to coupling to two inequivalent phosphorus atoms. The coupling was assigned on the basis of comparisons with the symmetrically oxidized analogs[59] and confirmed by performing $^{13}C\{^{31}P\}$ experiments on a few of the ligands. The chemical shift of the methylene carbon is not affected greatly by the introduction of a chalcogen, but the coupling constants $^1J_{CP(X)}$ and $^1J_{CP(N)}$ do exhibit some changes upon oxidation of the phosphorus. The coupling of the carbon to the chalcogen phosphorus is seen to decrease in the order O, S, Se (59.3, 47.3 and 39.8 Hz, respectively). This is in agreement with previous observations for bisphosphine dichalcogenides and reflects the decreasing electronegativity of the chalcogen (3.5, 2.5 and 2.4, respectively). With a decrease in coupling to the chalcogen phosphorus comes an increase in coupling to the imino phosphorus, though the effect is much smaller.

Selected $^1$H NMR data, specifically the resonance for the methylene or methine protons in the dppm backbone are gathered in Table 2.5. Unlike their bisphosphinimine analogs these imino-chalcogenide bisphosphines do not exhibit facile H/D exchange with the deuterated solvent; the resonance for the protons of the $CH_2$ backbone, which appeared as a doublet of doublets arising from coupling to two inequivalent phosphorus atoms, did not disappear with time. The chemical shifts for methylene protons are deshielded with the addition of chalcogen X in the order O, S and Se (δ 3.83, 4.08 and 4.22 ppm, respectively). This follows trends observed for the unsymmetrical bisphosphine dichalcogenides. If one assumes that chemical shifts are determined by diamagnetic shielding then the order should be reversed based on the electronegativity. The reason postulated for such a deviation is that the double bonded canonical form for the chalcogen-phosphoryl bond is more important for O than for S or Se, which favour the dipolar form.[54]



However, when one is dealing with nuclei other than hydrogen there is always the possibility that paramagnetic shielding effects[60] may become significant, in which case the explanation involving the different canonical forms becomes less certain. There is an observed increase in $^2J_{HP(X)}$ for the O, S and Se ligands (12.7, 13.6 and 14.0 Hz, respectively) and a concomitant decrease in $^2J_{HP(N)}$ (13.3, 12.8 and 12.6 Hz, respectively).

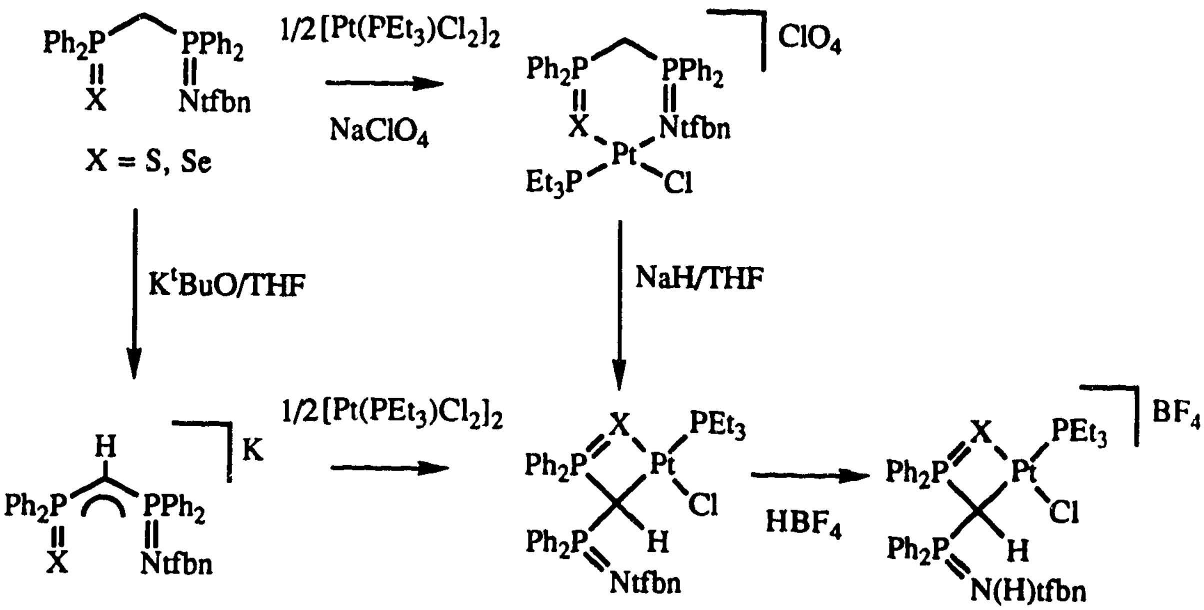
For the ligands $C_nH_m$ = $CH_2$ and X = O, S, and Se; $^{19}$F and $^{77}$Se NMR (Tables 2.7 and 2.8, respectively) provided further data which could be useful for assessing the effect complexation has on phosphorus-chalcogen bonding or chalcogen-fluorine interaction. This data includes the chemical shift for Se ($\delta$ -274.18 ppm), phosphorus-selenium coupling ($^1J_{PSe}$ 766 Hz), the chemical shifts for the *ortho* and *meta* fluorines of the tfbn ring ($\delta$ -153.20 to -152.70 and -140.19 to -139.75 ppm, respsectively) and phosphorus-fluorine coupling ($^4J_{PF}$ 5.5-6 Hz). The $^{19}F$ NMR spectra show that the chemical shifts for the *ortho* and *meta* fluorines are essentially unaffected by the nature of the chalcogen bonded to the second phosphorus centre. The measurement of phosphorus-fluorine coupling constants is ambiguous owing to poor resolution and the presence of second order distortions in the spectra.

## 2.2 Complexation chemistry

Complexation involved reacting the neutral and deprotonated ligands $Ph_2P(X)CH_2P(Ntfbn)Ph_2$ (X = O, S, Se) with the neutral group 8B transition-metal dimers $[M(\mu\text{-}Cl)LL']_2$ where M = Pt, Pd, L = $PEt_3$, L' = Cl; M = Rh, L, L' = CO, LL' = cod.

With the platinum triad, complexation was successful only for the ligands containing the softer chalcogens (X = S, Se) and resulted in the formation of the cationic {-X,N}, {-X,C} and neutral {-X,C} bonded metal complexes. The {-X,N} bonded chelates were obtained by reacting the neutral ligand with the metal dimer in the presence of $NaClO_4$. The {-X,C} bonded metallacycle was obtained by reacting the deprotonated ligand with the metal dimer or by deprotonating the {-X,N}bonded chelate complex. The cationic {-X,C} bonded metallacycle was formed by reacting the neutral {-X,C} bonded complex with $HBF_4$. With time, the cationic {-X,C} bonded complex was found to rearrange to the {-X,N} bonded chelate. The reactions are outlined below in Scheme III:

**Scheme III**



This chemistry closely follows the coordination chemistry observed for the analogous bisphosphine dichalcogenide ligands, with the exception that protonation of the neutral {-X,C} bonded metallacycle occurs at the imino nitrogen rather than at the methine carbon. All the complexes can be easily identified from one another from $^1H$, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ chemical shift and coupling data. For instance, in the $^{31}P$ NMR spectra (see Figures 2.2 and 2.3) phosphorus centres whose chalcogen or imino substituents are complexed are found downfield from those whose substituents are uncomplexed. The six-membered {-X,N} bonded chelates may be differentiated from the four-membered {-X,C} bonded metallacycles since for the former only coupling between any two inequivalent phosphorus atoms is observed whereas in the latter we see coupling between all three of the inequivalent phosphorus atoms. A full analysis of all the data can be found in section 2.2.1 to 2.2.4.

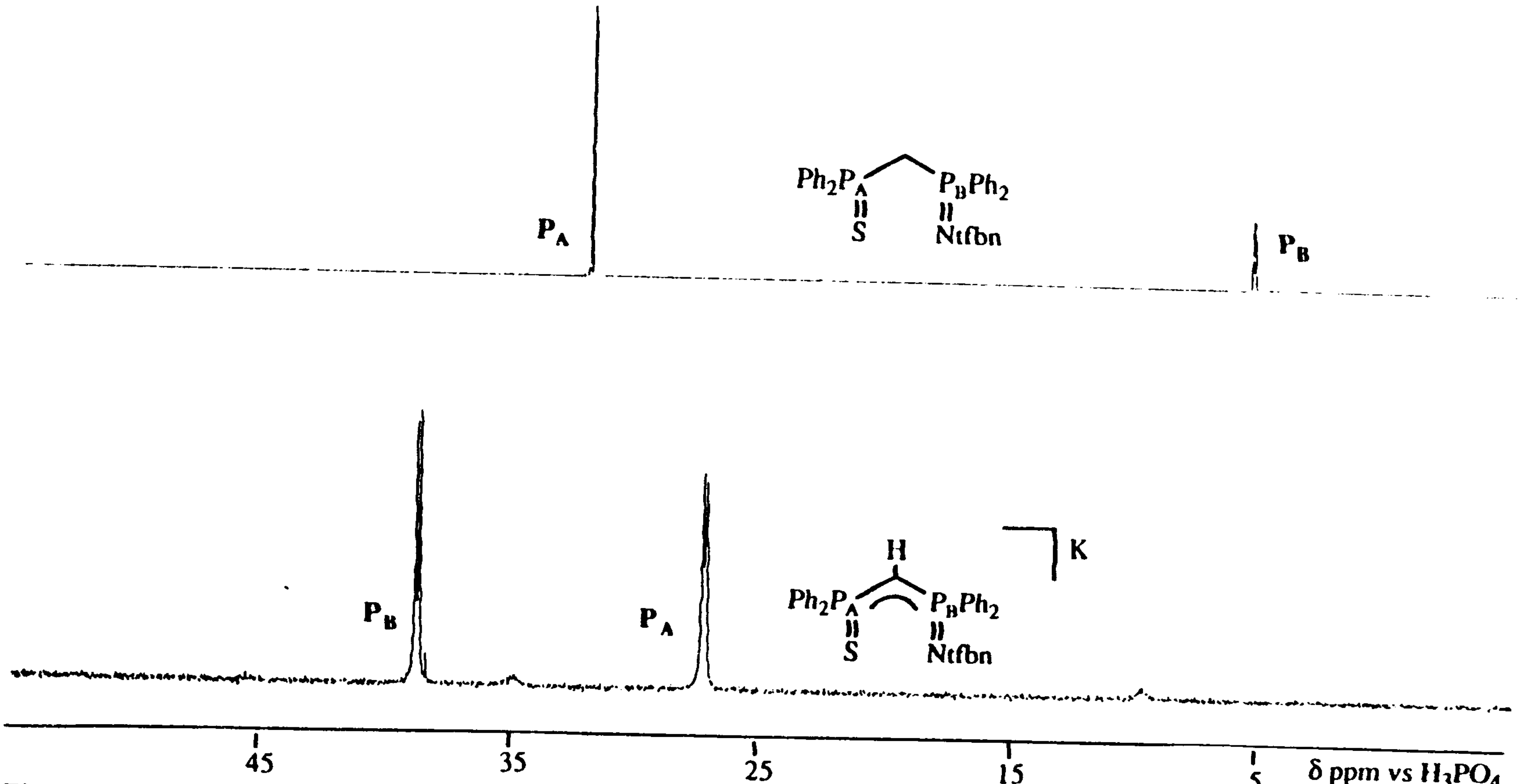


Figure 2.2

$^{31}P\{^1H\}$ NMR spectra of the neutral and deprotonated ligands, $(Ph_2P(S)CH_2P(Ntfbn)Ph_2)$ and $[Ph_2P(S)CHP(Ntfbn)Ph_2][K]$*

* solvent used for $(Ph_2P(S)CH_2P(Ntfbn)Ph_2)$ was $CD_2Cl_2$
solvent used for $[Ph_2P(S)CHP(Ntfbn)Ph_2][K]$ was $d^8$ THF

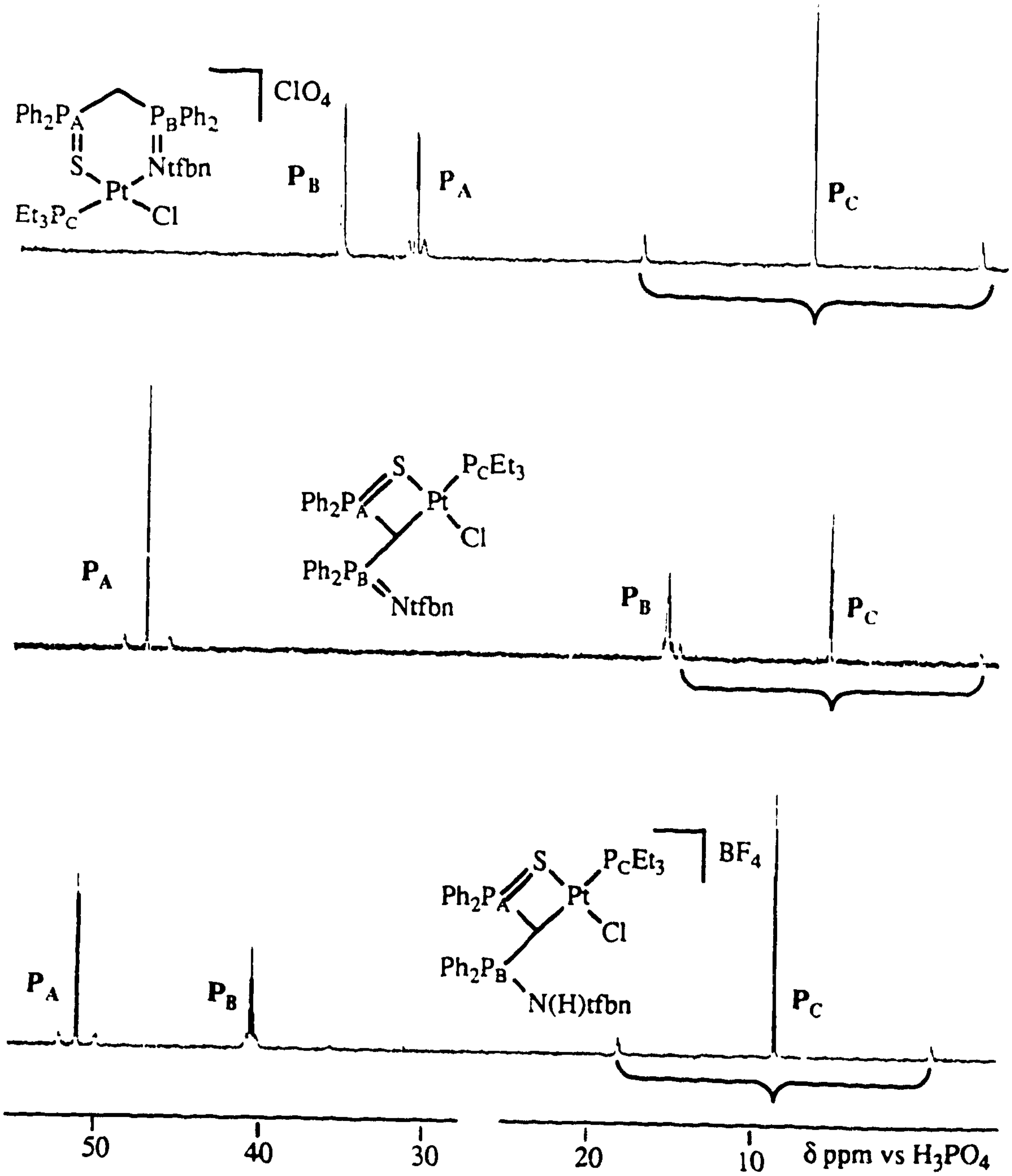
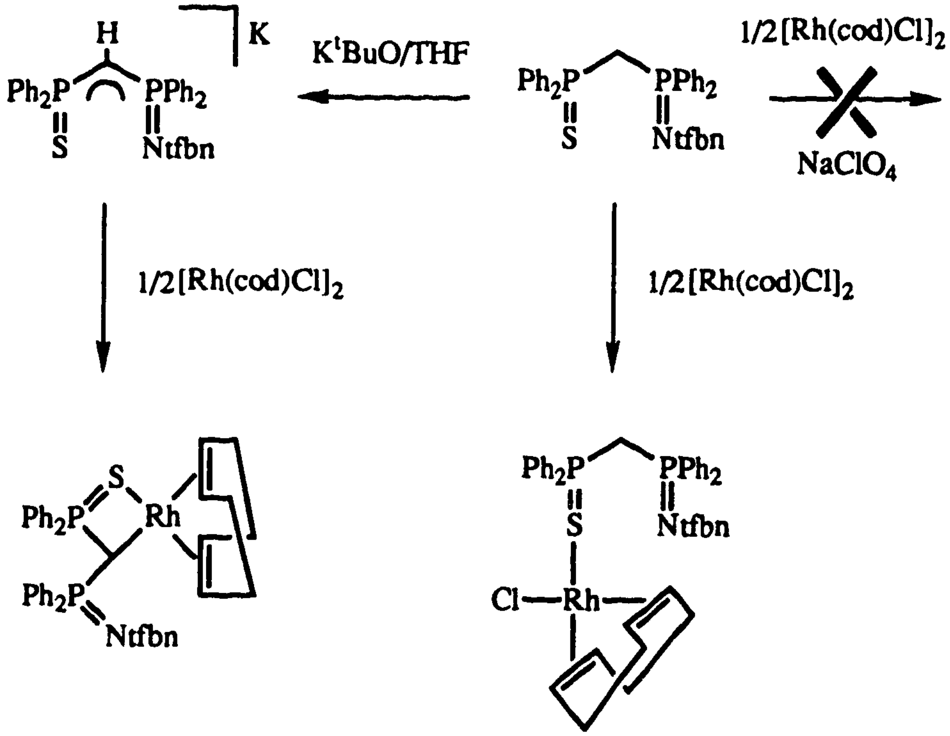


**Figure 2.3**

**$^{31}P\{^1H\}$ NMR spectra of $[(Ph_2P(S)CH_2P(Ntfbn)Ph_2\{\text{-}S,N\})Pt(PEt_3)Cl][ClO_4]$, $(Ph_2P(S)CHP(Ntfbn)Ph_2\{\text{-}S,C\})Pt(PEt_3)Cl$ and $[(Ph_2P(S)CHP(N(H)tfbn)Ph_2\{\text{-}S,C\})Pt(PEt_3)Cl][BF_4]$**

With the rhodium complexes only the sulfur containing ligands were investigated. Both {-S} and {-S,C} neutral metal complexes were synthesized. The coordination chemistry involving the Rh(cod) fragment is outlined below in Scheme IV:

**Scheme IV**



The {-S,C} metallacycle was obtained by reacting the rhodium dimer with two equivalents of the deprotonated ligand in THF. The same complex could not be synthesized by deprotonation of the {-X,N} chelate because all attempts to form the {-X,N} cationic chelates resulted in formation of the neutral monodentate {-X} chelate complex. It was mentioned in the introduction that the reaction of dppmS$_2$ with a carbonyl complex of iron resulted in a similar $\eta^1$-S bonded monodentate complex.[1] Its conversion to a bidentate {-S,S} coordinated complex was achieved by the photo-induced expulsion of CO. It is obvious that the nitrogen lone pair has little affinity for bonding to the rhodium metal centre. This is unusual considering that Rh(I) and Pt(II) would be expected to have the same hardness. One must now, however, consider the nature of the other groups bonded to the metal centre. The $PEt_3/Cl$ groups may be sufficiently electrophilic with respect to either CO/Cl or cod such that the platinum favours bonding with the Ntfbn nitrogen. We cannot conclude, however, that all {-S,N} ligands will not chelate to rhodium. The affinity that the imino nitrogen will have for bonding to the rhodium centre is obviously dependent upon the substituent on N. With an elecctron releasing tolyl substituent on nitrogen, it seems likely that the imino nitrogen would form a reasonably strong bond to the Rh.

A full analysis of the spectroscopic data for all reactions is given below:

### 2.2.1 Neutral Monodentate {-X} Bonded Complexes (X = S)

### $(Ph_2P(S)CH_2P(Ntfbn)Ph\{-S\})Rh(L)L'(Cl)$

Attempts to form neutral or cationic bidentate chelate complexes containing rhodium, through expulsion of CO or removal of $Cl^-$, were performed by reacting $Ph_2P(S)CH_2P(Ntfbn)Ph_2$ with $[Rh(CO)_2Cl]_2$, $[Rh(CO)_2Cl]_2/NaClO_4$ or $[Rh(cod)Cl]_2/NaClO_4$ in dichloromethane.

In the IR spectra (KBr) the bands for ν(P=N) (1510 $cm^{-1}$) show little change upon complexation (1511 $cm^{-1}$) and the bands for ν(P=S) (780 $cm^{-1}$), as expected, are shifted to lower frequency (581 and 611 $cm^{-1}$ for the CO and cod complexes, respectively). This seems to indicate that there is little or no bonding between nitrogen and the rhodium metal centres. In order to maintain a satisfactory electron count around rhodium(I) the anticipated loss of CO or $Cl^-$ must not have occurred. Two strong bands for ν(CO) are observed at 2072 and 2002 $cm^{-1}$. According to Group Theory analysis (Scheme V)

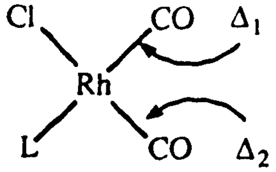
## Scheme V

## Group Theory analysis of the carbonyl region in the IR spectrum of $(Ph_2P(S)CH_2P(Ntfbn)\{\text{-}S\})Rh(CO)_2Cl$

Assume $C_s$ symmetry.

| $C_s$ | E | $\sigma_h$ |
|---|---|---|
| A' | 1 | 1 |
| A'' | 1 | -1 |

For the calculations consider only those unit vectors representing the CO bond axes.



$L = Ph_2P(S)CH_2P(Ntfbn)Ph_2\ \{\text{-}S\}$

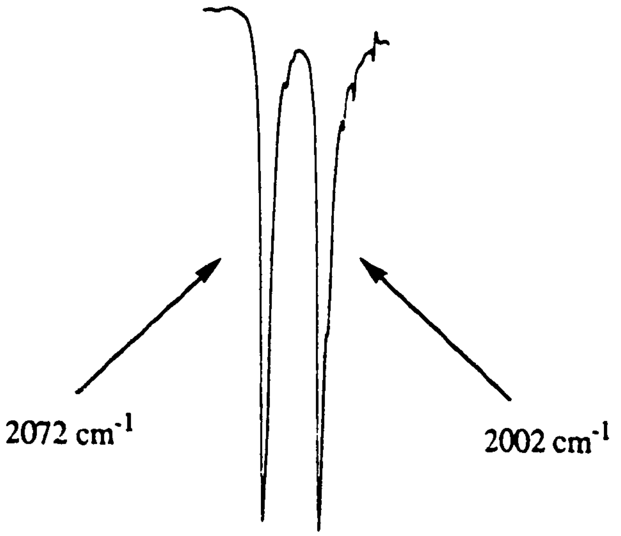
| $C_s$ | E | $\sigma_h$ |
|---|---|---|
| unshifted vectors | 2 | 0 |

$n_{irr} = 1/h\ \Sigma\ g_r \cdot \chi_{red}(R) \cdot \chi_{irr}(R)$

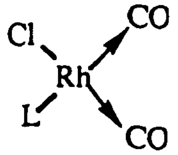
$n_{A'} = 1/2\ [(1 \cdot 1 \cdot 2) + (1 \cdot 1 \cdot 0)] = 1$

$n_{A''} = 1/2\ [(1 \cdot 1 \cdot 2) + (1 \cdot (-1) \cdot 0)] = 1$

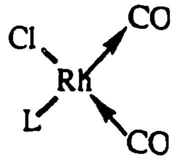
$\Gamma_{red} = A' + A''$; both are infrared active



A' symmetric stretching motion

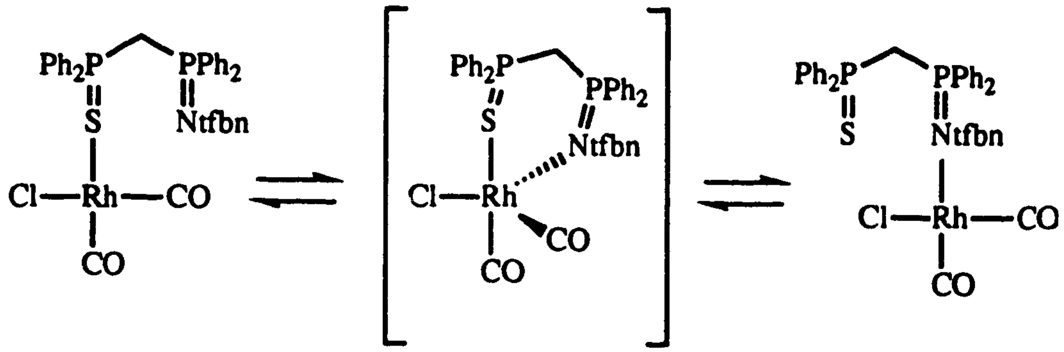


A'' asymmetric stretching motion

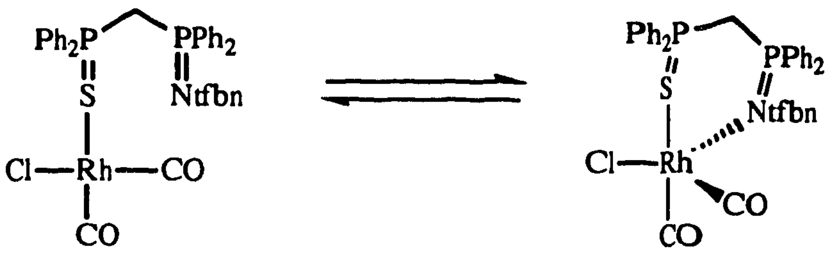


this indicates the presence of two CO ligands, therefore the expected loss of CO must not have occurred. The positions, in the infrared spectrum, of the ν(CO) bands indicate a terminal bonding mode for the CO ligands.

The NMR data for the monodentate complexes are, unfortunately, ambiguous. The $^{31}P\{^1H\}$ NMR spectrum for each compound contains two resonances both of which are very broad (CO, δ 32.93 and 6.90; cod, 32.05 and 5.48 ppm). Their assignment is based on comparing the phosphorus chemical shifts with those observed for the free ligand (δ 32.22, 5.50 ppm) and in rhodium-sulfur (~37 ppm) and rhodium-imino (~δ 30 ppm) chelates. This places P(N) upfield of P(S). These resonances cannot be resolved even at low temperatures. It is possible that it is the overlap of two-bond rhodium-phosphorus coupling through an imino nitrogen (typically 5 Hz),[31] four-bond fluorine-phosphorus coupling (typically 5 Hz; see Tables 2.4 and 2.7) and two-bond phosphorus-phosphorus coupling (typically 15-5 Hz; see Table 2.4) w[illegible] responsible for poor resolution. However, it may also imply some sort of fluxional process which is too fast to be resolved on the NMR time scale (at least down to *ca.* -80°C). One such process would involve the exchange of sulfur for the imino nitrogen in one coordination site on the metal. This could be envisioned as passing through a five coordinate intermediate.



Alternatively, the exchange process may involve only a brief attachment of the imino nitrogen.



The absence of any noticeable affect on ν(P=N) in the IR tends to support the latter. Five-coordinate rhodium metal centres have been previously proposed in a number of fluxional processes.[31,61,62]

Most diagnostic in the $^1$H NMR spectrum of the CO complex is the resonance for the methylene protons of the PCP backbone which appears as a triplet but is actually an overlapping doublet of doublets due to coupling to the two inequivalent phosphorus atoms. The values of the coupling were determined by $^1$H{$^{31}$P} experiments ($^2J_{HP(S)}$ 14.9 Hz, $^2J_{HP(N)}$ 12.5 Hz). Unfortunately, in the $^1$H NMR spectrum of the cod complex the backbone methylene resonance (δ 4 ppm) appears as a very broad singlet and was also overlapped by a broad resonance for one set of the methylene protons of the cod moiety (δ 4.25 ppm). There is a second broad resonance for the rest of the methylene protons of the cod (δ 2.48 ppm) and finally a broad resonance for the methine protons of cod at 1.79 ppm, which displays 8.3 Hz coupling to the $^{103}$Rh metal centre.

In the $^{13}$C{$^1$H} NMR spectrum the methylene carbon chemical shifts (L = L' = CO, δ 33.17 and LL' = cod 34.15 ppm) are comparable to those for other Rh/Ir complexes containing dppm(NR)$_2$ and dppmS$_2$ ligands.[7,31,34,61] The one-bond carbon-phosphorus coupling constants ($^1J_{CP(N)}$ = 49.9 and 54.2 Hz) support the notion that the imino nitrogen is not bonded to the rhodium centre (c.f. the values for the platinum and palladium {-S,N} cationic chelate complexes ($^1J_{CP(N)}$ = 66.4 and 69.4 Hz, respectively) and the free ligand ($^1J_{CP(N)}$ = 52.3 Hz)).

The $^{19}$F NMR spectrum possesses very broad resonances which were also unresolvable at low temperature. Thus, we cannot be sure if the broadening of the $^{31}P\{^1H\}$ resonances is due to a fluxional process or multiple, poorly resolved couplings. The $^{19}$F chemical shift difference for Pt/Pd complexed and uncomplexed Ntfbn (see Table 2.7) is significant (for *ortho* and *meta* F; $\Delta\delta$ ~13 and 4 ppm, respectively).

### 2.2.2 Cationic {-X,N} Bonded Chelates (X = S, Se)

#### $[(Ph_2P(X)CH_2P(Ntfbn)Ph_2\{-X,N\})Pt(PEt_3)Cl][ClO_4]$ (X = S, Se)

Synthesis of the platinum chelate compounds was accomplished by reacting the imino-chalcogenide bisphosphine with a solution of $[Pt(PEt_3)Cl_2]_2$ and $NaClO_4$ in acetone. The reaction succeeded only in the cases of the S and Se containing ligands and not for X = O. An attempt to complex the bisphosphinimine, $Ph_2P(Ntfbn)CH_2P(Ntfbn)Ph_2$, also failed. It appears that the nitrogen substituted tfbn is not sufficiently basic by itself nor in conjugation with a P(O) moiety to allow the ligand to coordinate.

The relevant data can be found in Tables 2.1, 2.4 through 2.12 and Figures 2.2 and 2.3.

Upon complexation there is a general shift of ν(P=N) (1510-09 cm$^{-1}$) and ν(P=S) (780 cm$^{-1}$) to lower frequencies (1489, 576 cm$^{-1}$, respectively) and this is indicative of the donation of the electron pairs on N and S to the metal centre. ν(CN) is clearly identifiable between 2233-2239 cm$^{-1}$, shifted to slightly higher frequencies by complexation. A new broad, strong band appears between 1100-1103 cm$^{-1}$ which can be assigned to the $ClO_4^-$ anion and is particularly useful in confirming the presence of the cationic chelate complex since in the mass spectrum only the pattern for the $Ph_2(X)CH_2P(Ntfbn)Ph_2)Pt(PEt_3)Cl$ fragment was observed.

The $^{31}P\{^1H\}$ NMR now contains three resonances which can be assigned to the three inequivalent phosphorus atoms in the product. The imine P(V) is shifted furthest downfield, P(III) on platinum is found furthest upfield and the P(X) phosphorus is in between. Assignments were made on the basis of observed one-bond phosphorus-selenium (581 Hz) and one-bond phosphorus-platinum (3342-3336 Hz) coupling. It is interesting that the imino phosphorus is now downfield of the chalcogen phosphorus. Strangely, there is coupling between the $Ph_2P(S)$ phosphorus and platinum (144-153 Hz) but there doesn't seem to be any resolvable coupling between the platinum metal centre and the imino phosphorus. This is significant in terms of the *trans* effect which will be discussed later to predict which geometrical isomer is formed. The resonance for the imino phosphorus experiences the greatest coordination shift (S = $\Delta\delta$ 29.9, Se = $\Delta\delta$ 30.3 ppm) indicating P=S has more of a dipolar form ($P^+$-$S^-$) vs P=N in the free ligand.

In general, there is shielding of the chalcogen phosphorus, a deshielding of the imino phosphorus and a decrease in $^2J_{PP}$ as the softness of the chalcogen increases. There is no effect on the chemical shift or $^1J_{CP(N)}$ for the methylene carbon (66.4 Hz), but $^1J_{CP(X)}$ decreases in the order S, Se ($\delta$ 41.2, 35.9 ppm, respectively). These values reflect the decreasing electronegativity of N, S, and Se (3.0, 2.5 and 2.4, respectively). The signal for the methylene protons is shifted downfield, while $^2J_{HP(X)}$ increases and $^2J_{HP(N)}$ decreases when S is replaced by Se.

The chemical shifts for the $^{19}F$ nuclei in the coordinated ligands $Ph_2P(X)CH_2P(Ntfbn)Ph_2$ (X = S , Se) are not greatly affected by coordination. The resonance for the Se atom is highly deshielded (from $\delta$ -274.13 to -131.51 ppm) and the coupling of the phosphorus to the selenium atom is greatly reduced (766 to 581

Hz). This is a direct measure of the donation of the electrons from the chalcogen to the metal centre and back donation from the metal into the $\pi^*$ orbital of the P=Se bond.

There are two possible geometrical isomers for the {-X,N} metal chelates. One has the $PEt_3$ group on platinum *trans* to the chalcogen while the other has the $PEt_3$ group *trans* to the nitrogen. An assignment can be made by considering how the magnitude of the phosphorus-platinum coupling between the metal centre and the phosphorus atoms in the bisphosphine ligand backbone is influenced by the antipodal groups on platinum (ie. the relative *trans* influences of the ligands on platinum). The *trans* influence is defined as the extent to which a coordinated ligand, L, weakens the bond *trans* to itself in the equilibrium state of the substrate.[63] This should not be confused with the *trans* effect which is defined as the effect that L has upon the rate of substitution of a ligand, L', *trans* to it.[64] Strong σ-donors and strong π-acid ligands are the most powerful *trans* influencing ligands. Both directly bonded and one-bond remote spin active nuclei in L' will experience a decrease in coupling to the NMR active metal when stronger *trans* influencing ligands, L, are located in a position opposite to them. It is believed that the decrease in coupling is the result of the monopolization of metal valence electron density by the *trans* ligand. This would in turn strengthen the M-L bond and weaken the M-L' bond. The literature has furnished the following *trans* influence series:[64,65]

$$H_2O < OH^- < NH_3, RNH_2, py < Cl^-, Br^- < SCN^- < I^- < NO_2^- < SO_3H^- < PR_3, SR_2,$$
$$SC(NH_2)_2 < CH_3^- < H^- < NO, CO, CN^-$$

For the cationic chelate complexes the remote spin active nucleus under consideration is phosphorus and the NMR active metal is platinum. Since coupling to the platinum metal centre is largest for the phosphorus nucleus bonded to the chalcogen and $PEt_3$ has a much stronger *trans* influence than Cl, it is safe to predict that the $PEt_3$ group is most probably located opposite to the imino phosphino group.

Indeed, the x-ray crystallographic determination of $[(Ph_2P(S)CH_2P(Ntfbn)Ph_2\{-S,N\})Pt(PEt_3)Cl]ClO_4$ confirms this conclusion:

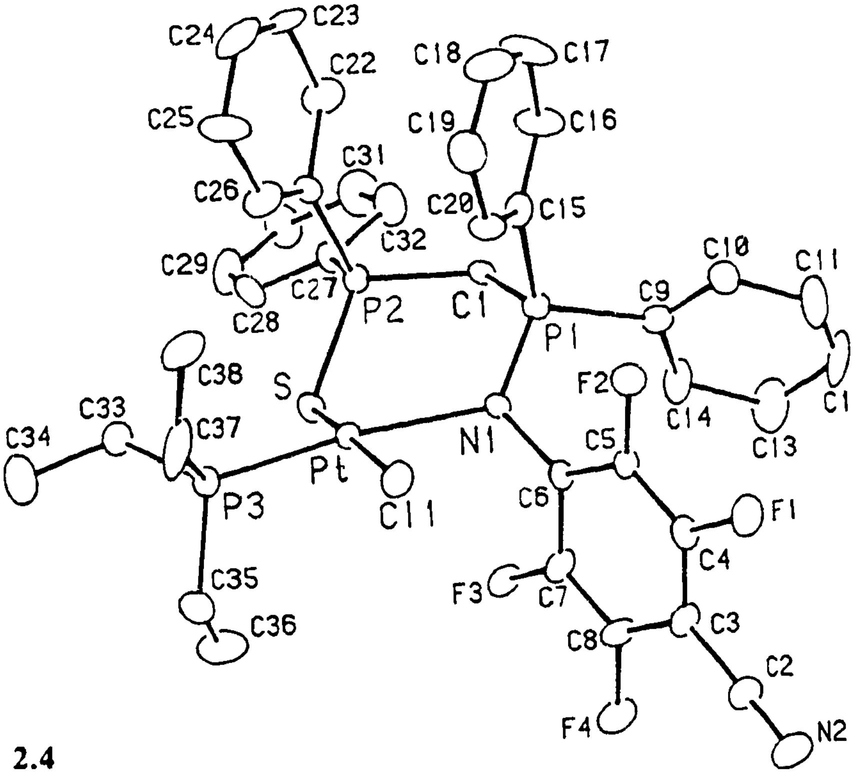


**Figure 2.4**

**The molecular structure for the cationic portion of $[(Ph_2P(S)CH_2P(Ntfbn)Ph_2\{-S,N\})Pt(PEt_3)Cl][ClO_4]$, hydrogen atoms have been omitted for clarity**

Pertinent crystallographic data is given in Tables 2.9-2.12. Though not shown, a discreet cation/anion pair was found with the counter anion being $ClO_4^-$. The ORTEP plot of the cationic fragment clearly shows the expected six-membered {-S,N} chelate ring. Crystal structures for related bistolylimino bisphosphine and bisphosphine disulfide complexes are available in the literature; namely $[Ph_2P(Ntolyl)CH_2P(Ntolyl)Ph_2\{-N,N\})Rh(cod)][PF_6]$, 1,[31,34] and

$[Ph_2P(S)CH_2P(S)(NEt_2)_2\{-S,S\})Pd(PEt_3)Cl][BF_4]$, 2[26]. The P=N bond length (1.598(9) Å) is comparable to those found in **1** (1.59(1) and 1.61(1) Å). The same can be said for the P=S bond length (2.001(5) Å) with respect to the P=S *trans* to the Cl atom in **2** (2.018(7) Å). Though there is no crystal structure for the free ligand, $Ph_2P(S)CH_2P(Ntfbn)Ph_2$, the shift of ν(P=N) and ν(P=S) to lower frequencies indicates the P=N and P=S bond lengths are longer than those in the free ligand. Indeed, related P=N bond lengths for various bisphosphinimine ligands (1.58-1.53 Å) and P=S bond lengths for the trisphosphinesulphide methanide ligand (1.944 Å) are shorter. An unusual feature is that the six-membered ring is in a chair conformation rather than the boat conformations observed for **1** and **2**.

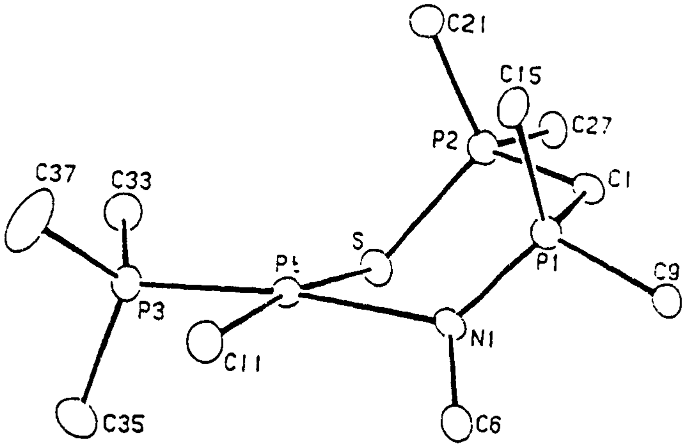


**Figure 2.5**

**Side-view $[(Ph_2P(S)CH_2P(Ntfbn)Ph_2\{-S,N\})Pt(PEt_3)Cl]^+$, substituents on N and P and hydrogen atoms have been omitted for clarity**

This could be due to the presence of a substituent on nitrogen which, for steric reasons, causes the phenyl rings to be eclipsed rather than staggered. The PCP angle of the ligand is larger (118.3°) than those observed in **1** and **2** (112.7 and 112.9°, respectively) also a result of having the phenyl rings eclipsing one another. There is approximately square planar geometry about the Pt metal with the metal raised slightly above the square plane.

### $[(Ph_2(S)CH_2P(Ntfbn)Ph_2\{-N,S\})Pd(PEt_3)Cl][ClO_4]$

The desired complex was made upon reaction of $Ph_2P(S)CH_2P(Ntfbn)Ph_2$ with a mixture of $[Pd(PEt_3)Cl_2]_2$ and $NaClO_4$ in acetone. The primary purpose of this reaction was to determine how the stability or reactivity of {-N,S} chelate complexes is affected by changing the metal centre. The palladium dimer was chosen because it gave stable {-S,S} chelate complexes with the bisphosphine disulfides.[26,59]

Upon complexation there is again a shift in ν(P=N) (1510 $cm^{-1}$) and ν(P=S) (780 $cm^{-1}$) to lower frequencies (1487 and 583 $cm^{-1}$, respectively) and the appearance of a band for $\nu(ClO_4)$ (1100 $cm^{-1}$) consistent with the formation of a cationic chelate complex. There is a shift in ν(CN) of the ligand (2218 $cm^{-1}$) to higher frequency (2233 $cm^{-1}$).

The $^{31}P\{^1H\}$ NMR showed three resonances which can be assigned to the three inequivalent phosphorus atoms in the product. The assignment is not as straightforward as it was in the case of the platinum complexes because there is no strong coupling between the metal and the phosphorus centres. The broad doublet located farthest upfield (δ 34.24 ppm) was assigned to the imino phosphorus and the broadening is attributed to poorly resolved phosphorus-fluorine coupling. A clearly resolved doublet of doublets was assigned to the P(S) phosphorus (δ 36.80 ppm). The singlet furthest downfield (δ 41.53 ppm) was assigned to the $PEt_3$ group on Pd. Dixon *et al*[59] have observed that the $PEt_3$ phosphorus resonance in the closely related bisphosphine disulfide complex is generally found downfield from the P(S) phosphorus resonance. Unlike in the platinum complex, P(N) has remained upfield of

P(S). Coordination shifts of $\Delta\delta$ 18.74 and 4.58 ppm are shown by the P(Ntfbn) and P(S) resonances, respectively.

The carbon and proton resonances for the methylene group are shielded ($\delta$ 32.40 ppm) and deshielded ($\delta$ 4.52 ppm) relative to the corresponding chemical shift values in the free ligand ($\delta$ 34.57 and 4.08ppm, respectively) and differ only slightly from those in the platinum complex ($\delta$ 31.41 and 4.54 ppm). The values of $^1J_{CP(S)}$ (43.3 Hz), $^2J_{HP(S)}$ (12.1 Hz) and $^2J_{HP(N)}$ (11.0 Hz) decrease and $^1J_{CP(N)}$ (69.4 Hz) increases with respect to their values in the free ligand (47.3, 13.6, 12.8 and 52.3 Hz, respectively). Again, the values of the former two are comparable with those for the platinum complex. In general, replacing Pt with Pd has little effect upon NMR parameters. There may be, however, a noticeable difference in bond lengths but this cannot be deduced without a crystal structure.

### 2.2.3 Neutral {-X,C} Bonded Metallacycles (X = S, Se)

#### (Ph$_2$(X)CHP(Ntfbn)Ph$_2${-X,C})Pt(PEt$_3$)Cl

The {-X,C} bonded complexes can be formed either through: (i) Deprotonation of the ligand using K$^t$BuO followed by subsequent reaction with $[Pt(PEt_3)Cl_2]_2$, or (ii) Deprotonation of the {-X,N} bonded chelate complexes with NaH (Figure 2.1). As with the cationic chelate complexes, the reactions were only successful with the S and Se chalcogens.

Complexation causes ν(P=N) to shift to lower frequency (1509-1504 cm$^{-1}$), though not quite as much as for the cationic chelates, and ν(CN) is shifted to higher frequencies (2239-2238 cm$^{-1}$). Bands for ν(P=X) were unresolved.

The $^{31}P\{^1H\}$ NMR spectrum contains three resonances which can be assigned to the three inequivalent phosphorus atoms in the product. The imine phosphorus in the

{-X,C} bonded complex does not experience as great a change in chemical shift relative to that in the free ligand as it does in the {-X,N} bonded chelate. The chalcogen bonded phosphorus is now found furthest downfield, the P(III) phosphorus is still the furthest upfield while the imine phosphorus resonates in an intermediate position. This assignment was based upon selenium satellite data (441 Hz), long range phosphorus-fluorine coupling ($^4J_{P(N)F}$ and $^7J_{P(Et_3)F}$ 5.6-5.3 and 3.2-3.1 Hz, respectively) and the magnitude of $^1J_{PEt_3Pt}$ (3000-2988 Hz). The coupling between P(X) and platinum (460-495 Hz) is significantly larger than that between P(N) and platinum (64 Hz). Interestingly, for the {-X,C} bonded complexes we observe P(N)-Pt coupling, which was not resolved in the {-X,N} chelates. This indicates that net coupling of P(N) to platinum through the framework of the four-membered ring is much stronger than the two bond coupling of P(N) to platinum through a datively-bonded nitrogen.

Information concerning the bonding of the Pt metal centre to the methine carbon can be obtained from the $^1H$ and $^{13}C\{^1H\}$ NMR spectra, which contain resonances for both the methine carbon and the methine proton. Both nuclei appear as a doublet of doublets of doublets due to coupling to all three inequivalent phosphorus atoms.

As with the {-X,N} chelates, there are two possible structures (geometrical isomers) for the {-X,C} bonded complexes. One has the $PEt_3$ group *trans* to the chalcogen and one has the $PEt_3$ group *trans* to the methine carbon. An x-ray structural analysis indicated that the latter geometry is adopted in the solid state.

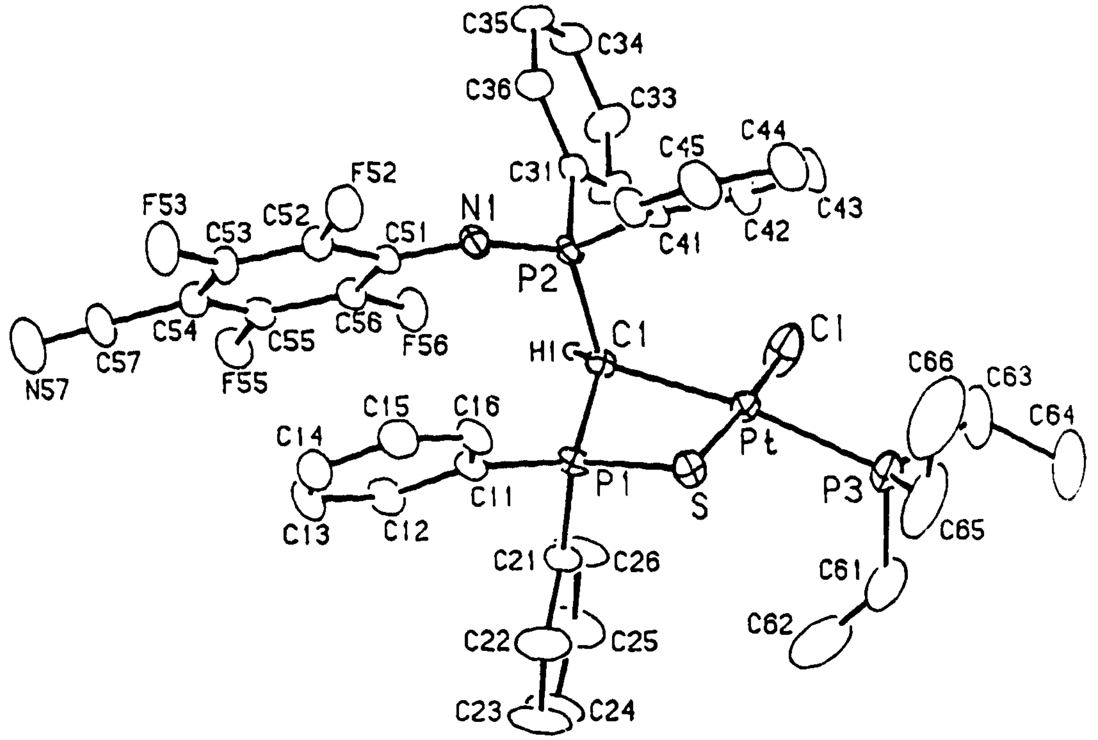


**Figure 2.6**

**The molecular structure of (Ph$_2$P(S)CHP(Ntfbn)Ph$_2${-S,C})Pt(PEt$_3$)Cl, hydrogen atoms have been omitted for clarity**

Pertinent structural information can be found in Tables 2.12 through 2.16. There are three complexes in the literature that we can use for comparison, these are (Ph$_2$P(Ntolyl)CHP(Ntolyl)Ph$_2${-N,C})Ir(cod), 3,[31] (Ph$_2$P(S)CHP(S)Ph$_2${-S,C})Pt(PEt$_3$)Cl, 4,[20] and [(Ph$_2$P(Ntolyl)CHP(N(H)tolyl)Ph$_2${-N,C})Rh(cod)]$^+$, 5.[31,34] The ORTEP diagram clearly shows that there is a four-membered {-S,C} bonded metallacycle in which the chalcogen is bonded to the platinum metal centre and the imino group remains uncomplexed. The ring is folded through the C-S axis (25.18 °). The four-membered metallacycles, 3, 5 and 4, are also folded along their C-N and C-S axes, respectively. The geometry about platinum is square planar with the metal raised slightly above the square plane. There is a loss in P-N-Ar planarity for the complexed imino group, this is consistent with the loss in planarity observed for the complexed imino group in **3** and **5**.

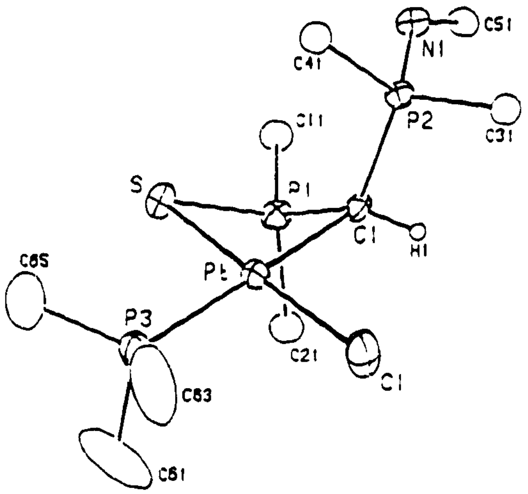


**Figure 2.7**

**Side-view of (Ph$_2$P(S)CHP(Ntfbn)Ph$_2${-S,C})Pt(PEt$_3$)Cl, substituents off of N and P and hydrogens have been omitted for clarity**

The uncomplexed imino group points away from the metal centre. This is consistent with the placement of the uncomplexed sulfur atom in **4** and the uncomplexed amino group in **5**, positions that appear sterically favourable for these substituents. It is , however, inconsistent with its bisphosphinime analog, **3**, whose uncomplexed imino group points towards the metal centre a position considered to be sterically favourable since the bonding interaction between the metal and the imino nitrogen in **3** may be considered to be negligible (d(N1-Ir) = 3.84(1) Å). Since the free ligand is most closely related to that of **3** it is strange that it should mimic **4** and **5**. Upon closer examination, however, we see that electronic arguments may now become important. It appears that there may be a favourable interaction between the π-clouds of the electron-deficient tfbn and an electron-rich phenyl group on the P(S) phosphorus. This phenomenon has been seen with a number of ligands, that our group has synthesized, containing Ph$_2$P=NR where R is highly electron withdrawing (dppmNtfbn, dppm(NT)(Ntfbn) and dppm(N-$C_6H_4$-2,4-$(NO_2)_2$-5-F)).[66-68] This is, however, the first metal complex in which we have observed this behaviour. The planes which contain the rings of interest deviate from parallel by an angle of 5.5°. The distance between the centre of one of the rings and the plane of the other varies between 3.410 and 3.368 Å. The average interatomic distance between the layers in graphite, *ca.* 3.35 Å, suggests that these are reasonable distances over which an interaction between two arene rings could occur. The data is far from conclusive, however, since this is a distance that is frequently seen between phenyl rings on adjacent phosphorus atoms, in many A-frame complexes containing bridging dppm, whose orientation one would expect to be due strictly to packing and not electronic effects. The P=S bond length (2.016(2) Å) is close to that observed in **4** (2.014(5) Å) and its lengthening with respect to a free P=S linkage (1.936(4) Å) reflects the use of the lone pair on S for coordination to the metal centre and perhaps some backbonding into the P=S $\pi^*$ orbital. The P(1)-C(1) bond length (1.771(4) Å) is virtually identical to that observed in **3** (1.77(1) Å) but is shorter than that observed for **2** (1.821(12) Å) suggesting that there is some ylide character to the bonding.[69] The Pt-S bond (2.312(1) Å) is shorter than that of **4** (2.390(4) Å) since the P(S) group in **4** is *trans* to $PEt_3$ while in our structure the P(S) group is bonded across from a much more weakly *trans* influencing $Cl^-$ ligand. The P=N bond length (1.591(4) Å) is slightly longer that that of a free P=N (1.57 Å) but shorter than the complexed P=N in **1** (1.62(1) Å). It seems likely that inductive effects alter the P=N and such effects can perhaps explain the loss of planarity in the P-N-Ar linkage.

## ($Ph_2$P(S)CHP(Ntfbn)$Ph_2${-C,S})Rh(cod)

The {-S,C} bonded rhodium metallacycle, ($Ph_2$P(S)CHP(Ntfbn)$Ph_2${-C,S})Rh(cod), was synthesized by deprotonating

$Ph_2P(S)CH_2P(Ntfbn)Ph_2$ with $K^tBuO$ and reacting the anion so formed with $[Rh(cod)Cl]_2$. High quality orange-yellow crystals were obtained from a dichloromethane/hexane layer.

Complexation does not seem to affect ν(P=N) (1511 $cm^{-1}$), however there is a decrease in ν(P=S) (604 $cm^{-1}$) and a decrease in ν(CN) (2222 $cm^{-1}$).

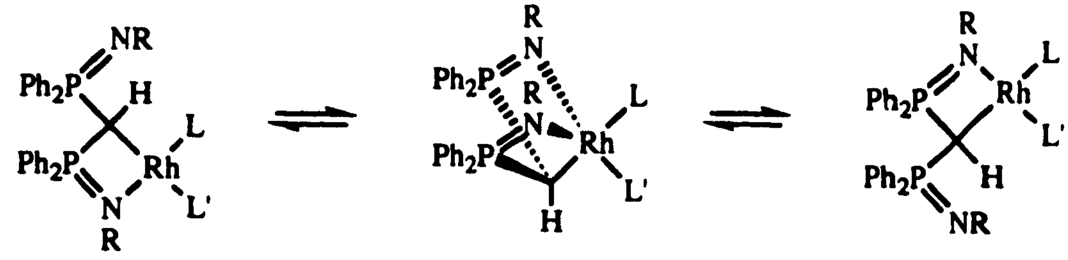
Dramatic affects of complexation are seen in the NMR spectra. The $^{31}P\{^1H\}$ NMR spectrum contains one broad doublet (δ 28.85, $^2J_{PP}$ 14.58 Hz) and one very broad singlet (δ 14.47). The doublet was shown by $^{31}P\{^{31}P\}$ decoupling experiments to arise from intra-chelate $^{31}P$-$^{31}P$ coupling. We were unable, however, to further resolve these resonances during low temperature NMR studies. This suggests that a fluxional process may be occurring or alternatively that the coupling of the phosphorus atoms to rhodium (typically 3-4 Hz through the P=N)[31] may be sufficiently large to prevent resolution on the 400 MHz instrument. If we follow the previously observed trend for the Pt and Pd complexes and place the P(S) phosphorus downfield from the (N) phosphorus and compare the chemical shifts with those observed for the Pt/Pd {-N,C} metallacycles (δ 47.00/42.84 and 15.00/15.42, ppm respectively) we see that the environment about P(N) is similar but that around P(S) is quite different. However, the resolution of coupling in P(N) is quite poor compared to that of P(S).

The $^{19}F$ NMR chemical shifts (*meta* F δ -140.94 and *ortho* F -153.15 ppm) compare nicely to the platinum/palladium analogs (δ -140.76/-141.55 and -152.85/-153.81 ppm).

The $^1H$ NMR spectrum is poorly resolved. The methine proton resonance is a broad signal at δ 2.76 ppm. The cod methylene and methine proton resonances are broad singlets at δ 1.95/1.67 and 4.12 ppm, respectively.

The $^{13}C\{^1H\}$ NMR spectrum shows a doublet of doublets of doublets for the methine carbon of the PCP backbone (δ 6.33 ppm, $^1J_{CP(S)}$ 51.5 , $^1J_{CP(N)}$ 33.7, $^1J_{CRh}$ 17.2 Hz)

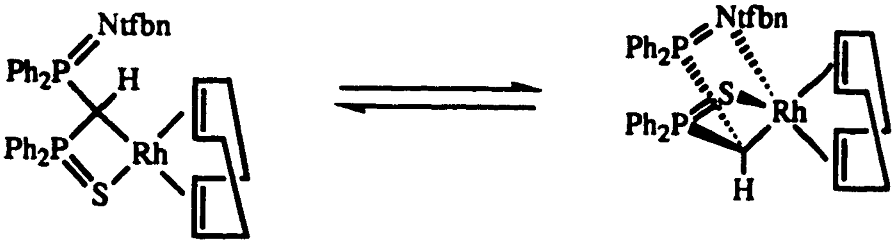
Referring to the $^1H$ and $^{31}P\{^1H\}$ NMR spectra of the analogous compound, (Ph$_2$P(Ntolyl)CHP(Ntolyl)Ph$_2${-N,C})Rh(cod) (**6**)[31] the two halves of the bisphosphinimine as well as both ligands *trans* to the N and C atoms became equivalent on the NMR time scale. A fluxional process involving a five-coordinate intermediate for the rhodium centre was postulated.



LL' = cod

R = tolyl

Because of the similarity of the data for complex **6** and (Ph$_2$P(S)CHP(Ntfbn)Ph$_2${-S,C})Rh(cod) it is also possible to invoke a fluxional process for the latter but since δ P(N) and ν(P=N), ν(CN) are not greatly different from those values for the static Pt/Pd {-S,C} bonded complexes, the mechanism for exchange may only involve a brief attachment of the N to the metal centre and not involve the formation of a {-C,N} bonded metallacycle.



The proposed formulation for the {-C,S} rhodium complex is supported by elemental and mass spectral analyses and compares favourably to the NMR data obtained for the analogous {-C,S} bonded platinum species. It is clearly imperative that these crystals be analyzed by x-ray diffraction to verify the structure for the {-C,S} bonded rhodium complex.

To sum up, the reaction of rhodium with the deprotonated ligand results in the formation of the {-C,X} metallacycle. Thus, the imino-chalcogenide ligands mimic the coordination chemistry of the bisphosphinimines. In contrast the bisphosphine dichalcogenides in rhodium complexes prefer to form the {-X,X} anionic chelate (X = S, Se).[19]

### 2.2.4 Cationic {-X,C} Bonded Metallacycles (X = S)

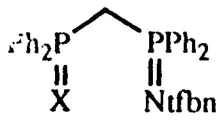
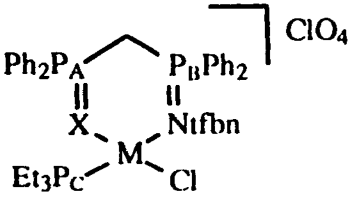
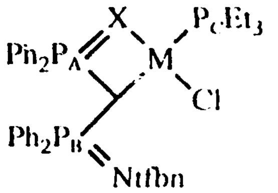
#### [($Ph_2P(S)CHP(N(H)tfbn)Ph_2${-S,C})Pt($PEt_3$)Cl][$BF_4$]

The reaction of the {-S,C} metallacycle, ($Ph_2P(S)CHP(Ntfbn)Ph_2${-S,C})Pt($PEt_3$)Cl, with $HBF_4$ was investigated. There were two possible sites of attachment for the proton, the carbon on the PCP backbone and the imino nitrogen. The former is observed for the analogous bisphosphine dichalcogenide ligands while the latter is observed for analogous bisphosphinimine ligands.[31,33,34] Spectroscopic data for the product indicated the four-membered metallacycle remained intact and it was the imino nitrogen that had been protonated forming [($Ph_2P(S)CHP(N(H)tfbn)Ph_2${-S,C})Pt($PEt_3$)Cl][$BF_4$]. Three resonances are observed in the $^{31}P\{^1H\}$ NMR spectrum. The chalcogen-bonded P(V) is found furthest downfield, the P(III) on platinum is found furthest upfield and the nitrogen-bonded phosphorus is found in between. Assignments were based on phosphorus-platinum coupling data ($^1J_{PPt}$ 3081, $^2J_{P(S)Pt}$ 360, $^2J_{P(N)Pt}$ 85 Hz).

Interestingly, the resonances for the P(N) and $PEt_3$ phosphorus atoms no longer exhibit coupling to the *ortho*-fluorines of the tfbn group. Since attachment of the proton to the carbon on the PCP backbone would have led to the formation of the {-S,N} chelate (δ 35.41 ppm), the chemical shift of P(N) (δ 40.09 ppm) indicated the formation of an amino group. Indeed, in the $^1H$ NMR spectrum the N(H) proton was a clearly visible as a doublet at δ 9.13 ppm. $^1H\{^{31}P\}$ decoupling experiments assigned the coupling ($^2J_{HP}$ 4.3 Hz) to the imino phosphorus. The methine proton (δ 3.02 ppm) remained coupled to all three phosphorus atoms ($^2J_{HP(S)}$ 5.0, $^2J_{HP(N)}$ 13.2, $^3J_{HPEt_3}$ 6.1 Hz) which indicated that the {-S,C} metallacyclic unit remained intact. In the $^{13}C\{^1H\}$ NMR spectrum the methine carbon, even further shielded (δ 2.02 ppm), remains coupled to all three phosphorus atoms ($^2J_{CP(S)}$ 72.5, $^2J_{CP(N)}$ 69.2, $^3J_{CPEt_3}$ 44.0 Hz). Recrystallization of the cationic {-S,C} metallacycle, from a deuterated solvent mixture resulted in the formation of the cationic {-S,N} chelate which would require the transfer of the proton on the amino nitrogen to the methine carbon of the PCP backbone. It would seem that protonation of the imino nitrogen is kinetically favourable while the protonation of the PCP backbone is thermally favourable; therefore, for {-S,C} bonded metallacycles such chemistry could likely be tailored by the choice of substituent on the imino nitrogen.

**Table 2.1**

**IR Stretching Frequencies for the Imino-Chalcogenide Bisphosphine Ligands $Ph_2P(X)CH_2P(Ntfbn)Ph_2$ (X = O, S, Se) and the metal complexes $[(Ph_2P(X)CH_2P(Ntfbn)Ph_2\{-X,N\})M(PEt_3)Cl][ClO_4]$ and $(Ph_2P(X)CHP(Ntfbn)Ph_2\{-X,C\})M(PEt_3)Cl$ (X = S, Se; M = Pt, Pd)**

| Compound | X | M | v(P=N) (cm$^{-1}$) | v(P=X) (cm$^{-1}$) | v(CN) (cm$^{-1}$) | v(ClO$_4$) (cm$^{-1}$) |
|---|---|---|---|---|---|---|
|  | O | - | 1511 s | 1213 m | 2233 w | - |
| | S | - | 1510 s | 780 m | 2218 w | - |
| | Se | - | 1509 s | 520 w | 2229 w | - |
|  | S | Pt | 1489 s | 576 m | 2239 w | 1100 s br |
| | Se | Pt | 1489 s | nr | 2238 w | 1103 s br |
| | S | Pd | 1487 s | 583 m | 2233 w | 1100 s br |
|  | S | Pt | 1509 s | nr | 2228 w | - |
| | Se | Pt | 1504 s | nr | 2227 w | - |
| | S | Pd | 1506 s | nr | 2224 w | - |

m medium
s strong
w weak

br broad
nr not resolved

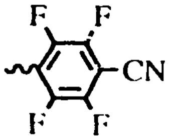
tfbn = 

**Table 2.2**

**The Influence of $C_nH_m$ in $Ph_2P(S)C_nH_mP(Ntfbn)Ph_2$ on Selected IR Frequencies:**

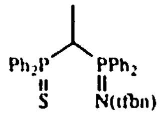
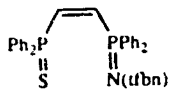
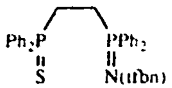
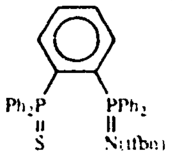
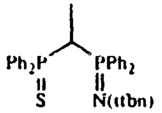
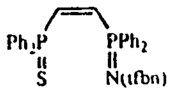
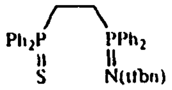
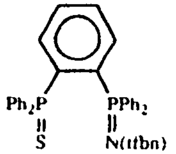
| Compound | ν(P=N) $(cm^{-1})$ | ν(CN) $(cm^{-i})$ |
|---|---|---|
|  | 1510 | 2218 |
|  | 1519 | 2231 |
|  | 1507 | 2227 |
|  | 1506 | 2232 |
|  | 1507 | 2124 |

**Table 2.3**

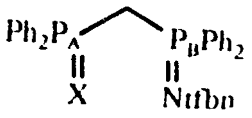
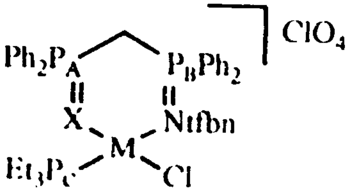
**Effect of Changing $C_nH_m$ of $Ph_2P_A(S)C_nH_mP_B(Ntfbn)Ph_2$ on the $^{31}P\{^1H\}$ Parameters**

| Compound | $P_A$ (ppm) | $P_B$ (ppm) | $J_{PP}$ (Hz) |
|---|---|---|---|
|  | 32.22 | 5.50 | 9.5 |
|  | 45.47 | 14.72 | nr |
|  | 28.93 | -1.68 | 19.8 |
|  | 44.31 | 17.22 | 56.7 |
|  | 44.93 | 12.16 | 7.3 |

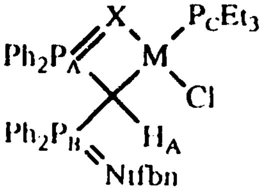
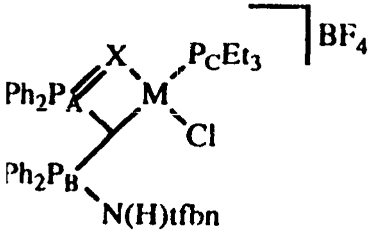
nr     not resolved

**Table 2.4**

$^{31}P\{^1H\}$ NMR data* for $Ph_2P(X)CH_2P(Ntfbn)Ph_2$ (X = O, S, Se) and the metal complexes $[(Ph_2P(X)CH_2P(Ntfbn)Ph_2\{\text{-}X,N\})M(PEt_3)Cl][ClO_4]$, $(Ph_2P(X)CHP(Ntfbn)Ph_2\{\text{-}X,C\})M(PEt_3)Cl$ and $[(Ph_2P(S)CHP(N(H)tfbn)Ph_2\{\text{-}S,C\})Pt(PEt_3)Cl][BF_4]$ (X = S, Se; M = Pt, Pd)

| Compound | M | X | δ $P_A$ (ppm) | δ $P_B$ (ppm) | δ $P_C$ (ppm) | $J_{PP}$ (Hz) | $J_{PPt}$ (Hz) | $J_{PSe}$ (Hz) | $J_{PF}$ (Hz)** |
|---|---|---|---|---|---|---|---|---|---|
|  | - | O | 21.84 d | 7.15 dt | - | $^2J_{P_AP_B}$ 11.9 | - | - | $^4J_{P_BF}$ 5.6 |
| | - | S | 32.22 d | 5.50 dt | - | $^2J_{P_AP_B}$ 9.5 | - | - | $^4J_{P_BF}$ 5.2 |
| | - | Se | 20.63 d | 5.61 dt | - | $^2J_{P_AP_B}$ 8.8 | - | $^1J_{P_ASe}$ 766 | $^4J_{P_BF}$ 6.1 |
|  | Pt | S | 30.94 dd | 35.41 ddt | 6.88 ddt | $^2J_{P_AP_B}$ 14.6 | $^2J_{P_APt}$ 144<br>$^1J_{P_CPt}$ 3342 | - | $^4J_{P_BF}$ nr |
| | Pt | Se | 12.00 dd | 35.86 ddt | 5.29 ddt | $^2J_{P_AP_B}$ 13.7 | $^2J_{P_APt}$ 153<br>$^1J_{P_CPt}$ 3336 | $^1J_{P_ASe}$ 581 | $^4J_{P_BF}$ nr |
| | Pd | S | 36.80 dd | 34.24 d br | 41.53 s br | $^2J_{P_AP_B}$ 15.6 | - | - | $^4J_{P_BF}$ nr |

## Table 2.4 Continued

| Compound | M | X | δ $P_A$ (ppm) | δ $P_B$ (ppm) | δ $P_C$ (ppm) | $J_{PP}$ (Hz) | $J_{PPt}$ (Hz) | $J_{PSe}$ (Hz) | $J_{PF}$ (Hz)** |
|---|---|---|---|---|---|---|---|---|---|
|  | Pt | S | 47.00 dd | 15.00 ddt | 5.30 ddt | $^2J_{P_AP_B}$ 6.2<br>$^3J_{P_AP_C}$ 13.7<br>$^3J_{P_BP_C}$ 8.5 | $^2J_{P_APt}$ 460<br>$^2J_{P_BPt}$ 64<br>$^1J_{P_CPt}$ 3000 | - | $^4J_{P_BF}$ 5.6<br>$^7J_{P_CF}$ 3.2 |
| | Pt | Se | 26.90 dd | 15.00 ddt | 4.70 ddt | $^2J_{P_AP_B}$ 5.7<br>$^3J_{P_AP_C}$ 13.7<br>$^3J_{P_BP_C}$ 9.9 | $^2J_{P_APt}$ 495<br>$^2J_{P_BPt}$ 64<br>$^1J_{P_CPt}$ 2988 | $^1J_{P_ASe}$ 441 | $^4J_{P_BF}$ 5.3<br>$^7J_{P_CF}$ 3.1 |
| | Pd | S | 42.84 dd | 15.42 ddt | 24.51 ddt | $^2J_{P_AP_B}$ 4.5<br>$^3J_{P_AP_C}$ 12.5<br>$^3J_{P_BP_C}$ 11.8 | - | - | $^4J_{P_BF}$ 6.2<br>$^7J_{P_CF}$ 4.6 |
|  | Pt | S | 50.69 dd | 40.09 dd | 8.45 dd | $^2J_{P_AP_B}$ 17.0<br>$^3J_{P_AP_C}$ 13.8<br>$^3J_{P_BP_C}$ 15.6 | $^2J_{P_APt}$ 360<br>$^2J_{P_BPt}$ 85<br>$^1J_{P_CPt}$ 3081 | - | - |

| | |
|---|---|
| s | singlet |
| d | doublet |
| dd | doublet of doublets |
| dt | doublet of triplets |
| ddt | doublet of doublets of triplets |

| | |
|---|---|
| * | Chemical shifts δ in ppm in $CD_2Cl_2$ with respect to 85% $H_3PO_4$ |
| ** | *ortho* fluorine of tfbn |
| br | broad |
| nr | not resolved |

Table 2.5

$^1H$ NMR data* for the methylene and methine protons in $Ph_2P(X)CH_2P(Ntfbn)Ph_2$ (X = O, S, Se) and the metal complexes $[(Ph_2P(X)CH_2P(Ntfbn)Ph_2\{-X,N\})M(PEt_3)Cl][ClO_4]$, $(Ph_2P(X)CHP(Ntfbn)Ph_2\{-X,C\})M(PEt_3)Cl$ and $[(Ph_2P(S)CHP(N(H)tfbn)Ph_2\{-S,C\})M(PEt_3)Cl][BF_4]$ (X = S, Se; M = Pt, Pd)

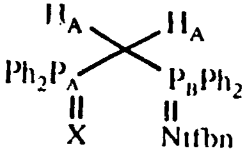
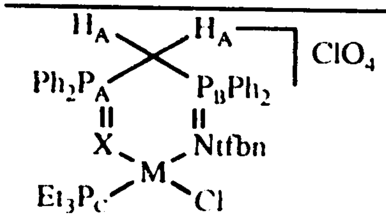
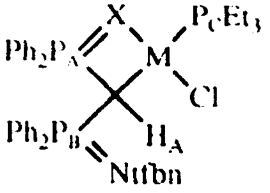
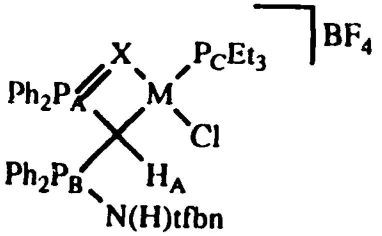
| Compound | M | X | $\delta$ $H_A$ (ppm) | $^2J_{H_AP_A}$ (Hz) | $^2J_{H_AP_B}$ (Hz) | $^2J_{H_AP_C}$ (Hz) |
|---|---|---|---|---|---|---|
|  | - | O | 3.83 dd | 12.7 | 13.3 | - |
|  | - | S | 4.08 dd | 13.6 | 12.8 | - |
|  | - | Se | 4.22 dd | 14.0 | 12.6 | - |
|  | Pt | S | 4.54 dd | 12.3 | 13.4 | - |
|  | Pt | Se | 4.63 dd | 14.8 | 12.9 | - |
|  | Pd | S | 4.52 dd | 12.1 | 11.0 | - |
|  | Pt | S | 3.48 ddd | 6.7 | 8.6 | 6.7 |
|  | Pt | Se | 3.47 ddd | 6.5 | 8.2 | 8.2 |
|  | Pd | S | 3.00 dddt | 4.7 | 6.8 | 6.8 |

**Table 2.5 continued**

| Compound | M | X | $\delta H_A$ (ppm) | $^2J_{H_AP_A}$ (Hz) | $^2J_{H_AP_B}$ (Hz) | $^2J_{H_AP_C}$ (Hz) |
|---|---|---|---|---|---|---|
|  | Pt | S | 3.02 ddd | 5.0 | 13.2 | 6.1 |

dd doublet of doublets
ddd doublet of doublets of doublets
dddt doublet of doublets of doublets of triplets

* Chemical shifts δ in ppm with respect to $SiMe_4$

**Table 2.6**

${}^{13}C\{{}^{1}H\}^{*}$ NMR data for the methylene and methine carbons in $Ph_2P(X)CH_2P(Ntfbn)Ph_2$ (X = O, S, Se) and the metal complexes $[(Ph_2P(X)CH_2P(Ntfbn)Ph_2\{-X,N\})M(PEt_3)Cl][ClO_4]$, $(Ph_2P(X)CHP(Ntfbn)Ph_2\{-X,C\})M(PEt_3)Cl$ and $[(Ph_2P(S)CHP(N(H)tfbn)Ph_2\{-S,C\})Pt(PEt_3)Cl][BF_4]$ (X = S, Se; M = Pt, Pd)

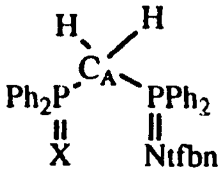
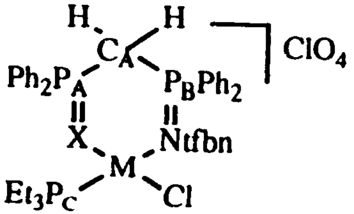
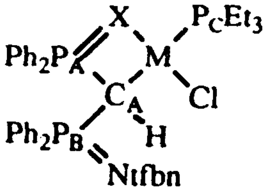
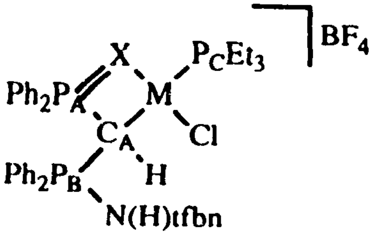
| Compound | M | X | δ $C_A$ (ppm) | $^1J_{C_AP_A}$ (Hz) | $^1J_{C_AP_B}$ (Hz) | $^2J_{C_AP_C}$ (Hz) |
|---|---|---|---|---|---|---|
|  | - | O | 33.04 dd | 59.3 | 49.9 | - |
| | - | S | 34.57 dd | 47.3 | 52.3 | - |
| | - | Se | 34.36 dd | 39.8 | 53.1 | - |
|  | Pt | S | 31.41 dd | 41.2 | 66.4 | - |
| | Pt | Se | 30.99 dd | 35.9 | 66.4 | - |
| | Pd | S | 32.40 dd | 43.3 | 69.4 | - |
|  | Pt | S | 9.89 ddd | 80.9 | 53.8 | 30.6 |
| | Pt | Se | 10.23 ddd | 81.4 | 52.4 | 21.9 |
| | Pd | S | 5.19 ddd | 89.0 | 53.3 | 36.0 |

Table 2.6 continued

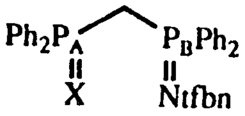
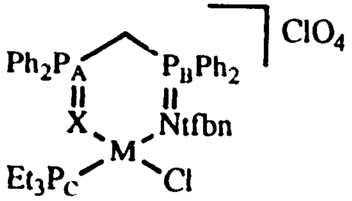
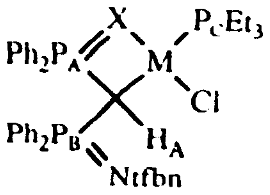
| Compound | M | X | δ $C_A$ (ppm) | $^1J_{C_AP_A}$ (Hz) | $^1J_{C_AP_B}$ (Hz) | $^2J_{C_AP_C}$ (Hz) |
|---|---|---|---|---|---|---|
|  | Pt | S | 2.02 ddd | 72.5 | 69.2 | 44.0 |

dd doublet of doublets
ddd doublet of doublets of doublets

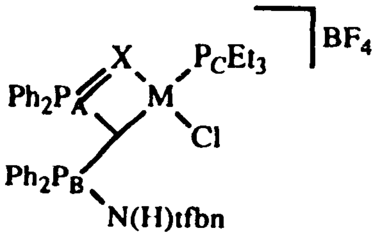
* Chemical shifts δ in ppm with respect to $SiMe_4$

**Table 2.7**

$^{19}F$ NMR data* for $Ph_2P(X)CH_2P(Ntfbn)Ph_2$ (X = O, S, Se) and the metal complexes $[(Ph_2P(X)CH_2P(Ntfbn)Ph_2\{-X,N\})M(PEt_3)Cl][ClO_4]$, $(Ph_2P(X)CHP(Ntfbn)Ph_2\{-X,C\})M(PEt_3)Cl$ and $[(Ph_2P(S)CHP(N(H)tfbn)Ph_2\{-S,C\})Pt(PEt_3)Cl][BF_4]$ (X = S, Se; M = Pt, Pd)

| Compound | M | X | δ $F_A$ (ppm)** | δ $F_B$ (ppm)** | $J_{FP}$ (Hz) | $J_{FH}$ (Hz) |
|---|---|---|---|---|---|---|
|  | - | O | -153.20 dd | -139.88 d | $^4J_{F_AP_B}$ 6.0 | - |
| | - | S | -152.81 dd | -139.77 d | $^4J_{F_AP_B}$ 6.0 | - |
| | - | Se | -152.70 dd | -139.75 d | $^4J_{F_AP_B}$ 5.5 | - |
|  | Pt | S | -139.98 d | -136.32 d | $^4J_{F_AP_B}$ nr | - |
| | Pt | Se | -139.79 d | -137.04 d | $^4J_{F_AP_B}$ nr | - |
| | Pd | S | -141.51 d | -136.85 d | $^4J_{F_AP_B}$ nr | - |
|  | Pt | S | -152.85 d | -140.76 d | $^4J_{F_AP_B}$ nr | - |
| | Pt | Se | -152.82 d | -140.90 d | $^4J_{F_AP_B}$ 5.0 | - |
| | Pd | S | -153.81 dddd | -141.55 dd | $^4J_{F_AP_B}$ 6.0<br>$^5J_{F_BP_B}$ 2.0<br>$^6J_{F_AP_A}$ 2.0 | $^6J_{F_AH_A}$ 5.0 |

## Table 2.7 continued

| Compound | M | X | δ $F_A$ (ppm)** | δ $F_B$ (ppm)** | $J_{FP}$ (Hz) | $J_{HH}$ (Hz) |
|---|---|---|---|---|---|---|
|  | Pt | S | -143.50 d | -133.15 d | - | - |

| | |
|---|---|
| d | doublet |
| dd | doublet of doublets |
| nr | not resolved |

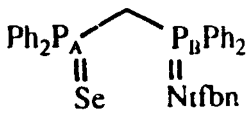
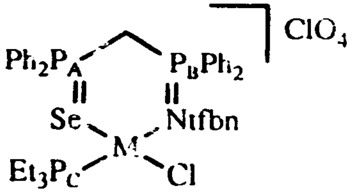
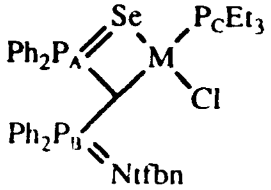
* Chemical shifts δ in ppm with respect to $CFCl_3$

** $F_A$ *ortho* fluorine on tfbn

$F_B$ *meta* fluorine on tfbn

**Table 2.8**

**$^{77}$Se NMR data* for $Ph_2P(Se)CH_2P(Ntfbn)Ph_2$ and the metal complexes $[(Ph_2P(Se)CH_2P(Ntfbn)Ph_2\{\text{-}Se,N\})Pt(PEt_3)Cl][ClO_4]$ and $(Ph_2P(Se)CHP(Ntfbn)Ph_2\{\text{-}Se,C\})Pt(PEt_3)Cl$**

| Compound | δ Se (ppm) | $J_{SeP}$ (Hz) | $J_{SePt}$ (Hz) |
|---|---|---|---|
|  | -274.18 d | $^1J_{SeP_A}$ 766 | - |
|  | -131.51 d | $^1J_{SeP_A}$ 579 | $^1J_{SePt}$ nr |
|  | -209.41 d | $^1J_{SeP_A}$ 443 | $^1J_{SePt}$ 101 |

* Chemical shifts δ in ppm with respect to $Me_2Se_2$

## Table 2.9

## X-RAY DATA FOR [($Ph_2P(S)CH_2P(Ntfbn)Ph_2\{\text{-}S,N\}$)Pt($PEt_3$)Cl][$ClO_4$] [Report Reference Code SDL:RGC9205]

### Crystal Data

| | |
|---|---|
| Empirical formula | $C_{38}H_{37}Cl_2N_2O_4P_3PtS$ |
| F.W. (g/mol) | 1044.73 |
| Space Group | Monoclinic $C_c$ |
| a (Å) | 18.369(3) |
| b (Å) | 13.987(2) |
| c (Å) | 16.040(3) |
| β (°) | 91.54(1) |
| Volume (Å$^3$) | 4119.6 |
| Density (g/cm$^{-3}$) | 1.684 |
| μ (cm$^{-1}$) | 37.88 |

### Data Collection and Refinement Parameters

| | |
|---|---|
| Radiation | MoKα (λ = 0.7107 Å ) |
| Monochromator | incident beam, graphite crystal |
| Take-off angle | 3.0° |
| Detector aperture | (3.00 + tan θ) mm horiz x 4.00 mm vert |
| Crystal-to-detector distance | 173 mm |
| Scan type | θ-2θ |
| Scan rate | 6.7-1.3 °/min |
| Scan width | 0.5 + 0.347 tan θ° |
| Data collection 2θ limit | 50.0° |
| Data collection index range | $h$, $k$, +/- $l$ |
| Reflections measured | 3916 total, averaged: 3335 with I > 3σ(I) |
| Observations: variables ratio | 3335: 469 |
| Agreement factors $R_1$, $R_2$, GOF | 0.046, 0.062, 2.277 |
| Corrections applied | absorption correction |

**Table 2.10**

**Selected Interatomic Bond s (Å) for**
**[(Ph$_2$P(S)CH$_2$P(Ntfbn)P )Pt(PEt$_3$)Cl][ClO$_4$]**

| Atoms | Distance (Å) | Atoms | Distance (Å) |
|---|---|---|---|
| Pt-Cl(1) | 2.293(3) | P(2)-C(1) | 1.82(1) |
| Pt-S | 2.325(3) | P(2)-C(21) | 1.78(1) |
| Pt-P(3) | 2.180(3) | P(2)-C(27) | 1.81(1) |
| Pt-N(1) | 2.239(9) | P(3)-C(33) | 1.79(1) |
| Cl(2)-O(1) | 1.42(1) | P(3)-C(35) | 1.80(1) |
| Cl(2)-O(2) | 1.42(1) | P(3)-C(37) | 1.79(2) |
| Cl(2)-O(3) | 1.36(2) | F(1)-C(4) | 1.32(1) |
| Cl(2)-O(4) | 1.40(2) | F(2)-C(5) | 1.33(1) |
| S-P(2) | 2.001(5) | F(3)-C(7) | 1.33(2) |
| P(1)-N(1) | 1.598(9) | F(4)-C(8) | 1.35(2) |
| P(1)-C(1) | 1.800(9) | N(1)-C(6) | 1.41(1) |
| P(1)-C(9) | 1.81(1) | N(2)-C(2) | 1.10(2) |
| P(1)-C(15) | 1.79(2) | C(2)-C(3) | 1.43(2) |

**Table 2.11**

**Selected Interatomic Angles (°) for**
**[(Ph$_2$P(S)CH$_2$P(Ntfbn)Ph$_2${-S,N})Pt(PEt$_3$)Cl][ClO$_4$]**

| Atoms | Angle (°) |
|---|---|
| Cl(1)-Pt-S | 172.2(1) |
| Cl(1)-Pt-P(3) | 90.6(1) |
| Cl(1)-Pt-N(1) | 86.9(2) |
| S-Pt-(P3) | 92.4(1) |
| S-Pt-N(1) | 89.3(2) |
| P(3)-Pt-N(1) | 173.1(2) |
| N(1)-P(1)-C(1) | 110.4(5) |
| S-P(2)-C(1) | 110.7(4) |
| Pt-N(1)-P(1) | 124.1(5) |
| P(1)-C(1)-P(2) | 118.3(6) |

## Table 2.12

**Selected* Atomic Coordinates (x $10^3$) and Equivalent Isotropic Displacement Parameters (Å, x $10^2$) for $[(Ph_2P(S)CH_2P(Ntfbn)Ph_2\{-S,N\})Pt(PEt_3)Cl][ClO_4]$**

| Atom | *x* | *y* | *z* | *U* |
|---|---|---|---|---|
| Pt | 0 | 51.26(4) | 250 | 3.15(1) |
| Cl(1) | -26.1(2) | 0.[illegible](3) | 381.8(2) | 5.0(1) |
| S | 41.1(2) | 91.0(3) | 118.6(2) | 3.9(1) |
| P(1) | 114.4(2) | 234.6(3) | 301.4(2) | 3.5(1) |
| P(2) | 51.9(2) | 233.3(3) | 119.1(2) | 3.5(1) |
| P(3) | -89.2(2) | -34.4(3) | 197.7(3) | 4.0(1) |
| F(1) | 181.4(6) | 49.7(8) | 586.8(6) | 6.1(4) |
| F(2) | 104.6(5) | 159.5(7) | 480.6(6) | 5.3(3) |
| F(3) | 178.8(5) | -35.8(7) | 259.1(5) | 4.8(3) |
| F(4) | 251.8(6) | -147.4(9) | 366.1(7) | 7.0(4) |
| N(1) | 98.4(7) | 122.6(8) | 307.2(7) | 3.4(3) |
| N(2) | 284(1) | -159(1) | 584(1) | 8.1(6) |
| C(1) | 122.8(8) | 270(1) | 194.2(8) | 3.2(4) |
| C(2) | 254(1) | -112(1) | 540(1) | 5.6(6) |
| C(3) | 218(1) | -51(1) | 480(1) | 5.2(5) |
| C(4) | 178.9(9) | 28(1) | 506.7(9) | 4.0(5) |
| C(5) | 141.3(9) | 84(1) | 452.7(9) | 3.9(4) |
| C(6) | 138.3(8) | 67(1) | 365.7(8) | 3.3(4) |
| C(7) | 176.1(8) | -17(1) | 340(1) | 4.5(5) |
| C(8) | 214(1) | -71(1) | 394(1) | 4.8(5) |
| C(33) | -119(1) | -5(1) | 94(1) | 5.2(6) |
| C(34) | -176(1) | -72(2) | 56(1) | 8.8(9) |
| C(35) | -64(1) | -159(1) | 193(1) | 6.0(6) |
| C(36) | 1(1) | -180(2) | 142(2) | 10(1) |
| C(37) | -165(1) | -26(2) | 265(1) | 10(1) |
| C(38) | -193(1) | 68(1) | 280(2) | 8.0(8) |

* Hydrogens and carbon atoms of phenyl groups on phosphines omitted.

## Table 2.13

## X-RAY DATA FOR $(Ph_2P(S)CHP(Ntfbn)Ph_2\{-S,C\})Pt(PEt_3)Cl$ [Report Reference Code SDL:RGC9208]

### Crystal Data

| | |
|---|---|
| Empirical formula | $C_{38}H_{36}N_2F_4P_3PtClS$ |
| F.W. (g/mol) | 952.25 |
| Space Group | $P\bar{1}$ |
| a (Å) | 12.279(2) |
| b (Å) | 17.146(2) |
| c (Å) | 9.769(3) |
| $\alpha$ (°) | 94.69(2) |
| $\beta$ (°) | 94.15(2) |
| $\gamma$ (°) | 74.56(1) |
| Volume (Å$^3$) | 1973.1 |
| Density (g/cm$^{-3}$) | 1.603 |
| $\mu$ (cm$^{-1}$) | 38.78 |

### Data Collection and Refinement Parameters

| | |
|---|---|
| Radiation | MoK$\alpha$ ($\lambda$ = 0.7107 Å) |
| Monochromator | incident beam, graphite crystal |
| Take-off angle | 3.0° |
| Detector aperture | (3.00 + tan $\theta$) mm horiz x 4.00 mm vert |
| Crystal-to-detector distance | 173 mm |
| Scan type | $\theta$-2$\theta$ |
| Scan rate | 6.7-1.3 °/min |
| Scan width | 0.5 + 0.347 tan $\theta$° |
| Data collection 2$\theta$ limit | 50.0° |
| Data collection index range | *+/- h, k, +/- l* |
| Reflections measured | 6836 total, averaged: 5606 with $I > 3\sigma(I)$ |
| Observations: variables ratio | 5606: 451 |
| Agreement factors $R_1$, $R_2$, GOF | 0.034, 0.046, 1.604 |
| Corrections applied | absorption correction |

## Table 2.14

**Selected Interatomic Bond Lengths (Å) for (Ph$_2$P(S)CHP(Ntfbn)Ph$_2${-S,C})Pt(PEt$_3$)Cl**

| Atoms | Distance (Å) | Atoms | Distance (Å) |
|---|---|---|---|
| Pt-Cl | 2.305(2) | P(3)-C(63) | 1.756(7) |
| Pt-S | 2.312(1) | P(3)-C(65) | 1.727(9) |
| Pt-P(3) | 2.263(2) | F(52)-C(52) | 1.338(6) |
| Pt-C(1) | 2.182(4) | F(53)-C(53) | 1.342(6) |
| S-P(1) | 2.016(2) | F(55)-C(55) | 1.347(6) |
| P(1)-C(1) | 1.771(4) | F(56)-C(56) | 1.352(5) |
| P(1)-C(11) | 1.814(5) | N(1)-C(51) | 1.337(6) |
| P(1)-C(21) | 1.819(5) | N(57)-C(57) | 1.114(7) |
| P(2)-N(1) | 1.591(4) | C(11)-C(12) | 1.395(7) |
| P(2)-C(1) | 1.794(4) | C(11)-C(16) | 1.371(7) |
| P(2)-C(31) | 1.816(5) | C(12)-C(13) | 1.370(7) |
| P(2)-C(41) | 1.808(4) | C(13)-C(14) | 1.354(8) |
| P(3)-C(61) | 1.80(1) | C(14)-C(15) | 1.367(8) |

## Table 2.15

**Selected Interatomic Angles (°) for (Ph$_2$P(S)CHP(Ntfbn)Ph$_2${-S,C})Pt(PEt$_3$)Cl**

| Atoms | Angle (°) |
|---|---|
| Cl-Pt-S | 173.18(6) |
| Cl-Pt-P(3) | 90.87(6) |
| Cl-Pt-C(1) | 95.0(1) |
| S-Pt-P(3) | 94.03(5) |
| S-Pt-C(1) | 79.6(1) |
| P(3)-Pt-C(1) | 171.7(1) |
| Pt-S-P(1) | 78.49(6) |
| S-P(1)-C(1) | 98.8(2) |
| Pt-C(1)-P(1) | 87.4(2) |
| P(1)-C(1)-P(2) | 117.8(2) |
| P(2)-N(1)-C(51) | 133.5(3) |

## Table 2.16

**Selected* Atomic Coordinates (x $10^3$) and Equivalent Isotropic Displacement Parameters (Å x $10^2$) for $(Ph_2P(S)CHP(Ntfbn)Ph_2\{-S,C\})Pt(PEt_3)Cl$**

| Atom | x | y | z | U* |
|---|---|---|---|---|
| Pt | 5.85(2) | 215.75(1) | -84.57(2) | 4.273(6) |
| Cl | -76.5(1) | 130.9(1) | -226.5(2) | 9.31(6) |
| S | 90.3(1) | 308.32(9) | 34.5(2) | 5.35(5) |
| P(1) | 119.2(1) | 322.07(8) | -161.5(2) | 4.32(4) |
| P(2) | 266.2(1) | 150.20(8) | -221.2(1) | 3.70([illegible]) |
| P(3) | -126.9(1) | 229.5(1) | 71.1(2) | 6.54(6) |
| F(52) | 571.8(3) | 219.5(2) | -207.2(4) | 7.3(1) |
| F(53) | 644.8(3) | 298.9(3) | -390.9(5) | 9.9(2) |
| F(55) | 320.6(4) | 300.6(2) | -678.8(4) | 7.8(1) |
| F(56) | 246.6(3) | 220.9(2) | -498.1(3) | 6.6(1) |
| N(1) | 374.0(3) | 182.2(3) | -241.0(5) | 4.4(1) |
| N(57) | 548.9(7) | 385.2(4) | -705.6(8) | 12.7(3) |
| C(1) | 129.8(4) | 221.6(3) | -230.0(5) | 3.8(2) |
| C(11) | 234.6(5) | 369.4(3) | -164.9(6) | 4.6(2) |
| C(12) | 246.0(5) | 413.2(3) | -27[illegible]9(7) | 6.1(2) |
| C(13) | 333.7(6) | 448.6(4) | -273.7(8) | 7.5(2) |
| C(14) | 411.4(6) | 439.7(4) | -166.6(8) | 7.3(2) |
| C(15) | 402.4(5) | 396.1(4) | -58.9(8) | 6.8([illegible] |
| C(16) | 315.6(5) | 361.5(3) | -59.1(7) | 5.7(2 |
| C(51) | 405.1(4) | 218.3(3) | -342.4(6) | 4.0(2) |
| C(52) | 508.7(5) | 239.3(3) | -323.0(6) | 5.2(2) |
| C(53) | 545.3(5) | 280[illegible]) | -417.2(7) | 6.2(2) |
| C(54) | 484.4(5) | 30[illegible]4) | -538.8(7) | 6.3(2) |
| C(55) | 383.9(5) | 280.0(4) | -562.3(6) | 5.7(2) |
| C(56) | 346.0(4) | 240.1(3) | -469.0(6) | 4.5(2) |
| C(57) | 520.8(7) | 348.6(4) | -632.9(8) | 8.5(3) |
| C(61) | -2248.1(8) | 310.7(8) | 26(1) | 20.3(6) |
| C(62) | -252.1(9) | 375.4(8) | -29(1) | 17.8(7) |
| C(63) | -185.0(8) | 146.9(5) | 79(1) | 16.5(4) |
| C(64) | -285.8(8) | 157.6(7) | 165(1) | 19.7(5) |
| C(65) | -96.2(8) | 262.7(9) | 238(1) | 16.7(6) |
| C(66) | 1(1) | 205(1) | 306(1) | 24(1) |

* Hydrogens and carbon atoms of non-interacting phenyl groups omitted.

# CHAPTER 3

# THE MIXED IMINO CHALCOGENIDE LIGANDS $Ph_2P(X)CH_2P(NT)Ph_2$ ($X = S, Se; T = SiMe_3$)

## 3.1 Synthesis

The synthesis of the title ligands had actually been attempted before the tfbn-containing ligands were prepared. It was hoped that the presence of an $SiMe_3$ group would allow for the facile attachment of new R groups to nitrogen via the elimination of $SiMe_3Cl$. This was preferred to using different azides to introduce new R groups, since many of the desired azides could not be formed or were highly dangerous to handle. The $Ph_2P(X)CH_2P(NT)Ph_2$ ligands were, however, very unstable, as were their metal complexes. This work was temporarily set aside in favour of the $Ph_2P(X)CH_2P(Ntfbn)Ph_2$ ($X = O, S, Se$) chemistry. Once it was realized, however, that the tfbn moiety lessened the coordinating power of the lone pair on nitrogen, interest in the $SiMe_3$ derivatives was revived.

Since the attachment of the silylimino group to phosphorus could only be achieved through the reaction of azide and phosphine at reflux without solvent, the imino-chalcogenide ligands were synthesized by adding the chalcogen to a mono-oxidized phosphinimine, (the aforementioned route B). The reaction of elemental chalcogen with $Ph_2PCH_2P(NT)Ph_2$ had to be closely monitored. The reactions were complete within 15 minutes (Se) to 1 hour (S) producing yields of 100 and 80%, respectively.

The ligands are not soluble in low polarity solvents (hexane, ether). They are, however, very soluble in halogenated solvents, THF, benzene, and acetonitrile. The ligands are sensitive to hydrolysis losing the $SiMe_3$ group and forming the P=NH compound. As a result no useful elemental analyses, mass spectral or infrared data could be obtained. These species did not crystallize but rather formed oils. An amorphous solid could however be obtained after prolonged stirring in hexane (1 hour).

## 3.2 NMR data

The $^{31}P\{^1H\}$ NMR spectra for the ligands contain two resonances for the chemically different phosphorus atoms (X = S, Se; δ 36.57/-6.45 and 25.49/-5.37 ppm, respectively). Unlike the tfbn analogs, however, the P(N) signals could not be identified through coupling of phosphorus to the R group on nitrogen (although the spin active nucleus $^{29}Si$ is present its natural abundance (4.7%) was too low to obtain useful satellite information). The P(Se) signal, the resonance that was most deshielded, was clearly identified through coupling of P to $^{77}Se$ ($^1J_{PSe}$ 734 Hz). Using this information the downfield resonance, in the $^{31}P\{^1H\}$ spectrum of the sulfur analog, was assigned as the P(S) phosphorus. This placement is consistent with assignments made for the tfbn ligands. Both resonances are split into doublets displaying mutual coupling ( X = S; 17.5 Hz and X = Se; 19.1 Hz).

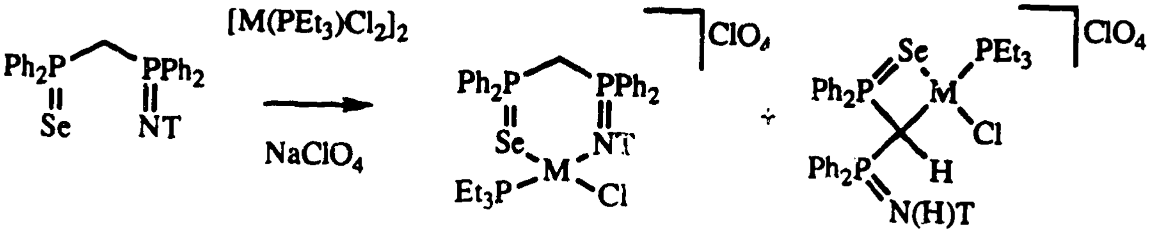
In the $^1H$ NMR spectrum the methylene protons (X = S, Se δ 3.70 and 3.85 ppm, respectively) appear as a doublet of doublets due to coupling with the two inequivalent phosphorus atoms ($^2J_{HP(X)}/^2J_{HP(N)}$ X = S, Se 14.8/12.3 and 14.8/11.8 Hz, respectively). As with the tfbn ligands, there is no evidence for the facile exchange of external sources of hydrogen and deuterium with the $CH_2$ protons in the PCP backbone.

In the $^{13}C\{^1H\}$ NMR spectra the methylene carbons (X= S, Se δ 39.28 and 39.41, respectively) appear as a doublet of doublets, again due to coupling to two inequivalent phosphorus atoms ($^1J_{CP(X)}/^1J_{CP(N)}$ X = S, Se 44.7/67.7 and 38.3/67.4, respectively).

## 3.3 Coordination of the $Ph_2P(X)CH_2P(NT)Ph_2$ Ligands (X = S, Se) to Platinum and Palladium

The coordination chemistry was restricted to reactions of only $Ph_2P(Se)CH_2P(NT)Ph_2$ since this ligand was prepared in the highest yield and had the added benefit of showing $^{77}Se$ satellites. In an attempt to duplicate the chemistry observed with $Ph_2P(Se)CH_2P(Ntfbn)Ph_2$, $Ph_2P(Se)CH_2P(NT)Ph_2$ was reacted with $[M(PEt_3)Cl_2]_2$ (M = Pt, Pd) in acetone in the presence of $NaClO_4$. This resulted in the formation of a mixture of $[(Ph_2P(Se)CH_2P(NT)Ph_2\{-Se,N\})M(PEt_3)Cl][ClO_4]$ and $[(Ph_2P(Se)CHP(N(H)T)Ph_2\{-Se,C\})M(PEt_3)Cl][ClO_4]$. Thus the complexation chemistry of this ligand resembles that observed for the bisphosphinimine ligands.[32,34]

e.g.



It is interesting to note that the {-Se,C} complex is favoured over the {-Se,N} complex, particularly in the case of the platinum complexes (90:10) vs the palladium complexes (60:40). Due to the facile hydrolysis of the $SiMe_3$ group, the complexes were characterized only by their $^1H$ and $^{31}P\{^1H\}$ NMR spectra.

The $^{31}P\{^1H\}$ NMR spectrum showed of two sets of three resonances (Figure 3.1). The resonances for the imino and chalcogenide phosphorus atoms were found downfield from the resonance for the $PEt_3$ phosphorus. The latter was identified by the large $J_{PPt}$ coupling (3007 Hz). The {-Se,C} bonded metallacyclic complex was

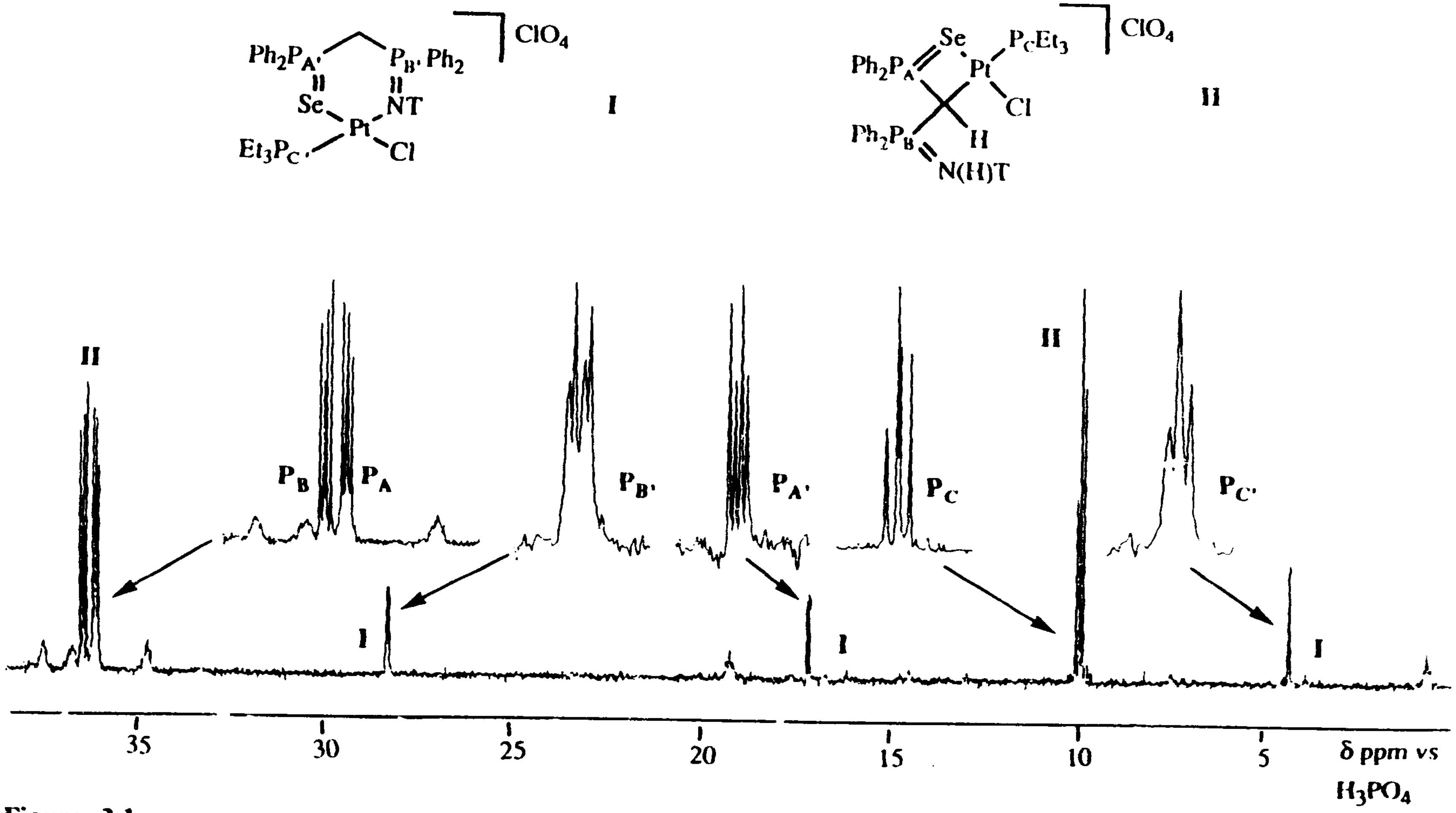


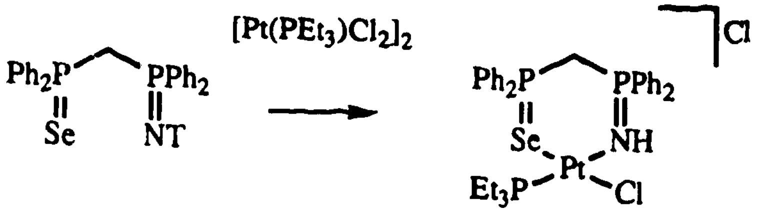
**Figure 3.1**

$^{31}P\{^1H\}$ NMR spectra of $[(Ph_2P(S)CH_2P(NT)Ph_2\{\text{-}S,N\})Pt(PEt_3)Cl][ClO_4]$ (I) and $[(Ph_2P(S)CHP(N(H)T)Ph_2\{\text{-}S,C\})Pt(PEt_3)Cl][ClO_4]$ (II) identified by the coupling of both the imino and the selenoyl phosphorus atoms ($^2J_{PPt}$ 86, 439 Hz,. respectively) to the platinum metal centre. The chemical shifts for the P(Se) and P(N) phosphorus atoms are very close (δ 32.87 and 33.18 ppm, respectively), assignment is made by observing $^1J_{PSe}$ (926 Hz). All phosphorus atoms are coupled to each other ($^2J_{P(Se)P(N)}$ 10.3, $^3J_{P(Se)PEt_3}$ 12.8 and $^3J_{P(N)PEt_3}$ 15.5 Hz). The {-Se,N} bonded chelate complex is identified by recalling that the analogous tfbn complexes displayed $J_{PPt}$ through P=Se ($^2J_{P(Se)Pt}$ 156 Hz) but not through P=N. The imino and selenoyl phosphorus resonances are much farther apart in the {-Se,N} bonded chelate as compared to the {-Se,C} bonded metallacycle. Assignment based on comparison with the analogous tfbn complexes (δ 25.11 and 13.89 ppm, respectively). All phosphorus centres are still coupled to one another but $^3J_{PP}$ is greatly reduced ($^2J_{P(Se)P(N)}$ 9.2, $^3J_{P(Se)PEt_3}$ 4.6, $^3J_{P(N)PEt_3}$ 3.4 Hz).

The $^1$H NMR afforded the proof that the {-Se,C} bonded complex was obtained through hydrogen migration of a proton from the methylene backbone onto the imino nitrogen. There is a resonance for the N(H)T proton at δ 6.05 ppm which integrates as one hydrogen. This resonance is split into a doublet due to coupling to the imino phosphorus ($^2J_{PH}$ Hz). The chemical shift of the imino hydrogen is much lower than the imino hydrogen in the Rh or Ir bistolylimino bisphosphine complexes (δ 8.84-11.90 ppm) but the range is large and apparently is dependant upon the metal centre and the other ligands present. $^1$H NMR spectroscopy also indicated that the $SiMe_3$ group remained attached to to nitrogen. In the {-Se,C} bonded complex the $SiMe_3$ protons are shielded by the introduction of the proton on the imino nitrogen (δ -0.37 ppm) while in the {-Se,N} bonded chelate they are deshielded (δ 0.18 ppm). The resonances for the $PEt_3$ methylene and methyl protons and the methylene and methine protons on the backbone are most easily identified for the {-Se,C} bonded metallacycle. Unfortunately, the chemical shifts of both the {-Se,C} and {-Se,N} bonded complexes overlap, which obscures the resonances of the low yield {-Se,N} chela

The $^{31}P\{^{1}H\}$ NMR spectrum obtained for the product of the reaction of the palladium dimer with $Ph_2P(Se)CH_2P(NT)Ph_2$ also consisted of two sets of three resonances for the {-Se,C} and {-Se,N} complexes. The resonances for P(Se) were easily identified by their $^{77}Se$ satellites (δ 32.94 ppm, $^{1}J_{PSe}$ 479 Hz and δ 18.16 ppm, $^{1}J_{PSe}$ 582 Hz) and by assuming a larger two-bond phosphorus-phosphorus coupling for P(Se) with P(N) (16.2 and 13.1 Hz) relative to P(Se) with $PEt_3$ (11.7 and 10.9 Hz). The remaining resonances at 27.99/29.73 and 35.00/30.82 ppm are then assigned to $Ph_2P(NT)$ and $PEt_3$ groups, respectively.

Treatment of $[Pt(PEt_3)Cl_2]_2$ with two equivalents of $Ph_2P(Se)CH_2P(NT)Ph_2$ in acetone in the absence of $NaClO_4$ was attempted as a possible route to a complex with a σ-bonded nitrogen.[30] Unfortunately, the $SiMe_3$ was eliminated through hydrolysis, probably as $(SiMe_3)_2O$, and $Cl^-$ was retained as a counter-ion to form $[(Ph_2P(Se)CH_2P(NH)Ph_2\{-Se,N\})Pt(PEt_3)Cl][Cl]$.[57,70]



In the $^{31}P\{^{1}H\}$ spectrum of the reaction product there are three resonances. The lack of any coupling between platinum and the imino phosphorus suggests that the imino nitrogen is not σ-bonded (i.e. we would expect to see *ca.* 50-100 Hz $^{195}Pt$-$^{31}P$ coupling through a σ-bonded nitrogen)[59] The imino phosphorus resonance was found furthest downfield (δ 30.07 ppm), followed by the selenoyl phosphorus (δ 8.37 ppm) and finally at highest field the $PEt_3$ phosphorus (δ 0.40 ppm). Unambiguous identification was provided by satellite couplings ($^{2}J_{P(Se)Pt}$ 161, $^{1}J_{PEt_3Pt}$ 3165 Hz) and

$^1J_{PSe}$ (583 Hz) couplings. Mutual coupling between all the phosphorus centres was observed ($^2J_{P(Se)P(N)}$ 13.2, $^3J_{P(Se)PEt_3}$ 9.7, $^3J_{P(N)PEt_3}$ 7.4 Hz). Mass spectral analysis on the crude solid indicated the presence of $SiMe_3$. However, the recrystallized complex showed no $SiMe_3$ in the $^1H$ NMR spectrum indicating that hydrolytic cleavage had likely occurred. The $PEt_3$ methylene and methyl resonances are clearly identifiable (δ 1.91 ppm, $^2J_{PH}$ 10.2, $^3J_{HH}$ 7.6 Hz; δ 1.39 ppm, $^3J_{PH}$ 17.2, $^3J_{HH}$ 7.6 Hz, respectively) as are the methylene protons on the PCP carbon (δ 4.58 ppm, $^2J_{HP(Se)}$ 14.8, $^2J_{HP(N)}$ 12.7 Hz).

The $^{13}C\{^1H\}$ NMR spectrum obtained from the crystalline product showed doublet and singlet resonances for the carbons of the methylene and methyl groups of $PEt_3$ (δ 15.10 ppm, $^1J_{CP}$ 40.2 Hz; δ 8.11 ppm, respectively). The carbon in the PCP backbone was found to resonate at 30.21 ppm ($^1J_{CP(Se)}$ 37.4 $^1J_{CP(N)}$ 68.6 Hz).

The crystals were mixed with $NaClO_4$ to confirm the presence of a counterion by the appearance of a ν($ClO_4$) stretch at 1103 cm$^{-1}$ in the IR spectrum (KBr). Mass spectroscopy could only identify the positive fragment $(Ph_2P(Se)CH_2P(NH)Ph_2\{-Se,N\})Pt(PEt_3)Cl$. With exchange of $Cl^-$ with $ClO_4^-$, however, ν(P=N) unfortunately becomes masked by the $ClO_4^-$ band. The location of ν(P=Se) remains uncertain.

## 3.4 Deprotonation of $Ph_2P(Se)CH_2P(NT)Ph_2$

The methylene carbon of $Ph_2P(Se)CH_2P(NT)Ph_2$ was readily deprotonated using LDA. The resonances for the P(Se) (δ 17.77 ppm) and P(N) (δ 19.20 ppm) in the deprotonated ligand fall between the signals for the starting compound (δ 26.04 and -5.63 ppm). The $^{31}P$-$^{31}P$ coupling has increased ($^2J_{PP}$ 20.9 to 27.0 Hz) though not to the same degree as [illegible] previously observed for the deprotonated unsymmetrical bisphosphine disulfide ligands.[59] The methine proton proved to be too broad to be resolved. The central carbon atom is shielded and $^1J_{CP}$ (*ca* 100 Hz)) increases, consistent with an increase in the s character of the hybrid orbitals used in bonding ough the PCP backbone. Complexation of with the anion with metals was not ssful. This failure may be due, in part, to the thermal instability of the ligand.

## Table 3.1

$^{31}P\{^1H\}$ NMR data* for $Ph_2P(X)CH_2P(NT)Ph_2$ (X = S, Se) and the metal complexes $[(Ph_2P(Se)CH_2P(NT)Ph_2\{\text{-}Se,N\})M(PEt_3)Cl][ClO_4]$, $(Ph_2P(Se)CHP(N(H)T)Ph_2\{\text{-}Se,C\})M(PEt_3)Cl][ClO_4]$, (M = Pt, Pd) and $[(Ph_2P(Se)CH_2P(NH)Ph_2\{\text{-}Se,N\})Pt(PEt_3)Cl][Cl]$

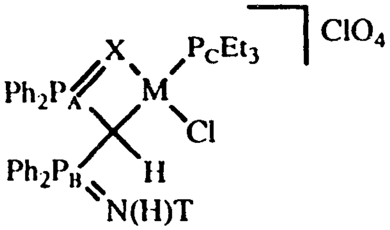
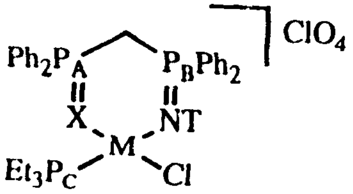
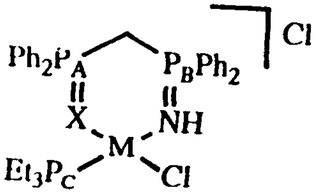
| Compound | M | X | δ $P_A$ (ppm) | δ $P_B$ (ppm) | δ $P_C$ (ppm) | $J_{PP}$ (Hz) | $J_{PPt}$ (Hz) | $J_{PSe}$ (Hz) |
|---|---|---|---|---|---|---|---|---|
|  | - | S | 36.57 d | -6.45 d | - | $^2J_{P_AP_B}$ 17.5 | - | - |
| | - | Se | 26.04 d | -5.63 d | - | $^2J_{P_AP_B}$ 20.9 | - | $^1J_{P_ASe}$ 734 |
|  | Pt | Se | 32.87 dd | 33.18 dd | 6.64 dd | $^2J_{P_AP_B}$ 10.3<br>$^3J_{P_AP_C}$ 12.8<br>$^3J_{P_BP_C}$ 15.5 | $^2J_{P_APt}$ 439<br>$^3J_{P_BPt}$ 86<br>$^1J_{P_CPt}$ 3007 | $^1J_{P_ASe}$ nr |
| | Pd | Se | 35.00 dd | 27.99 dd | 32.94 dd | $J_{P_AP_B}$ 10.7<br>$^3J_{P_AP_C}$ 11.4<br>$^3J_{P_BP_C}$ 16.2 | - | $^1J_{P_ASe}$ 479 |

**Table 3.1 continued**

| Compound | M | X | δ $P_A$ (ppm) | δ $P_B$ (ppm) | δ $P_C$ (ppm) | $J_{PP}$ (Hz) | $J_{PPt}$ (Hz) | $J_{PSe}$ (Hz) |
|---|---|---|---|---|---|---|---|---|
|  | Pt | Se | 13.89 dd | 25.11 dd | 0.08 dd | $^2J_{P_AP_B}$ 9.2<br>$^3J_{P_AP_C}$ 4.6<br>$^3J_{P_BP_C}$ 3.4 | $^2J_{P_APt}$ 156<br>$^1J_{P_CPt}$ 3275 | $^1J_{P_ASe}$ nr |
| | Pd | Se | 18.16 dd | 29.73 dd | 30.82 dd | $^2J_{P_AP_B}$ 13.1<br>$^3J_{P_AP_C}$ 10.9<br>$^3J_{P_BP_C}$ 7.3 | - | $^1J_{P_ASe}$ 582 |
|  | Pt | Se | 8.37 dd | 30.07 dd | 0.40 dd | $^2J_{P_AP_B}$ 13.2<br>$^3J_{P_AP_C}$ 9.7<br>$^3J_{P_BP_C}$ 7.4 | $^2J_{P_APt}$ 161<br>$^1J_{P_CPt}$ 3165 | $^1J_{P_ASe}$ 583 |

| | |
|---|---|
| d | doublet |
| dd | doublet of doublets |
| n r | not resolved |

* Chemical shifts in δ ppm in $CD_2Cl_2$ with respect to 85% $H_3PO_4$

# CHAPTER 4

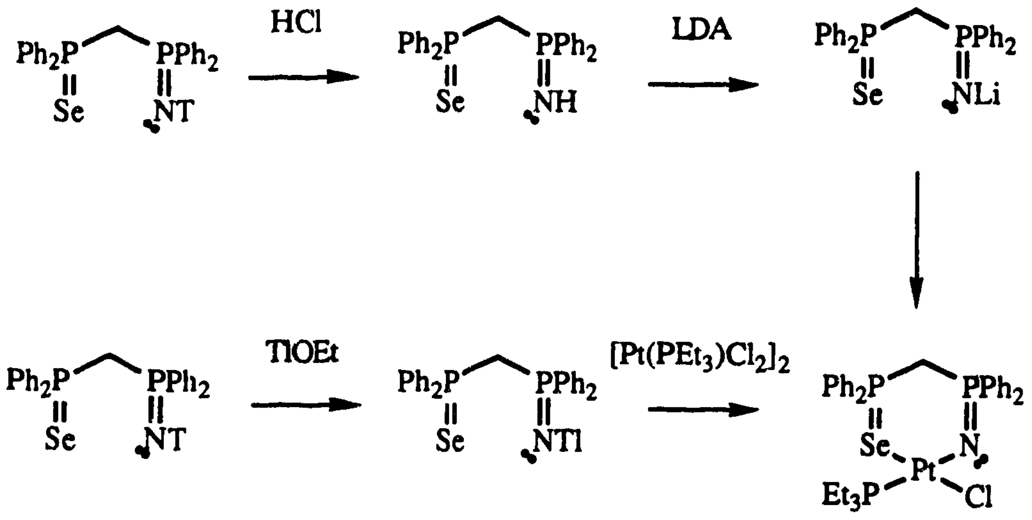
# CONCLUSIONS and PROPOSALS FOR FUTURE WORK

In summary, a new series of the mixed imino-chalcogenide bisphosphine ligands $Ph_2P(X)CH_2P(NR)Ph_2$ (X = O, S, Se; R = tfbn, $SiMe_3$) was prepared. They were synthesized, in most cases, in high yield

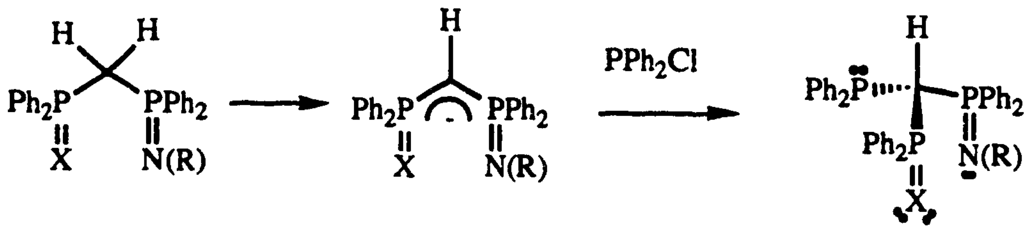
All combinations of P(NR)/P(O), P(NR)/P(S) and P(NR)/P(Se) were obtained with R = tfbn. The ligands did not display facile exchange of the methylene protons with deuterium sources as was exhibited by their bisphosphinimine counterparts. Complexation to the softer group 8B transition-metals was possible only for the S and Se containing ligands. The types of coordination modes encountered were diverse (neutral {-X} bonded, cationic {-X,X} bonded, cationic and neutral {-X,C} bonded modes). The platinum triad metals form static structures having the $P(S)Ph_2$ group coordinated through sulfur *trans* to Cl. The rhodium complexes seem to be fluxional species in solution. Future work should, therefore, include the investigation of the catalytic properties of the rhodium complexes.

Only the P(NR)/P(S) and P(NR)/P(Se) combinations could be prepared for R = $SiMe_3$. These ligands also did not display facile exchange of the methylene protons with deuterium but, nevertheless, possessed coordination chemistries analogous to the bisphosphinimine ligands. The ligands and complexes were very sensitive to hydrolysis, which made their complete characterization difficult. Future studies should be centred around the N-$SiMe_3$ containing ligands with a view to forming nitrogen-sigma bonds to late transition-metal centres. It may be possible to exploit the facile cleavage of the N-$SiMe_3$ bond by metal halides to produce the desired $\sigma$-bonded metal complexes; however, competitive hydrolysis reactions must be prevented. This could be done by transforming the silyl imines to their lithium derivatives..

e.g.



In addition the chemistry of deprotonated ligands possessing both tfbn and T groups should be investigated more thoroughly. This includes investigating the synthesis of triphosphorus ligands which contain reactive imino, chalcogenide and phosphorus centres that can be attached to both late and early transition-metal centres.



# CHAPTER 5

# EXPERIMENTAL

All reactions were carried out using standard Schlenk tube techniques under an atmosphere of dry argon. All solvents used in the synthesis of the phosphinimine ligands and their complexes were distilled over appropriate the drying agents, under argon, before use ($CH_2Cl_2$, $CH_3CN$, THF; were distilled from $P_2O_5$, $P_2O_5/CaH_2$ and Na/benzophenone, respectively). Deuterated solvents, necessary for NMR experiments, were dried over molecular sieves and stored under argon immediately prior to their use (prior to combining with lithium salts the solvents were degassed by the freeze-thaw method). $N_3$tfbn and $N_3SiMe_3$, $[Rh(CO)_2Cl]_2$, $[Rh(cod)Cl]_2$, $[Pt(PEt_3)Cl_2]_2$ and $[Pd(PEt_3)Cl_2]_2$ were prepared according to published procedures.[71-77] $^1H$, $^1H\{^{31}P\}$, $^{31}P$, $^{31}P\{^{31}P\}$, $^{13}C$, $^{13}C\{^{31}P\}$, $^{19}F$ and $^{77}Se$ NMR were collected on Bruker 200 and 400 NMR instruments (respective operating frequencies: $^1H = 400.135$ and 200.133 MHz, $^{13}C = 100.614$ and 50.323 MHz, $^{31}P = 161.978$ and 81.015 MHz, $^{19}F = 376.503$ and 188.313 MHz, $^{77}Se$ 76.312 MHz). External standards used were $SiMe_4$ (C and H), 85% $H_3\underline{P}O_4$, $C\underline{F}Cl_3$ and $Me_2\underline{Se}$. Elemental Analysis were preformed by the Microanalytical Services Lab at the University of Alberta. IR spectra were recorded on a BOMEM Michelson MB-100 FT-IR instrument calibrated using the 1601 $cm^{-1}$ band of polystyrene. Low resolution mass spectral analyses (Electron Impact, EI) were preformed on an AEI MS12 instrument, those requiring fast atom bombardment (FAB), on an AEI MS9 instrument. Crystal Structure determination was carried out by Dr. R. McDonald at the Structure Determination Lab, Department of Chemistry, University of Alberta. Intensity data was collected on a Enraf Nonius CAD-4F diffractometer using graphite monochromated $MoK_\alpha$ radiation. The structure of $(Ph_2P(S)CHP(Ntfbn)Ph_2\{-S,C\})Pt(PEt_3)Cl$ was solved using the direct methods program SHELXS-86.[78] The structure of $[(Ph_2P(S)CH_2P(Ntfbn)Ph_2\{-S,N\})Pt(PEt_3)Cl]ClO_4$ was solved by determining the position of the Pt atom from a three-dimensional Patterson map and locating the remaining non-hydrogen atoms from a series of difference Fourier maps. Adjustment of atomic parameters was carried out by full-matrix least-squares refinement and the data was subsequently corrected for absorption by use of an empirical scheme based on the absorption surface method of Walker and Stuart.[79]

## Preparation of $Ph_2P(X)C_nH_mP(Ntfbn)Ph_2$ (X = O, S, Se)

The mixed imino-chalcogenides of various bisphosphines ($C_nH_m$ = $CH_2$, 1,2-$C_6H_4$, $CH(CH_3)$, *cis*-CHCH, $CH_2CH_2$) were prepared using procedures similar to the following example:

### Synthesis of $Ph_2P(S)CH_2P(Ntfbn)Ph_2$:

The mono sulphide of diphenylphosphinomethane (dppm) was prepared by the method of Grim *et al*[52]. Azidotetrafluorobenzonitrile (0.74ml, 5.11 x $10^{-3}$mol) was syringed dropwise at -78°C (dry ice/acetone) into a solution of the monosulfide (2.13g, 5.11 x $10^{-3}$mol) in dichloromethane (30 ml). The reaction mixture immediately turned a bright yellow. It was left to warm to room temperature and then stirred overnight (the resulting solution was straw yellow). The solvent is removed *in vacuo* and the desired product is crystallized from a minimum amount of acetonitrile to give light sensitive, beige crystals. Yield quantitative. mp 160-165°C Anal. Calc'd for $C_{32}H_{22}P_2N_2F_4S$ /0.1mol S: C 63.24, H 3.65 , N 4.61, S 5.81. Found: C 64.64, H 3.75, N 4.25, S 6.48. IR data (KBr disk): ν(P=N) 1510 $cm^{-1}$, ν(P=S) 780 $cm^{-1}$, ν(CN) 2218 $cm^{-1}$. MS (EI, *m/z*) 604 ($M^+$). NMR data ($CD_2Cl_2$) $^{31}P\{^1H\}$: P(S) δ 32.22 d ($^2J_{PP}$ 9.6 Hz), P(Ntfbn) δ 5.50 dt ($^2J_{PP}$ 9.3 Hz, $^4J_{PF}$ 5.2 Hz). $^1H$: $PCH_2P$ δ 4.08 dd ($^2J_{P(S)H}$ 13.6 Hz, $^2J_{P(N)H}$ 12.8 Hz), phenyl H δ 7.3-7.8 m. $^{13}C\{^{1}H\}$: P$C$H$_2$P δ 34.57 dd ($^{2}J_{P(S)C}$ 47.3 Hz, $^{2}J_{P(N)C}$ 52.3 Hz). $^{19}F$ (second order): *meta* -F tfbn δ -139.77, *ortho* -F tfbn δ -152.81 ($^{4}J_{FP(N)}$ 6 Hz)

The relevant data for characterization of the other members of this class of compounds are given below. Published procedures were used to prepare the following bisphosphines: bis(diphenylphosphino)benzene,[80] *cis*-1,2-bis(diphenylphosphino)ethylene[81] and 1,1-bis(diphenylphosphino)ethane.[82] The monosulfides of these ligands and the monoselenide of dppm (dppmSe) were prepared by reacting the bisphosphines with elemental sulfur or selenium black in refluxing toluene. The mono oxide, and sulfide of dppm (dppmO and dppmS) were prepared by the methods of Grim *et al.*[52] Yields are based upon conversion of the monochalcogenide bisphosphine to the mixed imino-chalcogenide bisphosphine.

## Synthesis of $Ph_2P(Se)CH_2P(Ntfbn)Ph_2$:

The white product obtained from the reaction of dppmSe and N$_3$tfbn was recrystallized from a minimum amount of acetonitrile at -10°C. Yield of white crystals was essentially quantitative. mp 190°C. Anal. Calc'd for $C_{32}H_{22}P_2N_2F_4Se/0.4$mol Se: C 55.65, H 3.21, N 4.06. Found: C 55.61, H 3.03, N 4.25. IR data (KBr disk): ν(P=N) 1509 cm$^{-1}$, ν(P=Se) 520 cm$^{-1}$, ν(CN) 2229 cm$^{-1}$. MS (EI, *m/z*) 652 (M$^{+}$). NMR data ($CD_2Cl_2$) $^{31}P\{^{1}H\}$: P(Se) δ 20.63 d Se sat. 8% ($^{2}J_{PP}$ 9.0 Hz, $^{1}J_{PSe}$ 766 Hz), P(Ntfbn) δ 5.61 dt ($^{2}J_{PP}$ 8.4 Hz, $^{4}J_{PF}$ 6.1 Hz). $^{1}H$: PCH$_2$P δ 4.22 dd ($^{2}J_{P(Se)H}$ 14 Hz, $^{2}J_{P(N)H}$ 12.6 Hz), phenyl H δ 7.3-7.8 m. $^{13}C\{^{1}H\}$: P$C$H$_2$P δ 34.36 dd ($^{1}J_{P(Se)C}$ 39.8 Hz, $^{1}J_{P(N)C}$ 53.1 Hz). $^{19}F$ (second order): *meta*-F tfbn δ -139.75, *ortho*-F tfbn δ -152.70 ( $^{4}J_{FP(N)}$ 5.5 Hz). $^{77}Se$: δ -274.18 d ($^{1}J_{SeP}$ 766 Hz).

**Synthesis of $Ph_2P(O)CH_2P(Ntfbn)Ph_2$:**

The white product obtained from the reaction of dppmO and $N_3$tfbn was recrystallized from a minimum amount of $CH_2Cl_2$ at -10°C. Yield of white crystals was essentially quantitative. <u>mp:</u> > 250°C dec. <u>Anal.</u> Calc'd for $C_{32}H_{22}P_2N_2F_4O$/0.12 mol $CH_2Cl_2$: C 64.27, H 3.45, N 4.74 Found: C 64.44, H 3.74, N 4.68. <u>IR data:</u> (KBr disk) $\nu$(P=N) 1511 $cm^{-1}$, $\nu$(P=O) 1213 $cm^{-1}$, $\nu$(CN) 2233 $cm^{-1}$ <u>MS (EI, *m/z*)</u> 588 ($M^+$). <u>NMR data</u> ($CD_2Cl_2$) $^{31}P\{^1H\}$: <u>P</u>(O) $\delta$ 21.84 d ($^2J_{PP}$ 12.0 Hz), <u>P</u>(Ntfbn) $\delta$ 7.15 dt ($^2J_{PP}$ 11.8 Hz, $^4J_{PF}$ 5.6 Hz) $^1H$: PC<u>H</u>$_2$P $\delta$ 3.83 dd ($^2J_{HP(O)}$ 12.7 Hz, $^2J_{HP(N)}$ 13.3 Hz), phenyl H $\delta$ 7.3-7.9 m. $^{13}C\{^1H\}$: P<u>C</u>H$_2$P $\delta$ 33.04 dd ($^1J_{CP(O)}$ 59.3 Hz, $^1J_{CP(N)}$ 49.9 Hz). $^{19}F$ (second order): *meta*-F tfbn $\delta$ -139.88, *ortho*-F tfbn $\delta$ -153.20 ($^4J_{FP(N)}$ 6 Hz).

**Synthesis of $Ph_2P(S)CH(CH_3)P(Ntfbn)Ph_2$:**

The yellow residue obtained from the reaction of $Ph_2P(S)CH(CH_3)PPh_2$ and $N_3$tfbn was recrystallized from a minimum amount of acetonitrile at -10°C. Yellow crystals obtained in essentially quantitative yield. <u>mp:</u> 225-228°C. <u>Anal.</u> Calc'd for $C_{33}H_{24}P_2N_2F_4S$/0.1mol S: C 63.75, H 3.89, N 4.51, S 5.67. Found: C 64.00, H 3.76, N 4.59, S 6.11. <u>IR data</u> (KBr disk): $\nu$(P=N) 1519 $cm^{-1}$, $\nu$(P=S) ~740 $cm^{-1}$, $\nu$(CN) 2231$cm^{-1}$ <u>MS (EI, *m/z*)</u> 618 ($M^+$). <u>NMR data</u> ($CD_2Cl_2$) $^{31}P\{^1H\}$: <u>P</u>(S) $\delta$ 51.95 d ($^2J_{PP}$ 94.3 Hz), <u>P</u>(Ntfbn) $\delta$ -12.26 dt ($^2J_{PP}$ 94 Hz, $^4J_{PF}$ 3.5 Hz). $^1H$: C<u>H</u> $\delta$ 4.33 ddq ($^2J_{HP(S)}$ 13.0 Hz, $^2J_{HP(N)}$ 15.3 Hz, $^3J_{HH}$ 7.2 Hz), C<u>H</u>$_3$ $\delta$ 1.54 ddd ($^3J_{HP(S)}$ 17.8 Hz, $^3J_{HP(N)}$ 17.1 Hz, $^3J_{HH}$ 7.2 Hz), phenyl H $\delta$ 7.2-8.0 m. $^{13}C\{^1H\}$: <u>C</u>H $\delta$ 35.61 dd ($^1J_{CP(S)}$ 47.1 Hz, $^1J_{CP(N)}$ 59.1 Hz), <u>C</u>H$_3$ $\delta$ 13.31 s. $^{19}F$ (second order): *meta*-F tfbn $\delta$ -140.19, *ortho*-F tfbn $\delta$ -152.22 ($^4J_{FP(N)}$ 3.5 Hz).

## Synthesis of *cis*-$Ph_2P(S)CHCHP(Ntfbn)Ph_2$:

The yellow solid obtained from the reaction of *cis*-$Ph_2P(S)CHCHPPh_2$ and $N_3$tfbn was recrystallized from a minimum amount of acetonitrile at -10°C to give yellow crystals. Yield: *ca*. quantitative mp: 145-150°C. Anal. Calc'd for $C_{33}H_{22}P_2N_2F_4S$/0.25mol S: C 63.46, H 3.55, N 4.49, S 6.41. Found: C 63.94, H 3.42, N 4.40, S 6.56. IR data (KBr disk): $\nu$(P=N) 1507 $cm^{-1}$, $\nu$(P=S) ~730 $cm^{-1}$, $\nu$(CN) 2227 $cm^{-1}$ MS (EI, *m/z*) 616 ($M^+$). NMR data ($CD_2Cl_2$) $^{31}P\{^1H\}$: P(S) $\delta$ 28.93 d ($^2J_{PP}$ 19.8 Hz), P(Ntfbn) $\delta$ -1.68 dt ($^2J_{PP}$ 19.8 Hz, $^4J_{PF}$ 6.6 Hz). $^{13}C\{^1H\}$: P(S)CH $\delta$ 146.51 d ($^1J_{CP(S)}$ 75.5 Hz), P(Ntfbn)CH $\delta$ 136.98 d ($^1J_{P(N)C}$ 79.5 Hz). $^{19}F$ (second order): *meta*-F tfbn $\delta$ -139.25, *ortho*-F tfbn $\delta$ -152.00 ($^4J_{FP(N)}$ 7 Hz).

## Synthesis of $Ph_2P(S)CH_2CH_2P(Ntfbn)Ph_2$:

The yellow product obtained from the reaction of $Ph_2P(S)CH_2CH_2PPh_2$ and $N_3$tfbn was recrystallized from a minimum amount of acetonitrile at -10°C to give yellow crystals. Yield: *ca*. quantitative. mp: 160-165°C. Anal. Calc'd for $C_{33}H_{24}P_2N_2F_4S$/0.1mol S: C 63.75, H 3.89, N 4.51, S 5.67. Found: C 64.20, H 3.85, N 4.49, S 5.83. IR data (KBr disk): $\nu$(P=N) 1506 $cm^{-1}$, $\nu$(P=S) ~730 $cm^{-1}$, $\nu$(CN) 2232 $cm^{-1}$. MS (EI, *m/z*) 618 ($M^+$). NMR data ($CD_2Cl_2$) $^{31}P\{^1H\}$: P(S) $\delta$ 44.31 d ($^2J_{PP}$ 56.6 Hz), P(Ntfbn) $\delta$ 17.22 dt ($^2J_{PP}$ 56.7 Hz, $^4J_{PF}$ 4.7 Hz). $^1H$ $CH_2$ $\delta$ 2.55 and 2.80 m. $^{13}C\{^1H\}$: P(S)$CH_2$ $\delta$ 25.04 d ($^1J_{CP(S)}$ 55.3 Hz), P(tfbn)$CH_2$ $\delta$ 23.33 d ($^1J_{P(N)C}$ 67.4 Hz). $^{19}F$ (second order): *meta*-F tfbn $\delta$ -139.13, *ortho*-F tfbn $\delta$ -153.31 ($^4J_{FP(N)}$ 4.5 Hz).

## Synthesis of $Ph_2P(S)C_6H_4P(Ntfbn)Ph_2$:

The brown product obtained from the reaction of $Ph_2P(S)C_6H_4PPh_2$ and $N_3$tfbn was recrystallized from a minimum amount of acetonitrile at -10°C to give light sensitive, beige crystals. Yield: *ca*. quantitative. mp: >200°C dec. Anal. Calc'd for $C_{37}H_{24}P_2N_2F_4S$/0.3 mol $CH_3CN$: C 66.52, H 3.70, N 4.75, S 4.72. Found: C 66.30, H 3.54, N 4.82, S 4.92. IR data (KBr disk): ν(P=N) 1507 $cm^{-1}$, ν(P=S) ~720 $cm^{-1}$, ν(CN) 2124 $cm^{-1}$. MS (EI, *m/z*) 666 ($M^+$). NMR data ($CD_2Cl_2$) $^{31}P\{^1H\}$: P(S) δ 44.93 d ($^2J_{PP}$ 7.5 Hz), P(Ntfbn) δ 12.16 dt ($^2J_{PP}$ 7 Hz, $^4J_{PF}$ 4.7 Hz). $^{19}F$ (second order): *meta*-F tfbn δ -140.92, *ortho*-F tfbn δ -151.73 ($^4J_{FP(N)}$ 4 Hz).

## Preparation of $(Ph_2P(S)CH_2P(Ntfbn)Ph_2\{\text{-}S\})Rh(CO)_2Cl$

A straw yellow solution of $Ph_2P(S)CH_2P(Ntfbn)Ph_2$, (0.100g 1.65 x $10^{-4}$ mol) in $CH_2Cl_2$ (~20 ml) was added to a yellow solution of $[Rh(CO)_2Cl]_2$ (0.32 g, 8.27 x $10^{-5}$ mmol) in $CH_2Cl_2$ (~20 ml) at room temperature. The mixture was allowed to stir for three hours. The solvent was then removed *in vacuo*, and the yellow-orange solid was recrystallized from a dichloromethane/hexane layer at room temperature to give amber crystals of the title complex. Yield: *ca*. quantitative. mp: 75°C dec. Anal. Calc'd for $C_{33}H_{22}P_3N_2F_4SCl_2O_5Rh$/0.75mol $CH_2Cl_2$: C 48.39, H 2.75, N 3.25, S 3.72, Cl, 10.27. Found: C 48.51, H 2.58, N 3.27, S 4.01, Cl 10.23. IR data (KBr disk): ν(P=N) 1511 $cm^{-1}$, ν(P=S) 581 $cm^{-1}$, ν(CN) 2227 $cm^{-1}$, ν(CO) 2072/2002 $cm^{-1}$. MS (FAB, *m/z*) 771 ($M^+$ - CO). NMR data ($CD_2Cl_2$) $^{31}P\{^1H\}$: P(S) δ 37.93 br s, P(Ntfbn) δ 6.90 br s. $^1H$: $PCH_2P$ δ 4.66 dd ($^2J_{HP(N)}$ 14.9 Hz, $^2J_{HP(S)}$ 12.5 Hz), phenyl H δ 7.4-7.8 m. $^{13}C\{^1H\}$: $PCH_2P$ δ 33.17 dd ($^1J_{CP(S)}$ 46.0 Hz, $^1J_{CP(N)}$ 49.9 Hz). $^{19}F$ (second order): *meta*-F tfbn δ -139.4 s br, *ortho*-F tfbn δ -153.5 s v br.

## Preparation of $[(Ph_2P(X)CH_2P(Ntfbn)Ph_2\{-X,N\})M(PEt_3)Cl]ClO_4]$ (M = Pt; X = S, Se / M = Pd; X = S)

All the cationic nitrogen-chalcogenide bisphosphine metal chelate complexes were prepared using procedures similar to the following example:

### Synthesis of $[(Ph_2P(S)CH_2P(Ntfbn)Ph_2\{-S,N\})Pt(PEt_3)Cl]ClO_4$:

To a solution of $[Pt(PEt_3)Cl_2]_2$ (0.077g, $8.27 \times 10^{-5}$ mol) and $NaClO_4$ (0.023g, $1.65 \times 10^{-4}$ mol) in acetone (30ml) was added dropwise a solution of the heterodifunctional ligand, $Ph_2P(S)CH_2P(Ntfbn)Ph_2$, (0.100g $1.65 \times 10^{-4}$ mol) in acetone (10ml). The reaction mixture was left to stir at room temperature for one hour after which time the solution had turned a light yellow and a white precipitate had formed. The solvent was removed *in vacuo* the yellow residue taken up in a minimum of dichloromethane then filtered through Celite to remove NaCl. The product was crystallized from a dichloromethane/hexane mixture to produce yellow crystals. Yield: *ca*. quantitative. mp >230°C dec. Anal. Calc'd for $C_{38}H_{37}P_3N_2SF_4Cl_2O_4Pt/0.85$mol $CH_2Cl_2$: C 41.48, H 3.47, N 2.49, S 2.85. Found: C 41.50, H 3.43, N 2.35, S 2.28. IR data (KBr disk): $\nu$(P=N) 1489 $cm^{-1}$, $\nu$(P=S) 576 $cm^{-1}$, $\nu$(CN) 2239 $cm^{-1}$, $\nu(ClO_4)$ 1100 $cm^{-1}$. MS (FAB, m/z) 953 ($M^+ - ClO_4$) NMR data ($CD_2Cl_2$) $^{31}P\{^1H\}$: $\underline{P}$(S) $\delta$ 30.94 dd Pt sat. 32% ($^2J_{PP(N)}$ 15.3 Hz, $^2J_{PPt}$ 144 Hz), $\underline{P}$(Ntfbn) $\delta$ 35.45 d ($^2J_{PP(S)}$ 13.9 Hz), $\underline{P}Et_3$ $\delta$ 6.88 dd Pt sat. 32% ($^1J_{PPt}$ 3342 Hz,) $^1H$: $PC\underline{H}_2P$ $\delta$ 4.54 dd ($^2J_{P(S)H}$ 12.3 Hz, $^2J_{P(N)H}$ 13.4 Hz), $PEt_3$ $C\underline{H}_2$ $\delta$ 1.95 dq ($^2J_{PH}$ 10.5 Hz, $^3J_{HH}$ 7.6 Hz), $PEt_3$ $C\underline{H}_3$ $\delta$ 1.15 dt ($^3J_{PH}$ 17.8 Hz, $^3J_{HH}$ 7.6 Hz), phenyl H $\delta$ 7.2-7.9 m. $^{13}C\{^1H\}$: $P\underline{C}H_2P$ $\delta$ 31.43 dd ($^1J_{CP(S)}$ 41.2 Hz, $^1J_{CP(N)}$ 66.4 Hz), $PEt_3$ $\underline{C}H_2$ $\delta$ 15.22 d ($^1J_{CP}$ 10.26 Hz), $PEt_3$ $\underline{C}H_3$ $\delta$ 8.11 d ($^2J_{CP}$ 7 Hz). $^{19}F$ (second order): *meta*-F tfbn $\delta$ -136.32, *ortho*-F tfbn $\delta$ -152.85 ($^4J_{FP(N)}$ 5 Hz).

The relevant data for characterization of the other members of this class of compounds is given below. Yields are based upon complete conversion of the imino-chalcogenide bisphosphine to the nitrogen-chalcogenide coordinated metal complex.

Rhodium and Palladium {-S,N} bonded chelate complexes of the $Ph_2P(S)CH_2P(Ntfbn)Ph_2$ ligand were synthesized from the metal dimers $[Rh(CO)_2Cl]_2$, $[Rh(cod)Cl]_2$ and $[Pd(PEt_3)Cl_2]_2$. It should be mentioned that in the case of the rhodium complexes although there was no facile deuterium exchange observed for the methylene protons, coupling could not be resolved for the $^{31}P$ resonances (variable temperature did not allow for resolution of the coupling).

**Synthesis of $[(Ph_2P(Se)CH_2P(Ntfbn)Ph_2\{-Se,N\})Pt(PEt_3)Cl][ClO_4]$:**

The yellow solid obtained from the reaction of $Ph_2P(Se)CH_2P(Ntfbn)Ph_2$, $[Pt(PEt_3)Cl_2]_2$ and $NaClO_4$ was recrystallized from a dichloromethane/hexane mixture at room temperature to give yellow crystals. Yield: *ca.* quantitative. mp: 185°C dec. Anal. Calc'd for $C_{38}H_{37}P_3N_2F_4SeCl_2O_4Pt/0.25mol\ CH_2Cl_2$: C 40.99, H 3.37, N 2.50, Cl, 7.91. Found: C 40.93, H ,3.17 N 2.50, Cl 7.59. IR data (KBr disk): v(P=N) 1489 $cm^{-1}$, v(P=Se) 509 $cm^{-1}$, v(CN) 2238 $cm^{-1}$, v($ClO_4$) 1103 $cm^{-1}$. MS (FAB, *m/z*) 1000 ($M^+ - ClO_4$). NMR data ($CD_2Cl_2$) $^{31}P\{^1H\}$: P(Se) $\delta$ 12.0 dd Pt sat. 32%, Se sat 8% ($^2J_{PP(N)}$ 13.7 Hz, $^2J_{PPt}$ 153 Hz, $^1J_{PSe}$ 581 Hz), P(Ntfbn) $\delta$ 35.86 d ($^2J_{PP(Se)}$ 13.7 Hz), $PEt_3$ $\delta$ 5.29 ddt Pt sat. 33% ($^1J_{PPt}$ 3336 Hz). $^1H$: $PCH_2P$ $\delta$ 4.63 dd ($^2J_{HP(N)}$ 12.9 Hz, $^2J_{HP(Se)}$ 14.8 Hz), $PEt_3$ $CH_2$ $\delta$ 2.00 dq ($^2J_{HPEt_3}$ 10.4 Hz, $^3J_{HH}$ 7.6 Hz), $PEt_3$ $CH_3$ $\delta$ 1.18 dt ($^3J_{HPEt_3}$ 17.8 Hz, $^3J_{HH}$ 7.6Hz), phenyl H $\delta$ 7.4-7.9 m. $^{13}C\{^1H\}$: $PCH_2P$ $\delta$ 30.99 dd ($^1J_{CP(Se)}$ 35.9 Hz, $^1J_{CP(N)}$ 66.4 Hz), $PEt_3$ $CH_2$ $\delta$ 15.85 d ($^1J_{PC}$ 41.3 Hz), $PEt_3$ $CH_3$ $\delta$ 8.30 s. $^{19}F$ (second order): *meta*-F tfbn $\delta$ -139.11, *ortho*-F tfbn $\delta$ -136.34 ($^4J_{FP(N)}$ 5 Hz), $^{77}Se$ -108.59 dd ($^1J_{SeP}$ 579, $^3J_{SeP}$ 6 Hz).

## Synthesis of $[(Ph_2P(S)CH_2P(Ntfbn)Ph_2\{-S,N\})Pd(PEt_3)Cl][ClO_4]$:

The yellow-orange solid obtained from the reaction of $Ph_2P(S)CH_2P(Ntfbn)Ph_2$, $[Pd(PEt_3)Cl_2]_2$ and $NaClO_4$ was recrystallized from a dichloromethane/hexane mixture at room temperature to give yellow crystals. Yield: *ca.* quantitative. mp: 210°C dec. Anal. Calc'd for $C_{38}H_{37}P_3N_2F_4SCl_2O_4Pd$/0.15 mol $CH_2Cl_2$: C 46.91, H 3.85, N 2.87, Cl, 8.35. Found: C 46.84, H 3.99, N 2.86, Cl 8.19. IR data (KBr disk): ν(P=N) 1487 $cm^{-1}$, ν(P=S) 583 $cm^{-1}$, ν(CN) 2233 $cm^{-1}$, $\nu(ClO_4)$ 1100 $cm^{-1}$. MS (FAB, *m/z*) 865 ($M^+$ $-ClO_4$). NMR data ($CD_2Cl_2$) $^{31}P\{^1H\}$: $\underline{P}$(S) δ 36.80 dd ($^2J_{PP(N)}$ 15.6 Hz, $^2J_{PPEt_3}$ 4.1 Hz), $\underline{P}$(Ntfbn) δ 34.24 br d ($^2J_{PP(S)}$ 15.6 Hz), $\underline{P}Et_3$ δ 41.53 br s. $^1H$: $PC\underline{H}_2P$ δ 4.52 dd ($^2J_{HP(N)}$ 11.0 Hz, $^2J_{HP(S)}$ 12.1 Hz), $PEt_3$ $C\underline{H}_2$ δ 2.00 dq ($^2J_{HPEt_3}$ 3.2 Hz, $^3J_{HH}$ 7.6 Hz), $PEt_3$ $C\underline{H}_3$ δ 1.21 dt ($^3J_{HPEt_3}$ 18.5 Hz, $^3J_{HH}$ 7.6Hz). $^{13}C\{^1H\}$: $P\underline{C}H_2P$ δ 32.40 dd ($^1J_{CP(S)}$ 43.3 Hz, $^1J_{P(N)C}$ 69.4 Hz), $PEt_3$ $\underline{C}H_2$ δ 17.34 d ($^1J_{PC}$ 34.2 Hz), $PEt_3$ $\underline{C}H_3$ δ 8.47 s. $^{19}F$ (second order): *meta*-F tfbn δ -136.85, *ortho*-F tfbn δ -141.51.

## Preparation of $(Ph_2P(X)CHP(Ntfbn)Ph_2\{-X,C\})M(L)L'$ (M = Pt, X = S, Se, L = $PEt_3$, L' = Cl; M = Pd, X = S, L = $PEt_3$, L' = Cl; M = Rh, X = S, LL' = cod)

The procedures used for synthesizing the chalcogen/carbon bonded bisphosphine metallacycles are given below. Both method A and B were used to prepare the platinum/sulfur complex. The platinum/selenium, palladium/sulfur and rhodium/sulfur complexes were prepared using method A.

**Synthesis of $(\mathrm{Ph_2P(S)CHP(Ntfbn)Ph_2\{\text{-}S,C\})Pt(PEt_3)Cl}$:**

## METHOD A

A mixture of the bisphosphine, $\mathrm{Ph_2P(S)CH_2P(Ntfbn)Ph_2}$, (0.100g, 1.65 x $10^{-4}$mol) and $\mathrm{K^tBuO}$ (sublimed, 0.0186g, 1.65 x $10^{-4}$mol) was dissolved in $d^8$ tetrahydrofuran. To the straw yellow solution was added dropwise a solution of $\mathrm{[Pt(PEt_3)Cl_2]_2}$ (0.077g, 8.27 x $10^{-5}$mol) in tetrahydrofuran (5ml). The solution was left to stir for 1 hour. The solvent was then removed *in vacuo*, the yellow residue taken up in a minimum of dichloromethane and filtered through Celite. The title complex was crystallized from a dichloromethane/hexane mixture to give yellow crystals.

## METHOD B

An alternate method of preparation was to dissolve the chelate complex, $\mathrm{[(Ph_2P(S)CH_2P(Ntfbn)Ph_2\{\text{-}S,N\})Pt(PEt_3)Cl]ClO_4}$ (0.100g, 9.5 x $10^{-5}$mol), in tetrahydrofuran (10ml) and add the solution slowly to a suspension of NaH (5 fold excess, washed with hexane) in tetrahydrofuran (10ml). This solution was left to stir for approximately three hours. The THF solution was then filtered through Celite (to remove excess NaH), the solvent removed *in vacuo* and the title complex recrystallized from dichloromethane/hexane to give yellow crystals. Yield: *ca*. quantitative. mp: 160°C dec. Anal. Calc'd for $\mathrm{C_{38}H_{36}P_3N_2F_4SClPt}$: C 47.93, H 3.81, N 2.94. Found: C 47.94, H 3.67, N 2.95. IR data: (KBr disk) $\nu$(P=N) 1509 $\mathrm{cm^{-1}}$, $\nu$(P=S) $\mathrm{cm^{-1}}$, $\nu$(CN) 2228 $\mathrm{cm^{-1}}$ MS (FAB, *m/z*) 953 ($\mathrm{M^+}$). NMR data ($\mathrm{CD_2Cl_2}$) $^{31}\mathrm{P}\{^1\mathrm{H}\}$: $\underline{\mathrm{P}}$(S) $\delta$ 47.00 dd Pt sat. 32% ($^2J_{\mathrm{PPt}}$ 460 Hz, $^3J_{\mathrm{PPEt_3}}$ 13.8 Hz, $^2J_{\mathrm{PP(N)}}$ 6.4 Hz) , $\underline{\mathrm{P}}$(Ntfbn) $\delta$ 15.00 ddt Pt sat. 32% ($^2J_{\mathrm{PPt}}$ 64 Hz, $^3J_{\mathrm{PPEt_3}}$ 8.3 Hz, $^2J_{\mathrm{PP(S)}}$ 5.9 Hz, $^4J_{\mathrm{PF}}$ 5.6 Hz), $\underline{\mathrm{P}}\mathrm{Et_3}$ $\delta$ 5.3 ddt Pt sat. 32% ($^1J_{\mathrm{PPt}}$ 3000 Hz, $^3J_{\mathrm{PP(N)}}$ 8.7 Hz, $^3J_{\mathrm{PP(S)}}$ 13.6 Hz, $^4J_{\mathrm{PF}}$ 3.2 Hz). $^1$H: $\mathrm{PC\underline{H}P}$ $\delta$ 3.48 ddd ($^2J_{\mathrm{HP(S)}}$ 6.7 Hz, $^2J_{\mathrm{HP(N)}}$.8.6 Hz, $^3J_{\mathrm{HPEt_3}}$ 6.7 Hz), $\mathrm{PEt_3}$ $\mathrm{C\underline{H}_2}$ $\delta$ 1.62 ddq ($^3J_{\mathrm{HH}}$ 7.7Hz, $^2J_{\mathrm{HPEt_3}}$ 10.1 Hz, $^5J_{\mathrm{HC\underline{H}}}$ 6.1 Hz), $\mathrm{PEt_3}$ $\mathrm{C\underline{H}_3}$ $\delta$ 0.85 dt ($^3J_{\mathrm{HPEt_3}}$ 16.6 Hz, $^3J_{\mathrm{HH}}$ 7.7 Hz), phenyl H $\delta$ 7.2-8.4 m. $^{13}\mathrm{C}\{^1\mathrm{H}\}$: $\mathrm{P\underline{C}HP}$ $\delta$ 9.89 ddd ($^1J_{\mathrm{CP(S)}}$ 80.9 Hz, $^1J_{\mathrm{CP(N)}}$ 53.8 Hz,

$^{2}J_{CPEt_3}$ 30.6 Hz) $PEt_3$ $\underline{C}H_2$ δ 14.50 d ($^{1}J_{CPEt_3}$ 34.2 Hz), $PEt_3$ $\underline{C}H_3$ 7.62 s. $^{19}F$ (second order): *meta*-F tfbn δ -140.76, *ortho*-F tfbn δ -152.85.

## Synthesis of $(Ph_2P(Se)CHP(Ntfbn)Ph_2\{\text{-}Se,C\})Pt(PEt_3)Cl$:

This complex obtained from the reaction of $Ph_2P(Se)CH_2P(Ntfbn)Ph_2$, $K^tBuO$ and $[Pt(PEt_3)Cl_2]_2$ was isolated as an amber solid in essentially quantitative yield. mp: 100°C Anal. Calc'd for $C_{38}H_{36}P_3N_2F_4SeClPt$/1.58 mol $CH_2Cl_2$: C 41.96, H 3.48, N 2.47. Found: C 41.96, H 3.38, N 2.53. IR data: (KBr disk) ν(P=N) 1504 cm$^{-1}$, ν(CN) 2227 cm$^{-1}$ MS (FAB, *m/z*) 1001 (M$^+$). NMR data ($CD_2Cl_2$ ) $^{31}P\{^{1}H\}$: $\underline{P}$(Se) δ 26.90 dd Pt sat. 32%, Se sat. 8% ($^{2}J_{PPt}$ 495 Hz, $^{3}J_{PPEt_3}$ 13.6 Hz, $^{2}J_{PP(N)}$ 5.9 Hz, $^{1}J_{PSe}$ 441 Hz) , $\underline{P}$(Ntfbn) δ 15.00 ddt Pt sat. 32% ($^{2}J_{PPt}$ 64 Hz, $^{3}J_{PPEt_3}$ 9.9 Hz, $^{2}J_{PP(Se)}$ 5.5 Hz, $^{4}J_{PF}$ 5.3 Hz), $\underline{P}Et_3$ δ 4.70 ddt Pt sat. 32% ($^{1}J_{PPt}$ 2988 Hz, $^{3}J_{PP(N)}$ 9.93 Hz, $^{3}J_{PP(Se)}$ 13.7 Hz, $^{4}J_{PF}$ 3.1 Hz). $^{1}H$: $PC\underline{H}P$ δ 3.47 ddd ($^{2}J_{HP(Se)}$ 6.5 Hz, $^{2}J_{HP(N)}$ 8.2 Hz, $^{3}J_{HPEt_3}$ 8.2 Hz), $PEt_3$ $C\underline{H}_2$ δ 1.61 ddq (not resolved), $PEt_3$ $C\underline{H}_3$ δ 0.83 dt ($^{3}J_{HPEt_3}$ 16.5 Hz, $^{3}J_{HH}$ 7.6 Hz), phenyl H δ 7.2-8.4 m. $^{13}C\{^{1}H\}$: $P\underline{C}HP$ δ 10.23 ddd ($^{1}J_{CP(Se)}$ 81.4 Hz, $^{1}J_{CP(N)}$ 52.4 Hz, $^{2}J_{CPEt_3}$ 21.9 Hz) $PEt_3$ $\underline{C}H_2$ δ 15.13 d ($^{1}J_{CPEt_3}$ 31.4 Hz), $PEt_3$ $\underline{C}H_3$ 7.75 s. $^{19}F$ (second order): *meta*-F tfbn δ -140.90, *ortho*-F tfbn δ -152.82 ($^{4}J_{FP(N)}$ 5.0 Hz). $^{77}Se$: δ -209.41 d Pt sat. 32% ($^{1}J_{SeP}$ 443 Hz, $^{2}J_{SePt}$ 101 Hz).

## Synthesis of $(Ph_2P(S)CHP(Ntfbn)Ph_2\{\text{-}S,C\})Pd(PEt_3)Cl$:

This complex obtained from the reaction of $Ph_2P(S)CH_2P(Ntfbn)Ph_2$, $K^tBuO$ and $[Pd(PEt_3)Cl_2]_2$ was isolated as an amber solid in essentially quantitative yield. mp: 170°C Anal. Calc'd for $C_{38}H_{36}P_3N_2F_4SClPd$/0.8 mol $CH_2Cl_2$: C 52.57, H 4.19, N 3.22. Found: C 52.62, H 4.00, N 3.20. IR data: (KBr disk) ν(P=N) 1506cm$^{-1}$, ν(CN) 2224 cm$^{-1}$ MS (FAB, *m/z*) 864 (M$^+$). NMR data ($CD_2Cl_2$ ) $^{31}P\{^{1}H\}$: $\underline{P}$(S) δ 42.84 dd

($^3J_{PPEt_3}$ 12.6 Hz, $^2J_{PP(N)}$ 3.6 Hz) , $\underline{P}$(Ntfbn) δ 15.42 ddt ($^3J_{PPEt_3}$ 11.3 Hz, $^2J_{PP(S)}$ 5.4 Hz, $^4J_{PF}$ 6.2 Hz), $\underline{P}$Et$_3$ δ 24.51 ddt ($^3J_{PP(N)}$ 12.3 Hz, $^3J_{PP(S)}$ 12.3 Hz, $^4J_{PF}$ 4.6 Hz). $^1$H: PC$\underline{H}$P δ 3.00 ddd ($^2J_{HP(S)}$ 4.7 Hz, $^2J_{HP(N)}$ 6.8 Hz, $^3J_{HPEt_3}$ 6.8 Hz), PEt$_3$ C$\underline{H}_2$ δ 1.17 dq ($^2J_{HP}$ 9.1 Hz, $^3J_{HH}$ 7.5 Hz), PEt$_3$ C$\underline{H}_3$ δ 0.82 dt ($^3J_{HP}$ 16.8 Hz, $^3J_{HH}$ 7.7 Hz), phenyl H δ 7.4-7.9 m. $^{13}$C{$^1$H}: P$\underline{C}$HP δ 5.19 ddd ($^1J_{CP(S)}$ 89.0 Hz, $^1J_{CP(N)}$ 53.3 Hz, $^2J_{CPEt_3}$ 36.0 Hz) PEt$_3$ $\underline{C}$H$_2$ δ 15.40 d ($^1J_{CPEt_3}$ 27.2 Hz), PEt$_3$ $\underline{C}$H$_3$ δ 7.91 s. $^{19}$F (second order): *meta*-F tfbn δ -141.55, *ortho*-F tfbn δ -153.81 ($^4J_{FP(N)}$ 6 Hz).

### Synthesis of (Ph$_2$P(S)CHP(Ntfbn)Ph$_2${-S,C})Rh(cod):

The complex obtained from the reaction of Ph$_2$P(S)CH$_2$P(Ntfbn)Ph$_2$, K$^t$BuO and [Rh(cod)Cl$_2$]$_2$ was isolated as a yellow solid in essentially quantitative yield. mp: 160°C dec. Anal. Calc'd for C$_{40}$H$_{34}$P$_2$N$_2$F$_4$SClRh/0.1 mol CH$_2$Cl$_2$: C 55.69, H 4.07, N 3.20. Found: C 57.13, H 4.09, N 3.31. IR data: (KBr disk) ν(P=N) 1511 cm$^{-1}$, ν(P=S) 604 cm$^{-1}$, ν(CN) 2222 cm$^{-1}$ MS (FAB, *m/z*) 814 (M$^+$). NMR data (CD$_2$Cl$_2$ ) $^{31}$P{$^1$H}: $\underline{P}$(S) δ 30.37 d ($^2J_{PP}$ 15.2 Hz), $\underline{P}$(Ntfbn) δ 14.62 br s. $^1$H: PC$\underline{H}$P δ 2.76 br s. cod C$\underline{H}$. δ 4.12 br s. cod C$\underline{H}_2$ δ 1.96 br s, 1.67 br s, phenyl H's 7.4-8.1 m. $^{13}$C{$^1$H}: P$\underline{C}$HP δ 6.56 dd ($^1J_{CP(S)}$ 51.5 Hz, $^1J_{CP(N)}$ 33.6 Hz, $^1J_{CRh}$ 17.2 Hz), cod $\underline{C}$H δ 132.97 br s, cod $\underline{C}$H$_2$ δ 82.46 br s, 31.24 br s. $^{19}$F (second order): *meta*-F tfbn δ -140.98, *ortho*-F tfbn δ -153.15.

### Preparation of [(Ph$_2$P(S)CHP(N(H)tfbn)Ph$_2${-S,C})Pt(PEt$_3$)Cl][BF$_4$]

To a solution of (Ph$_2$P(S)CHP(Ntfbn)Ph$_2${-S,C})Pt(PEt$_3$)Cl (0.011 g, 1.15 x 10$^{-5}$ mol) in dichloromethane (~20 ml) was added a solution of HBF$_4$ (1 µl, 1.1 x 10$^{-5}$ mol). There was no apparent colour change noted. The solvent was removed *in vacuo* and the yellow solid was recrystallized from a dichloromethane/hexane mixture. The yield was essentially quantitative. NMR data ($CD_2Cl_2$) $^{31}P\{^1H\}$: $\underline{P}$(S) $\delta$ 50.69 dd Pt sat. 32% ($^2J_{PPt}$ 360 Hz, $^3J_{PPEt_3}$ 13.1 Hz, $^2J_{PP(N)}$ 17.3 Hz) , $\underline{P}$(Ntfbn) $\delta$ 40.09 dd Pt sat. 32% ($^2J_{PPt}$ 85 Hz, $^3J_{PPEt_3}$ 16.7 Hz, $^2J_{PP(S)}$ 16.7 Hz), $\underline{P}Et_3$ $\delta$ 8.45 dd Pt sat. 32% ($^1J_{PPt}$ 3081 Hz, $^3J_{PP(N)}$ 14.4 Hz, $^3J_{PP(S)}$ 14.4 Hz). $^1H$: PC$\underline{H}$P 3.02 ddd ($^2J_{HP(S)}$ 5 Hz, $^2J_{HP(N)}$. 13.2 Hz, $^3J_{HPEt_3}$ 6.1 Hz), N($\underline{H}$) $\delta$ 9.13 d ($^2J_{HP}$ 4.3 Hz). $^{13}C\{^1H\}$: P$\underline{C}$HP $\delta$ 2.02 ddd ($^1J_{CP(S)}$ 72.5 Hz, $^1J_{CP(N)}$ 69.2 Hz, $^2J_{CPEt_3}$ 44 Hz) $PEt_3$ $\underline{C}H_2$ $\delta$ 14.73 d ($^1J_{CPEt_3}$ 36.2 Hz), $PEt_3$ $\underline{C}H_3$ 7.84 s. $^{19}F$ (second order): *meta*-F tfbn $\delta$ -143.49, *ortho*-F tfbn $\delta$ -133.15, $B\underline{F}_4$ $\delta$ -153.55 s.

## Preparation of $Ph_2P(X)CH_2P(NT)Ph_2$ (X = O, S, Se)

The mixed imino/chalcogen ligands were prepared using procedures similar to the following example. The synthesis of the oxo ligand in the series was unsuccessful. An attempt to synthesize the oxo ligand by reacting the mono oxide of dppm with trimethylsilyl azide was also unsuccessful.

### Synthesis of $Ph_2P(Se)CH_2P(NT)Ph_2$:

A mixture of dppm (25.02g, 0.065 mol) and trimethylsilyl azide (7.81g, 0.068 mol) were heated at reflux (using an oil bath) for two days. When cooled, the resulting straw yellow, gelatinous material was dissolved in a minimum of warm acetonitrile. The solution was allowed to stand for 48 hours at room temperature to yield colourless crystals. Yield: 42%. mp: 85°C. Anal. Calc'd for $C_{31}H_{37}P_2NSi$: C 71.31, H 6.63, N 2.97. Found: C 72.30, H 6.44, N 2.50. IR data (KBr disk): $\nu$(P=N) 1271 $cm^{-1}$. MS (EI, *m/z*) 471 ($M^+$). NMR data ($CD_2Cl_2$) $^{31}P\{^1H\}$: $\underline{P}$(e pair) $\delta$ -27.64 d ($^2J_{PP}$ 57.1 Hz), $\underline{P}$(NT) $\delta$ -1.69 d

($^2J_{PP}$ 57.1 Hz). $^1$H: $C\underline{H}_2$ δ 3.08 dd ($^2J_{HP(III)}$ 1.1 Hz, $^2J_{HP(NT)}$ 12.2 Hz), $C\underline{H}_3$ δ -0.06 s, phenyl H δ 7.3-7.7 m. $^{13}C\{^1H\}$: $\underline{C}H_2$ δ 33.36 dd ( $^1J_{CP(N)}$ 72.6 Hz, $^1J_{CP(III)}$ 31.3 Hz), $SiMe_3$ $\underline{C}H_3$ δ 4.01 s.

To a solution of the phosphinimine, $Ph_2PCH_2P(NT)Ph_2$, (0.200g, 4.24 x $10^{-4}$mol) in toluene (20 ml) was added selenium black (0.033g, 4.24 x $10^{-4}$mol). The mixture was heated at reflux until the selenium black had completely disappeared (approx. 15 minutes). The solution was cooled to room temperature, filtered through Celite and the solvent removed *in vacuo*. The complex was isolated as a white solid. The yield was essentially quantitative. Mass Spec. $M^+$ Calc'd: 550.52. Found: 551. NMR data ($CD_2Cl_2$) $^{31}P\{^1H\}$: .$\underline{P}$(Se) δ 26.04 d Se sat. 8% ($^2J_{PP}$ 21.1 Hz, $^1J_{PSe}$ 734 Hz), $\underline{P}$(NT) δ -5.63 d ($^2J_{PP}$ 20.7 Hz). $^1$H: $C\underline{H}_2$ δ 3.85 dd ($^2J_{HP(Se)}$ 14.8 Hz, $^2J_{HP(NT)}$ 11.8 Hz), $SiMe_3$ $C\underline{H}_3$ δ -0.09 s, phenyl H δ 7.3-8.0 m. $^{13}C\{^1H\}$: $\underline{C}H_2$ δ 39.41 dd ($^1J_{CP(Se)}$ 38.25 Hz, $^1J_{PCP(N)}$ 67.44 Hz), $SiMe_3$ $\underline{C}H_3$ δ 3.71 d ($^3J_{CP(N)}$ 3.0 Hz).. $^{77}$Se: δ -214.27 ($^1J_{SeP}$ 731 Hz, $^3J_{SeP(NT)}$ 4 Hz).

**Synthesis of $Ph_2P(S)CH_2P(NT)Ph_2$:**

The complex obtained from the reaction of $Ph_2PCH_2P(NT)Ph_2$ and elemental sulfur was isolated as a white solid. Yield: 80%. NMR data ($CD_2Cl_2$) $^{31}P\{^1H\}$: .$\underline{P}$(S) δ 36.57 d ($^2J_{PP}$ 17.3 Hz), $\underline{P}$(NT) δ -6.45 d ($^2J_{PP}$ 17.1 Hz). $^1$H: $C\underline{H}_2$ δ 3.70 dd ($^2J_{HP(S)}$ 14.8 Hz, $^2J_{HP(NT)}$ 12.3 Hz), $SiMe_3$ $C\underline{H}_3$ δ -0.05 s, phenyl H δ 7.2-8.0 m. $^{13}C\{^1H\}$: $\underline{C}H_2$ δ 39.28 dd ($^1J_{CP(S)}$ 44.7 Hz, $^1J_{CP(N)}$ 67.7 Hz), $SiMe_3$ $\underline{C}H_3$ δ 3.75 d ($^3J_{CP(N)}$ 3.3 Hz).

## Preparation of $[(Ph_2P(Se)CH_2P(NT)Ph_2\{-Se,N\})M(PEt_3)Cl][ClO_4]$ and $[(Ph_2P(Se)CHP(N(H)T)Ph_2\{-Se,C\})M(PEt_3)Cl][ClO_4]$ (M = Pt, Pd)

The reaction of the $Ph_2P(Se)CH_2P(NT)Ph_2$ with $[M(PEt_3)Cl_2]_2$ (M = Pt, Pd) resulted in spontaneous deprotonation of the methylene carbon and formation of a mixture of the {-X,C} and {-X,N} bonded complexes. The procedures used were similar to the example below. It is noteworthy that all of the complexes possessing the NT moiety could not be crystallized because they decomposed rapidly in solution, especially in $CH_2Cl_2$. NMR Spectra were obtained in both $CD_2Cl_2$ and $d^6$ acetone solutions.

### Synthesis of $[(Ph_2P(Se)CHP(N(H)T)Ph_2\{-Se,C\})Pt(PEt_3)Cl][ClO_4]$ and $[(Ph_2P(Se)CH_2P(NT)Ph_2\{-Se,N\})Pt(PEt_3)Cl][ClO_4]$:

To a solution of $[Pt(PEt_3)Cl_2]_2$ (0.07g, $9.05 \times 10^{-5}$mol) and $NaClO_4$ (0.026g, $1.81 \times 10^{-4}$mol) in acetone (20ml) was added dropwise a solution of the phosphinimine selenide, $Ph_2P(Se)CH_2P(NT)Ph_2$ (0.100g, $1.81 \times 10^{-4}$ mol), in acetone (20ml). The reaction mixture was left to stir at room temperature for one hour after which time the solution had turned a light yellow and a white precipitate had formed. The precipitate was removed by filtration through Celite. $^{31}P\{^1H\}$ NMR spectroscopy indicated the product was comprised of a mixture of the {-C,Se} and {-N,Se} bonded complexes with the major component being the {-C,Se} metallacycle (90:10). $^{31}P\{^1H\}$ NMR data ($d^6$ acetone) for $[(Ph_2P(Se)CHP(N(H)T)Ph_2\{-Se,C\})Pt(PEt_3)Cl][ClO_4]$: $\underline{P}$(Se) $\delta$ 32.87 dd Pt sat 33%, Se sat. 8% ($^2J_{PP(N)}$ 10.3 Hz, $^2J_{PPEt_3}$ 12.8 Hz, $^2J_{PPt}$ 439 Hz, $^1J_{PSe}$ ), $\underline{P}$(NT) $\delta$ 33.18 dd ($^2J_{PP(Se)}$ 10.4 Hz, $^2J_{PPEt_3}$ 15.4 Hz, $^2J_{PPt}$ 86 Hz) $\underline{P}Et_3$ $\delta$ 6.64 dd ($^2J_{PP(Se)}$ 12.8 Hz, $^2J_{PP(N)}$ 15.6 Hz, $^1J_{PPt}$ 3007 Hz). $^{31}P\{^1H\}$ NMR data ($d^6$ acetone) for $[(Ph_2P(Se)CH_2P(NT)Ph_2\{-Se,N\})Pt(PEt_3)Cl][ClO_4]$: $\underline{P}$(Se) $\delta$ 17.15 dd ($^2J_{PP(N)}$ 9.2 Hz,

$^3J_{PPEt_3}$ 4.6 Hz, $^2J_{PPt}$ 156 Hz), P(NT) $\delta$ 28.37 dd ($^2J_{PP(Se)}$ 9.2 Hz, $^3J_{PPEt_3}$ 3.4 Hz), PEt$_3$ $\delta$ 0.08 dd ($^3J_{PP(Se)}$ 4.4 Hz, $^3J_{PP(NT)}$ 3.3 Hz)

### Synthesis of [(Ph$_2$P(Se)CHP(N(H)T)Ph$_2$ {-Se,C})Pd(PEt$_3$)Cl][ClO$_4$] and [(Ph$_2$P(Se)CH$_2$P(NT)Ph$_2$ {-Se,N})Pd(PEt$_3$)Cl][ClO$_4$]:

The NMR analysis of the product mixture obtained from the reaction of Ph$_2$P(Se)CH$_2$P(NT)Ph$_2$ and [Pd(PEt$_3$)Cl$_2$]$_2$ indicated the major component was the {-C,Se} bonded complex in a 60:40 ratio over the {-N,Se} bonded complex. $^{31}$P{$^1$H} NMR data (d$^6$ acetone) for [(Ph$_2$P(Se)CHP(N(H)T)Ph$_2${-Se,C})Pd(PEt$_3$)Cl][ClO$_4$]: .P(Se) $\delta$ 35.00 dd, Se sat. 7% ($^2J_{PP(N)}$ 11 Hz, $^2J_{PPEt_3}$ 11 Hz, $^1J_{PSe}$ 479 Hz), P(NT) $\delta$ 27.99 dd ($^2J_{PP(Se)}$ 10.4 Hz, $^2J_{PPEt_3}$ 16.2 Hz, $^2J_{PPt}$ Hz) PEt$_3$ $\delta$ 32.94 dd ($^2J_{PP(Se)}$ 11.7 Hz, $^2J_{PP(N)}$ 16.2 Hz). $^{31}$P{$^1$H} NMR data (d$^6$ acetone) for [(Ph$_2$P(Se)CH$_2$P(NT)Ph$_2${-Se,N})Pd(PEt$_3$)Cl][ClO$_4$]: P(Se) $\delta$ 18.16 dd, Se sat. 7% ($^2J_{PP(N)}$ 12.9 Hz, $^3J_{PPEt_3}$ 11.3 Hz, $^1J_{PSe}$ 582 Hz), P(NT) $\delta$ 29.73 dd ($^2J_{PP(Se)}$ 13.2 Hz, $^3J_{PPEt_3}$ 6.9 Hz), PEt$_3$ $\delta$ 30.82 dd ($^3J_{PP(Se)}$ 10.5 Hz, $^3J_{PP(N)}$ 7.6 Hz)

### Preparation of [(Ph$_2$P(Se)CH$_2$P(NH)Ph$_2${-Se,N})Pt(PEt$_3$)Cl][Cl]

To a yellow solution of [Pt(PEt$_3$)Cl$_2$]$_2$ (0.07 g, 1.82 x 10$^{-4}$ mol) ) in dichloromethane (20 ml) was added dropwise a clear colourless solution of Ph$_2$P(Se)CH$_2$P(NT)Ph$_2$ (0.1 g, 1.82 x 10$^{-4}$ mol) in dichloromethane (20 ml). The yellow reaction mixture was left to stir for one hour, the solvent was removed *in vacuo* and a mass spectral analysis performed on the yellow residue. MS (EI, *m/z*) 828 (M$^+$). The mass spectral analysis indicates that the SiMe$_3$ group was retained on the ligand. The yellow residue was then recrystallized from a dichloromethane/hexane mixture to give a yellow crystalline solid. $^1$H NMR data indicated that the $SiMe_3$ group was lost during recrystallization. Yield: 50%. NMR data ($CD_2Cl_2$) $^{31}P\{^1H\}$: $\underline{P}$(Se) δ 8.37 dd Pt sat. 32%, Se sat. 8% ($^2J_{PP(N)}$ 12 Hz, $^2J_{PPEt_3}$ 11 Hz, $^2J_{PPt}$ 161 Hz, $^1J_{PSe}$ 583 Hz), $\underline{P}$(NT) δ 30.07 dd ($^2J_{PP(Se)}$ 13.2 Hz, $^2J_{PPEt_3}$ 7.1 Hz), $\underline{P}Et_3$ δ 0.40 dd Pt sat. 32 % ($^2J_{PP(Se)}$ 9.7 Hz, $^2J_{PP(N)}$ 7.6 Hz, $^2J_{PPt}$ 3165 Hz). $^1H$: $C\underline{H}_2$ δ 4.58 dd ($^2J_{HP(Se)}$ 14.8 Hz, $^2J_{HP(NT)}$ 12.7 Hz), $PC\underline{H}_2CH_3$ δ 1.91 dq ($^2J_{HPEt_3}$ 10.23 Hz, $^3J_{HH}$ 7.6 Hz), $PCH_2C\underline{H}_3$ δ 1.14 dt ($^3J_{HPEt_3}$ 17.24 Hz, $^3J_{HH}$ 7.6 Hz), phenyl H δ 7.5-7.9 m. $^{13}C\{^1H\}$: $\underline{C}H_2$ δ 30.21 dd ($^1J_{CP(Se)}$ 68.6 Hz, $^1J_{PCP(N)}$ 37.4 Hz), $P\underline{C}H_2CH_3$ δ 15.10 d ($^2J_{CP(N)}$ 40.2 Hz), $PCH_2\underline{C}H_3$ 8.11 s.

The yellow crystalline solid was dissolved in dichloromethane in the presence of $NaClO_4$. After 15 minutes the solution was filtered through Celite and the solvent was removed *in vacuo*. An IR spectrum (KBr) of the yellow residue showed the presence of $\nu(ClO_4)$ at 1104 $cm^{-1}$

## Deprotonation of $Ph_2P(X)CH_2P(NR)Ph_2$ (X = S, R = tfbn; X = Se, R = T)

Both of the ligands $Ph_2P(S)CH_2P(Ntfbn)Ph_2$ and $Ph_2P(Se)CH_2P(NT)Ph_2$ were successfully deprotonated using strong bases. The former was used in the synthesis of various {-X,C} bonded metal complexes while the latter did not lead to the successful formation of metal complexes due to the propensity of the imino nitrogen of the parent ligand to abstract $H^+$. An example of the procedure for deprotonation is given below and differs for the two ligands in that the tfbn ligand was deprotonated with $K^tBuO$ because LDA was found to promote $F^-$ abstraction instead of deprotonation.

### Synthesis of $[Ph_2P(Se)CHP(NT)Ph_2][Li]$:

To a clear and colourless THF solution (20 ml) of $Ph_2P(Se)CH_2P(NT)Ph_2$ (0.100 g, 1.82 x $10^{-4}$ mmol), cooled to -78°C (dry ice/acetone bath), was added dropwise an $Et_2O$/hexane solution of LDA (1.35M, 0.13 ml). The solution turned a light yellow colour. The solvent was removed *in vacuo* and various multinuclear NMR measurements conducted. NMR data ${}^{31}P\{{}^{1}H\}$: P(Se) $\delta$ 17.77 d, Se sat 8% (${}^{1}J_{PSe}$ 591 Hz, ${}^{2}J_{PP}$ 26.9 Hz), P(N) $\delta$ 19.19 d (${}^{2}J_{PP}$ 26.7 Hz). ${}^{1}H$: $SiMe_3$ $C\underline{H}_3$ $\delta$ -0.17 s, phenyl H $\delta$ 7.2-7.9 m.

### Synthesis of $[Ph_2P(S)CHP(Ntfbn)Ph_2][K]$:

The straw yellow solution gave the following NMR data: ${}^{31}P\{{}^{1}H\}$: $\delta$ 35.26 d (${}^{2}J_{PP}$ 23.8 Hz), $\delta$ 23.79 d (${}^{2}J_{PP}$ 23.5 Hz). ${}^{1}H$: $\delta$ 3.42 br s, phenyl H $\delta$ 7.2-8.0 m. ${}^{13}C\{{}^{1}H\}$: 18.92 dd (${}^{1}J_{CP(S)}$ 103.4 Hz, ${}^{1}J_{CP(N)}$ 116.4 Hz) ${}^{19}F$ *ortho*-F -153.98 dd (${}^{3}J_{FF}$ 18, ${}^{4}J_{FP(N)}$ 7 Hz), *meta*-F -143.57 d (${}^{3}J_{FF}$ 18 Hz).

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