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SYNTHESES AND CHARACTERIZATION OF TRANSITION METAL COMPLEXES WITH SULFUR DONOR LIGANDS (DTC)

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tarafından değerlendirilmiş olup, yapılan Tez Savunma Sınavında aday oy birliği ile başarılı bulunmuştur.

ABSTRACT

SYNTHESES AND CHARACTERIZATION OF TRANSITION METAL COMPLEXES WITH SULFUR DONOR LIGANDS (DTC)

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PhD. in Department of Chemistry

Supervisors:

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A series of new palladium complexes with dithiocarbamate ligands, and various allyl groups, $[(\eta^3\text{-allyl})Pd(S_2CNR_2)]$ (allyl: 2-methylallyl, 1,1,2-trimethylallyl, R: Me, Et, ^nPr, Bz; allyl: cyclohexenyl, R: Me, Et) have been synthesized and characterized by elemental analysis, FT-IR, ^1H- NMR and FAB-Mass spectrometry. And also, X-ray crystal structure of $[(\eta^3\text{-}CH_2CMeCH_2)Pd(S_2CN^nPr_2)]$ has been resolved.

The spectroscopic studies suggest that the palladium atom is tetra-coordinated with a distorted square-planar geometry of two sulfur atoms of bidentate dithiocarbamate chelate and three carbon atoms of π-allyl group.

Key Words: Palladium dithiocarbamate complexes, palladium allyl complexes.

ÖZET

GEÇİŞ METALLERİNİN KÜKÜRT DONORLU (DTC) KOMPLEKSLERİNİN SENTEZ VE KARAKTERİZASYONU

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Çeşitli allil grupları ve ditiyokarbamat ligandlarının, koordine olduğu bir seri, yeni palladyum kompleksleri; [(η^3-allil)Pd(S_2CNR_2)] (allil: 2-metilallil, 1,1,2-trimetilallil, R: Me, Et, ^{n}Pr, Bz; allil: siklohegzenil, R: Me, Et) sentezlenmiş ve yapıları elemental analiz, FT-IR, ^{1}H-NMR ve FAB-Mass spektrometri yöntemleri ile aydınlatılmıştır. Ayrıcaη [(^{3}-CH_2CMeCH_2)Pd ($S_2CN^nPr_2$)] kompleksinin X-ışını kristal yapısı da açıklanmıştır.

Spektroskopik çalışmalar sonucunda, π-allil grubunun üç karbon atomundan ve iki dişli ditiyokarbamatın, iki kükürt atomundan kelat olarak palladyum atomuna koordinasyonu ile bozulmuş kare düzlem yapı oluşturduğu saptanmıştır.

Anahtar sözcükler: Palladyum ditiyokarbamat kompleksleri, palladyum allil kompleksleri.

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ABBREVIATIONS AND SYMBOLS

Abbreviations

IR	Infrared
FT-IR	Fourier Transform Infra-Red
UV	Ultra Violet
NMR	Nuclear Magnetic Resonance
CVD	Chemical Vapour Deposition
TOPO	Trioctylphosphine oxide
Dtc	Dithiocarbamate
Acac	Acetylacetonate
Cp	Cyclopentadien, C_5H_6
TMS	Tetramethylsilane
Me	Methyl
Et	Ethyl
^{n}Pr	*n*-Propyl
Ph	Phenyl
Bz	Benzyl
L	Ligand
M	Metal
THF	Tetrahydrofurane
m.p	melting point

Symbols

α	Alpha	η	Eta	δ	Delta
β	Beta	π	Pi	λ	Lambda
γ	Gamma	σ	Sigma	θ	Theta

1. INTRODUCTION

Transition metal complexes with sulfur ligands are active catalysts in a considerable number of homogeneous reactions, although they have been less investigated than complexes with other donor atoms. The use of different types of sulfur ligands and the characteristics of the coordination complexes have been described together with the results of the catalytic reactions (Bayon, Claver and Masdeu-Bulto, 1999). The coordination chemistry of sulfur ligands has been extensively studied and has shown a unique variety of structures with most of the transition metals in different oxidation states. However, the use of sulfur ligands in reactions catalysed by transition metals is still relatively unexplored compared with other ligands.

1.1 Palladium Sulfides

Platinum group metal chalcogenides (M_xE_y; M= Pd or Pt; E= S, Se, Te) have found extensive applications in catalysis and materials science. Examples of the latter include; the manufacture of semiconductors and solar cells, lithographic films/plates with high resolution, and optical disc recording films (Malik, O'Brien, Paul, and Revaprasadu, 2002).

Palladium sulfides have been used as heterogeneous catalysts in organic reactions, including the hydrogenation of olefins and the hydrodesulfurization of thiophenes (Mashkina, and Zirka, 2000). They also have a range of interesting magnetic and electrical properties. They are semiconductors (E_g=~2eV) and have been studied as a constituent of a Pd-P-S photoelectrode (Folmer, Turner and Parkinson, 1987) and they have also been used for electrolytic plating due to their layered structures (Bladon, Lamola, and Lytle, 1996). Traditional synthetic methods to these materials have involved direct combination of elements, and reaction of hydrogen sulfide with palladium metal or palladium chlorides. Materials produced in this way are difficult to process and engineer (Harvey and Hogarth, 2002), and with increasing industrial demands for smaller-scale applications, a cleaner method of synthesizing palladium sulfides from molecular precursors would be advantageous, in order for it to be laid down in thin films, as nanoparticles or incorporated them into zeolites.

The two main sulfides of palladium are PdS, prepared as a brown powder and grey crystals, and PdS_2, a grey solid (Greenwood and Earnshaw, 1984). Other less common palladium sulfide materials include Pd_4S and a range of non-stoichiometric sulfides, including $Pd_{2.2}S$, $Pd_{2.5}S$, *etc.* which show strong temperature dependance. In common with many other metal sulfides they are difficult to process or engineer. Industry increasingly demands nanoscale materials and thin films, and the lack of palladium sulfides in this form severely restricts their effective use. A cleaner method of synthesizing these materials would be chemical vapour deposition, using a single source molecular precursor, which would be easy to process (Gleizes, 2000). This technique has been used widely to produce early transition metal chalcogenides but there have been few reports of their late transition metal analogues, including palladium, being formed in this way.

1.2 Chemical Vapour Deposition: The Single-Source Approach

Chemical vapour deposition (CVD) of metal particles was first demonstrated in 1890 by Mond, who prepared highly pure nickel by decomposition of nickel tetracarbonyl (Mond, 1890). Since then, CVD has been a rapidly developing technology for laying down thin films or finely dispersed particles of materials. It relies on the reaction of gase phase molecules to form film precursors, followed by adsorption and diffusion of the precursors onto a heated substrate, and desorption and removal of surface reaction by-products (Gleizes, 2000). The first CVD strategies involved reactions between two gas phase, or very volatile reactants, that formed and deposited the required product on the substrate.

$$e.g.\ Me_3Ga + AsH_3 \longrightarrow GaAs + 3CH_4$$

Opposed to this dual-source approach, is the single source approach. Here a pre-formed single molecule, containing all the element-element bonds required in the product, is transported into the gas phase. When heated, it decomposes to give the required material as a film, or nanoscale particles on the substrate, which can be glass, silicon, TiO_2 *etc.*

The best method for laying down thin films of palladium sulfides is the single-source approach, so as to avoid the use of toxic H_2S, and to have better control over the purity of the film. It has already been noted that palladium sulfide materials produced from dual sources are difficult to process and are often of variable composition. The conditions that need to be met are that a suitable precursor should:

- Contain Pd-S bonds. This is a relatively straightforward as Pd is a "*soft*" metal atom and has a large affinity for "*soft*" donor atoms, such as phosphorus, arsenic, sulfur and selenium.
- Be volatile enough to allow it to be transported into the vapour phase.
- Decompose cleanly at a relatively low temperature.

Ideally, the precursor should also be neutral, monomeric with weak intermolecular bonds, easily synthesised, produced in high yield, and preferably non-toxic and air-stable.

1.3 Designing Precursors to Palladium Sulfide

There has been considerable attention given in the past to laying down films of palladium metal for use in microelectronic devices and designing suitable precursors. A review of such work, involving palladium and various π-allyl, *acac*, and phosphine ligands has been given by Hierso *et al.* (Hierso, Feurer, and Kalck, 1998). Another group used liquid precursors, giving obvious benefits in terms of increased volatility, (Zhang, Yuan, and Puddephatt, 1998) and such precursors also act as catalysts in the CVD of yttrium oxide (Zhang and Puddephatt, 1999). CVD routes and single-source precursors to early transition and main group metal sulfides have been widely studied (Gleizes, 2000). To date little work has been carried out on late transition metal sulfides including palladium (Cheon, Talaga, and Zink, 1997 and Malik, O'Brien, and Revaprasadu, 2002). In finding a precursor for palladium sulfide, it is important to design materials that allow the deposition if palladium sulfide as an intermediate process, rather than depositing metal immediately. The temperature of deposition will probably be important in determining the stoichiometry of the sulfide produced.

Palladium forms many compounds with sulfur-donating ligands, both in monodentate and bidentate fashion (Figure 1.1). Examples include xanthates S_2COR^-, dithiocarbamates $S_2CNR_2^-$ and dithiophosphinates $S_2PR_2^-$ (Cotton, Wilkinson, Murillo and Bochmann, 1999). The groups attached to the coordinated sulfur should ideally increase the volatility of the complexes and make a good leaving group at moderate temperature, leaving behind PdS or PdS_2. There is a wide variety of compounds of the following anions;

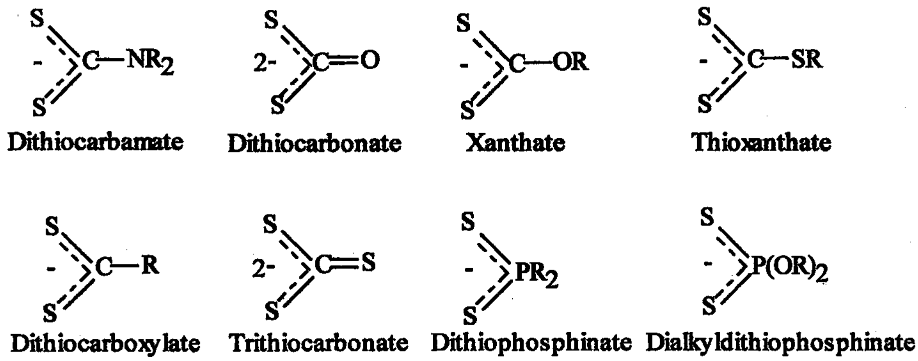


Figure 1.1 Some sulfur containing anions.

Xanthates are bidentate sulfur donating ligands. Simple alkyl xanthates [$M(S_2COR_2)$] are well known and easily prepared, *e.g.* ethyl xanthate and methyl xanthate are available as alkali metal salts, which can be reacted with the relevant metal halide or nitrate (Wilkinson *et al.*, 1987). The most important example of this series are dithiocarbamate and dithiophosphinate complexes (Cotton and Wilkinson, 1988, 537); the former are used as fungicides and for solvent extraction and the latter as high pressure lubricants.

The production of NiS and PdS films was reported by Laser and Thermal Vapour Deposition from *bis*(isopropylxanthate)metal [$M(S_2COCHMe_2)_2$] (where M= Ni, Pd) (Cheon, Talaga and Zink, 1997), (Figure 1.2).

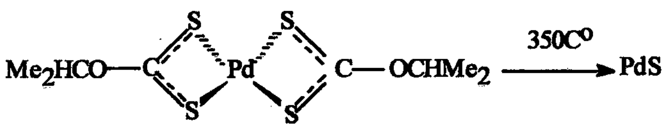


Figure 1.2 CVD of Bis(isopropylxanthate)palladium (II).

Zinc and Cadmium dialkyl dithiocarbamates have been extensively studied as precursors to ZnS and CdS. Saunder *et al.* prepared ZnS, CdS and

$Zn_xCd_{1-x}S$ thin films from $[Zn(S_2CNEt_2)_2]$ in a low pressure reactor (Saunders, Vecht, Tyell, 1988). O'Brien *et al.* (Motevalli, O'Brien, Walsh, Watson, 1996) compared the volatilities of symmetrically substituted $[Zn(S_2CNEt_2)_2]$ with asymmetrically substituted $[Zn(S_2CN(Me)Et)_2]$, $[Zn(S_2CN(Me)^nPr)_2]$ and $[Zn(S_2CN(Me)^nBu)_2]$. They found that the symmetrically substituted complex sublimed as a solid, whereas the asymmetric compounds sublimed above their melting points. They prepared a film of ZnS from $[Zn(S_2CN(Me)^nBu)_2]$ in a cold-wall, low-pressure CVD reactor, with a source temperature of 150°C and a substrate temperature of 450-490°C. Zinc and cadmium are soft metals like palladium and therefore palladium dithiocarbamates might reasonably be expected to be suitable precursors to palladium sulfides.

The simplest dithiocarbamate of palladium, $[Pd(S_2CNH_2)_2]$ was reported by Nakamoto *et al.* (Nakamato, 1963) It was prepared by the addition of a solution of ammonium dithiocarbamate to an aqueous solution of palladium(II). Since then a wide range of compounds, usually binding through both sulfur atoms have been reported (Ibers, 1982). A crystal structure of an interesting trinuclear complex of palladium diethyldithiocarbamate, where the dithiocarbamate bridges the Pd atoms, has been reported (Blake, Kathirgamanathan, Toohey, 2000), (Figure 1.3).

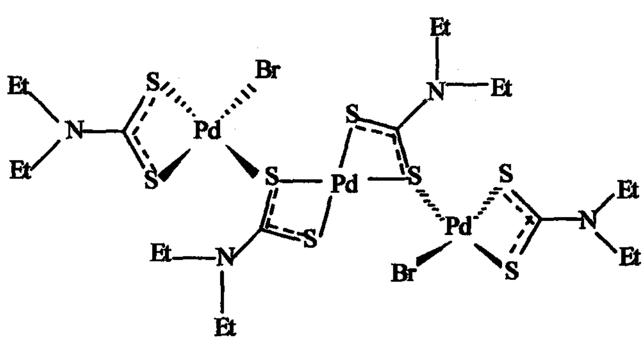


Figure 1.3 A novel trinuclear palladium(II) dithiocarbamate.

The properties of the palladium dithiocarbamate complexes can be altered by variation of the alkyl groups on the nitrogen. A study into a series of such compounds determined the X-ray crystal structures, and measured volatility and melting points (Riekkda, Pakkanen, Niinisto, 1983), (Table 1.1).

Table 1.1 Melting points of $[Pd(S_2CNR_2)_2]$ (R: Et, ^{i}Pr, ^{n}Bu, ^{i}Bu, (CF_3CH_2)).

R	Et	^{i}Pr	^{n}Bu	^{i}Bu	(CF_3CH_2)
m.p./ C°	243	149	109	189	161

Gas chromatography showed that the most volatile complex was $[Pd(S_2CN(CF_3CH_2)_2)_2]$, due to the electronegativity of the fluorine substituents, which repel other atoms. The melting points of the compounds decreased with the alkyl group chain lengths but no pattern could be observed between their volatility and the carbon chain length. However, the compounds are less crystalline and generally harder to purify as the alkyl group increases in size.

This work demonstrated that most of the *bis*(dialkyldithiocarbamate) palladium complexes are quite involatile with high melting points, seemingly making them undesirable for use as molecular precursors to palladium sulfides. More volatile molecular systems would lead to faster growth rates and lower temperatures of film deposition.

Recently however, O'Brien *et al.* reported the synthesis of PdS and PtS, as both thin films on a GaAs substrate, and as nanoparticles capped by trioctylphosphine oxide (TOPO) (Malik, O'Brien, and Revaprasadu, 2002). The films were laid down thermally at 10^{-2} torr and 400°C from $[Pd(S_2CN(Me)^nHex)_2]$ and $[Pt(S_2CN(Me)^nHex)_2]$, and characterized by EDAX, XRD, and SEM. Both films were in the tetragonal phase, and the PdS and PtS nanoparticles were of approximately 5 and 3 nm diameter respectively. The same group successfully used [Cd($Se_2CN(Me)^nHex)_2$] as a precursor to CdSe (Lazell, Norager, O'Brien, and Revaprasadu, 2001). The asymmetric combination of methyl and hexyl groups on the amine appears to make the dithiocarbamate more volatile than a symmetrically substituted analogue. However, the temperatures of deposition are relatively high compared to those used by Zink *et al.* (Zink, Cheon, Talaga, 1997) to lay down PdS from xanthates, and very high compared to the 350°C temperature used to deposit Pd metal from [Pd(η^5-C_5H_5)(allyl)] (Shaw, 1960). The growth rates of the films are low, but this is not a problem when forming the mono-dispersed nanoparticles where volatility is not a prerequisite for a precursor.

The lability of an allyl group in allylpalladium compounds is well documented. This has been exploited in the deposition of palladium films from allylpalladium compounds, such as [Pd(η^3-allyl$)_2$] (allyl=C_3H_5, C_4H_7), [CpPd(η^3-C_3H_5)], at moderately low temperatures (Hierso, Feurer, Kalck, 1998). Volatile compounds of palladium are slightly less numerous than those of platinum. Due to the importance of palladium films for microelectronic applications, there has been much interest in the design and study of palladium complexes for use as precursors for CVD over the past few years. The complexes considered to be sufficiently volatile to be used for CVD are given in Table 1.2, (Hierso, Feurer, Kalck, 1998).

Table 1.2. Volatile complexes to be used for CVD.

Pd complexes	Yield	Volatility	Deposit quality
Pd(η^3-allyl)(Cp)	****	VP: 25 Torr, 100 °C	***
Pd(η^3-allyl)$_2$	****	_	****
Pd(η^3-methyl-2-allyl)$_2$	****	_	****
Pd(η^3-allyl)(acac)	***	_	****
Pd(η^3-methyl-2-allyl)(acac)	***	Sublim.70 °C, 10^{-2} Torr	***
Pd(η^3-allyl)(hfacac)	****	VP: 2.5 Torr, 100 °C	****
Pd(η^3-methyl-2-allyl)(hfacac)	_	_	****
Pd($S_2COCHMe_2$)	_	Sublim.95 °C, 10^{-2} Torr	***

A good way of increasing the volatility of the complexes is by substituting one of the dithiocarbamate ligands for a more volatile group, such as the π-allyl group (η^3-C_3H_5), found in many complexes with palladium.

The first such compound, [Pd(η^3-C_3H_5)(η^5-C_5H_5)] was prepared by Shaw in 1960, (Shaw, 1960) and was extensively studied as a CVD precursor to palladium metal. The *bis*(allyl)palladium complex [Pd(η^3-C_3H_5)$_2$] was synthesized by Wilke in 1963, from the reaction of $PdCl_2$ with allyl magnesium chloride (Wilke, 1963). It can be precipitated as pale yellow crystals from pentane, which are stable in ether at 80°C, but which explode on exposure to air at room temperature, as bound allyl groups react together in a Diels-Alder type reaction. Faller and Incorvia, (Faller and Incorvia, 1967), made the even less stable *bis*(methylallyl)palladium [Pd(η^3-C_4H_7)$_2$], but a complete synthesis was not reported until 1980 (Henc *et al.*, 1980).

Clearly the allyl group is very labile, but these unstable compounds are not suitable for transferring the allyl group onto the dithiocarbamates.

A good method of synthesizing [(allyl)Pd(dtc)] is by adding a solution of dithiocarbamate to the allyl chloride dimer $[(\eta^3\text{-}C_3H_5)Pd(\mu\text{-}Cl)]_2$ or the 2-methylallyl chloride dimer $[(\eta^3\text{-}C_4H_7)Pd(\mu\text{-}Cl)]_2$, (Figure 1.4). The latter are air-stable, thermally stable crystalline, yellow solids, which have a straightforward, high yielding synthesis and can be stored for months (Zhang, Yuan, Puddephatt, 1998). The stability of the chelate complex formed also helps drive the reaction.

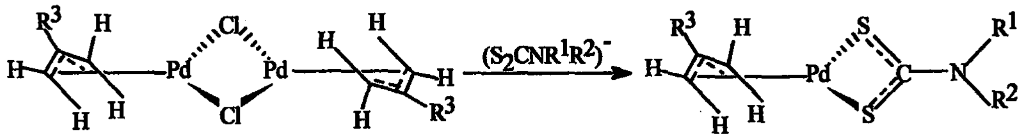


Figure 1.4 Formation of allyl palladium dithiocarbamates.

Powel and Chan, using low temperature ^1H NMR, to investigate the lability of the allyl group in allylpalladium dithiocarbamates (Powell and Chan, 1972). They found that when the phosphine PMe_2Ph was reacted with $[(\eta^3\text{-}C_4H_7)Pd(\eta^2\text{-}S_2CNMe_2)]$, the allyl group underwent a $\pi \rightarrow \sigma$ interconversion and the phosphine added to the metal centre, briefly forming the σ-allyl complex $[(\eta^1\text{-}C_4H_7)Pd(S_2CNMe_2)(PMe_2Ph)]$, (Figure 1.5). The dithiocarbamate remained coordinated through both sulfur atoms. This is a measure of the chelating power of the dithiocarbamate ligand, and its ability to briefly stabilise the less stable σ-allyl coordination. Further addition of phosphine yielded ionic, conducting species as phosphorus is a better σ-donor than sulfur, and addition of the phosphine breaks the metal-sulfur bond *trans* to it.

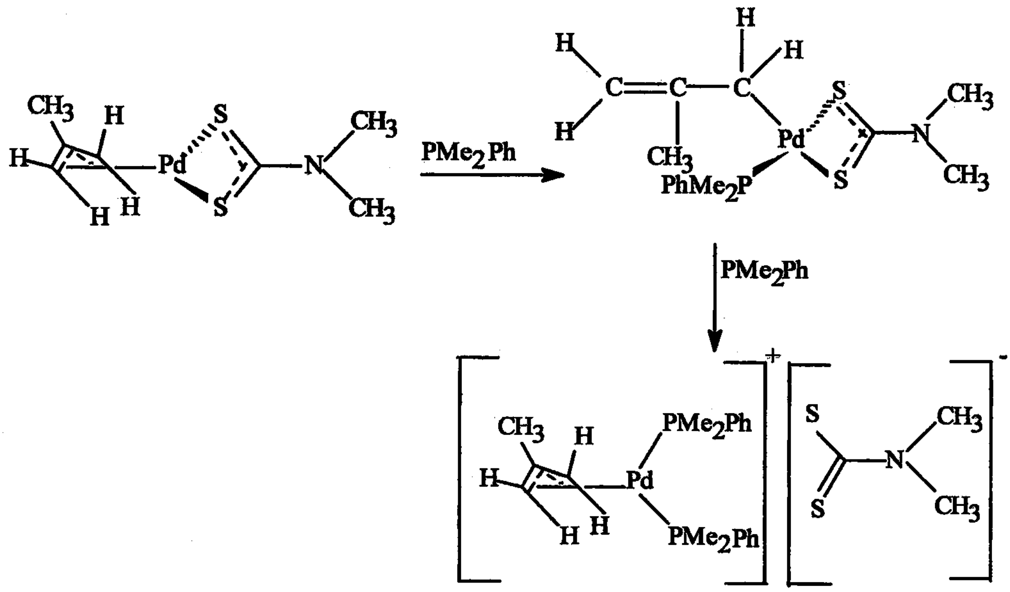


Figure 1.5 $\pi \rightarrow \sigma$ **interconversion in a dithiocarbamate complex.**

Jain *et al.* used TGA to investigate whether dimeric (2-methylallyl) palladium with organochalcogenide bridging ligands would form palladium chalcogenides when heated (Figure 1.6), (Singhal, Jain, Mishra, Varghese, 2000). They found that when $[\{(\eta^3\text{-}C_4H_7)Pd(\mu\text{-}ER)\}_2]$, (ER=$S^tBu$, SC_6F_5, SePh, TePh), were heated to ~200°C, they decomposed to Pd_4E, confirmed by *XRD*. The formation of these palladium-rich chalcogenides indicates that the temperature of deposition is important in determining the palladium: sulfur ratio.

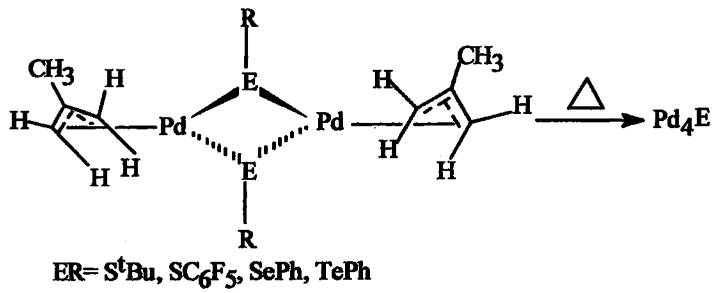


Figure 1.6 **Palladium-rich chalcogenides from organochalcogenide-bridged dimers.**

1.4 Dithiocarbamates

Dithiocarbamate ligands display a rich and varied coordination chemistry providing a wide range of transition and main group metal complexes, many of which have important chemical and biological properties.

1.4.1 Preparation of Dithiocarbamates

Dithiocarbamates are bidentate, sulfur donating ligands and normally prepared as alkali metal salts by the reaction of primary or secondary amines on CS_2 in the presence of NaOH (Wilkinson, Gillard, and McCleverty, 1987). The zinc, manganase, and iron dithiocarbamates are extensively used as agricultural fungucides and zinc salts as accelarators in the vulcanization of rubber. Alkali metal dithiocarbamates are usually hydrated and are dissociated in aqueous solution. When anhydrous, they are soluble in organic solvents in which they are associated. They have the formula $(S_2CNR_2)^-$ or $(S_2CNR^1R^2)^-$ (R=H, alkyl), depending on whether the nitrogen atom is symmetrically or asymmetrically substituted. The first such compound prepared was ammonium dithiocarbamate $[NH_4][S_2CNH_2]$ (Sceney and Magee, 1974). It is formally a salt of the unstable dithiocarbamic acid (HCS_2NH_2). The free acid can be prepared as an oily liquid by dissolving the ammonium salt in concentrated sulfuric acid at low temperatures. Addition of metal salts to solutions of this compound, yields metal dithiocarbamate complexes. Little information is available as to their characterisation or stabilities.

Dialkyldithiocarbamates, such as *N,N*-diethyldithiocarbamate, are available commercially as alkali metal salts such as $NaS_2CNEt_2.3H_2O$. The synthesis of dithiocarbamates with more complex *N*-alkyl groups is straightforward, consisting of addition of metal salt to a pre-stirred aqueous solution of excess amine, carbon disulfide and base at room temperature. These compounds are more stable and inert than those with hydrogen substituents and dithiocarbamates of nearly all main group and transition elements have been prepared (Sceney and Magee, 1974). One important use of dithiocarbamates is in heavy metal extraction. The bonding to the central metal atom is through both sulfur atoms and both M-S bonds are identical in transition metal complexes.

Although dithiocarbamates are usually made from sodium salts such as NaS_2CNMe_2 or by oxidations using thiuram disulfides, they can also be made by insertion reactions of CS_2 with dialkylamides, for example, (Cotton and Wilkinson, 1988).

$$Ti(NR_2)_4 + 4CS_2 \longrightarrow Ti(S_2CNR_2)_4$$

1.4.2 Resonance forms of Dithiocarbamates

The sulfur atoms are strongly donating, and consequently there is high electron density at the metal. Extensive π-delocalisation occurs throughout the MS_2CN plane and this contributes to the resonance structures (Figure 1.7), (Job, 1967).

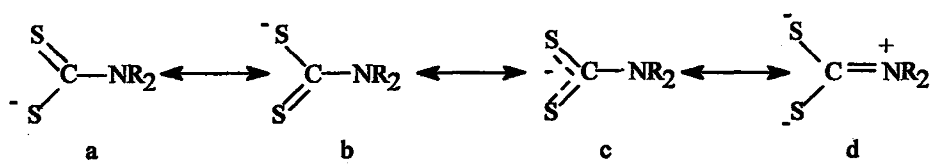


Figure 1.7 Resonance forms in dithiocarbamates.

Structure (d) is important for simple alkyl derivatives, less important for more complex aliphatic chains, and makes a relatively low contribution when R is an aliphatic heterocyclic group such as piperidine. Possibly this is because the rigid heterocycle system has less tendency to release electrons, and consequently there is less double bond character to the C-N bond (Franchini, *et al.,* 1985). Dithiocarbamates have interesting redox properties: they are not prone to reduction, but can oxidised fairly readily. The dithiocarbamate ligand can stabilise high formal oxidation states on the metal centre, such as Fe^{IV}, Cu^{III} and Ni^{IV}. *Bis*(diethyldithiocarbamato) palladium(II) is oxidised by elemental bromine to *bis*(diethyldithiocarbamato)dibromo palladium(IV) (Blake and Kathirgamanathan, *et al.,* 2000). Dithiocarbamates stabilize high oxidation states as in $[Fe^{IV}(dtc)_3]^+$ or $[Ni^{IV}(dtc)_3]^+$.

Main group dithiocarbamates often have unsymmetrical M-S bonds. They are pure σ-donors, owing to lack of pπ-dπ interactions and they are usually only stable in low oxidation states, unless strong σ-donors such as halogens, are introduced onto the metal.

1.4.3 Bonding types of Dithiocarbamates

The typical bonding modes of dithiocarbamates are shown below, (Cotton, and Wilkinson, 1988, 537), (Figure 1.8);

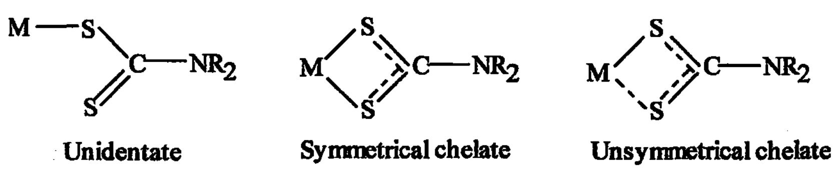


Figure 1.8 Bonding types of dithiocarbamates

When bridging the dithiocarbamate groups (shown diagrammatically) can have several forms (Figure 1.9)

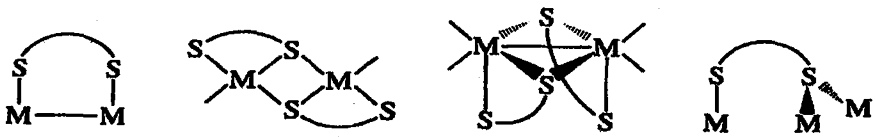


Figure 1.9 The bridging $^{-}S_2CNR_2$ groups

The unidentate and chelate types can be distinguished by IR and NMR spectra. The latter, particularly for chelate ligands, are commonly temperature dependant due to dynamic processes, involving non equivalence of the R groups resulting from restricted rotation about the C-N bond. The *tris*-(chelates) $Mdtc_3$, have intramolecular, metal-centered dynamic processes proceeding *via* a trigonal twist mechanism (Cotton and Wilkinson, 1988).

Most transition metals form *bis*- and/or *tris*-(dithiocarbamato) complexes in which the sulfur atoms of chelate dithiocarbamate ligands possess non bonding lone pairs. Such complexes should in principle be capable of acting as S-donor ligands to other metal centers and thereby generating homo- or hetero-polynuclear complexes. This behaviour pattern is commonly encountered with transition metal aminothiolate complexes *cis*-$[M(N\text{-}S)_2]$ and *fac*-$[M(N\text{-}S)_3]$ (N-S=2-aminoethane thiolate or *L*-cysteinate) which form S-bridged polynuclear species by acting as bidentate or tridentate S-donor ligands respectively towards a variety of class (b) metal ions (Konno, and Okamoto, 1997). However, it is a relatively rare phenomenon in dithiocarbamate coordination chemistry. The few structurally characterised homonuclear examples in which the chelate dithiocarbamate ligands bridge through sulfur to a second metal centre include the ruthenium complexes; $[Ru_2(Et_2NCS_2)_5][BF_4]$, $[\{Ru(CO)(S_2CNEt_2)_2\}_2]$, $[Ru_3(CO)_3Cl_2(S_2CNEt_2)_4]$

and the cobalt $[Co_2(S_2CNEt_2)_5][BF_4]$ and rhodium $[Rh_2(S_2CNMe_2)_5][BF_4].0.5CH_2Cl_2$, complexes (Exarchos, Nyburg and Robinson, 1998).

The $M(NR_2)_5$ compounds undergo insertion reactions with CS_2 (Cotton, and Wilkinson, 1988, 794). The metal atoms in the resulting dithiocarbamates are eight-coordinate, with two monodentate and three bidentate ligands;

$$Ta(NMe_2)_5 + 5CS_2 \longrightarrow Ta(S_2CNMe_2)_5$$

Besides the $M(S_2CNMe_2)_5$ compounds just mentioned, many other dithiocarbamates are known, of which the cationic species, $[M(S_2CNR_2)_4]^+$ are most important. They have generally dodecahedral structures in which the S_2CNR_2 ligands span four *m* edges of the dodecahedron but many are fluxional. Compounds of this type can be made by the reaction;

$$TaCl_5 + 4NaS_2CNR_2 \xrightarrow[\text{reflux}]{CH_2Cl_2} [Ta(S_2CNR_2)_4]Cl$$

Sulfur ligands are especially important for Zn and Cd and have been much studied partly because of the biological importance of the elements and partly because of the use of zinc dithiocarbamate and related compounds as accelerators in the vulcanisation of rubber by sulfur (Cotton, and Wilkinson, 1988, 925). Dithiocarbamate complexes, $[Zn(S_2CNR_2)_2]$ are antioxidants and anti wear lubricants as well as vulcanisation accelerators. The dimers achieve five-coordination, where one M-S bond is longer than the other. The dimers may be cleaved by amines to give five-coordinate 1:1 adducts. In the $[Zn(S_2CNR_2)_3]^-$ anion, the Zn is in a distorted tetrahedral environment with one chelate and two formally unidentate S_2CNR_2 groups. (Figure 1.10)

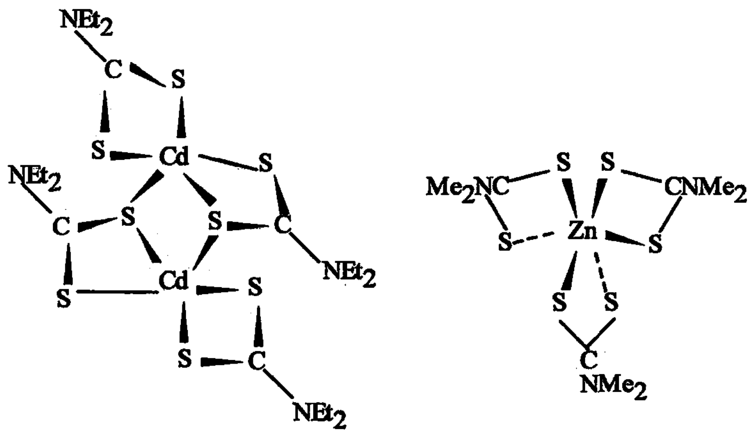


Figure 1.10 The structures of $[Cd(S_2CNR_2)_2]_2$ and $[Zn(S_2CNR_2)_3]$

In addition several bis(dithiocarbamato) complexes exist in the solid state as dimers *e.g.* $[Cu(S_2CNEt_2)_2]_2$ and $[Zn(S_2CNEt_2)_2]_2$ (Bonamico, Dessy, Magnoli, Vaciago, and Zambonelli, 1965) or polymers *e.g.* $[Mn(S_2CNEt_2)_2]_n$ (Ciampolini, Mengozzi, and Orioli, 1975) with chelate dithiocarbamate ligands bridging through sulfur to a second metal atom. Structurally characterised examples of heteronuclear complexes in which chelate dithiocarbamate ligands bridge through sulfur to a second metal atom are even less common. The best established examples are the iron/zinc species $[(p\text{-}ClPhNC)_2Fe(S_2CNEt_2)_2ZnI_2]$, and some adducts of copper(I) halides with tris(dithiocarbamato) complexes $[M(S_2CNR_2)_3]$ (M=Co, Rh, Cr), (Exarchos, Nyburg and Robinson, 1998). Some dithiocarbamato-bridged heterobimetallic complexes $[M'\{M(S_2CNR_2)_3\}_2]$ and $[\{M'M(S_2CNR_2)_4\}_n]$, obtained by successive addition of stoichiometric amounts of bivalent metal salts MX_2 (M=Zn, Cd or Hg) and $M'Y_2$ (M′= VO, Mn, Fe, Co, Ni, Cu, or Zn) to a solution of a sodium dithiocarbamate, are reformulated as mixtures of homonuclear complexes involving, in some instances (M′= Mn, Fe or Co), trivalent $[M'(S_2CNR_2)_3]$ species (Exarchos and Robinson, 1997). Thio ligands of various kinds readily complex both Mo and W (Cotton, and Wilkinson, 1988, 839). There are two interesting binuclear tungsten complexes that both contain the same planar $Et_2NCS_2W(\mu\text{-}S)_2W(S_2CNEt_2)$ group but differ in the other four ligands (Figure 1.11).

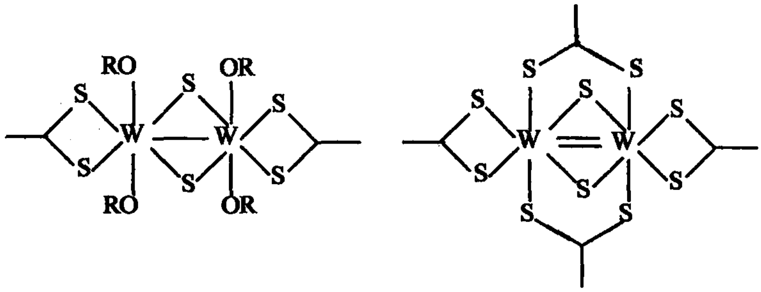
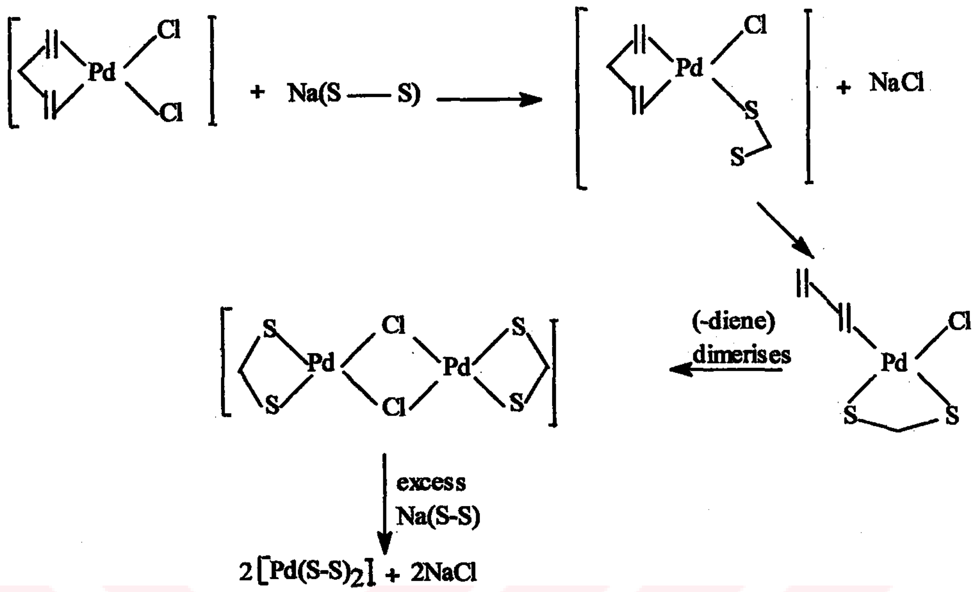


Figure 1.11 Dithiocarbamate compelexes of Tungsten

Dithiocarbamates and related sulfur ligands form stable complexes with both Pt and Pd. Stable complexes include $[Pd(S_2CNR_2)_3]^+$, and $[Pd(S_2CNR_2)_2X_2]$ (Cotton, and Wilkinson, 1988, 925).

The activation of olefins towards nucleophilic attack by coordination to palladium (II) was well established and of commercial importance. Extensive studies on reactions of $[(diene)PdCl_2]$ complexes with various nucleophiles containing oxygen or nitrogen donor atoms (*e.g.* $^-$OR, $^-$OCOR, NH_2R *etc.*) show that, usually, attack on one of the coordinated double bonds occurs to give substituted alkenyl complexes (Corcock and *et al.*, 1976). The reaction between $[C_8H_{12}PdCl_2]$ (C_8H_{12}= 1,5-cyclooctadiene) and S-containing nucleophiles such as *N,N'*-dialkyl- and *O*-alkyl-dithiocarbamate anions ($S\text{-}S^-$) (1:1 molar ratios) leads, in contrast, to complete diene displacement with formation of compounds of empirical formula $[PdCl(S\text{-}S)]^-_n$. The probable mechanism of formation is given in Scheme 1.1.



Scheme 1.1. Mechanism of formation of $[PdCl(S\text{-}S)]_n$

The X-ray crystal structures of $[Pd(S_2CNEt_2)(Ph_2PCH_2CH_2PPH_2)][CuCl_2]$ and $[Pd(S_2CNEt_2)(Ph_2PCH_2CH_2PPH_2)][AgCl_2].0.5CH_2Cl_2$ were reported (Exarchos, Nyburg and Robinson, 1998). Once again, ligand exchange was the preferred reaction pathway and chlorometallate salts of the general form $[Pd(S_2CNEt_2)(Ph_2PCH_2CH_2PPh_2)]_2[MCl_4]$ were obtained in good yield.

The interest in platinum(II) and palladium(II) complexes containing N and S donors has increased in recent years, with the aim to synthesize anti tumor drugs having a reduced toxicity with respect to *cis*-platin and analogues (Faraglia, Fregona, Sitran, 2001). The molecules containing sulfur are currently under study as chemoprotectants in platinum-based chemotherapy. In particular, thiocarbonyl and thiol donors have shown promising properties for chemical use in modulating *cis*-platin nephrotoxicity. The dithiocarbamato complexes, $[M(S_2CNEt_2)(L)]NO_3$

(M=Pt or Pd; L=2,2'-bipyridiyl or 1,10-phenanthroline), showed antitumor activity against leukemic cells.

1.5 Allyl and Related Complexes

The possibility that the allyl group CH_2=CH-CH_2- can act as an η^3 ligand was recognized independently by several groups in 1960 and since then the field has flourished, partly because of its importance in homogeneous catalysis, and partly because of the novel steric possibilities and interconversions that can be studied by ^1H NMR spectroscopy (Greenwood, and Earnshaw, 1984, 362 p).

1.5.1 MO Theory in η^3-Allylic Complexes

The bonding in η^3-allylic complexes can be described in terms of the qualitative MO theory illustrated in Figure1.12 (Greenwood, and Earnshaw, 1984, 362 p).

The p_z orbitals on the three allylic C atoms can be combined to give the 3 orbitals shown in the upper part of figure 1.12; each retains π symmetry with respect to the C_3 plane but has, in addition, 0, 1, or 2 nodes perpendicular to this plane. The metal orbitals of appropriate symmetry to form bonding MOs with these 3 combinations are shown in the lower part of Figure 1.12. The extent to which these orbitals are, in fact, involved in bonding depends on their relative energies, their radial diffuseness, and the actual extent of orbital overlap. Electrons to fill these bonding MOs can be thought of as coming both from the allylic π-electron cloud and from the metal, and the possibility of "*back donation*" from filled metal hybrid orbitals also exists.

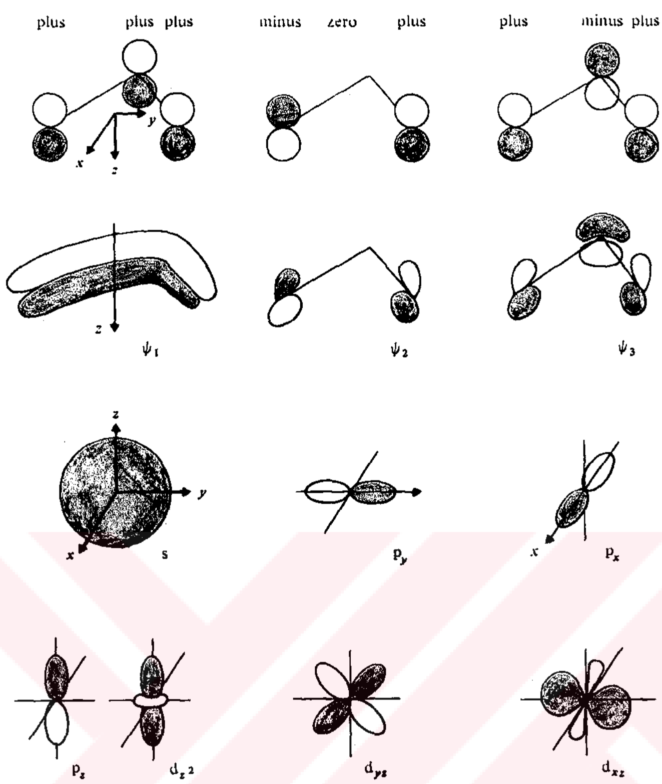


Fig.1.12 Schematic illustration of possible combinations of orbitals in the π-allytic complexes.

1.5.2 Bonding Types of Allyls

Groups of the formal type can interact with a metal atom so as to serve as (2n+1)-electron ligands. The two cases of greatest interest are the allyl and pentadienyl groups (Cotton and Wilkinson, 1988, 76).

$$\begin{matrix} & \mathrm{H}\ \ \mathrm{H} & \\ \mathrm{H} & (\mathrm{C{=}C})_n & -\mathrm{CH_2} \end{matrix}$$

The allyl system displays both η^1 (also often denoted σ behavior) and η^3 behavior. This group, and substituted derivatives of it, may act as σ-bonded ligands, but it is as 3-electron π-donor ligands that they are most important. Many allyls show nonrigid behavior in solution (Figure 1.13).

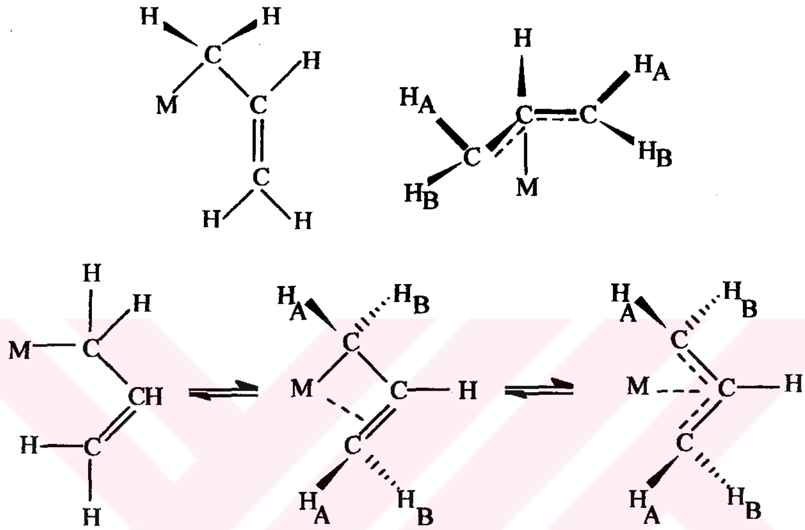


Figure 1.13 η^1 or σ-allyl and η^3 or π-allyl

Allylic complexes have delocalised three-carbon open or closed moieties bound to a metal. They can be considered as arising from a η^1-allyl by further binding of the C=C π bond and indeed both η^1- and η^3-allyls are known and nonrigid behavior arises from this equilibrium in some cases (Cotton, and Wilkinson, 1988, 1162 p), (Figure 1.13).

In addition to acting as an η^1 and an η^3 ligand, the allyl group can also act as a bridging ligand by η^1 bonding to one metal atom and η^2 bonding via the alkene function to a second metal atom (Greenwood, and Earnshaw, 1984, 365 p). For example, $[Pt_2(acac)_2(\eta^1, \eta^2\text{-}C_3H_5)_2]$ has the dimeric structure.

The η^5-pentadienyl ligand, as a five-electron donor in its semicircular, delocalised form represented schematically is capable of forming a variety of metal complexes, including a so-called "open" ferrocene, $(C_5H_7)_2Fe$. (Figure 1.14)

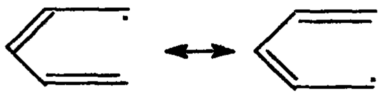


Figure 1.14 The η^5-pentadienyl ligand

It may also be noted that η^3-allyl and η^5-pentadienyl units are often found within rings, especially six-membered rings, namely, (Figure 1.15).

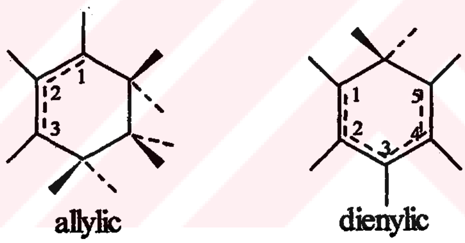
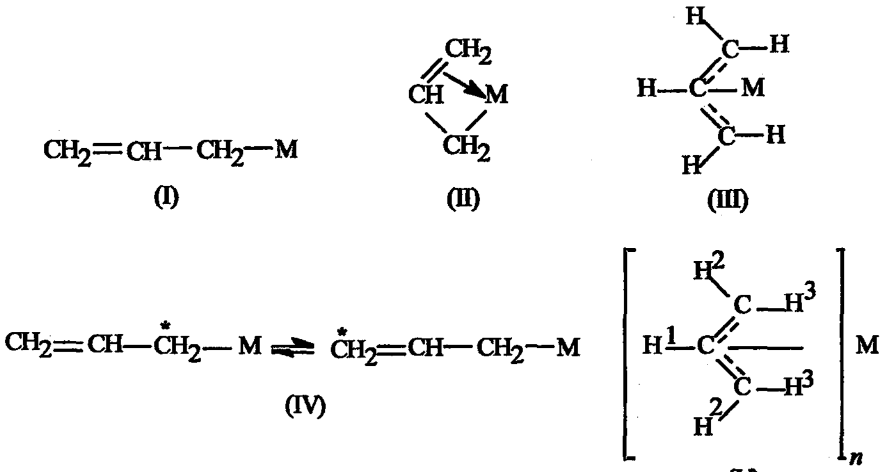


Figure 1.15 η-1,3-Cyclohexenyl and η-1,5-Cyclohexadienyl

Several modes of bonding of allylic ligands to metal atoms are recognised (Becconsall, Job and O'Brien, 1967). The complexes are usually classified according to their proton n.m.r. spectra, which reveal the extent of symmetry within the allyl group. For unsubstituted allylic ligands (C_3H_5), three types of spectrum have been found and corresponding bonding situations postulated as follows (Scheme 1.2):



(I) (II) (III) (IV) (V)

Scheme 1.2 Bonding situations of allyl group

(a) $ABCX_2$ spectra: σ-bonded structures (I) in which the carbon-carbon double bond takes no part in bonding to the metal atom (M), e.g., $(C_3H_5)Mn(CO)_5$, or structures with a combination of σ- and π-bonding (II), e.g., allylpalladium complexes with phosphines or dimethyl sulphoxide as additional ligands, and $[(C_3H_5)_2RhCl]_2$; (b) AM_2X_2 spectra: symmetrical π-allyl structures (III) as in $[(C_3H_5)PdCl]_2$; (c) AX_4 spectra: "dynamic" structures (IV) involving a rapid exchange in which each CH_2 group in turn is σ-bonded to the metal atom; analogous exchanging species based on structures of the type (II) have also been suggested (Becconsall, Job and O'Brien, 1967). For substituted allylic ligands (*e.g.*, methallyl, crotyl), analogous situations are found, with the spectra modified as expected.

Acording to the same literature, the evidence for the "dynamic" structures (IV), however, rests entirely on the apparent equivalence of four of the protons in the C_3H_5 group. Complexes showing this equivalence include some main-group allyl compounds (*e.g.*, Grignard reagents, diallylmagnesium, and diallylzinc), and the transition-metal complexes

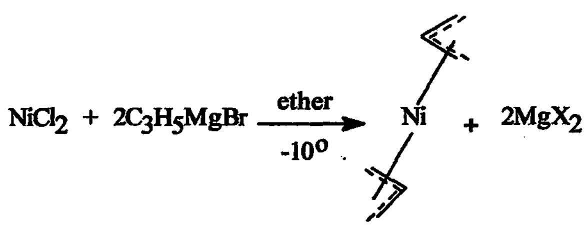
$Zr(C_3H_5)_4$ and $Th(C_3H_5)_4$ at sufficiently high temperatures. Similarly AX_4-type or analogous spectra are found for the addition products of phosphines to $[(C_3H_5)NiBr]_2$ and π-methallylpalladium chloride and of dimethyl sulphoxide to $[(C_3H_5)PdCl]_2$ and π-crotylpalladium chloride.

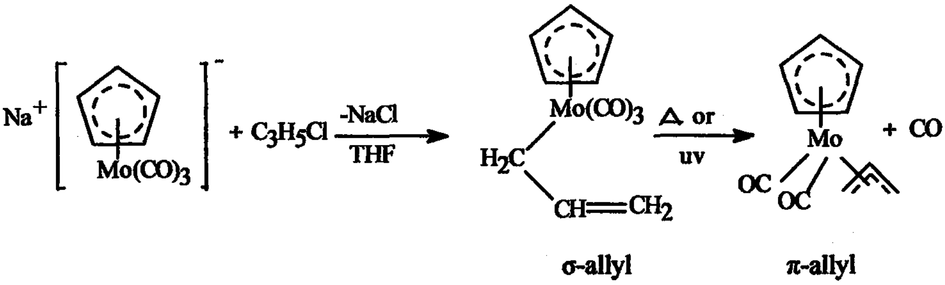
Spectra of $Zr(C_3H_5)_4$ as a solution in $CFCl_3$ at several temperatures from -66 to 20 °C were shown. As the temperature is raised through this range, the two CH_2 doublets of the AM_2X_2 spectrum broaden and move together, coalescing at –40 °C, and sharpening at still higher temperatures to the single CH_2 doublet of the AX_4 spectrum. Simultaneously the resonance of the central proton (nine lines at –74°C) simplifies at –20°C to a quintet. All these spectra are accounted for by the single structure (V) (M=Zr, *n*=4) in which the four allylic ligands occupy equivalent positions, and rotation of the CH_2 groups about the bonds linking them to the central carbon atom occurs at a rate depending on the temperature (Becconsall, Job and O'Brien, 1967).

1.5.3 Preparation of Allyl complexes

Many synthetic routes are available of which the following are representative;

1. ***From Allyl Grignard Reagents or Allyl Halides.*** Examples are the following:

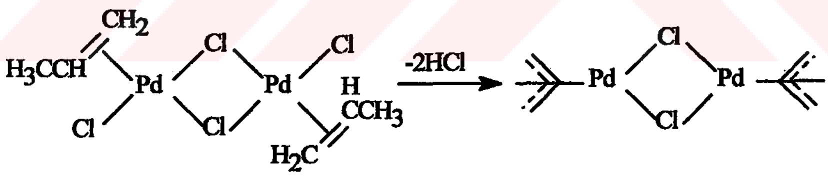




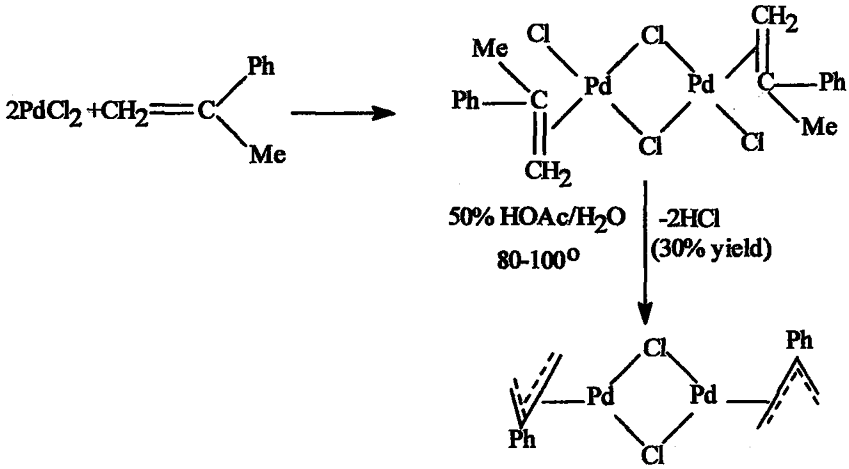
The second example shows the initial formation of a σ- or η^1-allyl that is subsequently converted into a η^3-allyl with loss of CO. There are numerous examples of η^1=η^3 allylic conversions involving displacement of CO, PR_3, Cl^-, or other ligands.

2. ***By Hydrogen Transfer from Alkene Complexes and Loss of HCl or*** $\boldsymbol{H_2}$.

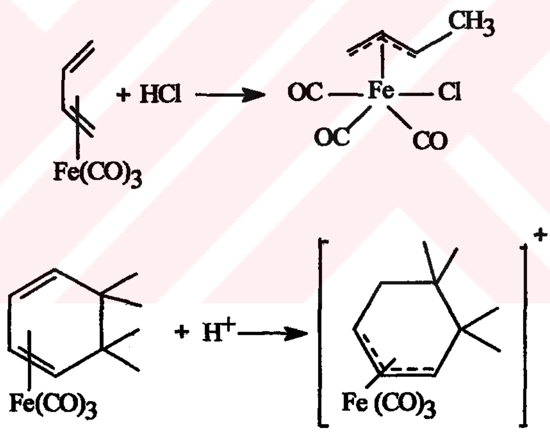
In some cases direct interaction of an alkene gives an allyl through loss of allylic hydrogen atoms:



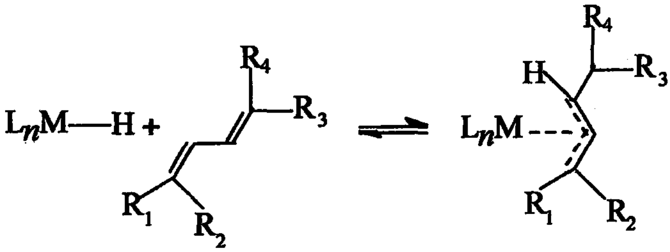
Elimination of HCl from an alkene metal halide complex, *e.g.* (Greenwood and Earnshaw, 1984, 362);



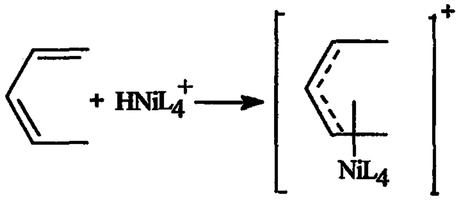
3. Protonation of 1,3-Diene Complexes. Two examples are;



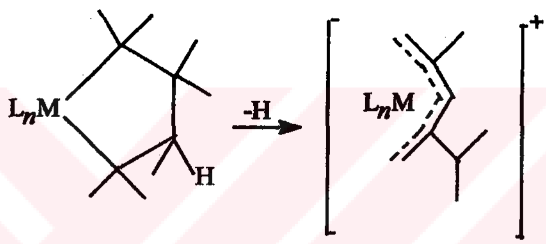
4. Hydrogen Transfer from MH to Dienes. This is a common reaction,



A specific example being;



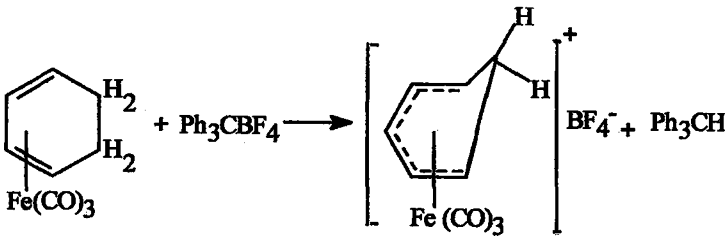
5. ***Hydrogen Abstraction From Metallacycles.*** Abstraction of a β-hydrogen from Rh, Ir, and Pd metallacycles by Ph_3C^+ is regio specific:

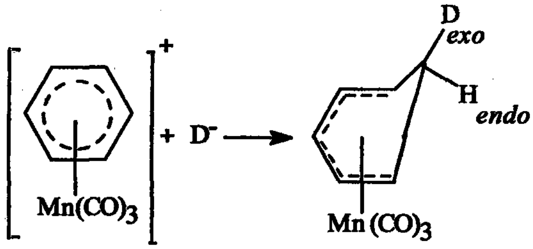


Allyl complexes are intermediates in a great variety of reactions. Cobalt, and especially Palladium, are very prone to form allyls and there are many Palladium catalysed diene transformations that proceed *via* allyl intermediates.

Some compounds have a carbocycle bound to a metal by only a three-carbon allylic grouping, for example, η^3-C_5H_5. Another class of compounds that may have 6, 7, 8, or more carbon atoms that give rise to η(1-5)dienyl systems, the most important of which are η(1-5)cyclohexadienyls (Cotton and Wilkinson, 1988, 1182).

(1-5)cyclohexadienyls; These are formed by hydride transfer reactions, either H abstraction or addition as in the following reactions.





1.5.4 Fluxionality of η^3-allyl complexes

Many η^3-allyl complexes are fluxional at room temperature or slightly above, and this property has been extensively studied by ^{1}H NMR spectroscopy. Exceedingly complex patterns can emerge. The simplest interchange that can occur is between the *syn* and *anti* H atoms probably *via* a short-lived η^1-allyl metal intermediate. The fluxional behavior can be slowed down at lower temperatures, and separate resonances from the various types of hydrogen atoms are observed. Fluxionality can also sometimes be quenched by incorporating the allylic group in a ring system which restricts its mobility (Greenwood, and Earnshaw, 1984, 365).

Fluxionality is characteristic of certain classes of organometallic compound and is found sporadically in others. Allyl complexes are characteristically fluxional, the principal pathway being the η^3-η^1-η^3 process shown in Figure 1.16 (Cotton, and Wilkinson, 1988, 1333).

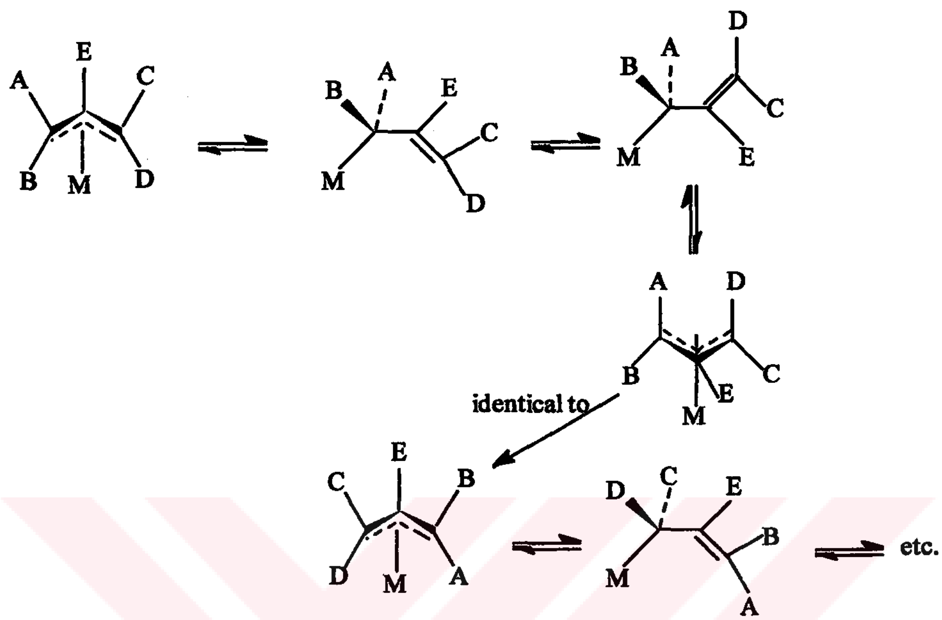
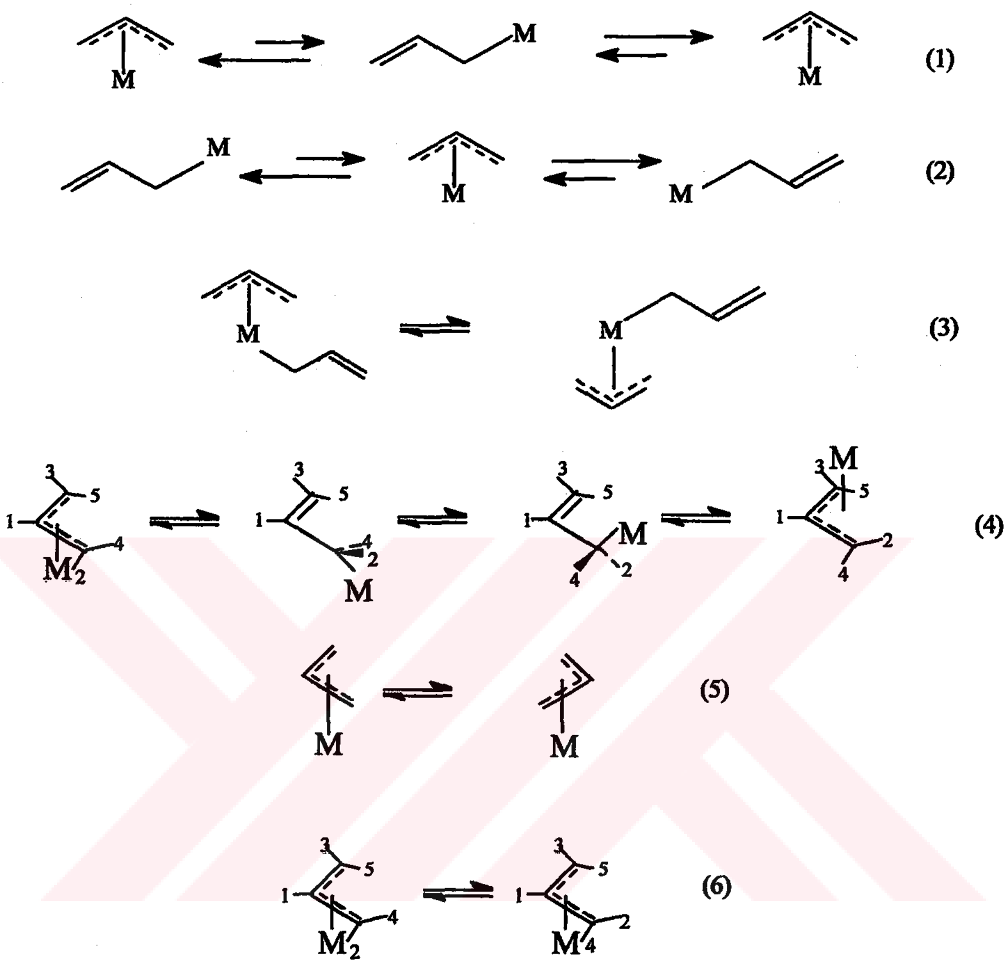


Figure 1.16 Fluxionality of allyl ligand

Three fluxional processes can be distinguished (Henc, Wilke, and *et al.* 1980), (Scheme 1.3) 1) dynamic η^3-allyl (eq.1), 2) dynamic η^1-allyl (eq.2), 3) dynamic η^3-allyl, η^1-allyl (eq.3). The last possibility is, of course, restricted to complexes containing at least two allyl groups.

If the rate of exchange for these three processes is faster than the NMR time scale, then spectra derived from the simple AX_4 spin system will be observed in the ^{1}H NMR as the result of equilibration of the *syn-* and *anti-* protons due to rotation about the C-C single bond in the η^1-allyl form (eq.4).



Scheme 1.3 Fluxional process of allyl group

On the other hand, if the rate of exchange of the processes shown in eqs.1-3 is slower than the NMR time scale, then the spectra corresponding to the so-called static η^3-allyl or η^1-allyl- or η^1-allyl, η^3-allyl-metal complexes, respectively, will be observed.

Additional intramolecular fluxional processes which may be considered include rotation of the η^3-allyl group about the metal-allyl axis (eq.5) and rotation about a C-C bond within the η^3-allyl system (eq.6).

Rotation about the metal-allyl axis (eq.5) was first confirmed with the help of spin saturation transfer experiments for complexes of Fe, Mo and W while an intramolecular twist mechanism has been proposed to account for the observed equivalence of the allyl groups, in $(\eta^3\text{-}C_3H_5)_2Ru(CO)_2$. For $(\eta^3\text{-}C_3H_5)_2Ni$, however, a qualitative MO treatment indicates that simple rotation about the allyl-metal axis is symmetry forbidden and hence a high energy process. Although rotation about a C-C bond (eq.6) may occur in ionic allyl-metal complexes, the barrier for (η^3-allyl) complexes of the transition metals having filled d-orbitals can be expected to be prohibitively high; an MO calculation indicates that for $(\eta^3\text{-}C_3H_5)_2Ni$ the barrier to rotation is ca. 90 kcal/mol. In addition to these various possibilities, many examples of fluxional behaviour in allyl-metal complexes which involve ligand exchange have been studied (Wilkinson, Stone, and Abel, 1982).

1.6 Allylic Complexes of Palladium (II)

The role of η^3-allyl-palladium compounds in several palladium-catalysed organic syntheses was well established. Review have focused on reactions such as; carbonyl allylation, carbonylation, allyl alkylation, decarbopalladation or on their application as enantioselective homogeneous catalysts. In contrast with other derivatives of allyl-palladium complexes, those bearing sulfur-containing ligands are relatively scarce.

In the chemistry of η^2- and η^4- bonded π-complexes derived from alkenes and dienes, the ligand is usually stable in the free state (Wilkinson, Stone, and Abel, 1982, 385). In addition, a large number of π-complexes are known in which the organic ligand is not stable in the free state. The simplest of these are those derived from the allyl radical ($C_3H_5\cdot$) in which the three carbon atoms are bonded equivalently to the metal in an η^3-fashion. The allyl ligand can also be σ-bonded (η^1) where it only occupies one coordination site. The η^3-bonded allyl is usually considered to act as a bidentate four-electron donor. Complexes of palladium may be regarded as consisting of an allylic anion bonded to Pd(II) (d^8). In a typical complex, *bis*(η^3-allyl)dichlorodipalladium (Figure 1.17), the metal has a square-planar geometry and is a 16-electron species.

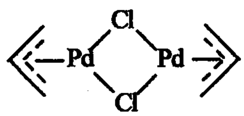


Figure 1.17 $[Pd(\eta^3\text{-}C_3H_5)X]_2$ (X= Cl)

The π-allyl complexes of Pd^{II}, *e.g.* $[Pd(\eta^3\text{-}C_3H_5)X]_2$ (X= Cl, Br, I), are very stable and more numerous than for any other metal, and neither Ni nor Pt form as many of these complexes (Greenwood, and Earnshaw, 1984, 1362). Indeed, the contrast between Pd and Pt is such that in reactions with alkenes, where a particular compound of Pt is likely to form an alkene complex, the corresponding compound of Pd is more likely to form a π-allyl complex. The role of the Pd and Ni complexes as intermediates in the oligomerization of conjugated dienes (of which 1,3-butadiene, C_4H_6, is the most familiar) was extensively studied, particularly by G. Wilke and his group (Wilke, 1963).

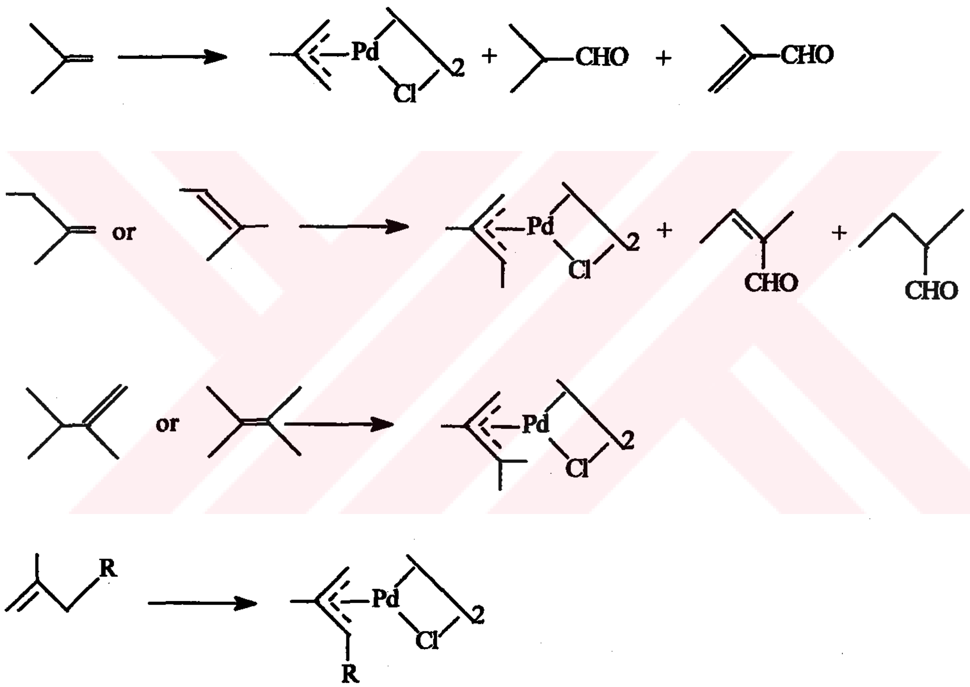
A large number of η^3-allylic palladium (II) complexes are known and these have been studied in considerable detail. This is a consequence of the ease of preparation of these complexes and also because they play an important role in a number of catalytic reactions.

1.6.1 Preparation of η^3-Allylic Palladium Complexes

The principal routes to η^3-allylic complexes involve the reaction of palladium salts with olefins, dienes or allylic halides in alcoholic solvents.

1.6.1.a From Monoolefins (Substituted Propenes)

Palladium chloride reacts with numerous olefins in protic solvents to form aldehydes, ketones or products arising from coupling reactions (Scheme 1.4).



R: Me, Et, Pr^n with $PdCl_2$-CH_3CO_2H

Scheme 1.4 Preparation of η^3-allylic complexes from monoolefins

The substituents at C-1 or C-3 in η^3-allylic compounds can be either on the same side as the 2-substituent (*syn*) or on the opposite side (*anti*). In general, steric repulsions are minimized when the substituents are *syn* and consequently this geometry predominates. However, 2,4,4-trimethylpent-2-ene gave a mixture of *syn* and *anti* complexes, (Figure 1.18.a) and (Figure 1.18.b). The *anti* complex is kinetically favoured and is the major product using short reaction times in AcOH/NaOAc, but with longer reaction times the *syn* complex predominates. This reaction has been explained in terms of the initial formation of an olefin complex in which the steric interaction between the Cl and the t-butyl group is minimized and consequently the *anti*-η^3-allylpalladium isomer is formed initially. (Wilkinson, Stone and Abel, 1982, 392)

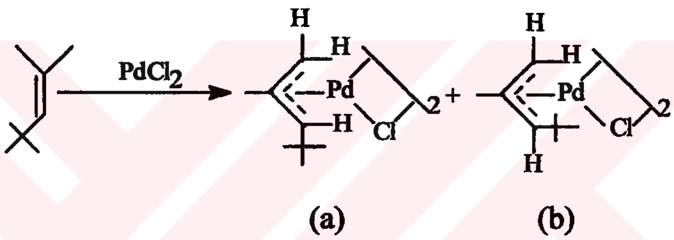


Figure 1.18 (a) *syn*-[Pd(η^3-allyl)Cl]$_2$ and (b) *anti*-[Pd(η^3-allyl)Cl]$_2$

1.6.1.b From Dienes

Sodium tetrachloropalladate reacts with penta-1,3-diene to form either (Figure 1.19.a) at 0-10 °C or (Figure 1.19.b) at 50-60 °C. (Rowe, and White, 1967)

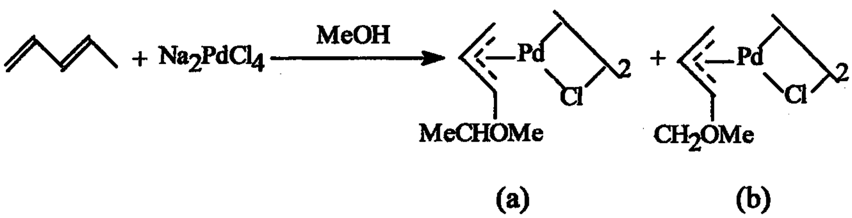


Figure 1.19 (a) Product formed at 0-10 °C, (b) Product formed at 50-60 °C

Cyclic dienes also react with $PdCl_2$, (Wilkinson, Stone, and Abel, 1982, 393 p). In methanol at low temperatures the methoxy adduct was formed from cyclohexa-1,3-diene, whereas at high temperatures the unsaturated η^3-allyl complex was formed (Figure 1.20).

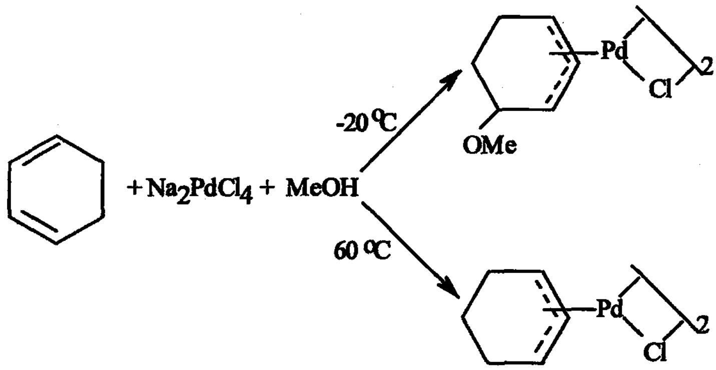
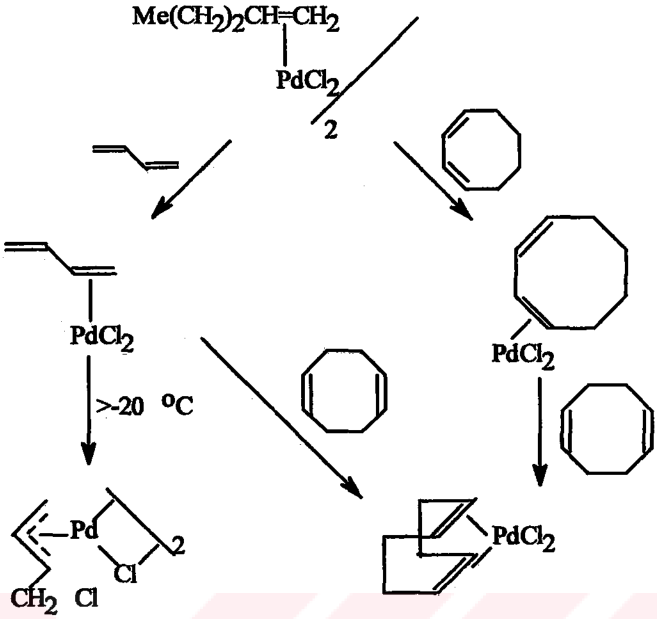
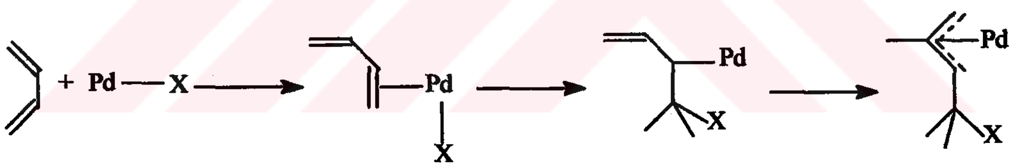


Figure 1.20 Preparation of η^3-allylic complexes from cyclohexa-1,3-diene

At low temperatures (-40 and –20 °C) both butadiene and cyclooctadiene formed η^2-olefin complexes from which the diene could be recovered unchanged (Donati, and Conti, 1966). The η^2-cyclooctadiene complex remained unchanged up to 110 °C, whereas the butadiene complex was quantitatively converted into the η^3-allyl at –20 °C. These results, which are presented in Scheme 1.5, imply that these reactions occur *via* initial coordination of one double bond which is followed by the addition of Pd-X to the double bond, giving the allylic complex (Scheme 1.6). Other by-products arise by loss of X^- and the H^+ from the resultant carbonium ion which may also rearrange.



Scheme 1.5 Formation of η^3-allyl and η^4-diene compounds



Scheme 1.6 Formation of η^3-allyl complexes from dienes

1.6.1.c From allyl halides, allyl alcohol and related compounds

The reaction of allyl alcohol with palladium chloride in aqueous acid or without added solvent gave dichloro*bis*(η^3-allyl)dipalladium in addition to palladium metal and organic products (Wilkinson, Stone and Abel, 1982, 401), (Figure 1.21).

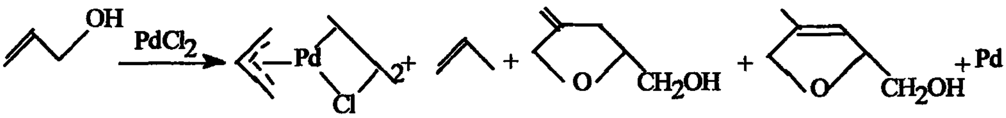
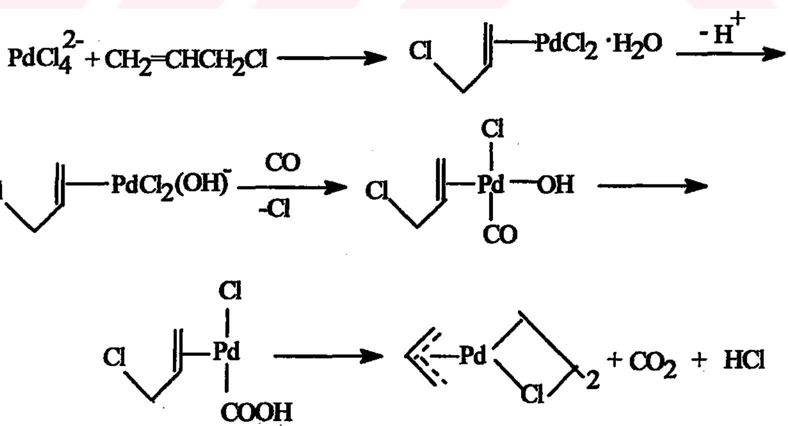


Figure 1.21 Preparation of η^3-allylic complex from allyl alcohol

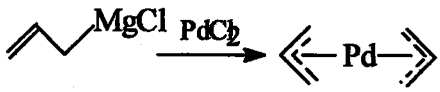
The synthesis of allylpalladium complexes from the reaction of allylic chlorides with palladium chloride in aqueous acetic acid was reported (Hüttel, and Bechter, 1961). This method was extended to the preparation of other allyl complexes. It was also found that the reaction of the allylic chloride with sodium tetrachloropalladate in methanol, in the presence of carbon monoxide and traces of water, led to an improved yield (Dent, Long, and Wilkinson, 1964).

The mechanism was proposed in Scheme 1.7 wherein the intermediate hydroxo(carbonyl)(η^2-olefin) complex is attacked by hydroxide ion at the carbonyl group (Nickolson, Powell and Shaw, 1966). This species then undergoes a rearrangement with the formation of the product η^3-allyl complex together with CO_2 and HCl.

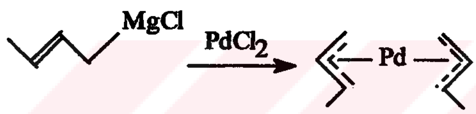


Scheme 1.7 The proposed mechanism of formation of η^3-allylic complexes from allyl chlorides

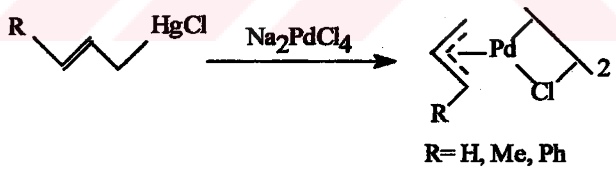
Wilke described the preparation of *bis*(η^3-allyl)palladium from allylic Grignard reagents (Wilke, 1963).



Powell and Shaw (Powell, and Shaw, 1968) also prepared the methyl substituted complex by this route;



Allylmercury compounds have also been used to synhesize the allylic palladium complexes (Wilkinson, Stone, and Abel, 1982, 404).



1.6.2 Structures and Spectra of (η^3-Allyl) Palladium Complexes

Numerous X-ray crystal-structure determinations have been carried out on η^3-allyl complexes of palladium. The most accurate was interpreted by Smith at –140 °C in order to minimize thermal vibrations (Smith, 1965). The structure showed that the allyl group is bonded to the metal in an η^3-fashion and occupies two coordination sites with the remaining sites being occupied by the bridging chlorines (Figure 1.22).

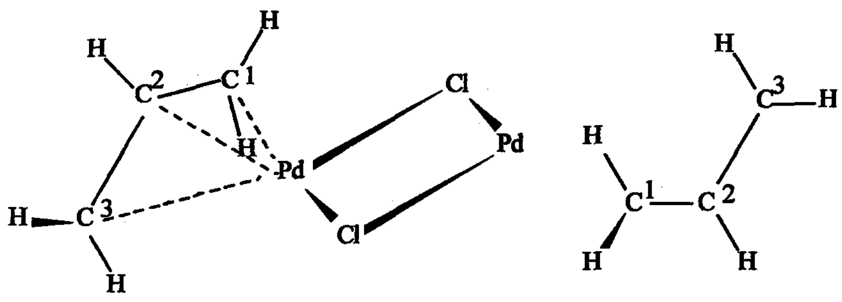


Figure 1.22 The structure of $[Pd(\eta^3\text{-}C_3H_5)X]_2$ (X= Cl)

The molecule has C_2 symmetry. The carbon-carbon bond lengths are equal [1.357(15) and 1.395(15) Å respectively] and the angle C(1)-C(2)-C(3) [119.8±0.9°] shows that C(2) is sp^2 hybridized. The three carbon atoms are approximately equidistant from palladium [Pd-C(1), 2.121(7); Pd-C(2), 2.108(9); Pd-C(3), 2.132(7) Å], but the central carbon atom may be slightly closer to the palladium than the other two carbon atoms. The Pd_2Cl_2 unit is very nearly square planar (ClPdCl, 88°; PdClPd, 92°), but the plane of the allyl group is at an angle of 111.5±0.9° to the Pd_2Cl_2 unit and is not perpendicular to it. This feature appears to be common to all η^3-allylpalladium complexes. The hydrogen atoms were not located accurately in any of these determinations, however, Smith calculated that the *anti* protons were significantly closer to the metal than the *syn* hydrogens and consequently are more shielded by the palladium. This has been used to interpret the ^1H NMR chemical shifts of the *syn* and *anti* protons in these complexes.

Further information has been obtained from the elucidation of the structures of substituted η^3-allyl palladium chloride complexes (Mason and

Wheeler, 1968). The structural determination of the η^3-2-methylallyl complex has shown that the methyl group is not in the same plane as the other carbon atoms but is bent towards the metal. For this complex (Figure 1.23.a) the angle at the central carbon was contracted to 112.4±1.6°, while the dihedral angle between the allyl plane and the Pd_2Cl_2 plane remained 111.6°.

The tetramethylallyl complex (Figure 1.23.b) was shown to have a similar geometry with all four methyl groups displaced out of the plane of the allyl groups; the *anti* methyl groups are displaced towards the metal whereas the *syn* methyls are displaced away from the palladium (Mason and Wheeler, 1968). For this complex the angle at the central carbon atom is 118.5° and the dihedral angle between the planes is 121.5°.

The structure of the 1,3-dimethylallyl complex (Figure 1.23.c) was reported (Davies, Mais and Owston, 1967). The methyls are not coplanar with the allylic carbons and in this complex the Pd_2Cl_2 unit is not planar but is bent at an angle of 150° along the Cl-Cl axis; the dihedral angles in this complex are 123° and 126°.

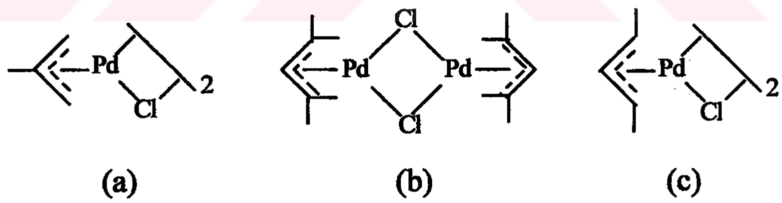


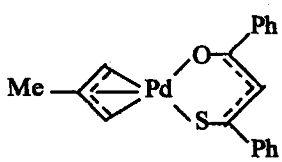
Figure 1.23 (a) 2-methylallyl complex, (b) tetramethylallyl complex, (c) 1,3-dimethylallyl complex

An X-ray crystal structure determination of $[Pd_3(2\text{-methylallyl})_2Cl_4]$ shows it to be centrosymmetric with a rippled near-planar arrangement of $PdCl_2PdCl_2Pd$, the terminal Pd atoms being η^3-bonded to the 2-methylallyl ligand (Bailey, Kelley, Maitlis, 1978).

A series of π-allylic palladium (II) complexes containing the anionic, asymmetrically chelating picolinate or oxinate ligands have been prepared and structurally characterised (Ban, Chanand, Powell, 1972).

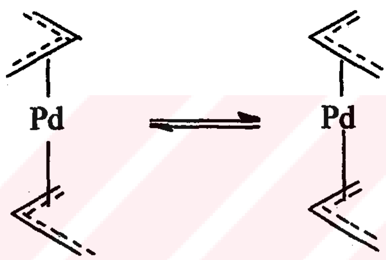
A more common type of asymmetric η^3-allyl complex may be obtained by the replacement of the halide bridge by ligands which contain two different atoms and the X-ray structure determinations of several of these asymmetric η^3-allyl palladium complexes have been carried out. The mono nuclear triphenylphosphine adducts $[PdCl(\eta^3\text{-}C_3H_5)(PPh_3)]$ and $[PdCl(\eta^3\text{-}2\text{-}MeC_3H_4)(PPh_3)]$ showed the palladium-carbon distances *trans* to the phosphine to be longer than those *trans* to the chloride. In each case the bond length of the C-C *trans* to PPh_3 was longer than that *trans* to the Cl (Wilkinson, Stone, and Abel, 1982, 406).

The structure of the monothiodibenzoylmethanato complex shows that the Pd-C distance *trans* to the sulphur is significantly longer than that *trans* to the oxygen. Powell and Shaw suggested that, since electronegative elements such as O and Cl are poor σ-donors whereas P, C, S or Sn are good σ-donors, when the σ-donor ability of the ligands attached to the palladium is significantly different than very asymmetric η^3-allyls result.



Although *bis*(η^3-allyl)metal complexes of nickel, palladium and platinum were isolated in the early sixties and have since been shown to be formed as intermediates in a variety of metal-catalyzed cyclooligomerization and cyclocooligomerization reactions involving 1,3-dienes, detailed information on their structure and reactivity is surprisingly limited. The NMR spectra of the isoleptic (all the ligands attached to the central metal atom are identical in constitution) complexes $M(C_3H_5)_2$ (M= Ni, Pd, Pt) and $M(C_3H_5)_4$ (M= Zr, Hf) were reported (Becconsall, Job, and O'Brien, 1967).

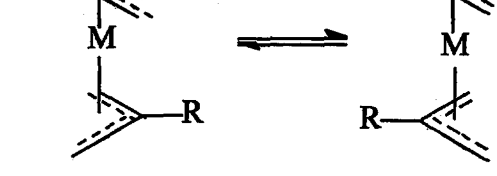
Bis(η^3-allyl) palladium(II) complexes also show some interesting features in the ^1H NMR spectra. An equilibrium exists in solution between the *trans* form (Figure 1.24.a), which is favoured in the solid state, and the *cis* form (Figure 1.24.b). In this case, again, the chemical shifts of the *syn* and *anti* protons were assigned on the basis of their expected relative proximity to the metal.



(a) (b)

Figure 1.24 (a) *trans-bis*(η^3-allyl)palladium(II), and (b) *cis-bis*(η^3-allyl)palladium(II)

The symmetrical (η^3-allyl)$_2$M (M=Ni, Pd, Pt) complexes can be adopt at least two configurations. Similar behaviour has been reported for the (η^3-2-$CH_3C_3H_4$)$_2$M complexes (Figure 1.25), (Henc, Jolly and Wilke, *et al.*, 1980).



(a) (b)

Figure 1.25 (a) *trans-bis*(η^3-2-methylallyl)palladium(II), and (b) *cis-bis*(η^3-2-methylallyl)palladium(II)

In the particular case of (η^3-1-$CH_3C_3H_4$)$_2$Ni a total of twelve isomers are possible due to *syn-* or *anti-*substitution of the (η^3-allyl) groups as shown below (Figure 1.26):

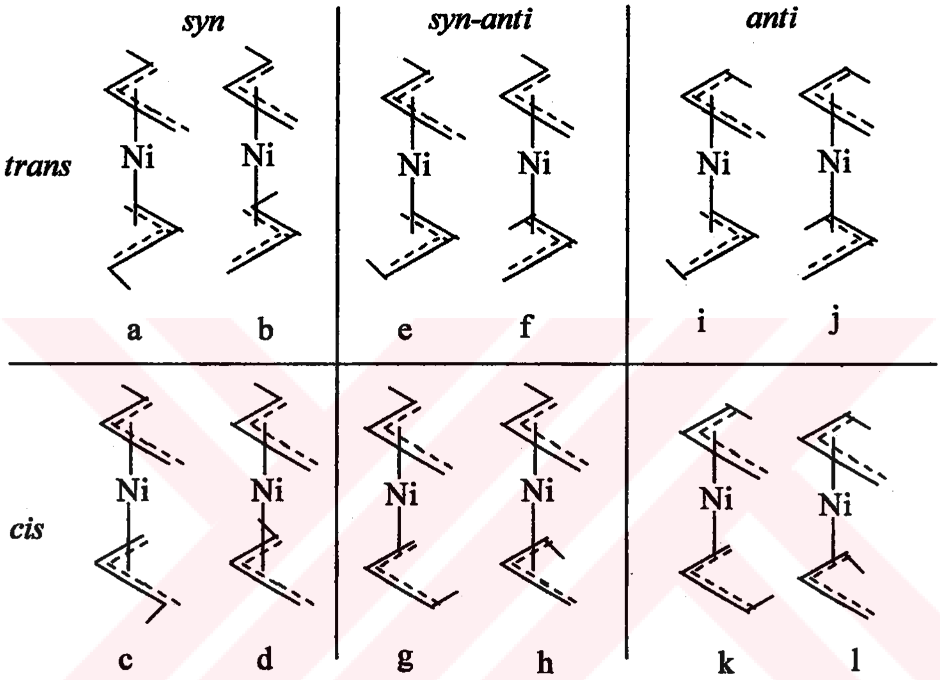


Figure 1.26 Isomers of (η^3-1-$CH_3C_3H_4$)$_2$Ni

The situation in the case of the analogous η^3-1-$CH_3C_3H_4$-complexes of palladium and platinum has not been completely resolved: in the case of platinum the ^{1}H NMR spectrum proved too complex to analyse, while in the case of palladium four isomers containing *syn*-CH_3 groups have been identified with certainty, while two other species probably contain *anti*-CH_3 groups. (η^3-1,1′-$(CH_3)_2C_3H_3$)$_2$Ni also exists as a mixture of the four possible isomers (Figure 1.27), (Henc, Jolly and Wilke, *et al.*, 1980).

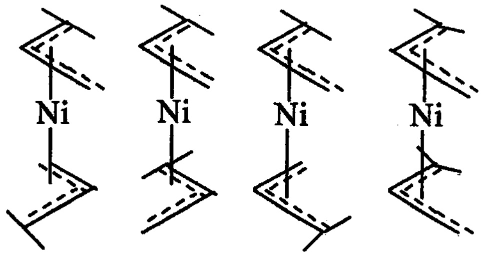


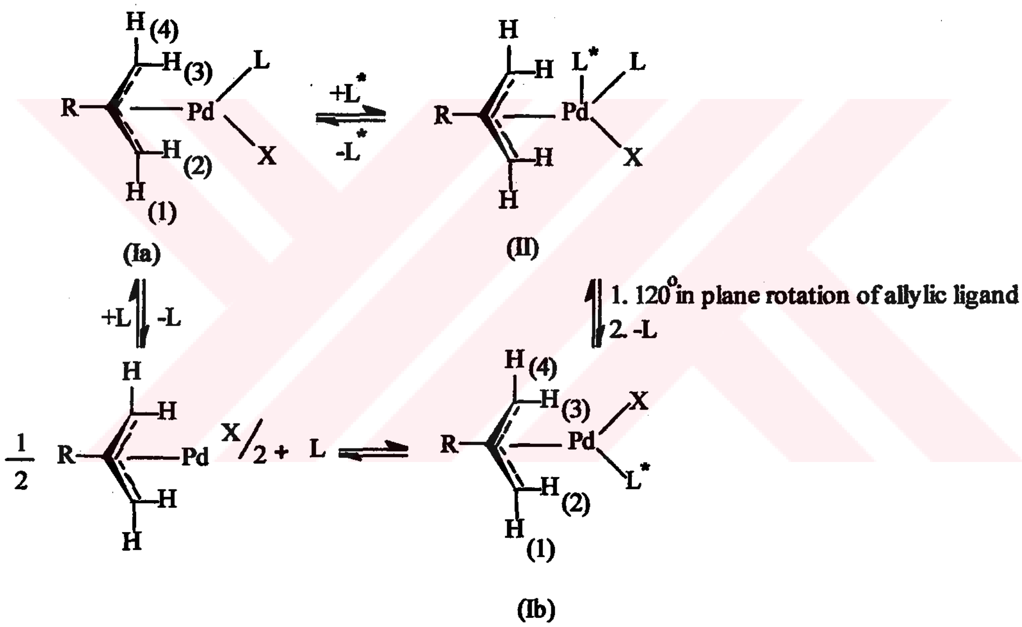
Figure 1.27 Isomers of [η^3-1,1'-$(CH_3)_2C_3H_3)_2$Ni]

Comparison of the ^{13}C-chemical shifts for the η^3-C_3H_5 and η^3-2-$CH_3C_3H_4$ complexes of Ni, Pd, and Pt shows, surprisingly, that the chemical shifts increase in the order Pt < Ni< Pd (Henc, Jolly and Wilke, *et al.*, 1980).

Dehm and Chien reported in 1960 that symmetric (η^3-allyl) palladium complexes normally shown an AM_2X_2 type ^1H NMR spectrum. However, they noted that when the measurement was carried out in coordinating solvents dramatic changes occurred; for example, dichloro *bis*(η^3-allyl) dipalladium in DMSO gave an AX_4 spectrum (Dehm and Chien, 1960).

For the complex of [Pd(η^3-C_4H_7)(PO_2F_2)L] L=$PMePh_2$, $P(OMe)_3$, $P(OEt)_3$, $P(OPh)_3$ the ^1H- and $^{13}C\{^1H\}$-NMR data were collected (Fernández-Galán, Manzano, Otero, 1999). In the ^1H-NMR spectra of all the neutral complexes an asymmetric allyl group is seen with two H_{syn} and two H_{anti} signals. The protons situated *trans* to phosphorus appear at higher chemical shift and exhibit the corresponding coupling constant (higher for the H_{anti} than for the H_{syn}). The $^{13}C\{^1H\}$ NMR data confirmed the asymmetric nature of the allyl groups showing two different signals for the terminal carbons with a chemical shift at lower field for those situated *trans* to phosphorus. This results is in accordance with the higher *trans* influence of the phosphine or phosphite ligands as compared to the PO_2F_2- group.

Since 1965 the dynamic stereochemistry of π-allylicpalladium(II) complex-ligand systems has received considerable attention (Ban, Chan and Powell, 1972). Whilst *syn-anti* proton exchange in π-allylic complexes occurs *via* σ-allylic intermediates, *syn-syn* (protons 1 and 4) and *anti-anti* (protons 2 and 3) exchange in asymmetric π-allylic systems such as (Ia) may occur via a dissociative process (as has been observed in several π-allylic palladium (II) halide-amine systems) or *via* an associative, base promoted process (Scheme 1.8)



Scheme 1.8 *Syn-anti* proton exchange in π-allylic complexes

Several mechanisms have been proposed to account for the *syn-syn, anti-anti* interconversion. Although the simple rotation of the allyl ligand is a mechanism often proposed to explain some isomerizations in complexes of metals as Mo, W and Fe, it is not widely accepted for square–planar palladium complexes and orbital considerations suggest a high activation barrier in square-planar geometries (Vrieze, *et al.*, 1975). This rotation is apparently a more facile process *via* a possible pentacoordinate intermediate. Dissociative pathways, *via* tricoordinate palladium intermediates, with monodentate ligands such as CO, $SnCl_3$, amines, macrocycles, polyenes, and also N-donor chelate ligands have been proposed to explain the dynamic behavior in asymmetric allyl palladium complexes.

A series of allyl-palladium dinuclear complexes, $[(\eta^3\text{-}C_3H_5)Pd(\mu\text{-}SR)_2Pd(\eta^3\text{-}C_3H_5)]$ (R=fluorinated substituents), and the reactivity of, $[(\eta^3\text{-}C_3H_5)Pd(\mu\text{-}SC_6F_5)_2Pd(\eta^3\text{-}C_3H_5)]$ towards *para*-substituted phosphines were studied (Redón, Cramer, Bernès and Morales, 2001). The ^1H NMR spectra of the dinuclear complexes of $[(\eta^3\text{-}C_3H_5)Pd(\mu\text{-}SR)_2Pd(\eta^3\text{-}C_3H_5)]$ (R=1; C_6F_5, 2; C_6HF_5-4, 3; C_6H_4F-2, 4; C_6H_4F-3, 5; C_6H_4F-4) at room temperature exhibit only one set of resonances for the allyl group, i.e. three resonances with the expected intensity ratio of 1:2:2.

In the complex of $[Pd(L^n\text{-}S,N)(\eta^3\text{-}C_3H_5)]$ the $(L^n)^-$ anions form six-membered S,N chelate rings at the metal centre, in a manner analogues with β-diketonates and imidodiphosphinates (Bhattacharyya, Slawin and Woollins, 2001).

1.6.3 Reactions of (η^3-allyl)palladium complexes

1.6.3.1 Nucleophilic attack at the metal

η^3-allylic complexes react with donor ligands to form compounds which show dynamic behaviour in solution. In complexes of the type [Pd(allyl)XL], in which the allyl is substituted at the 1-position, the ^1H NMR spectra may be best interpreted by considering the phosphine as being *trans* to the more heavily substituted carbon atom (Fernández-Galán, Manzano and Otero, 1999).

Powell and Shaw have prepared and characterized a number of complexes from the reaction of (η^3-allyl)palladium halide complexes with phosphines in aqueous acetone or from the reaction of $[PdCl_2(PPh_3)_2]$ with allyl Grignard reagents (Figure 1.28). The ^1H NMR spectrum (L= PPh_3) with BPh_4^- as the anion, in the absence of added phosphine, showed the η^3-2-methylallyl ligand to be symmetrically bonded to the metal. (Powell, and Shaw, 1968)

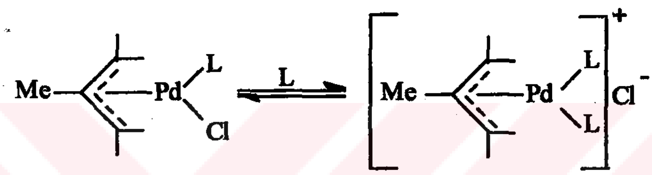


Figure 1.28 $[(\eta^3\text{-allyl})Pd(PPh_3)_2]^+$ complexes

Conductivity measurements on the reaction (Crosby, and Kemmitt, 1971);

$$[Pd_2X_2(\eta^3\text{-allyl})_2] + 4L \rightarrow 2[Pd(\eta^3\text{-allyl})L_2]^+X^-$$

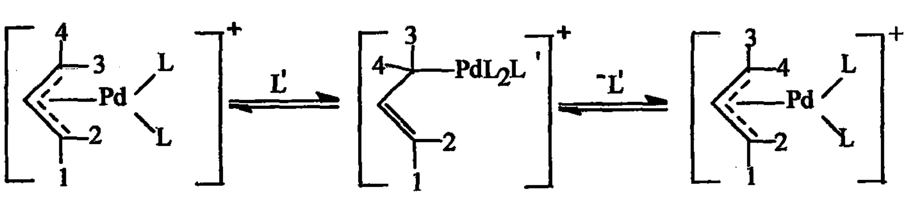
indicated that the relative reaction rates for the formation of the cation decreased in the order; L= $PMe_2Ph \approx PEt_2Ph \approx PEt_3 > PPh_3 > AsPh_3 > SbPh_3 >$ py; allyl= 2-$MeC_3H_4 > C_3H_5 >$ 1-$MeC_3H_4 >$ 1,3-$Me_2C_3H_3 >$ 1,1-$Me_2C_3H_3$; and X= Cl> Br> I.

Powell and Chan have reported the reaction of η^3-allylpalladium xanthate, dithiocarbamate, picolinate and oxalate with dimethylphenylphosphine. The addition of one equivalent of phosphine resulted in the formation of η^1-allyl complexes. When two moles of phosphine were added to [Pd(η^3-

$C_3H_5)(S_2CNMe_2)]$ the ionic species $[Pd(\eta^3\text{-}C_3H_5)(PMe_2Ph)_2]^+(S_2CNMe_2)^-$ was formed (Powell, and Chan, 1972).

Issleib *et al.* have also reported the isolation of the cationic species $[Pd(\eta^3\text{-}C_3H_5)(Ph_2PCH_2PPh_2)]^+[AlClBr_3]^-$ from the reaction of $[Pd_2(\eta^3\text{-}C_3H_5)_2Cl_2]$ with two equivalents of $Ph_2PCH_2PPh_2$ in the presence of $AlBr_3$. When one equivalent of diphosphine was added then the mononuclear complex $[Pd(\eta^3\text{-}C_3H_5)Cl(Ph_2PCH_2PPh_2)]$ was formed (Issleib, Abicht and Winkelmann, 1972).

Paiaro and Musco have prepared cationic η^3-allylpalladium complexes containing chelating amines (bipy, en) (Paiaro, Musco, 1965). The low-temperature NMR spectra of the complexes $[PdCl(\eta^3\text{-}2\text{-}MeC_3H_4)L]$ with an excess of the more basic phosphines suggest that the η^3-allyl group is bound to the metal symmetrically. At high temperatures or, in the case of less basic phosphines such as PPh_3, at lower temperatures the spectra are consistent with the presence of a dynamic η^1-allyl species. These facts have been interpreted in terms of equilibria between η^3- and η^1-allyl species, (Scheme 1.9), (Wilkinson, Stone, and Abel, 1982, 413).



Scheme 1.9 Equilibria between η^3- and η^1-allyl species

In the intermediate η^1-allyl complex, the C-C single bonds and C-Pd bonds can rotate freely, allowing the H_3 and H_4 protons to interchange; the H_1 and H_2 protons can exchange by means of an identical process when the η^1-allyl is found at the other terminal carbon. The (η^3-allyl) palladium(II) chloride-phosphine system shows the same behaviour in solution whereas certain di- and tri-methylallyl complexes do show some interesting differences.

The trimethylallyl complex, which is symmetric, forms the asymmetric complex on reaction with PPh_3 (or $AsPh_3$), (Figure 1.29), (Vrieze, Praat and Cossee, 1968). Isomerization of *syn* and *anti* groups occurred at higher temperatures or with higher phosphine:metal ratios. These results again implicate the presence of η^1-allylpalladium intermediates.

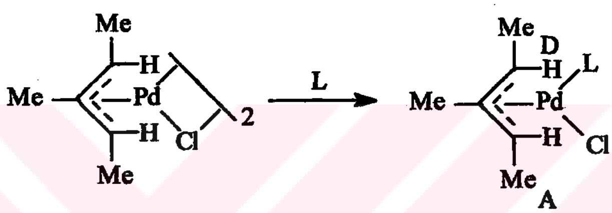
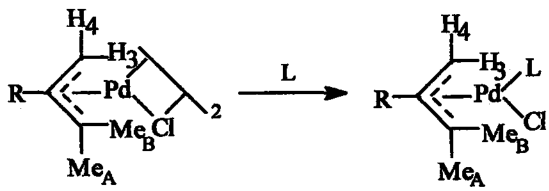


Figure 1.29 The asymmetric trimethyl allyl complex

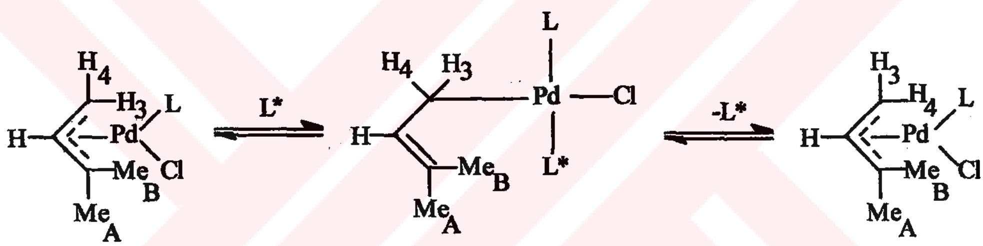
Reaction of triphenylphosphine or triphenylarsine with the trimethylallyl complex (Figure1.30; R=Me) resulted in the formation of the adduct (Figure 1.30; R=Me). Coalescence of the protons H_3 and H_4 occurred at higher temperatures, or increasing the ligand to metal ratios, without line broadening of Me_A or Me_B.



R= Me, H ; L=PPh_3, $AsPh_3$

Figure 1.30 Asymmetric 1,1,2- trimethylallyl and 1,1-dimethylallyl complexes

Reaction of the analogous 1,1-dimethyl complex (Figure 1.30 ; R=H) with triphenylphosphine gave (Figure 1.30 ; R= H) (Powell and Shaw, 1967). Powell and Shaw argued that steric effects prevent the facile addition of a second phosphine to form a five-coordinate complex and that a four-coordinate η^1-allyl complex was formed instead as indicated in Scheme 1.10. A fast process of this type results in the protons H_3 and H_4 becoming equivalent while the groups Me_A and Me_B retain their identities. A further consequence of such a mechanism is that L* is bound to palladium less strongly than L.



Scheme 1.10. Possible mechanism of the formation of 1,1-dimethylallyl complex

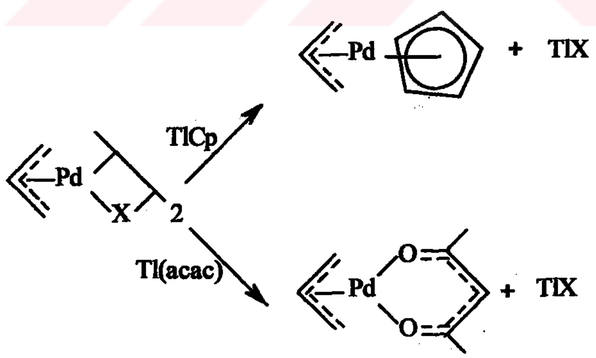
The bridge cleavage reactions of allylpalladium chloride by phosphines was reported (Virieze *et al.*, 1968). The principal effect is to increase the electron density at palladium. This results in an increase in the energy of the metal orbitals. The overall consequence of this is a decrease in π-bonding and a stabilization of the antibonding π*-orbital, circumstances which cause the allyl group to become more negative and stabilize the formation of an η^1-allyl complex.

Numota *et al.* have prepared trans η^1-allyl complexes of the type trans-$[Pd(\eta^1\text{-allyl})(Ar)L_2]$ (allyl=CH_2CHCH_2, $MeCHCHCH_2$, CH_2CMeCH_2; Ar = 2,3,5,6-C_6HCl_4, C_6F_5; L=PPh_3) from the corresponding $[Pd(\eta^3\text{-allyl})ClL]$

complexes (Numota *et.al.*, 1977). They reported that the ease of formation of the η^1-allyl complexes decreased in the order $MeCHCHCH_2 \approx CH_2CHCH_2$ >> CH_2CMeCH_2 and PMe_2Ph> PPh_3. If either diphos or diars were used then the *cis*- η^1-allyl complexes were formed.

1.6.3.2 Halide exchange in $[Pd_2Cl_2(\eta^3\text{-allyl})_2]$ and related reactions

The halide in $[Pd_2(\eta^3\text{-}C_3H_5)_2Cl_2]$ may be readily displaced by other halides (I> Br> Cl) and by cyanide or by thiocyanate through reaction with the appropriate alkali metal salt in solvent. Other replacements which have been widely used involve reaction with sodium cyclopentadienide or acetylacetone in the presence of base (Scheme 1.11). The products are monomeric and usually have greater solubility than the dihalide dimers. An alternative route is to use the corresponding thallium (I) salts; this method is particularly attractive in that the co-product, a thallium(I) halide, is quite insoluble in the reaction medium.



Scheme 1.11 Displacements of halide in $[Pd_2(\eta^3\text{-}C_3H_5)_2Cl_2]$ by $acac^-$ and Cp^-

Reaction of these monomeric complexes with HCl, halogen, *N*-bromosuccinimide or metal halides ($AlCl_3$, $FeCl_3$, $HgCl_2$) caused the cleavage of the η^5-cyclopentadienyl or acetylacetonato ligand and regenerated the allylic halide complexes.

Exchange reactions have also resulted in the formation of the monomeric allyl palladium xanthate, dithiocarbamate, picolinate and oxinate complexes, (Powell and Chan, 1972 and Bau, Chan and Powell, 1972). The formation of β-ketoamine η^3-allylpalladium complexes, (Musco, Rampone, *et al.*, 1972) and the amino acid complexes $[Pd(\eta^3\text{-}C_3H_5)(AA)]$ (AA= glycinato or D,L-β-phenylalinato) have been reported (Benedetti and Nakagawara, 1973).

The preparation of the sulphurdiimine complexes $[Pd(\eta^3\text{-}2\text{-}RC_3H_4)(R^1NSR^2NR^1)]$ (R=Me; R^1=aryl, R=Me, Bu^t) from reaction of the lithium sulphur diimine salts with the halide dimers were reported (Henriks, *et al.*, 1976). These complexes decomposed on heating to form azoarenes together with the thiolato dimers $[Pd(\eta^3\text{-allyl})(SR^2)]_2$.

1.6.3.3 Reactions in which the η^3-allyl group is transferred to another metal

The allyl group in palladium allyl complexes is extremely labile and this is manifested in its facile transfer to other metals. Mono- or di-σ-allylmercury complexes are formed from the reaction of a number of η^3-allylic palladium compexes with mercury, *e.g.* (Wilkinson, Stone, Abel, 1982);

$$[Pd(C_3H_5)X]_2 + Hg \rightarrow Pd + Hg(C_3H_5)X \text{ or } Hg(C_3H_5)_2$$

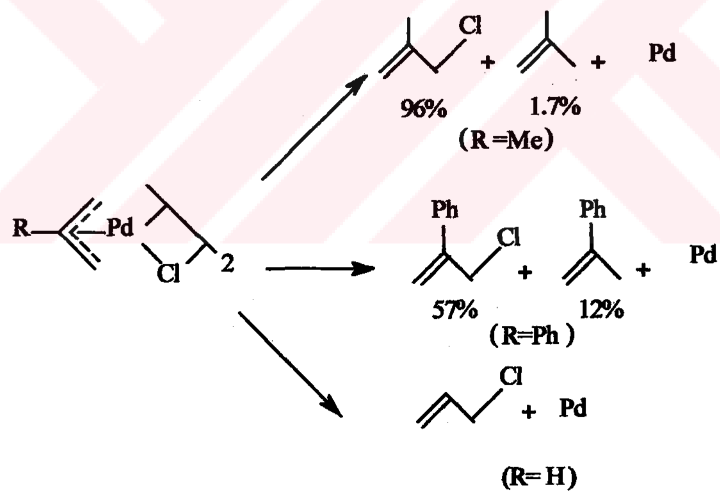
however, η^3-allylic palladium complexes did not react with magnesium, copper or gallium. The suggested mechanism involves the insertion of mercury into a palladium-chloride bond followed by intramolecular transfer of the allyl moiety.

1.6.3.4 Decomposition Reactions of (η^3-Allyl)palladium Complexes

The following reactions in which the allylic group is attacked will be considered here: (1) thermal decomposition; (2) oxidation; (3) halogenation; (4) reduction; (5) reactions with acids.

1.6.3.4.a Thermal Decomposition

Hüttel *et al.* have shown that allylic palladium chloride complexes decomposed to form the allylic chloride, olefin and metal (Scheme 1.12), (Hüttel and Bechter, 1961).

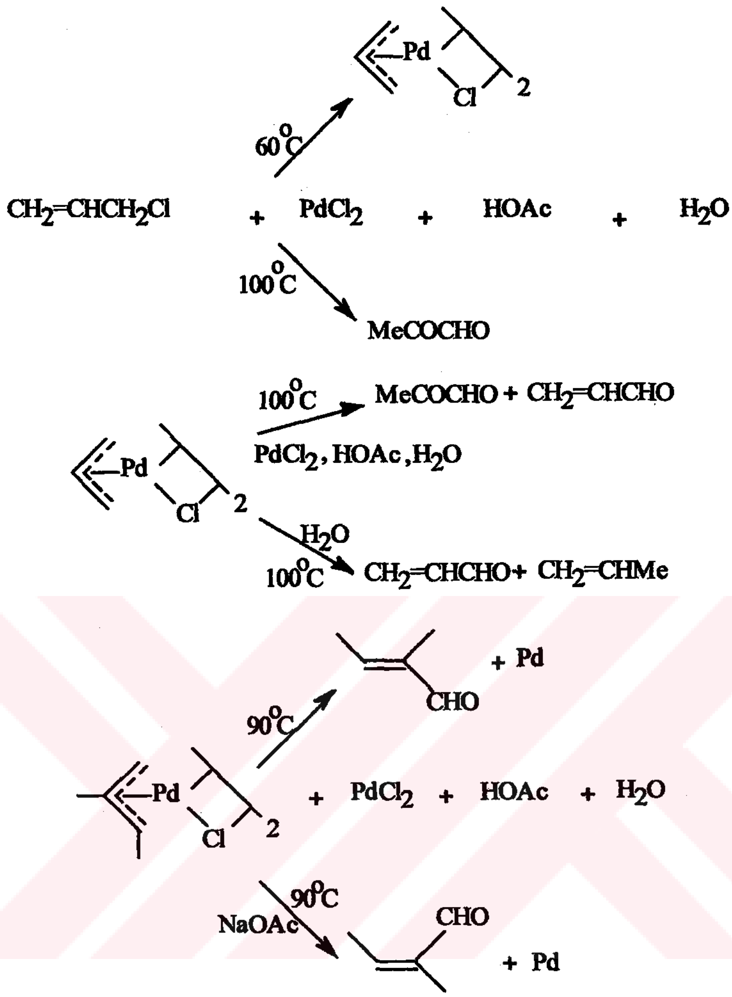


Scheme 1.12 Decomposition of allylic palladium chloride complexes

1.6.3.4.b Oxidation of Allylic Complexes to Aldehydes and Ketones

There are three reaction types; (1) the reaction of olefins with $PdCl_2$ to give aldehydes and ketones under conditions in which the η^3-allylic complexes are formed, such as in aqueous acetic acid; (2) the oxidation of η^3-allylic complexes by, for example, palladium chloride; (3) the hydrolysis of η^3-allylic complexes. These reactions are not well understood as the roles of the numerous variables (pH, presence or absence of atmospheric oxygen, presence of ligands such as acetate or chloride) have not been studied in sufficient detail.

Hüttel and coworkers (Wilkinson, Stone and Abel, 1982) have noted that the oxidation of η^3-allyl complexes normally resulted in the formation of unsaturated aldehydes or ketones, whereas oxidation of the olefin gave rise to saturated carbonyl products. Different products have been obtained from oxidation of η^3-allyl complexes at different pHs (Scheme 1.13).



Scheme 1.13 Oxidation of allylic complexes

These reactions have been interpreted in terms of an attack by HO^- at an allylic carbon, followed by the loss of H^- to the uncomplexed Pd^{II}. Other oxidizers such as MnO_2 or $[Cr_2O_7]^{-2}$ gave similar results; however, as they are more powerful oxidants than $PdCl_2$ they were able to oxidize η^3-allyl groups of greater steric bulk, for example;

$$[Pd_2(1,2,3\text{-}Me_3C_3H_2)_2Cl_2] + [Cr_2O_7]^{2-} \text{ or } MnO_2 \rightarrow MeCH{=}CMeCOMe$$

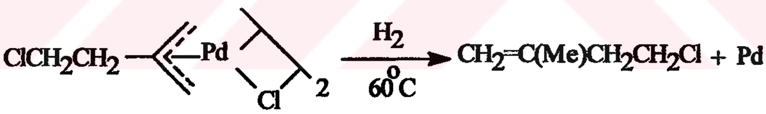
1.6.3.4.c Halogenation

Allyl bromide was formed from the reaction of $[Pd(C_3H_5)Cl]_2$ with bromine in methanol in the presence of sodium bromide; when excess bromine was used then 1,2,3-tribromopropane was formed (Wilkinson, Stone and Abel, 1982).

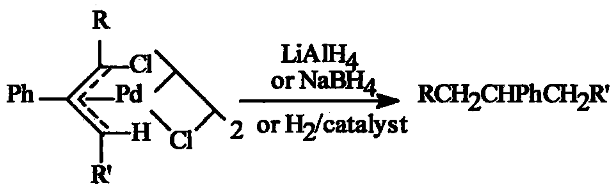
The reaction of $[Pd(\eta^3\text{-}C_3H_5)X(SbPh_3)]$ with halogens and triphenylantimony: with Cl_2 or Br_2 at 100°C, palladium metal and SbX_2Ph_3 were formed whereas I_2 gave $[PdI_2(SbPh_3)_2]$ and palladium metal.

1.6.3.4.d Reduction

The hydrogenation of η^3-allylic complexes usually results in the formation of a monoolefin or the saturated organic compound (Wilkinson, Stone and Abel, 1982).



In general, the use of $LiAlBH_4$ or $NaBH_4$ results in the formation of similar products to those obtained from hydrogenataion.



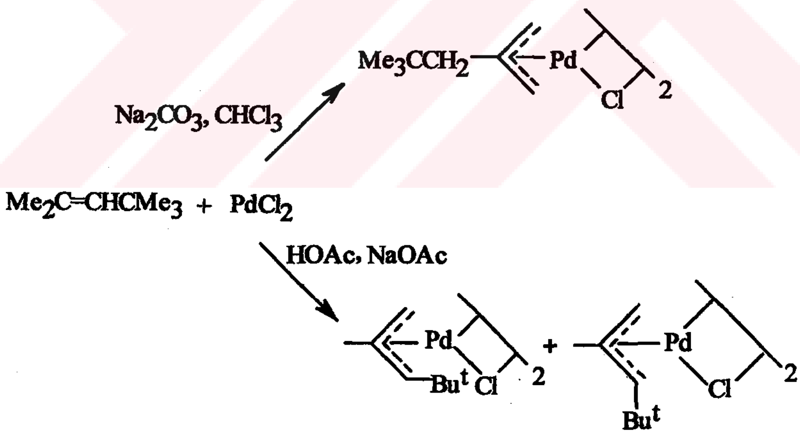
R=R'=Ph; R=But, R'=Me

1.6.3.4.e Reactions with Acids

Bis(η^3-2-methylallyl)dichlorodipalladium was converted to tetrachloro *bis*(propylene) dipalladium quantitatively by HCl in ether. This result has been used to interpret a number of reactions in terms of equilibria between allyl and olefin complexes (Wilkinson, Stone and Abel, 1982).

$$[Pd_2(C_nH_{2n-1})_2X_2] \underset{-HX}{\overset{HX}{\rightleftharpoons}} [Pd_2X_4(C_nH_{2n})_2]$$

2,4,4-Trimethylpent-2-ene in the presence of sodium carbonate has been shown to form η^3-2-neopentylallyl complexes, whereas in acetic acid-sodium acetate media the major products are the *syn-* and *anti*-η^3-1-*t*-butyl-2-methylallyl complexes (Scheme 1.14).



Scheme 1.14 The equilibria between olefin and allyl complexes

1.6.3.5 Nucleophilic Attack at Carbon

Nucleophilic substitution at an allylic carbon normally results in decomposition. However, nucleophilic displacement at carbons attached to C(1) or C(3) of the allyl group is quite easy, e.g. Figure 1.31, (Robinson and Shaw, 1963).

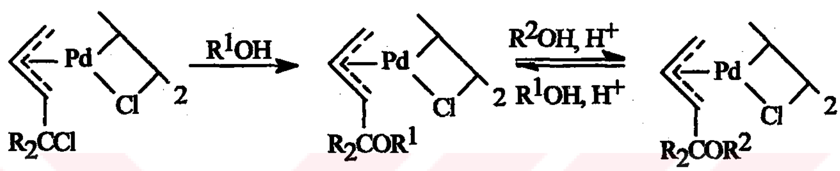
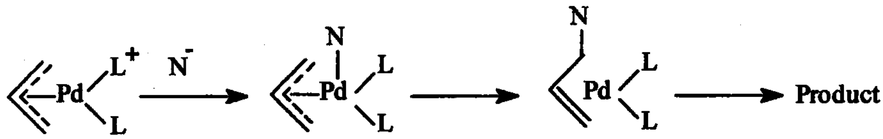


Figure 1.31 Nucleophilic displacement at carbons attached to C(1) or C(3) of the allyl group

In these reactions the complex serves as an electrophile and so the addition of alkyl substituents which increase the electron density on the alkyl group results in a decreased rate of reaction. The stereoselectivity of the reaction is such that attack takes place at the less-substituted carbon atom. The ideal ligand is a good σ-donor, which decreases the attack of the anion at palladium; however, it should also possess π-acceptor properties in order to delocalize the electron density when nucleophilic addition has occurred. These results can be interpreted in kinetic terms with initial attack at the metal followed by rearrangement (Scheme 1.15). Alternatively, on thermodynamic grounds the formation of carbon-carbon single and double bonds is a more favourable process than the formation of a palladium-carbon bond and thus attack by the soft nucleophile may occur at carbon.



Scheme 1.15 The mechanism of nucleophilic attack at an allylic carbon

2.MATERIALS AND METHODS

2.1 Instruments

Infrared Spectroscopy: IR spectra were measured as KBr disks using a Perkin Elmer 1600 Fourier Transform Spectrophotometer. (Department of Chemistry, University College London, England)

^{1}H NMR: ^{1}H NMR spectra in $CDCl_3$ solution were recorded by using a BRUKER-Fx 400 FT spectrometer and chemical shifts are referenced to tetramethylsilane (TMS). (Department of Chemistry, University College London, England)

FAB-Mass Spectroscopy: VG Autospec instrument using caesium ion bombardment at 25 KV of the sample dissolved in 3-nitrobenzyl alcohol. (Department of Chemistry, University College London, England)

Elementel Analyses: Elementel analyses were performed on a Carlo Erba Strummentaione Model 1106. (Department of Chemistry, University College London, England)

X-ray Crystallography: X-ray diffraction measurements were made on a Nicolet R3mV diffractometer, operated with monochromated Cu-K_α radiation. (Department of Chemistry, University College London, England)

2.2 Chemicals

Solvents: Diethylether, dichloromethane, methanol (Merck).

Drying Agents: Na_2SO_4, $MgSO_4$

Reactants: KCl, NaCl, Na_2PdCl_4, $PdCl_2$, $NaOAc.3H_2O$ and $Cu(Oac)_2.H_2O$, CS_2, NaOH, ***allylchloride:*** 2-methylallylchloride, ***olefines:*** tetramethylethene and cyclohexene, ***amines:*** *n*-propylamine, benzylamine, ***dithiocarbamates:*** $Na(Me_2NCS_2).3H_2O$, $Na(Et_2NCS_2).3H_2O$.

2.2.1 Purification of Solvents

The solvents used were refluxed over the special drying agents under the nitrogen atmosphere. The solvents were prepared for the use as described below (Perrin *et al.*, 1980);

Diethylether: Very dry ethers were obtained by refluxing the sodium dried material (1L) over sodium (3g) and benzophenone (1g) until the mixture develops the deep purple color of the sodium benzophenon ketyl.

Dichloromethane: The solvent kept in the bottle containing Na_2SO_4 was distilled over P_2O_5 (b.p= 40.0°C).

Methanol: The solvent kept in the bottle containing Na_2SO_4 was distilled over Mg powder and iodide. The mixture was heated until iodine was removed. The 900 ml absolute ethanol was added to this mixture. The mixture was refluxed for 30 minutes and distilled directly. The first 25 ml was spilled (b.p= 64.5°C).

2.3 Preparation of $[(\eta^3\text{-}CH_2CHCH_2)Pd(\mu\text{-}Cl)]_2$, (1a); $[(\eta^3\text{-}CH_2CMeCH_2)Pd(\mu\text{-}Cl)]_2$, (1b); $[(\eta^3\text{-}CMe_2CMeCH_2)Pd(\mu\text{-}Cl)]_2$, (1c); $[(\eta^3\text{-}C_6H_9)Pd(\mu\text{-}Cl)]_2$, (1d):

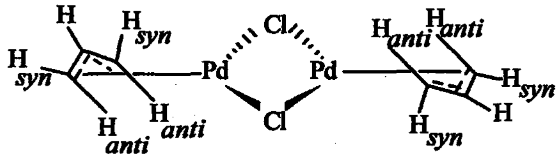
Typical synthetic procedures, modified from literature (Zhang, *et al.* 1998 and Palenik, 1992) methods are given below;

Sodium tetrachloropalladate (II) (1.00 g, 2.87 mmol) and 3-chloropropene (allyl chloride) (66 mg, 8.47 mmol) were stirred together in water (20 ml) for 8 hours at 70 °C. The mixture was extracted with chloroform (3x20 ml) and the organic layer was dried over magnesium sulfate, and the solvent was removed under reduced pressure. The product was obtained as a yellow solid, (yield, **1a**, 62%). (Figure 2.1)

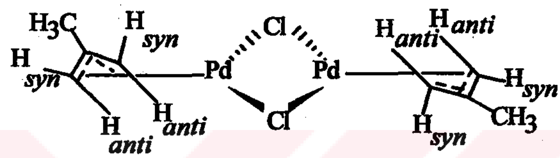
Also synthesized in the same way was $[(\eta^3\text{-}CH_2CMeCH_2)Pd(\mu\text{-}Cl)]_2$, **(1b)** using 3-chloro-2-methylpropene (methylallyl chloride), (yield, 80%). (Figure 2.1)

A mixture of $PdCl_2$ (0.10 g; 0.56 mmol), $NaOAc.3H_2O$ (1.03 g, 7.5 mmol), NaCl (0.42 g, 7.2 mmol), and $Cu(OAc)_2.H_2O$ (0.485 g, 3.4 mmol) in a solvent mixture of glacial acetic acid (10 ml) and acetic anhydride (1 ml) was stirred at 90°C for 2 h and then cooled to 60°C. A solution of $Me_2C{=}CMe_2$ in THF (1.3 ml of 1M solution) was added, and the mixture was allowed to react at 60°C for 3h, then cooled to room temperature, and poured into distilled water (250 ml). The product was extracted with benzene (3x5ml). The benzene layer was collected, washed with distilled water (3x20 ml), saturated aqueous $NaHCO_3$ (10 ml), and saturated aqueous NaCl solution (10 ml), and dried over anhydrous sodium sulfate, and the solvent was removed under vacuum to give a yellow solid, $[(\eta^3\text{-}CMe_2CMeCH_2)Pd(\mu\text{-}Cl)]_2$, **(1c)** (yield, 88%) (Figure 2.1).

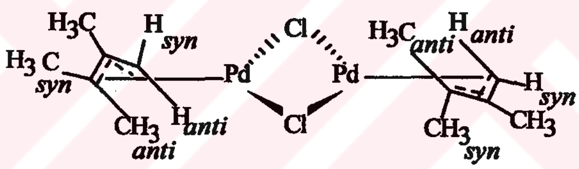
Similarly, from cyclohexene, the cyclohexenyl complex $[(\eta^3\text{-}C_6H_9)Pd(\mu\text{-}Cl)]_2$, **(1d)** (yield, 68%) was prepared (Fig.2.1).



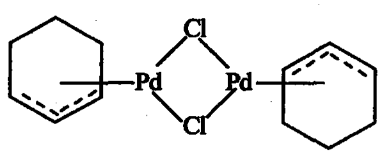
(1a)



(1b)



(1c)



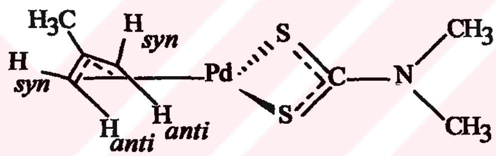
(1d)

Figure 2.1 $[(\eta^3\text{-allyl})Pd(\mu\text{-}Cl)]_2$ allyl ; 1a) allyl, 1b) 2-methylallyl, 1c) 1,1,2-trimethylallyl, 1d) cyclohexenyl

2.4 Preparation of (η^3-Allyl)Palladium(Dithiocarbamate) Complexes;

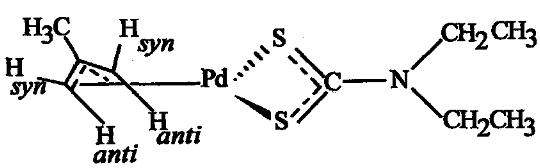
[Pd(η^3-CH_2CMeCH_2)(η^2-$S_2CN(CH_3)_2$)], 2a :

$Na((CH_3)_2NCS_2).H_2O$ (0.220 g, 1.36 mmol) was dissolved in MeOH. [Pd(η^3-CH_2CMeCH_2)(μ-Cl)]$_2$ (0.266 g, 0.68 mmol) in diethylether was added and stirring was continued for 3 hrs. The solvents were removed by reduced pressure to yield a yellow sticky solid, which was dissolved in Et_2O and washed with water (3x10 ml) and dried over $MgSO_4$. Organic part was filtrated and evaporated.



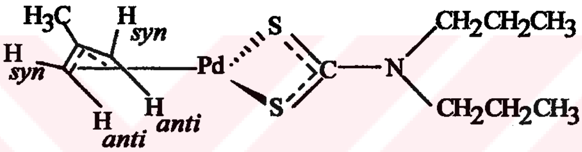
[Pd(η^3-CH_2CMeCH_2)(η^2-$S_2CN(C_2H_5)_2$)], 2b :

$Na((C_2H_5)_2NCS_2).3H_2O$ (0.275 g, 1.22 mmol) was stirred in MeOH until dissolved. [Pd(η^3-CH_2CMeCH_2)(μ-Cl)]$_2$ (0.240 g, 0.61 mmol) in diethylether was added and stirring was continued for 3 hrs. The solvents were removed by reduced pressure to yield a yellow viscous oily, which was dissolved in Et_2O and washed with water (3x10 ml) and dried over $MgSO_4$. Organic part was filtrated and evaporated.



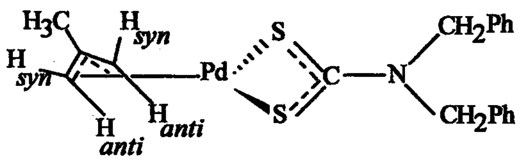
[Pd(η^3-CH_2CMeCH_2)(η^2-$S_2CN(C_3H_7)_2$)], 2c :

NaOH (0.040 g, 1mmol) was stirred in MeOH until dissolved. *N,N*-dipropylamine (0.097 g, 0.96 mmol) was added with stirring, followed by carbon disulfide (0.073 g, 0.96 mmol). Stirring was continued for 30 minutes. [Pd(η^3-CH_2CMeCH_2)(μ-Cl)]$_2$ (0.160 g, 0.40 mmol) in diethylether (40 ml) was added and stirring was continued for 3 hours. The solvents were removed, leaving a yellow sticky solid, which was dissolved in Et_2O and washed with water (3x10 ml) and dried over $MgSO_4$. Organic part was filtrated and evaporated.



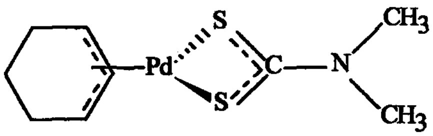
[Pd(η^3-CH_2CMeCH_2)(η^2-$S_2CN(CH_2C_6H_5)_2$)], 2d :

NaOH (0.048 g, 1.2 mmol) was stirred in MeOH until dissolved. *N,N*-dibenzylamine (0.245 g, 1.24 mmol) was added with stirring, followed by carbon disulfide (0.092 g, 1.2 mmol). Stirring was continued for 30 minutes. [Pd(η^3-CH_2CMeCH_2)(μ-Cl)]$_2$ (0.200 g, 0.50 mmol) in diethylether (40 ml) was added and stirring was continued for 3 hours. The solvents were removed, leaving a yellow sticky solid, which was dissolved in Et_2O and washed with water (3x10 ml) and dried over $MgSO_4$. Organic part was filtrated and evaporated.



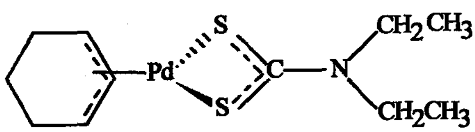
$[Pd(\eta^3\text{-}C_6H_9)(\eta^2\text{-}S_2CN(CH_3)_2)]$, 3a :

$[Pd(\eta^3\text{-}C_6H_9)(\mu\text{-}Cl)]_2$ (0.250 g, 0.56 mmol) was dissolved in dichloromethane and added to $Na((CH_3)_2NCS_2).H_2O$ (0.200 g, 1.24 mmol) / water solution. It was stirred for 3 hrs. The solvents were removed, leaving a yellow viscous oil, which was dissolved in Et_2O and washed with water (3x10ml) and dried over $MgSO_4$. Organic part was filtrated and evaporated.



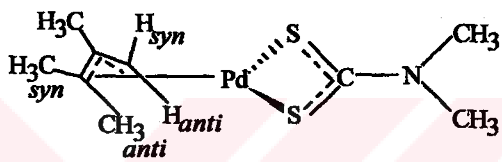
$[Pd(\eta^3\text{-}C_6H_9)(\eta^2\text{-}S_2CN(C_2H_5)_2)]$, 3b :

$[Pd(\eta^3\text{-}C_6H_9)(\mu\text{-}Cl)]_2$ (0.230 g, 0.51 mmol) was dissolved in dichloromethane and added to $Na((C_2H_5)_2NCS_2).3H_2O$ (0.230 g, 1.02 mmol) / water solution. It was stirred for 3 hrs. The solvents were removed, leaving a yellow viscous oil, which was dissolved in Et_2O and washed with water (3x10 ml) and dried over $MgSO_4$. Organic part was filtrated and evaporated.



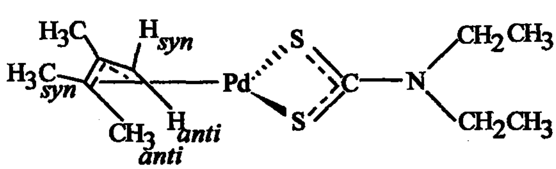
[Pd(η^3-C(Me$_2$)CMeCH$_2$)(η^2-S$_2$CN(CH$_3$)$_2$)], 4a :

$Na((CH_3)_2NCS_2).H_2O$ (0.063 g, 0.40 mmol) was dissolved in MeOH. [Pd(η^3- C(Me$_2$)CMeCH$_2$)(μ-Cl)]$_2$ (0.100 g, 0.22 mmol) in diethylether was added and stirring was continued for 3 hrs. The solvents were removed by reduced pressure to yield a brown sticky solid, which was dissolved in Et_2O and washed with water (3x10 ml) and dried over $MgSO_4$. Organic layer was filtrated and evaporated. Organic part was filtrated and evaporated.



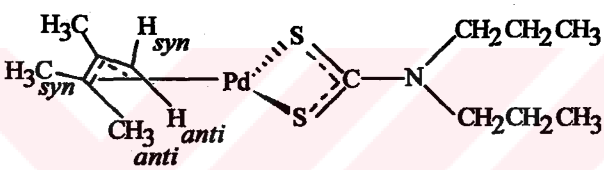
[Pd(η^3-C(Me$_2$)CMeCH$_2$)(η^2-S$_2$CN(C$_2$H$_5$)$_2$)], 4b :

$Na((C_2H_5)_2NCS_2).3H_2O$ (0.100 g, 0.44 mmol) was dissolved in MeOH. [Pd(η^3- C(Me$_2$)CMeCH$_2$)(μ-Cl)]$_2$ (0.100 g, 0.22 mmol) in diethylether was added and stirring was continued for 3 hrs. The solvents were removed by reduced pressure to yield a brown viscous oily, which was dissolved in Et_2O and washed with water (3x10 ml) and dried over $MgSO_4$. Organic part was filtrated and evaporated.



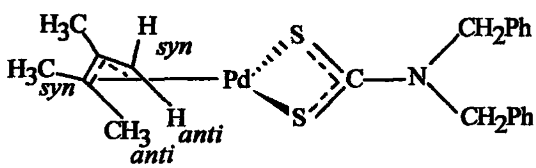
[Pd(η^3-C(Me$_2$)CMeCH$_2$)(η^2-S$_2$CN(C$_3$H$_7$)$_2$)], 4c :

NaOH (0.021 g, 0.52 mmol) was stirred in MeOH until dissolved. *N,N*-dipropylamine (0.053 g, 0.52 mmol) was added with stirring, followed by carbon disulfide (0.040 g, 0.52 mmol). Stirring was continued for 30 minutes. [Pd(η^3-C(Me$_2$)CMeCH$_2$)(μ-Cl)]$_2$ (0.100 g, 0.22 mmol) in diethylether (40 ml) was added and stirring was continued for 3 hours. The solvents were removed, leaving a brown sticky solid, which was dissolved in Et$_2$O and washed with water (3x10 ml) and dried over MgSO$_4$. Organic part was filtrated and evaporated.



[Pd(η^3-C(Me$_2$)CHMeCH$_2$)(η^2-S$_2$CN(CH$_2$C$_6$H$_5$)$_2$)], 4d :

NaOH (0.021 g, 0.52 mmol) was stirred in MeOH until dissolved. *N,N*-dibenzylamine (0.104 g, 0.52 mmol) was added with stirring, followed by carbon disulfide (0.040 g, 0.52 mmol). Stirring was continued for 30 minutes. [Pd(η^3-C(Me$_2$)CHMeCH$_2$)(μ-Cl)]$_2$ (0.100 g, 0.25 mmol) in diethylether (40 ml) was added and stirring was continued for 3 hours. The solvents were removed, leaving a brown sticky solid, which was dissolved in Et$_2$O and washed with water (3x10 ml) and dried over MgSO$_4$. Organic part was filtrated and evaporated.



3.RESULTS AND DISCUSSION

3.1 Scope of the Thesis:

The aim of this project was to synthesize and characterize a series of palladium complexes with sulfur-coordinating ligands, and various allyl groups, which are known to increase the volatility of complexes. These complexes might be ideal precursors for palladium sulfurs, therefore they would be tested for their suitability as precursors to palladium sulfide, using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). If successful, one of the precursors is used to lay down a thin film of palladium sulfide by CVD, and characterise any film produced in this way by materials analysis, including X-ray diffraction and energy dispersive X-ray spectrometry. The ultimate aim would be to incorporate the sulfide into zeolites are onto supports in order to test its function as a heterogeneous catalyst. (Figure 3.1)

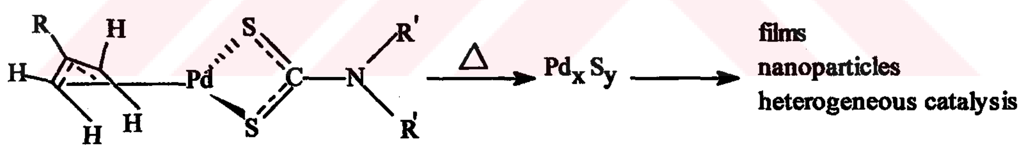
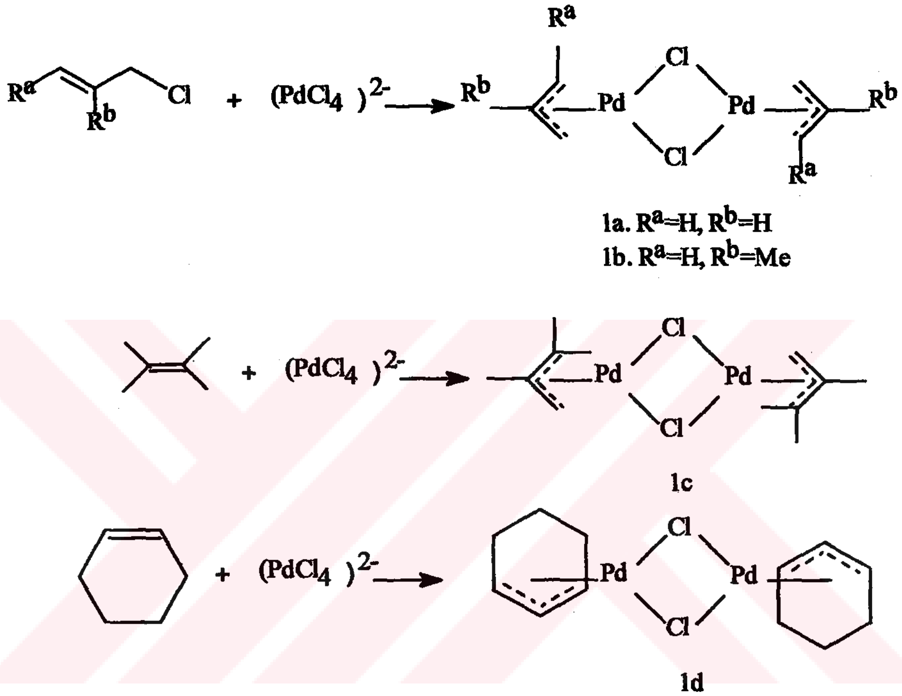


Figure 3.1 Usage of precursors

3.2 Analysis of Complexes

There are several methods available for synthesis of complexes of the type $[(\eta^3\text{-allyl})Pd(\mu\text{-}Cl)]_2$, and literature methods were modified to give optimum yields (Palenik *et al.*, 1992; Trost *et al.*, 1978 and Zhang *et al.*, 1998). Substituted allyl derivatives were obtained in almost quantitative yields and without the need for sophisticated equipment. The more highly substituted complex $[(\eta^3\text{-}CMe_2CMeCH_2)Pd(\mu\text{-}Cl)]_2$, **(1c)** and the cyclohexenyl derivative $[(\eta^3\text{-}C_6H_9)Pd(\mu\text{-}Cl)]_2$, **(1d)**, were prepared from the corresponding alkene, $Me_2C{=}CMe_2$ and cyclohexene, respectively.

The synthetic procedure is summarized in scheme 3.1;



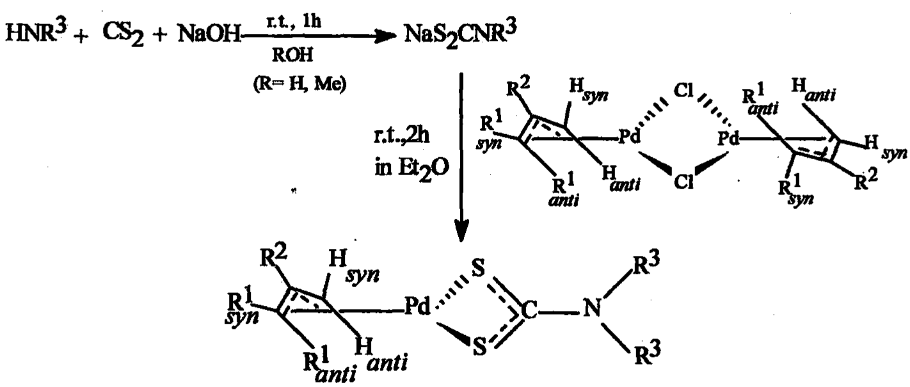
Scheme 3.1 Preparations of $[(\eta^3\text{-}allyl)Pd(\mu\text{-}Cl)]_2$ dimers

Ten original, $[(\eta^3\text{-}allyl)Pd(S_2CNR_2)]$ (***allyl***: 2-methylallyl, 1,1,2-trimethylallyl, ***R***: Me, Et, ^{n}Pr, Bz, (**2a, 2b, 2c, 2d, 4a, 4b, 4c** and **4d**); ***allyl:*** cyclohexenyl, ***R***: Me, Et, (**3a, 3b**) complexes were prepared and analysed (Table 3.1).

Table 3.1 Yields of allylpalladium dithiocarbamates

Complex	R^1	R^2	R^3	Yield/%
2a	H	Me	Me	78
2b	H	Me	Et	76
2c	H	Me	^{n}Pr	69
2d	H	Me	Bz	65
3a	cyclohexenyl		Me	65
3b	cyclohexenyl		Et	58
4a	Me	Me	Me	80
4b	Me	Me	Et	82
4c	Me	Me	^{n}Pr	74
4d	Me	Me	Bz	60

The syntheses were straightforward, consisting of creating a solution of sodium dithiocarbamate *in situ* from sodium hydroxide, carbon disulfide and a secondary amine (Sceney and Magee, 1974). When added to a solution of palladium allyl chloride dimer, the dithiocarbamate displaces chlorides to give (η^3-allyl)palladium dithiocarbamate and sodium chloride (Scheme 3.2).



Scheme 3.2 Preparation of allyl Palladium dithiocarbamates

The synthesis of dithiocarbamate was initially carried out in water, before addition of the allylpalladium chloride in diethylether. The two-phase mixture was then stirred for 4 hours. It was thought that the reaction would take place at the phase interface, keeping local concentrations of reactants low, and preventing formation of by-products such as *bis*(dithiocarbamates), which had been encountered in previous syntheses. However, despite prolonged drying over magnesium sulfate, the products obtained were dark brown and oily, and gave broad, overlapping peaks in the NMR, which proved impossible to identify. Repeated attempts to recrystallise the products from a variety of solvents including ether, chloroform, petroleum spirits and cyclohexane were also unsatisfactory.

The synthesis was repeated using methanol as the solvent; this gave better results and products that could be identified by NMR and mass spectrometry. One drawback was that the NaCl produced was fairly soluble in the methanol, so the organic layers had to be washed thoroughly with water.

The prepared compounds varied in appearance from pale yellow to brown solid. Some general trends were apparent. The compounds with the 2-methylallyl side chain (*i.e.* when R^1 = H, R^2 = Me) were pale yellow in appearance, prepared in moderate yield. By contrast, the compounds with an 1,1,2-trimethylallyl side chain were all light brown to dark-brown, diamagnetic solids and gave good NMR results and microanalysis. Compounds **(2b)** and **(4b)** were viscous oils and their elemental analysis could not be carried out. All of the compounds had a very low solubility except in chlorinated solvents, and also could not be recrystallised satisfactorily except for **(2c)**, which was recrystallised from hexane/chloroform solution and gave a crystalline yellow solid with good microanalysis and NMR spectra. Cyclohexenyl complexes of **(3a)** and **(3b)** were also obtained in a moderate yield and the compexes were pale yellow.

As they were oily their elemental analysis characterisation could not be carried out. The analytical data for the complexes $[(\eta^3\text{-allyl})Pd(S_2CNR_2)]$ are listed in the Table 3.2.

Table 3.2 The analytical data for $[(\eta^3\text{-allyl})Pd(S_2CNR_2)]$ complexes of **2a-d, 3a-b, 4a-d.**

Complex	C% (calcd.)	H%(calcd.)	N% (calcd.)	S% (calcd.)
2a	29.62(29.89)	4.01(4.63)	4.70(4.98)	22.82(22.77)
2b	-	-	-	-
2c	39.54(39.17)	6.02(6.23)	4.02(4.15)	18.92(19.00)
2d	52.86(52.65)	4.73(4.84)	3.02(3.23)	14.98(14.78)
3a	-	-	-	-
3b	-	-	-	-
4a	34.44(34.68)	5.70(5.78)	4.75(4.50)	20.75(20.55)
4b	-	-	-	-
4c	42.55(42.74)	6.51(6.85)	3.94(3.83)	17.88(17.53)
4d	54.49(54.60)	5.40(5.42)	3.07(3.03)	13.76(13.88)

All the compounds had so far been prepared on a small scale (≈100 mg), owing to the general expense of palladium compounds. The prepared compounds can be stored for long periods at room temperature without thermal decomposition.

All new complexes have been characterized by IR, ^1H NMR spectroscopy and mass spectrometry techniques. Assignments are made by reference to literature data on related complexes.

3.3 IR Characterisation of the Complexes

3.3.1 IR Spectra of σ- and π-Allyl Complexes

Complete vibrational assignments are available for σ-bonded allyl compounds such as $M(CH_2\text{-}CH{=}CH_2)_4$ (M=Si and Sn), and $M(CH_2\text{-}CH{=}CH_2)_3$ (M=P and As), and $M(CH_2\text{-}CH{=}CH_2)_2$ (M=Hg) (Davidson, Harrison, and Riley, 1973 and Mink and Pentin, 1970). Carbon-carbon and metal-carbon stretching frequencies of σ-bonded allyl compounds are shown in Table 3.3.

Table 3.3 ν(C=C) and ν(MC) stretching frequencies of σ-bonded allyl compounds

Compound	ν(C=C)	ν(MC)
$Si(CH_2\text{-}CH{=}CH_2)_4$	1592	732, 583
$Sn(CH_2\text{-}CH{=}CH_2)_4$	1583	527, 513
$P(CH_2\text{-}CH{=}CH_2)_3$	1590	715, 667
$Hg(CH_2\text{-}CH{=}CH_2)_2$	1603	541, 513

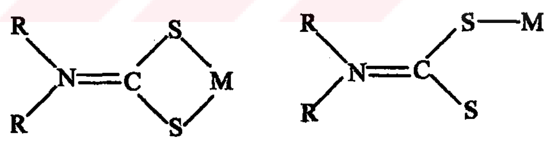
If the allyl group is π-bonded to a metal, the C=C stretching band characteristic of the σ-bonded allyl group does not appear. Instead, three bands of medium or strong intensity are observed at 1510-1375 cm^{-1} (Nakamato, 1986). In the low-frequency region, the metal-olefin vibrations appear in the range from 570 to 320 cm^{-1}.

Complete band assignments was reported for $[Pd(\pi\text{-}C_3H_5)(\mu\text{-}X)]_2$ (X=Cl and Br) (Shobatake and Nakamato, 1970). In the absence of other interfering vibrations, a band at 1455 cm^{-1}, assigned to ω_{cc}, is characteristic of the η^3-allyl ligand. A further band at 360-405 cm^{-1} was assigned to the Pd-allyl stretching frequency.

According to the literature data (Bailey, Kelley, Maitlis, 1978); the far-IR spectra of $[Pd_3(2\text{-}MeC_3H_4)_2Cl_4]$ complexes of this type show a very strong ν(Pd-Cl) in the region (>300 cm^{-1}) normally associated with a terminal Pd-Cl bond and only much weaker bands in the lower frequency region (<300 cm^{-1}) associated with bridging Pd-Cl bonds; for example, ν(Pd-Cl) for $[Pd_3(2\text{-}MeC_3H_4)_2Cl_4]$ are observed at 326 (vs), 268(m), 246(w), and 200(w) cm^{-1}. By comparison ν(Pd-Cl) for $[Pd(2\text{-}MeC_3H_4)(\mu\text{-}Cl)]_2$ occur at 259(vs) and 248(vs) cm^{-1} and for $M_2[PdCl_4]$, a very strong band is observed between 332 and 317 cm^{-1} the exact position depending on the nature of M^+ (Adams and Arnold, 1967).

3.3.2 IR spectra of dithiocarbamate complexes

The infrared spectra of *N,N*-dialkyldithiocarbamato complexes have been studied extensively. All these compounds are roughly classified into two types (Nakamato, 1986);



Bidentate coordination

Unidentate coordination

The former exhibits ν(CS) near 1000 cm^{-1} as a single band, (O'Connor, Gilbert, Wilkinson, 1969), whereas the latter shows a doublet in the same region (Bonati, and Ugo, 1967). Also the ν(C=N) of the former (above 1485 cm^{-1}) is higher than that of the latter (below 1485 cm^{-1}). The ν(MS) of the bidentate complexes are observed at 400-300 cm^{-1}.

IR data of $Ni(S_2CNMe_2)_2$ and $Pt(S_2CNH_2)_2$ complexes were reported (Durgaprasad, *et al.,* 1969 and Nakamoto, *et al.*, 1963). In these complexes there are only three pure bands belong to ν(C=N), ν(C-S) and ν(M-S), associated with the corresponding complexes shown in table 3.4. IR data of palladium dithiocarbamate complexes also show three strong bands assigned to ν(C=N), ν(C-S) and ν(M-S), respectively as shown in table 3.4, as well (Sceney and Magee, 1974).

Table 3.4 IR data of $M(S_2CNR_2)_2$ (M=Pd, R= Me, Et, ^nPr, Bz; M=Ni, R=Me; M=Pt, R=H) complexes

Complex	ν(C=N)	ν(C-S)	ν(M-S)
$Ni(S_2CNMe_2)_2$	1550s	975m	410m
$Pt(S_2CNH_2)_2$	1438, 1434s	622w	378m
$Pd(S_2CNMe_2)_2$	1541s	966m	349s
$Pd(S_2CNEt_2)_2$*	1514s	986m	357s
$Pd(S_2CN^nPr_2)_2$	1503s	968w	351s
$Pd(S_2CNBz_2)_2$	1493s	-	342s
$Pd(S_2CNEt_2)_2$**	1520s	987m	360s
$Pd(S_2CNEt_2)_2Br_2$	1523,1535sh	990m	363s
$[\{(Et_2NCS_2)BrPd\}_2Pd(Et_2NCS_2)_2]$	1537s	985m	352, 377m

* The data was given by Sceney and Magee, 1974, ** The data was given by Blake *et al.*, 2000.

The important bands in the IR spectra of $Pd(S_2CNR_2)_2$ and $Pd(S_2CNR_2)_2Br_2$ where the dithiocarbamates are coordinated bidentate to the metal and $[\{(Et_2NCS_2)BrPd\}_2Pd(Et_2NCS_2)_2]$; the structure can be described as a central $Pd(dtc)_2$ fragment, in which two *trans* sulfur atoms each bridge to a further Pd(Br)(dtc) fragment, the palladium coordination being square-planar in all cases are given in table 3.4, as well (Blake *et al.*, 2000). It was assumed that more than one ν(Pd-S) band (which generally appears in the 330-370 cm^{-1} region) is observed for the last complex because of the lower symmetry of this species.

3.3.3 IR Spectra Data of [(η^3-allyl)Pd(S_2CNR_2)] (allyl: 2-methylallyl, R: Me, Et, ^{n}Pr, Bz, (2a, 2b, 2c, 2d); allyl: 1,1,2-trimethylallyl, (4a, 4b, 4c and 4d); allyl: cyclohexenyl, R: Me, Et, (3a, 3b)) Complexes.

With the ten palladium dithiocarbamates available (**2a-d**, **3a-b**, **4a-d**), an attempt was made to determine and assign clearly the various absorption bands and investigate the variation with the different alkyl groups. It was found to be very difficult to assign the bands as most of them are highly coupled. Assignments are made by comparison with that of (Sceney and Magee, 1974) for a wide range of dialkyldithiocarbamate complexes of palladium(II). Some important stretching vibrations of IR spectra of the complexes are shown in Table 3.5.

Table 3.5 IR data of [(η^3-allyl)palladium(dtc)] complexes **2a-d; 3a-b, 4a-d.**

Complex	ν(allyl)	ν(C-N)	ν(C-S)
2a	1450m, 1375s, 1350m	1525vs	971s
2b	1440m, 1375s, 1350m	1525vs	988s
2c	1435s, 1375m, 1350m	1525vs	970s
2d	1450s, 1427m, 1375m	1500vs	987s
3a	1450m, 1400s	1530vs	966s
3b	1460m, 1430s, 1345m	1525vs	988s
4a	1450m, 1395vs, 1360m	1520vs	970s
4b	1450m, 1425s, 1365m	1505vs	989s
4c	1435s, 1375m, 1345m	1500vs	971s
4d	1455s, 1430m, 1375m	1500vs	987m

The IR spectra of the complexes do not show any unusual features. As in the other palladium dithiocarbamate complexes such as [Pd(dtc)$_2$], [Pd(dtc)$_2$Br$_2$] (shown in table 3.4), ν(C-S) and ν(C=N) stretching vibrations of **2a-b, 3a-b** and **4a-b** complexes are almost at the same regions (table.3.5). The IR spectra of dithiocarbamate ligands showed absorptions in the region of 1500-1525 cm^{-1} attributable to ν(C=N) and in the region 965-990 cm^{-1} due to ν(C-S) stretching modes, respectively. Three bands of medium or strong intensity observed at 1460-1345 cm^{-1} region due to η^3-allyl complexes.

Allyl group stretching frequencies are in good accordance with the literature assignments (Nakamato, 1986). ν(Pd-S) and ν(Pd-allyl) stretching vibrations are overlapping at 300-500 cm^{-1} region. Therefore presence of several absorptions in that region due to allyl and dithiocarbamate ligand thwarted unambiguous assignment of ν(Pd-S) and ν(Pd-allyl) stretching.

The dimethyldithiocarbamate complexes show a greater shift in the C=N stretching frequency than any other derivatives, indicating a greater contribution from canonical form (d), (in figure 1.7) (Van der Kerk, *et al.*, 1952), which they suggest decreases in the order; Me_2> Et_2> H, Me > iPr_2> nPr_2> nBu_2, for other alkyl groupings. On further examination of the ν(C=N) stretching frequencies several interesting trends showed up (Sceney and Magee, 1974);

(i) values for the $[Pd(S_2CNRR')_2]$, (R′=H) complexes are higher than the corresponding $[Pd(S_2CNR_2)_2]$ complexes, e.g., H, Me> Me_2; H, Me> Et_2; H, iPr> iPr_2; H, Ph> Ph_2;

(ii) for $Pd(S_2CNR_2)_2$ complexes, the ν(C=N) value decreases as Me_2 > Et_2 > nPr_2> nBu_2;

(iii) as branching increases the ν(C=N) value decreases, e.g., nPr_2> iPr_2; nBu_2 > iBu_2; $nHex_2$ > $CycHex_2$

It is possible to see a similar trend in the ν(C=N) values of the complexes, **2a-2d, 3a-b, 4a-d** in table 3.5. ν(C=N) stretching frequencies of **2a, 2b** and **2c** are same (1525 cm^{-1}), but the corresponding value for **2d** (1500 cm^{-1}) is decreased, due to benzyl groups in dithiocarbamato ligands. Here the reason is most likely attributed to the branching effects of the alkyl groups of dithiocarbamates. There is again a decrease in the ν(C=N) stretching frequencies because of the branching effect from **3a** (1530 cm^{-1}) to **3b** (1525 cm^{-1}). The ν(C=N) stretching frequency is apparently decreased from **4a** to

4d in the order; **4a** (1520 cm^{-1}) > **4b** (1505 cm^{-1}) > **4c** (1500 cm^{-1}) > **4d** (1500 cm^{-1}).

IR spectra of the complexes are shown in Figure 3.2-3.11.

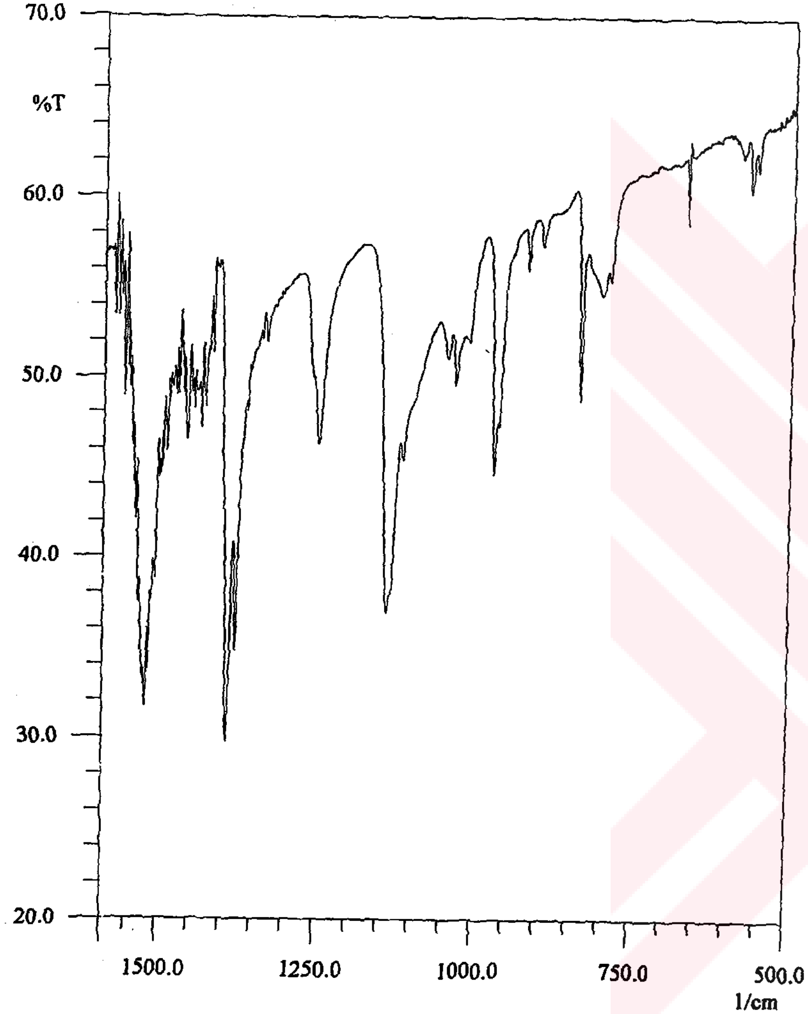


Fig. 3.2 FT-IR Spectrum of $[(\eta^3\text{-}CH_2CMeCH_2)Pd(S_2CNMe_2)]$, 2a

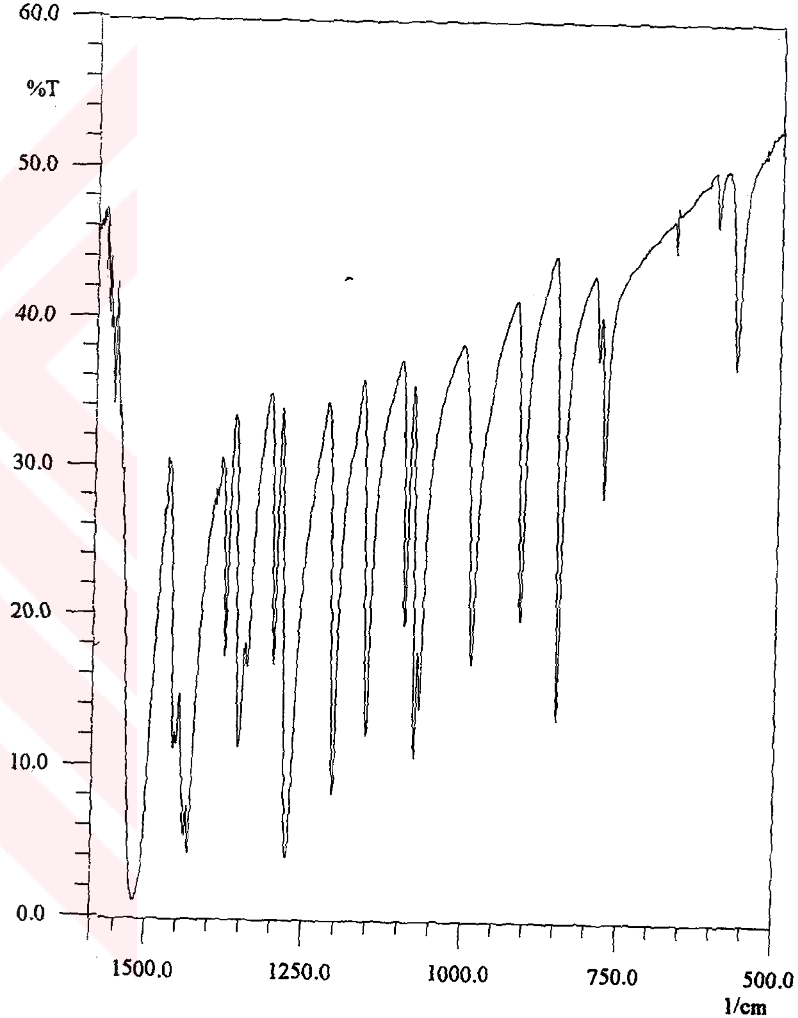


Fig. 3.3 FT-IR Spectrum of $[(\eta^3\text{-}CH_2CMeCH_2)Pd(S_2CNEt_2)]$, 2b

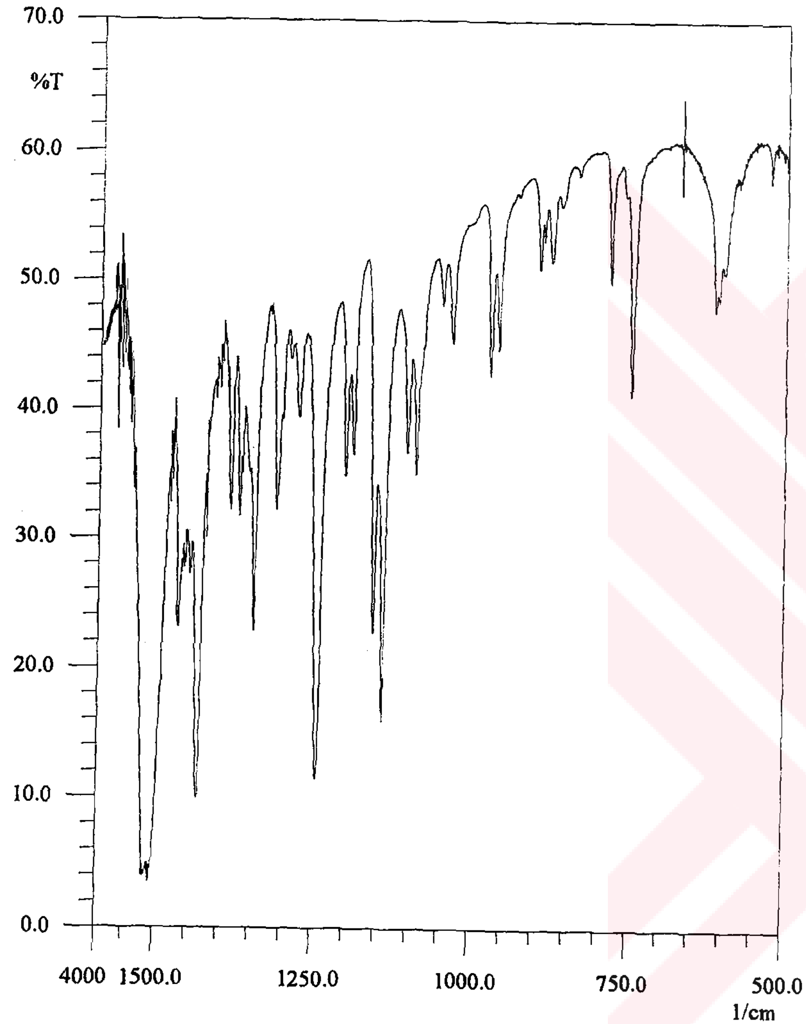


Fig. 3.4 FT-IR Spectrum of $[(\eta^3\text{-}CH_2CMeCH_2)Pd(S_2CN^nPr_2)]$, 2c

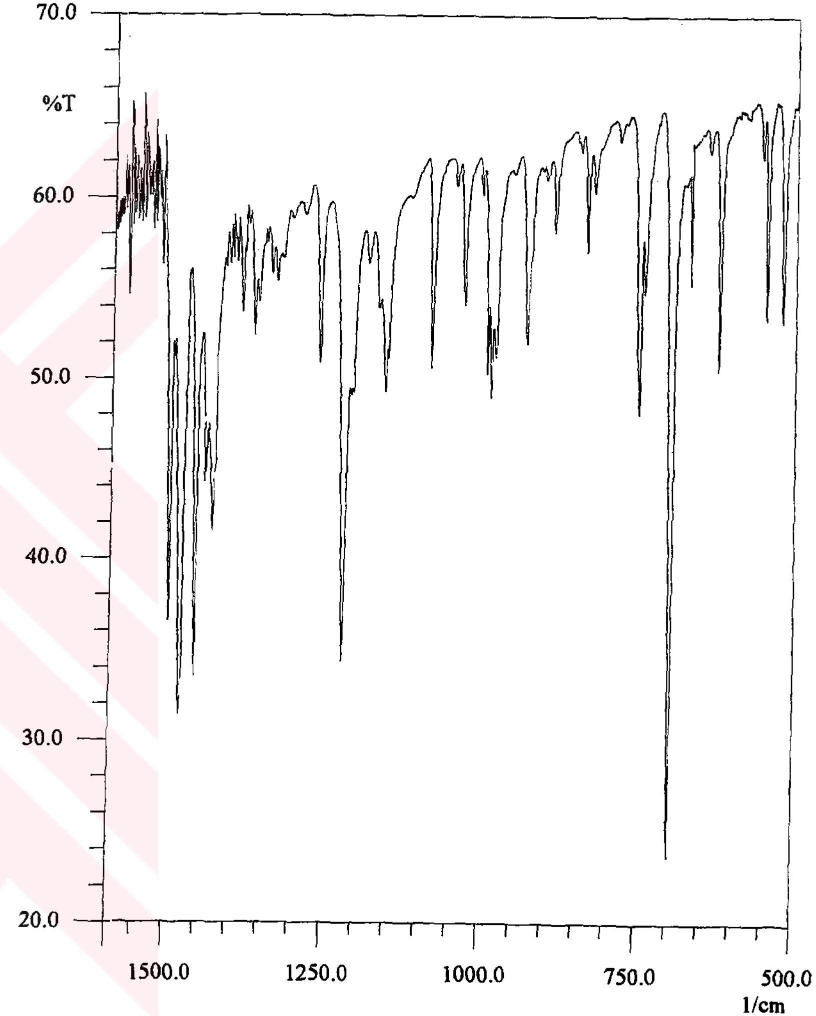


Fig. 3.5 FT-IR Spectrum of $[(\eta^3\text{-}CH_2CMeCH_2)Pd(S_2CNBz_2)]$, 2d

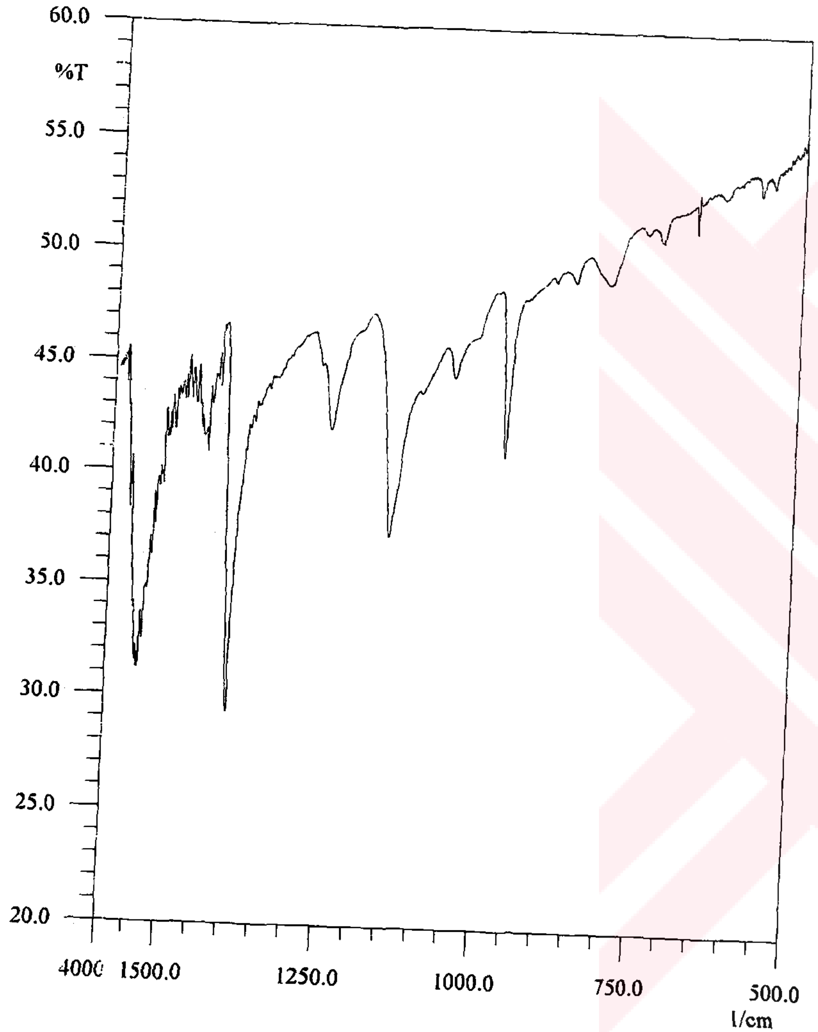


Fig. 3.6 FT-IR Spectrum of $[(\eta^3\text{-}C_6H_9)Pd(S_2CNMe_2)]$, 3a

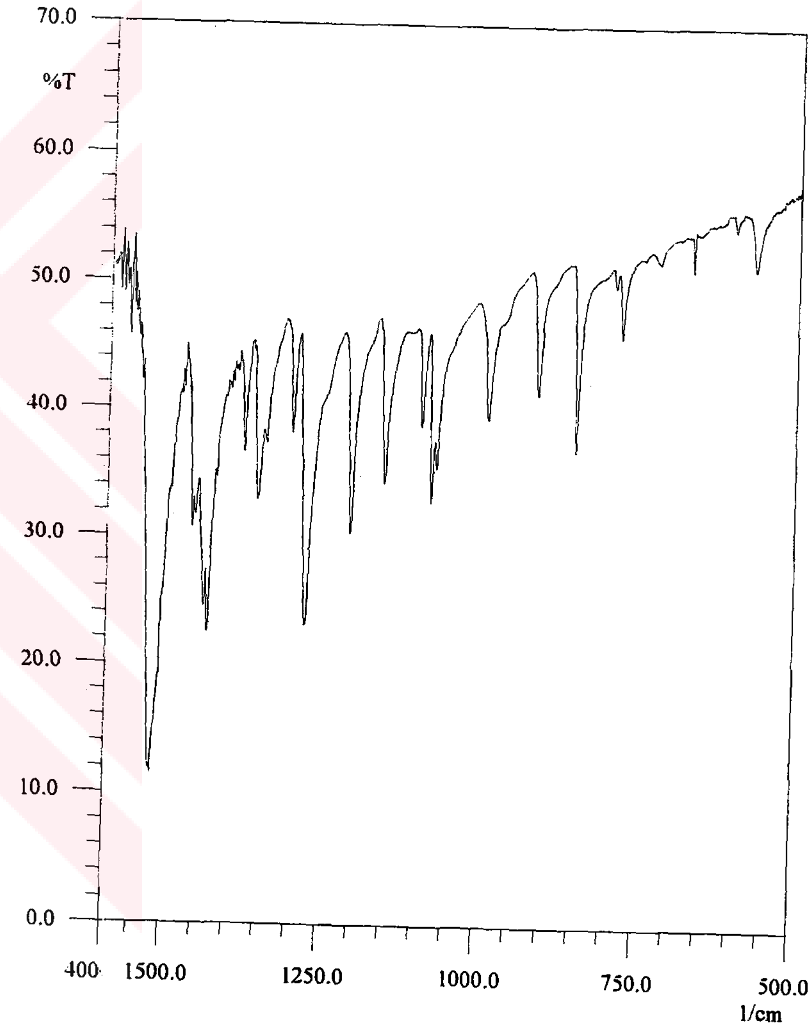


Fig. 3.7 FT-IR Spectrum of $[(\eta^3\text{-}C_6H_9)Pd(S_2CNEt_2)]$, 3b

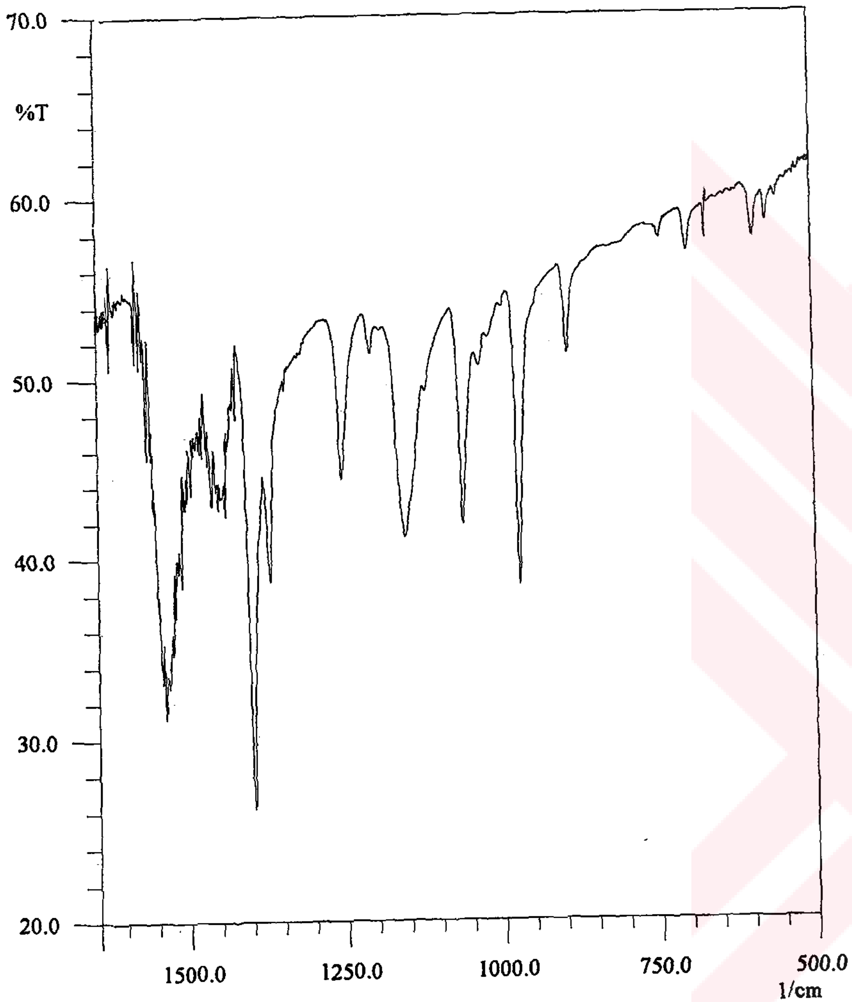


Fig. 3.8 FT-IR Spectrum of $[(\eta^3\text{-CMe}_2\text{CMeCH}_2)\text{Pd}(\text{S}_2\text{CNMe}_2)]$, 4a

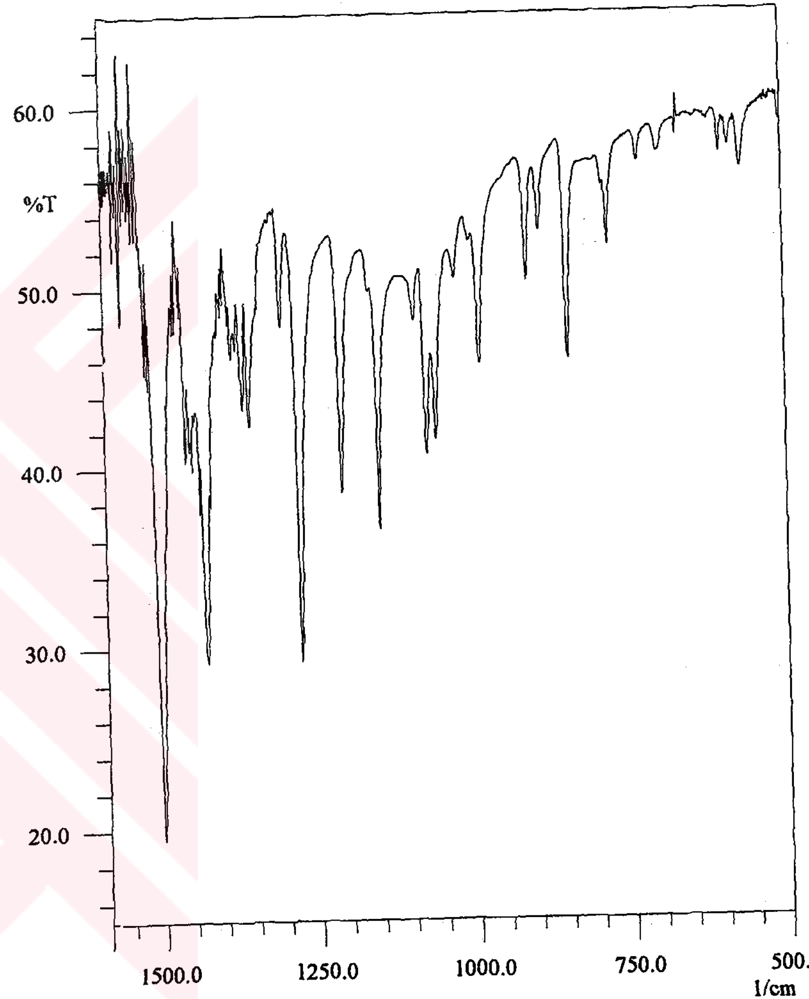


Fig. 3.9 FT-IR Spectrum of $[(\eta^3\text{-CMe}_2\text{CMeCH}_2)\text{Pd}(\text{S}_2\text{CNEt}_2)]$, 4b

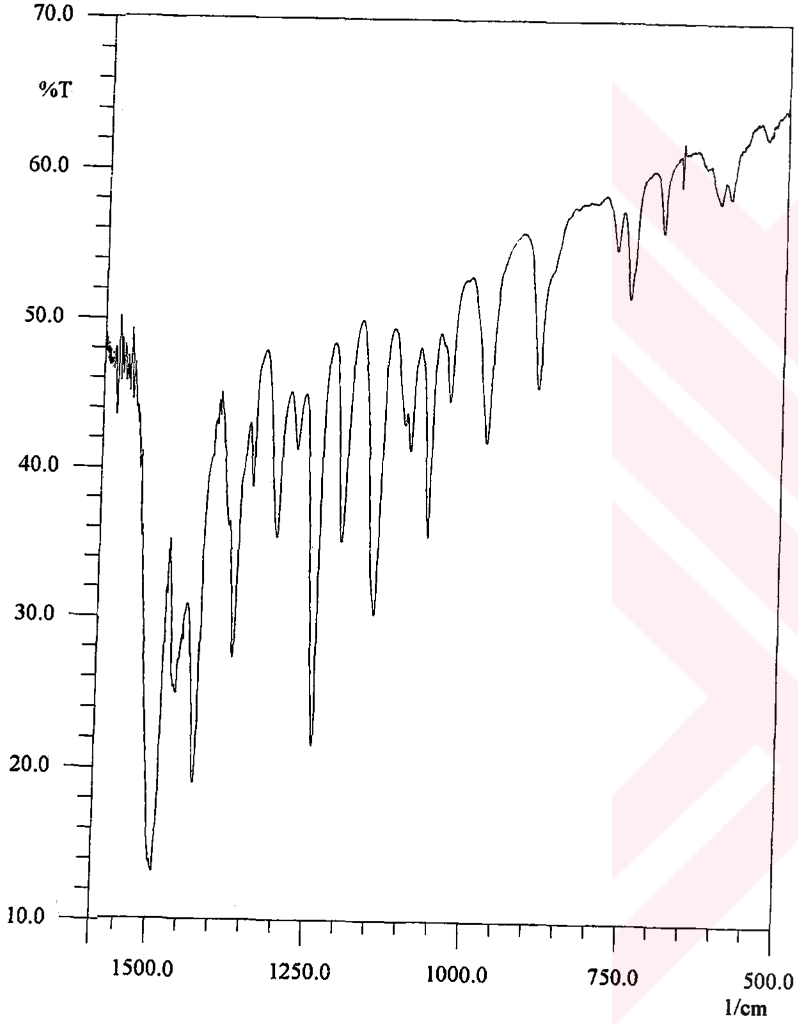


Fig. 3.10 FT-IR Spectrum of $[(\eta^3\text{-}CMe_2CMeCH_2)Pd(S_2CN^nPr_2)]$, 4c

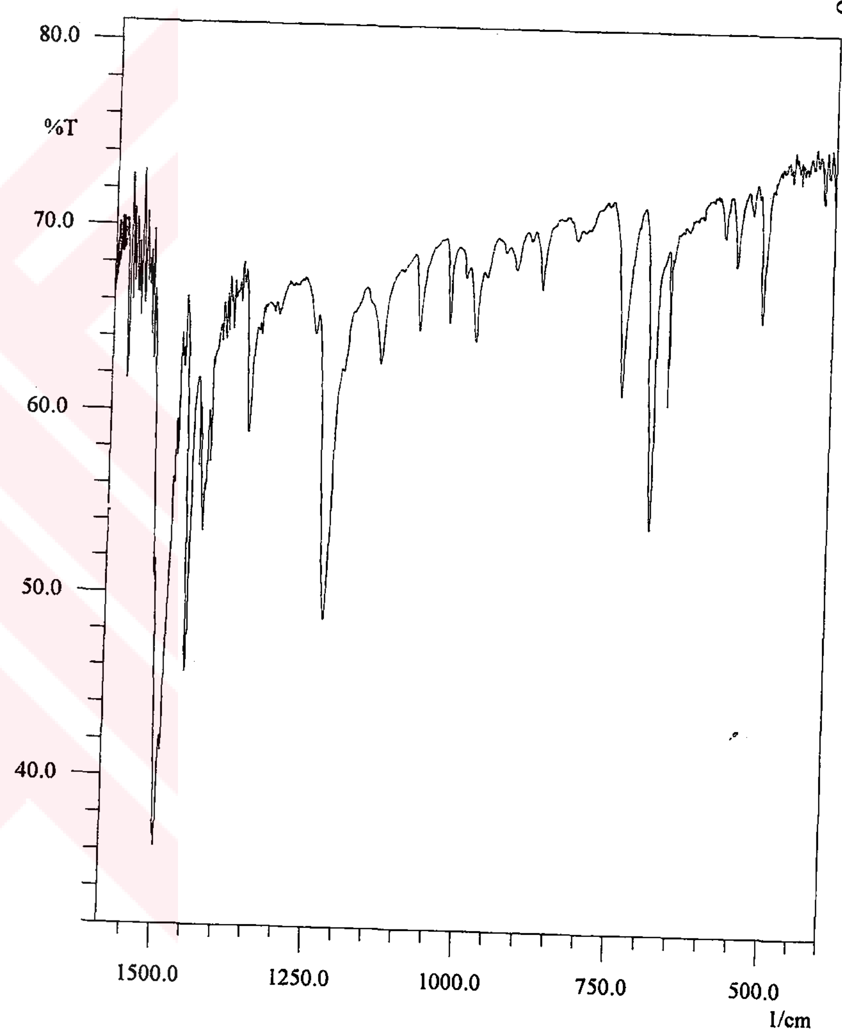


Fig. 3.11 FT-IR Spectrum of $[(\eta^3\text{-}CMe_2CMeCH_2)Pd(S_2CNBz_2)]$, 4d

3.4 NMR Characterisation of the Complexes

NMR spectroscopy is a powerful technique for investigating the structures of species in solution and this has proved invaluable in the interpretation of all types of stereochemical non-rigidity and exchange processes.

3.4.1 NMR Characterisation of $[(\eta^3\text{-allyl})Pd(\mu\text{-}Cl)]_2$ (*allyl*: allyl, 2-methylallyl, 1,1,2-trimethylallyl, cyclohexenyl, (1a, 1b, 1c, 1d)):

The assignment of chemical shifts and coupling constants has enabled NMR spectroscopy to become an extremely powerful method for the elucidation of the structure and dynamic behavior of allylpalladium species in solution. In the ^{1}H NMR spectrum of dichlorobis(η^3-allyl)dipalladium, H_5 appears as a multiplet at δ 5.42 (Fig.3.12), (Smith, 1965). It is coupled to the *syn* protons H_1 and H_4 with $J_{5,1(4)}$=6.8 Hz in the expected range for two protons *cis* in an olefin. The *syn* protons (H_1, H_4) appear as a doublet at higher field (δ 4.01) and are coupled to H_5; the coupling to the gem protons is small (0.1 Hz). The X-ray structural results suggested that the *anti* protons are closer to the metal and hence the higher field resonances (δ 3.05) are assigned to them as they are most shielded by the metal. They also appear as a doublet, coupled to H_5 ($J_{5,2(3)}$ =11.8 Hz); the magnitude of this coupling is similar to that for two *trans* olefinic protons.

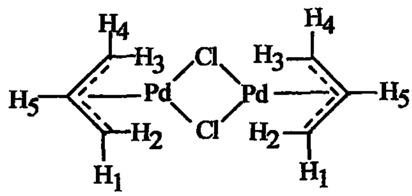
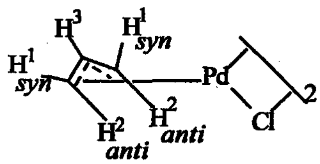


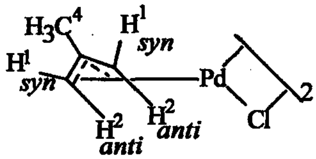
Figure 3.12 The protons of dichloro*bis*(η^3-allyl)dipalladium

These values of J and, to a lesser extent, the chemical shifts have enabled the stereochemistry of a large number of similar complexes to be assigned. ^{1}H NMR data of 1a, 1b, 1c and 1d was given in Table 3.6.

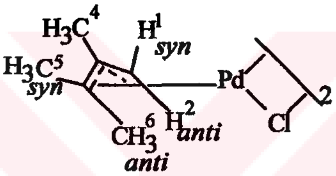
Table 3.6 ^{1}H NMR data for 1a, 1b, 1c, and 1d.



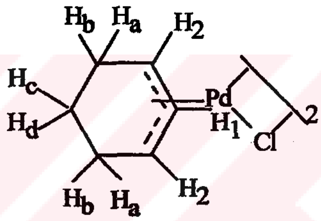
(1a)



(1b)



(1c)

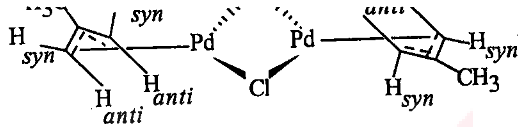


(1d)

Allylic ligand	Chemical shift δ(ppm) and spin-spin coupling constants, J_x(Hz)									
	H^1	**H^2**	**H^3**	**CH$_3^4$**	**CH$_3^5$**	**CH$_3^6$**	**H$_c$**	**H$_d$+H$_a$+H$_b$**	**H$_1$**	**H$_2$**
Allyl **(1a)**	4.01d $^3J_{(1,3)}$=6.8	3.05d $^3J_{(2,3)}$=12	5.42tt $^3J_{(3,2)}$=6.8 $^3J_{(3,1)}$=12							
2-Methylallyl **(1b)**	3.84s	2.86s		2.12s						
1,1,2-trimethylallyl **(1c)**	3.72s	3.18s		2.06s	1.37s	1.24s				
cyclohexenyl **(1d)**							1.08m	1.75-1.90m	5.50m	5.17m

Note: 400 MHz ^{1}H NMR for the allylic protons of π-allylic palladium(II) chloride complexes recorded in $CDCl_3$ solution.

^{1}H NMR spectra of $[(\eta^3\text{-allyl})Pd(\mu\text{-}Cl)]_2$ were shown in Figure 3.13, **1b**; Figure 3.14, **1c**; Figure 3.15, **1d**, in sequence.



(1b)

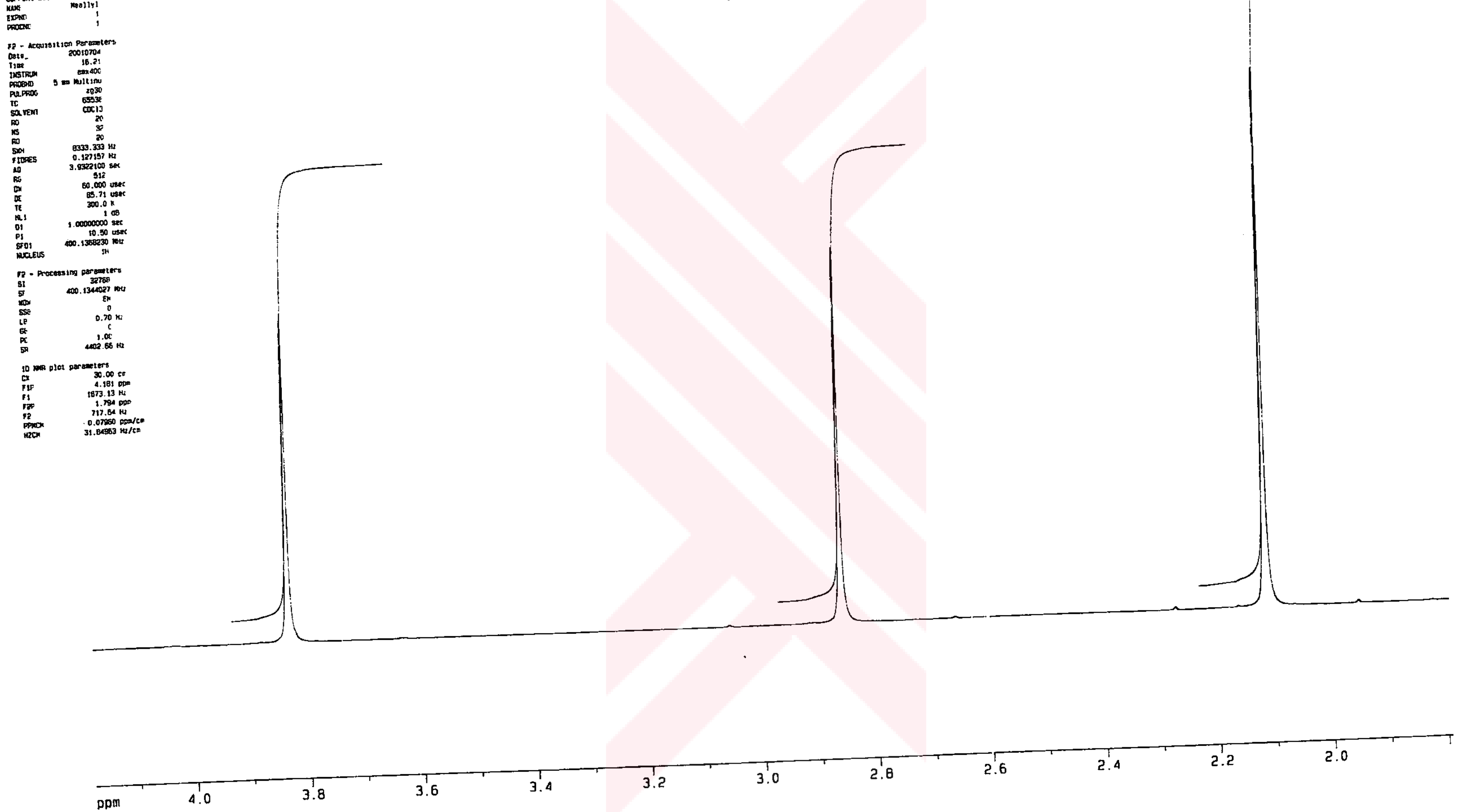
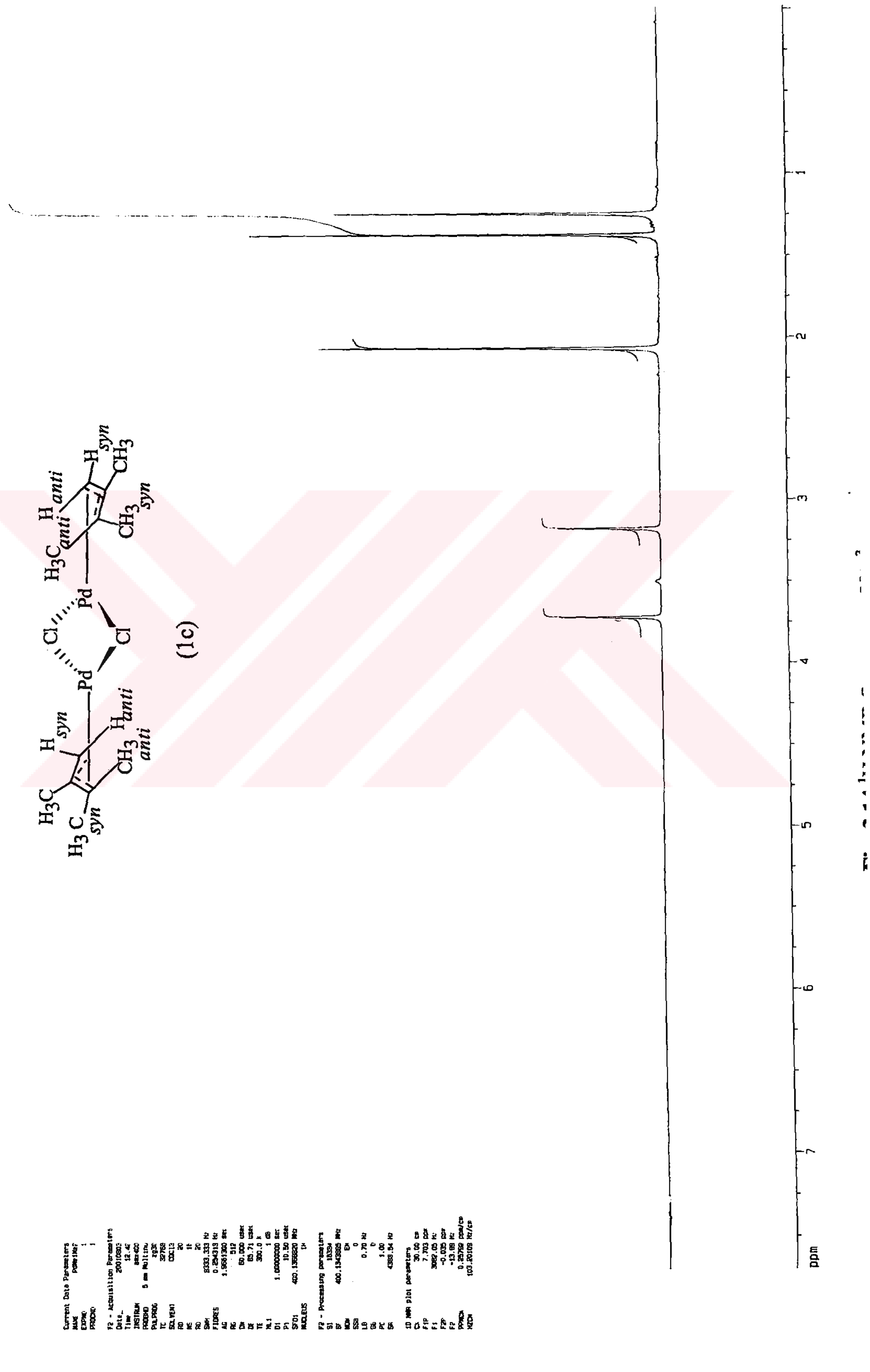


Fig. 3.13 ^{1}H NMR Spectrum of $[(\eta^3\text{-}CH_2CMeCH_2)Pd(\mu\text{-}Cl)]_2$, (1b)



(1c)
ppm

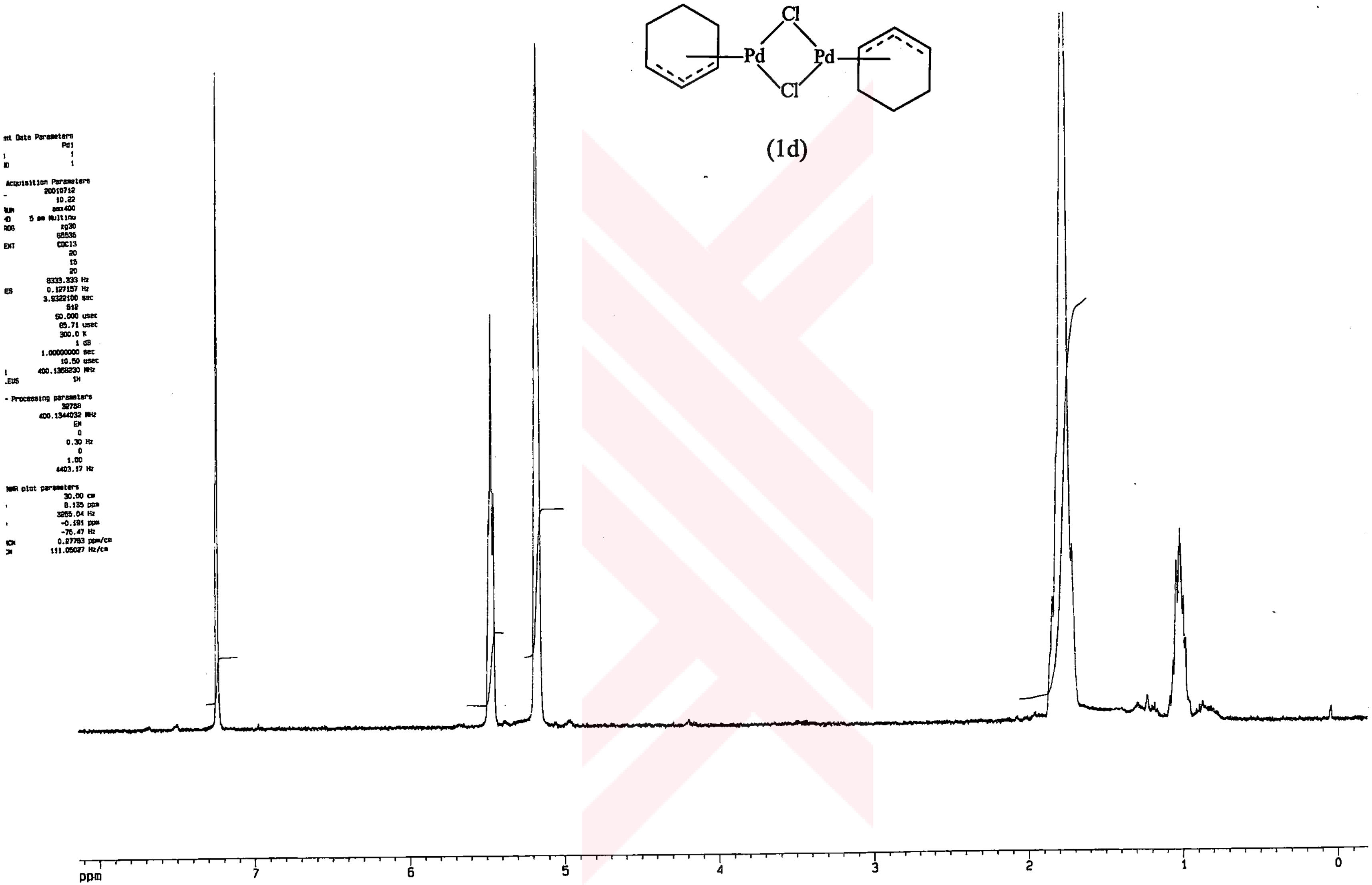


Fig. 3.15 ^{1}H NMR Spectrum of $[(\eta^3\text{-}C_6H_9)Pd(\mu\text{-}Cl)]_2$, (1d)

With the (η^3-C_4H_7) 2-methylallyl group, in (**1b**), (fig.3.13), there is no spin-spin coupling, the peaks are all singlets, slightly upfield to the corresponding (η^3-C_3H_5) protons. The *anti* protons are at δ 2.8 ppm, the *syn* protons are at δ 3.8 ppm and the central methyl protons are at δ 2.12 ppm.

With the 1,1,2-trimethylallyl group, in (**1c**), (fig.3.14) there is again no spin-spin coupling, the peaks belong to the *central*, *syn* and *anti* methyls and *syn*, *anti* protons are all singlets. The spectra show a unique set of two resonances of equal intensity for the allylic protons. The shielding order for the allylic protons is $H_{anti} > H_{syn}$ as a consequence of *anti* protons are more shielded than *syn* protons by palladium metal. The resonances for the *anti* protons are at δ 3.18, the *syn* protons at δ 3.72, respectively. The ^1H NMR spectrum of (**1c**), also shows only three resonances, one for each type of methyl protons of allyl groups. The shielding order for the methyl protons of the allyl group is $CH_{3\,anti} > CH_{3\,syn} > CH_{3\,central}$ and chemical shifts δ $CH_{3\,anti}$= 1.24 ppm; δ $CH_{3\,syn}$= 1.37 ppm; δ $CH_{3\,central}$= 2.02 ppm, respectively.

There are six kinds of protons in [(η^3-$CH^2CH^1CH^2CH_2{}^{a,b}CH_2{}^{c,d}CH_2{}^{a,b}$) Pd(μ-Cl)]$_2$ complex, (**1d**), (fig.3.15). Chemical shifts of the protons of cyclohexenyl groups were determined from the peak integrities. The ^1H NMR spectrum of (**1d**) exhibits four resonances with the intensity ratio 1:5:2:1 for the cyclohexenyl group. The most remarkable feature is the appearance of multiplets due to spin-spin coupling of the protons. These multiplets are resolved from their intensities. H_d and $2H_{a+}2H_b$ give signals at 1.75-1.90 ppm region with the intensity of 5 protons. H_c appears as a multiplet at 1.08 ppm and allylic protons of H_1 and H_2 give separate multiplets with the expected intensity of of 1:2. H_1 proton signal is shifted to the slightly lower field than that of H_2 proton.

All these assignments are in good agreement with the previous ^1H NMR data of the dichloro*bis*(η^3-allyl)dipalladium dimers (Zhang, 1998).

3.4.2. NMR Characterisation of [(η^3-allyl)Pd(S_2CNR_2)] (allyl: 2-methylallyl, R: Me, Et, ^{n}Pr, Bz, (2a, 2b, 2c, 2d); allyl: 1,1,2-trimethylallyl, (4a, 4b, 4c and 4d); allyl: cyclohexadienyl, R: Me, Et, (3a, 3b)) complexes.

Generally the compounds gave good NMR spectra. In order to explain all of the chemical shifts and resonances of the **2a-d, 3a-b, 4a-d** complexes, ^{1}H NMR spectra of Na(S_2CNMe_2); Na(S_2CNEt_2); [Pd(S_2CNMe_2)$_2$] and [Pd(S_2CNEt_2)$_2$] were also recorded. The resonances are given in Table 3.7.

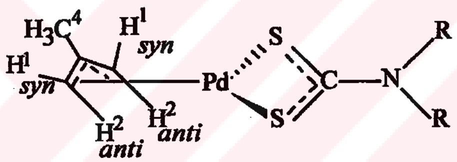
Table 3.7 ^{1}H NMR Data of Na(S_2CNMe_2); Na(S_2CNEt_2); Pd(S_2CNMe_2)$_2$ and Pd(S_2CNEt_2)$_2$ compounds

Assignments	Na(S_2CNMe_2)	Na(S_2CNEt_2)	Pd(S_2CNMe_2)$_2$	Pd(S_2CNEt_2)$_2$
δ(CH_3)	3.40-3.50m	1.20-1.40m	3.27s	1.12t $^3J_{HH}$=7.0 Hz
δ(CH_2)		3.70-4.00m		3.68q $^3J_{HH}$=7.0 Hz

$Na(S_2CNMe_2)$ and $Na(S_2CNEt_2)$ show resonances as multiplets corresponding to the methyl and methylene protons of the *N,N*-dimethyldithiocarbamates and *N,N*-diethyldithiocarbamates, respectively. However, ^1H NMR spectra of $[Pd(S_2CNMe_2)_2]$ gave a singlet at 3.27 ppm, slightly up field from $Na(S_2CNMe_2)$ and $[Pd(S_2CNEt_2)_2]$ showed a unique resonance set; a triplet at 1.12 ppm and a quartet at 3.68 ppm with the expected intensity ratio of (3:2). The resonances of $[Pd(S_2CNEt_2)_2]$ are at slightly higher field than of the corresponding $Na(S_2CNEt_2)$ compound.

^1H NMR data of the hitherto unknown series of the complexes were given in Table 3.8, Table 3.9 and Table 3.10, sequentially;

Table 3.8 ^1H NMR data of $[(\eta^3\text{-allyl})Pd(S_2CNR_2)]$ (allyl: 2-methylallyl, R: Me, Et, ^nPr, Bz, (2a, 2b, 2c, 2d)



R= Me **(2a)**, Et **(2b)**, ^{n}Pr **(2c)**, Bz **(2d)**

Note: 400 MHz ^1H NMR for the complexes of 2a, 2b, 2c and 2d were recorded in $CDCl_3$ solution .

$[(\eta^3\text{-allyl})Pd(S_2CNR_2)]$ allyl: 2-methylallyl R CH_3^5 (2a) $CH_3^5\,CH_2^6$ (2b) $CH_3^5\,CH_2^6CH_2^7$ (2c) $CH_2^8Ph^9$ (2d)	Chemical shift δ(ppm) and spin-spin coupling constants, ^3J_x(Hz)							
	H^1	H^2	CH_3^4	CH_3^5	CH_2^6	CH_2^7	CH_2^8	Ph^9
(2a)	3.79s	2.62s	1.91s	3.33s				
(2b)	3.71m	2.57s	1.87s	1.22t $^3J_{(5,6)}$=7.13	3.71m $^3J_{(6,5)}$=7.13			
(2c)	3.77s	2.62s	1.92s	0.92t $^3J_{(5,6)}$=3.3	1.73m $^3J_{(6,7)}$=7.8 $^3J_{(6,5)}$=3.3	3.67t $^3J_{(7,6)}$=7.8		
(2d)	3.86s	2.70s	2.15s				4.92s	7.35-7.27m

The ^{1}H NMR spectra of (**2a**), (Figure 3.16) exhibits only one set of resonances for *syn*, *anti* and methyl protons of the allyl group, i.e. three resonances with the expected intensity ratio of (2:2:3) according to (H_{syn}: H_{anti}: CH_3). There is no spin-spin coupling, the peaks are all singlets, slightly upfield to the corresponding (**1c**), (η^3-2-methylallyl) protons (in Table 3.6). The methyl group protons of *N,N*-dimethyldithiocarbamate ligand appear as a singlet at 3.33 ppm with the expected integrity of three.

In the ^{1}H NMR spectra of (**2b**), (Figure 3.17), there is again a unique set of resonances for *syn*, *anti* and methyl protons of the allyl group, i.e. three resonances with the expected intensity ratio of (2:2:3) according to (H_{syn}: H_{anti}: CH_3) slightly up field to the corresponding (**2a**) protons. The methylene protons of *N,N*-diethyldithiocarbamate are expected to give a quartet, but unfortunately chemical shifts of the methylene protons and H_{syn} protons of the 2-methylallyl ligand overlap at 3.71 ppm appearing as a multipled (J_{HH}= 7.13 Hz). Peak ratios (1:2) help us to explain identity of the chemical shifts. The methyl protons of *N,N*-diethyldithiocarbamate give rise to a triplet due to spin-spin coupling at 1.22 ppm (J_{HH}= 7.13 Hz) at higher field to the corresponding methylene protons.

In the ^{1}H NMR spectra of (**2c**), (Figure 3.18), the shielding order for the allylic *syn* and *anti* protons and allylic methyl protons is the same as that observed for (**1b**), (**2a**) and (**2b**) complexes, $\delta H_{anti} < \delta H_{syn} < \delta CH_3$ and the chemical shifts of the allylic group protons are very close to that of (**2a**). The set of resonances for the 2-methylallyl group i.e. three resonances with the intensity ratio of (2: 2:3) of (**2c**) complex shifted to lower field compared with that of (**2b**). The methyl protons of *N,N*-dipropyl dithiocarbamate appear as a triplet at 0.92 ppm (J_{HH}= 3.3 Hz), the methylene protons between the methyl and the other methylene of *N,N*-dipropyldithiocarbamate give rise to a multipletwith spin-spin coupling to both neighbour methyl and methylene protons at 1.73 ppm, and at slightly lower field are the other methylene protons, appearing at 3.67 ppm as a triplet (J_{HH}= 7.8 Hz).

A similar observation has been made for the corresponding complex **(2d)**, (Figure 3.19). However, the signals corresponding to the H_{anti}, H_{syn} and terminal allylic carbons are shifted to lower-field with respect to the other complexes **(2a)**, **(2b)**, **(2c)** due to the electronegativity of the benzyl group. Resonances are at 3.86 ppm for H_{syn}, 2.70 ppm for, H_{anti} and 2.15 ppm for allylic methyl protons as singlets. Aromatic protons of the benzyl groups are also resonanced at 7.35-7.27 ppm region as a multiplet.

The ^{1}H NMR spectra of **(2a)**, **(2b)**, **(2c)** and **(2d)** exhibit the expected resonances considering the symmetry of the allyl and *N,N*-dialkyldithiocarbamate groups. The resonance set of allylic protons and allylic methyl protons of **(1b)** dimer was slightly shifted to higher field compared with that in **(2a)**, **(2b)**, **(2c)** and **(2d)** due to the better σ-donor ability of bidentate dithiocarbamates versus allyl group. As can be seen from table 3.5, methyl and methylene protons of *N,N*-dialkyldithiocarbamates signals shift to higher field due to magnetic anisotropy from **(2a)** to **(2c)**. In the ^{1}H NMR spectrum of **(2d)** due to the electronegativity of benzyl group of dithiocarbamates, the resonance set of allylic protons and allylic methyl protons are shifted to lower field.

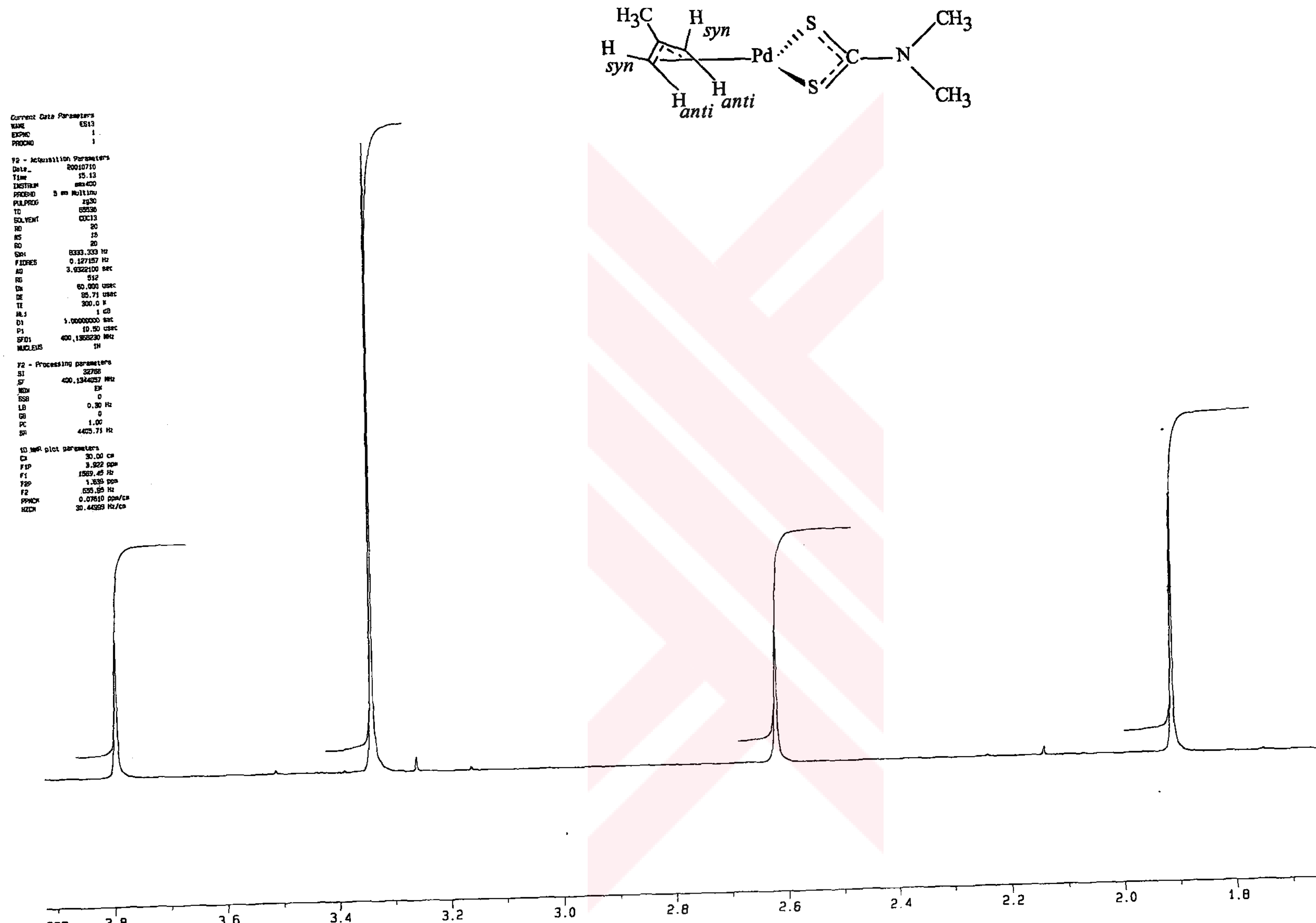


Fig. 3.16 ^{1}H NMR Spectrum of [(η^3-CH_2CMeCH_2)Pd(S_2CNMe_2)], 2a

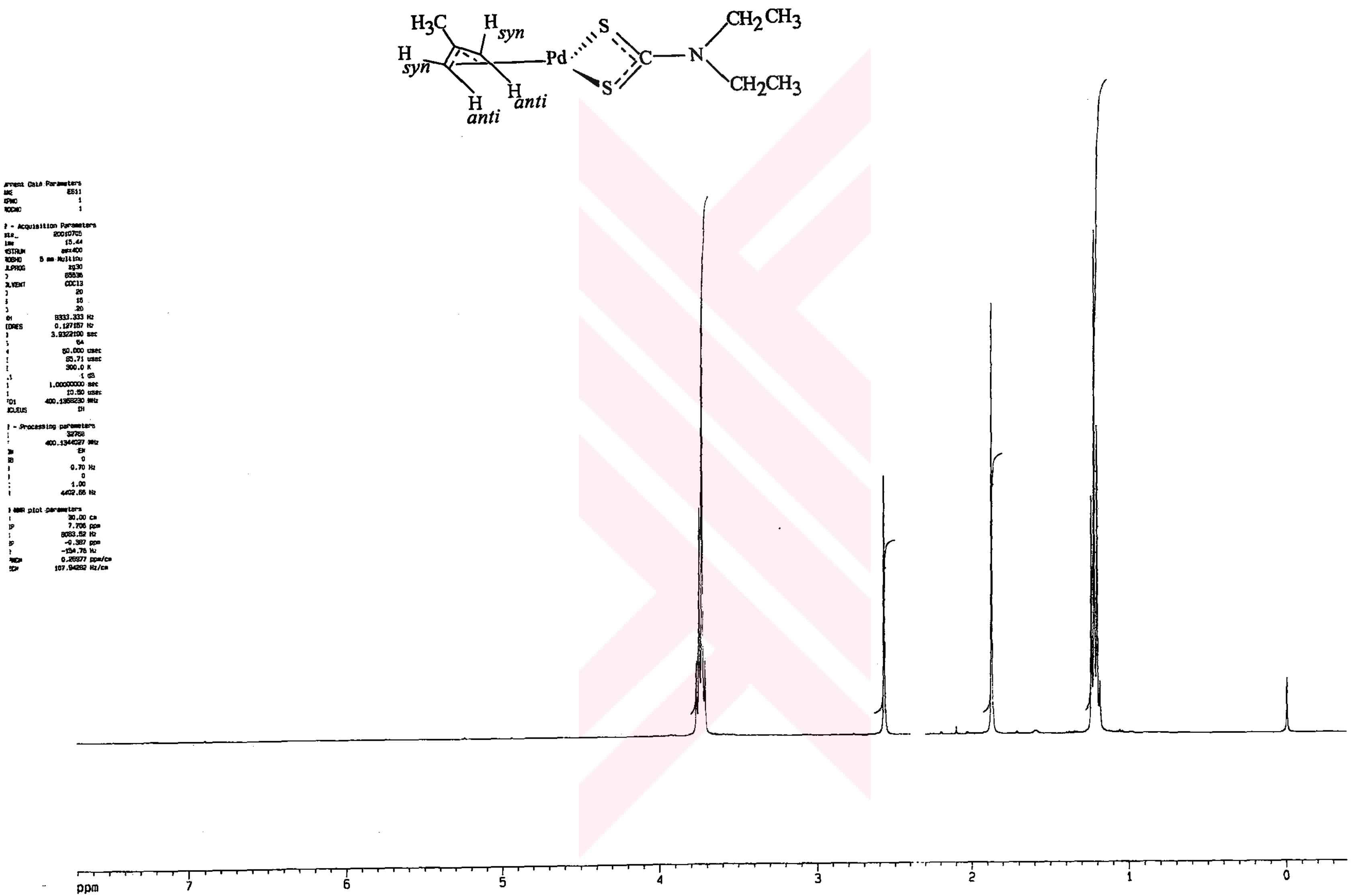


Fig. 3.17 ^{1}H NMR Spectrum of [(η^3-CH_2CMeCH_2)Pd(S_2CNEt_2)], 2b

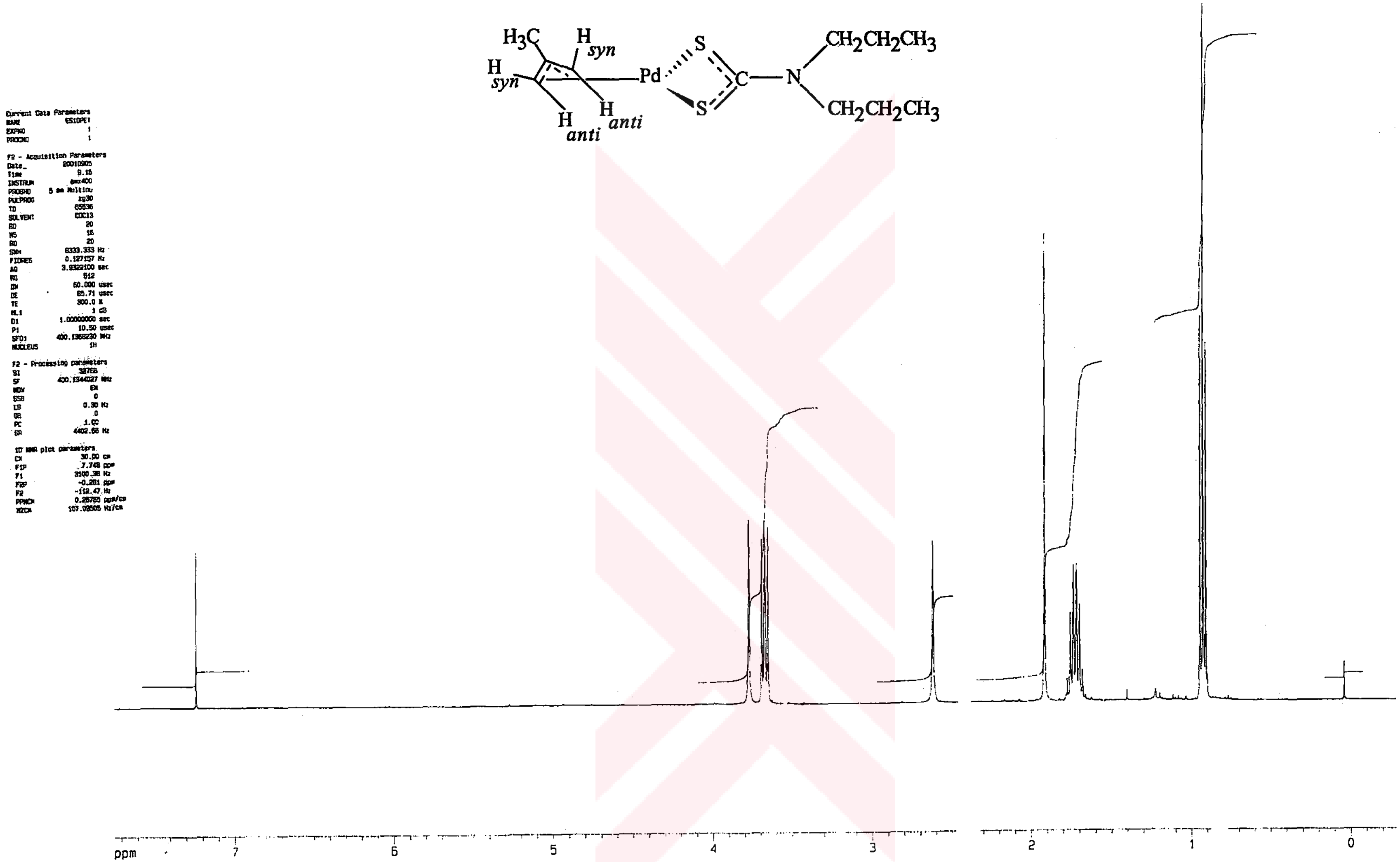


Fig. 3.18 ^{1}H NMR Spectrum of [(η^3-CH_2CMeCH_2)Pd($S_2CN\ ^nPr_2$)], 2c

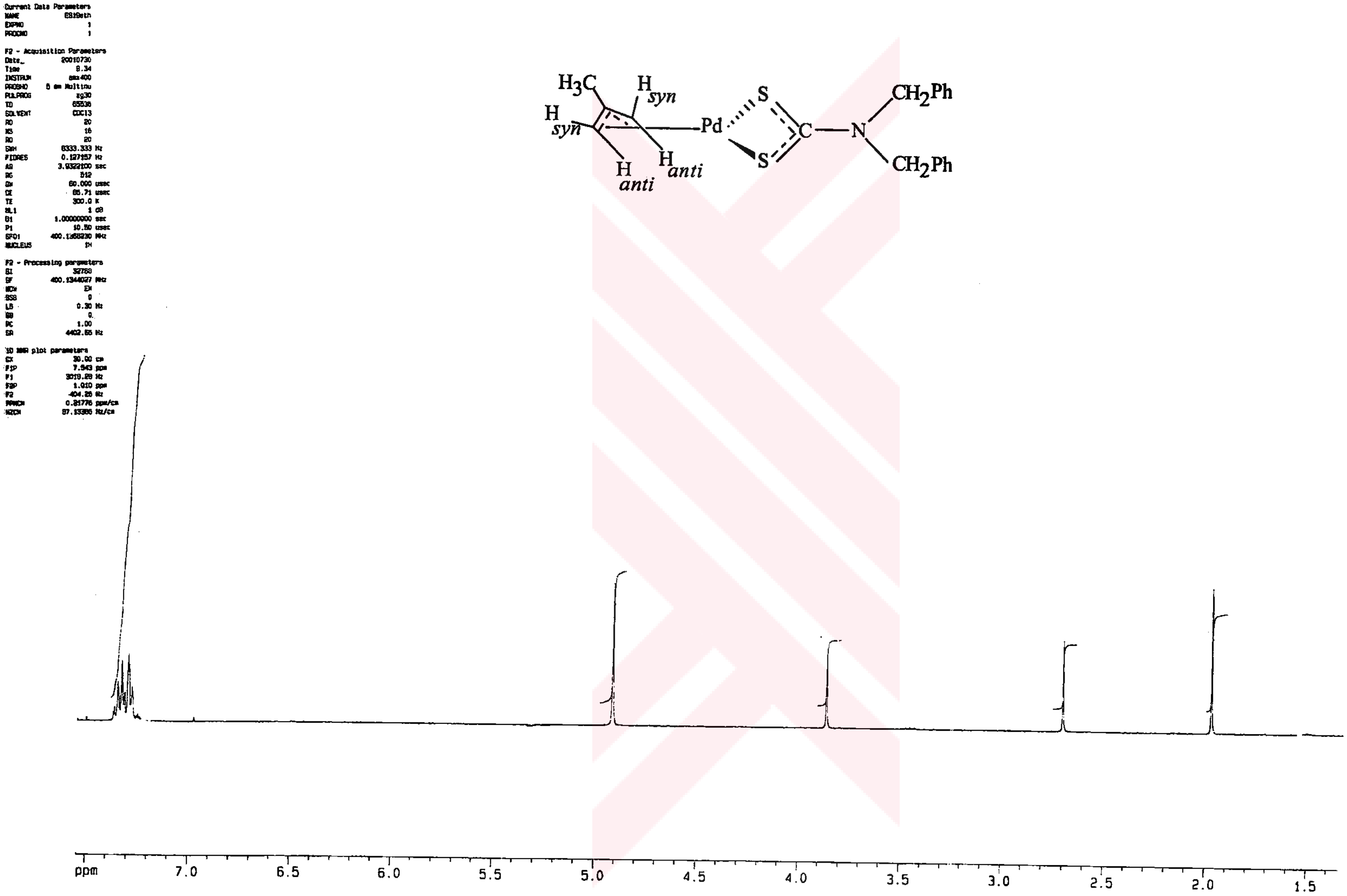
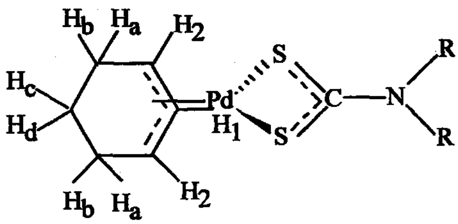


Fig. 3.10 ^{1}H NMR Spectrum of [(η^3-CH_2CMeCH_2)Pd(S_2CNBz_2)], 2d

Table 3.9 ^{1}H nmr data of [(η^3-allyl)Pd(S_2CNR_2)] (allyl: cyclohexenyl, R: Me, Et, **(3a, 3b)**)



[(η^3-C_6H_9)Pd(S_2CNR_2)] R CH_3^5 (3a) CH_3^5 CH_2^6 (3b)	Chemical shift δ(ppm) and spin-spin coupling constants, J_x(Hz)				
	H_c	H_d	H_a, H_b	H_1, H_2	CH_3^5	CH_2^6
(3a)	1.09m	1.78dq $^2J_{(d,c)}$=18.4 $^3J_{(d,a(b))}$=5.5	1.86m	5.17m	3.35s	
(3b)	1.08dtt $^2J_{(c,d)}$=12.7 $^3J_{(c,a(b))}$=8.1 $^4J_{(c,2)}$=6.0	1.76dq $^2J_{(d,c)}$=12.7 $^3J_{(d,a(b))}$=5.5	1.98-1.85m	5.17m	1.25t $^3J_{(5,6)}$=7.2	3.77q $^3J_{(6,5)}$=7.2

Note: 400 MHz ^{1}H NMR for the complexes of 3a and 3b were recorded in $CDCl_3$ solution

In the ^{1}H NMR spectrum of (3a), (Figure 3.20), there are four resonances with the intensity ratio of 1:1:4:3 assigned to H_c; H_d; H_a+H_b; H_1+H_2 of the cyclohexenyl group. The highest field resonance belongs to H_c and appears as a multiplet at 1.09 ppm. Owing to the coupling with H_c ($^2J_{(d,c)}$=18.4 Hz) and H_a+H_b protons ($^3J_{(d,a(b))}$=5.5 Hz), the H_d resonance appears as a doublet of quartets at 1.78 ppm. H_a+H_b protons appear as a multiplet at 1.86 ppm with the intensity ratio of four. Another multiplet resonance at 5.17 ppm with the intensity ratio of three belongs to allylic protons of cyclohexenyl group. The methyl groups of *N,N*-dimethyldithiocarbamate give rise to a singlet at 3.35 ppm with the intensity ratio of six protons.

In the ^{1}H NMR spectrum of (3b), (Figure 3.21), there are four resonances with the intensity ratio of 1:1:4:3 assigned to H_c; H_d; H_a+H_b; H_1+H_2 of the cyclohexenyl group as the same as (3a). In this spectrum, it was possible to interpret some of the multiplets. The highest field resonance is observed at 1.08 ppm as a doublets of triplet of triplets ($^{2}J_{(c,d)}$=12.7 Hz, $^{3}J_{(c,a(b))}$=8.1 Hz, $^{4}J_{(c,2)}$=6.0 Hz) belonging to H_c. H_d appears as a doublet of quartets at 1.76 ppm ($^{2}J_{(d,c)}$=12.7 Hz; $^{3}J_{(d,a(b))}$=5.5 Hz). H_a+H_b protons appear as a multiplet at 1.98-1.85 ppm, with the intensity ratio of four. Another multiplet resonance at 5.17 ppm with the intensity ratio of three belongs to allylic protons of cyclohexenyl. There is also one set of resonances belonging to methyl and methylene protons of *N,N*-diethyldithiocarbamate with the intensity ratio of (3:2). The methyl protons appear as a triplet at 1.25 ppm and methylene protons as a quartet at 3.77 ppm.

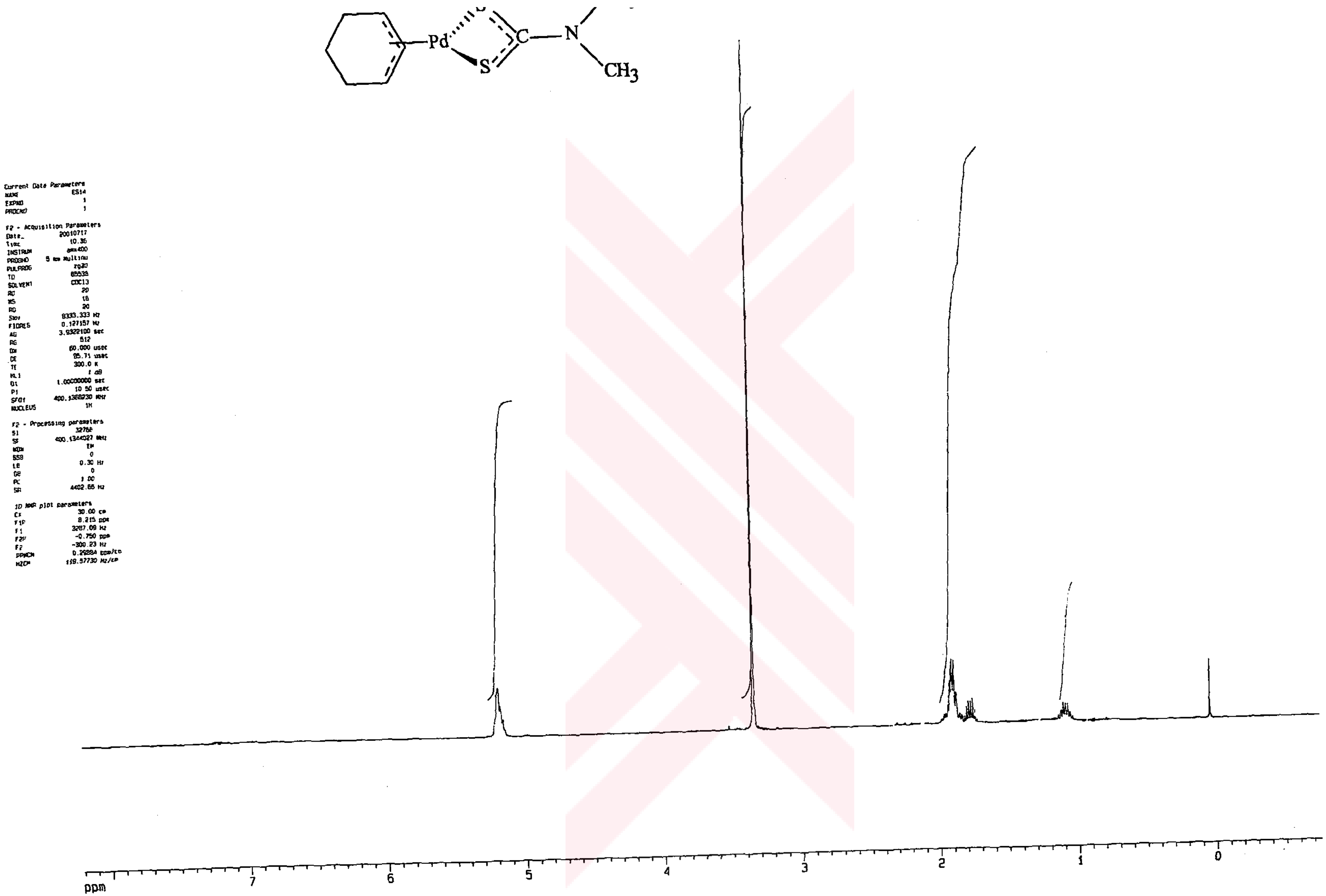


Fig. 3.20 ^{1}H NMR Spectrum of $[(\eta^3\text{-}C_6H_9)Pd(S_2CNMe_2)]$, 3a

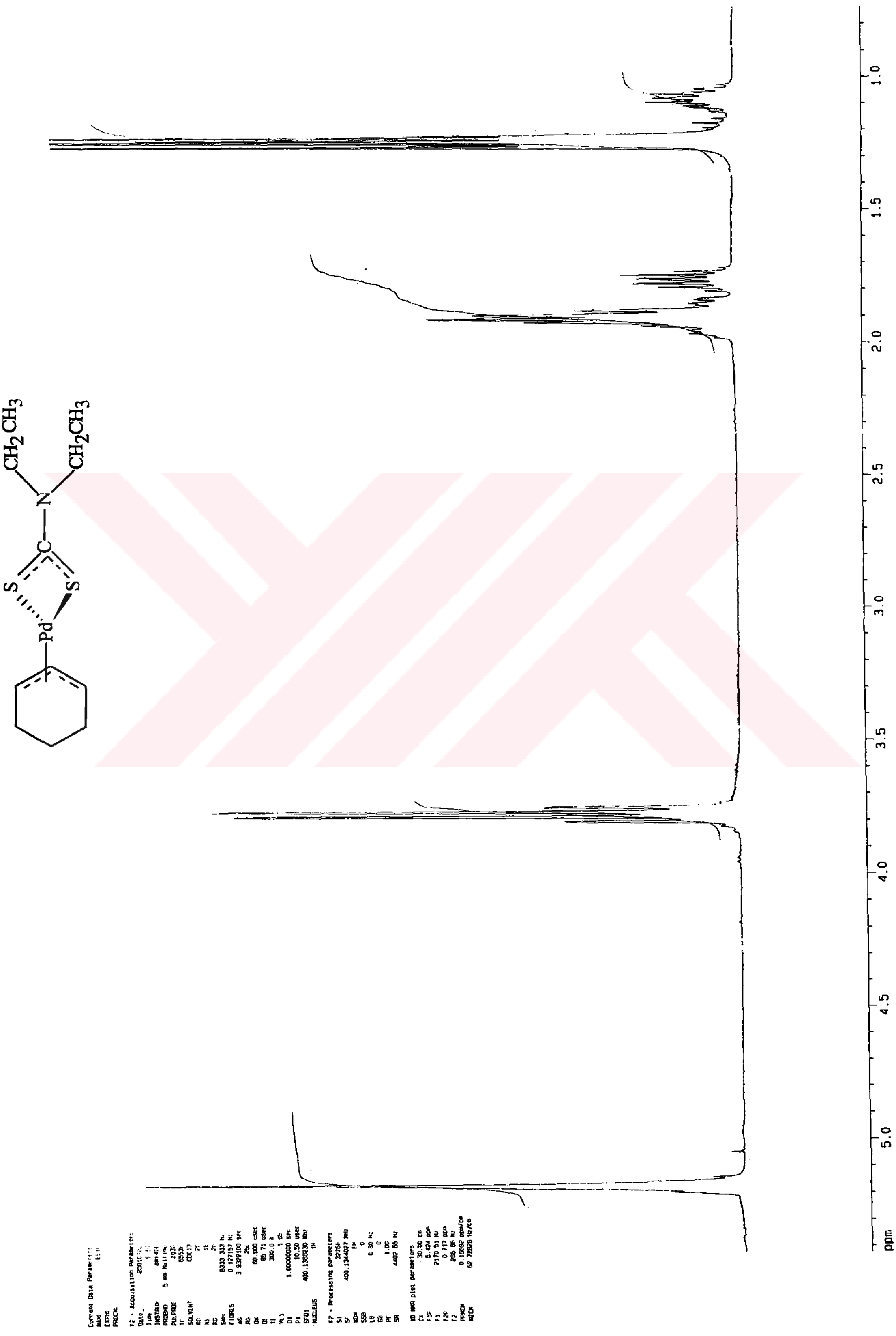
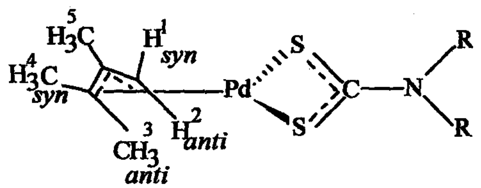

CH2CH3
CH2CH3
N
C
S
S
Pd
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
ppm

Table 3.10 ^{1}H NMR data of [(η^3-allyl)Pd(S_2CNR_2)] (allyl: 1,1,2-trimethylallyl, R: Me, Et, ^{n}Pr, Bz, (4a, 4b, 4c and 4d) complexes.



($\eta^3Me_2CCMeCH_2$)Pd (S_2CNR_2) **R** CH_3^6 (4a) $CH_3^6CH_2^7$ (4b) $CH_3^6CH_2^7CH_2^8$ (4c) $CH_2^9Ph^{10}$ (4d)	Chemical shift δ(ppm) and spin-spin coupling constants, J_x(Hz)								
	H^1	H^2	CH_3^3	CH_3^4	CH_3^5	CH_3^6	CH_2^7	CH_2^8	CH_2^9	Ph^{10}
(4a)	3.64br	2.94br	1.33s	1.67s	1.93s	3.35s				
(4b)	3.60s	2.84s	1.29s	1.64s	1.88s	1.20t $^3J_{(6,7)}$=7.10	3.70-3.75m			
(4c)	3.66s	2.92s	1.37s	1.72s	1.96s	0.94dt $^3J_{(6,7)}$=7.4 $^3J_{(6,8)}$=2.0	1.74hext. $J_{(7,6(8))}$=7.9	3.69q $J_{(8,7)}$=6.0		
(4d)	3.82s	3.08s	1.51s	1.84s	2.07s				5.0-5.03m	7.32-7.43n

Note: 400 MHz ^{1}H NMR for the complexes of 4a, 4b, 4c and 4d were recorded in $CDCl_3$ solution

In the ^{1}H NMR spectra of (4a), (Figure 3.22), there are two broad singlets at 3.64 and 2.94 ppm, respectively. The existence of an equilibrium might explain the broad appearance of the resonances. The broad signals obtained for the H_{anti} and H_{syn} allylic protons indicate that a fluxional process that interconverts the ends of the allylic group (*syn-syn*, *anti-anti* interconversion) may be taking place. The higher-field resonance belongs to the *anti* proton since *anti* proton are nearer to the metal and are consequently more shielded. The methyl protons of allyl group show one set of resonance, ie. three resonances with the expected intensity ratio of (3: 3: 3). The shielding order of the allylic methyl protons increase in the order; $CH_3^5 < CH_3^4 < CH_3^3$.

The methyl group protons of *N,N*-dimethyldithiocarbamate appear as a singlet at 3.35 ppm with the expected intensity of six.

In the ^1H NMR spectrum of (4b), (Figure 3.23), there are five resonances with the expected intensity ratio of (3:3:3:1:1) according to ($CH_{3,anti}$; $CH_{3,syn}$; $CH_{3,central}$; H_{anti}; H_{syn}). There is no spin-spin coupling, the peaks are all singlets, slightly up-field of the corresponding (1b), (η^3-1,1,2-trimethylallyl) protons (in Table 3.6). Methylene protons of *N,N*-diethyldithiocarbamate appear as a multiplet in the 3.70-3.75 ppm region and methyl protons as a triplet due to coupling with the methylene protons at 1.20 ppm ($^3J_{(6,7)}$=7.10 Hz).

In the ^1H NMR spectrum of (4c), (Figure 3.24), there is again a unique set of resonances for the allylic protons and methyls, ie. five resonances with the expected intensity ratio of 3:3:3:1:1 corresponding to $\delta CH_{3,anti}$= 1.37 ppm, $\delta CH_{3,syn}$= 1.72 ppm, $\delta CH_{3,central}$= 1.96 ppm, δH_{anti}= 2.92 ppm, δH_{syn}= 3.66 ppm, respectively. There is also a one set of resonances for the methyl and methylene groups of *N,N*-di-*n*-propyldithiocarbamato ligands, i.e. three resonances with the intensity ratio of (3:2:2) from high field to low field of the spectrum. Methyl group protons of *N,N*-di-*n*-propyldithiocarbamato ligands resonate at 0.94 ppm as a multiplet, methylene protons in the middle of *n*-propyl group give a hexted at 1.74 ppm ($^3J_{(7,8(6))}$= 7.9 Hz) and the methylene groups coordinating to the nitrogen atom of the dithio carbamato ligand resonate at 3.69 ppm as a quartet.

The ^1H NMR spectrum of (4d), (Figure 3.25), as its other analogues complexes such as (4a), (4b), (4c), besides the signals of the three methyl protons at $\delta CH_{3,anti}$= 1.51 ppm, $\delta CH_{3,syn}$= 1.84 ppm, $\delta CH_{3,central}$= 2.07 ppm which are all singlets, two resonances one for each type of allylic protons; δH_{anti}= 3.08 ppm and δH_{syn}= 3.82 ppm, respectively also appear. This is in accordance with the expected symmetric environment of the allyl group in this complex. The methylene and phenyl protons of *N,N*-dibenzyldithiocarbamato ligands resonate at 5.00-5.03 ppm due to methylene protons and at 7.32-7.43 ppm corresponding to phenyl protons these multiplets having the expected intensity ratio of (2:5).

These ^{1}H NMR assignments were made in accordance with the previous publications. (Zhang, 1998; Redón, *et al.*, 2001; Fernández-Galan, *et al.*, 1999) The ^{1}H NMR for all of these complexes show peaks representing the allyl group protons. The existence of a symmetric allyl group is deduced from the ^{1}H NMR spectrum (one type of H_{anti} and H_{syn}) where the corresponding resonances of the methyl and methylene protons of dithiocarbamate groups are also observed.

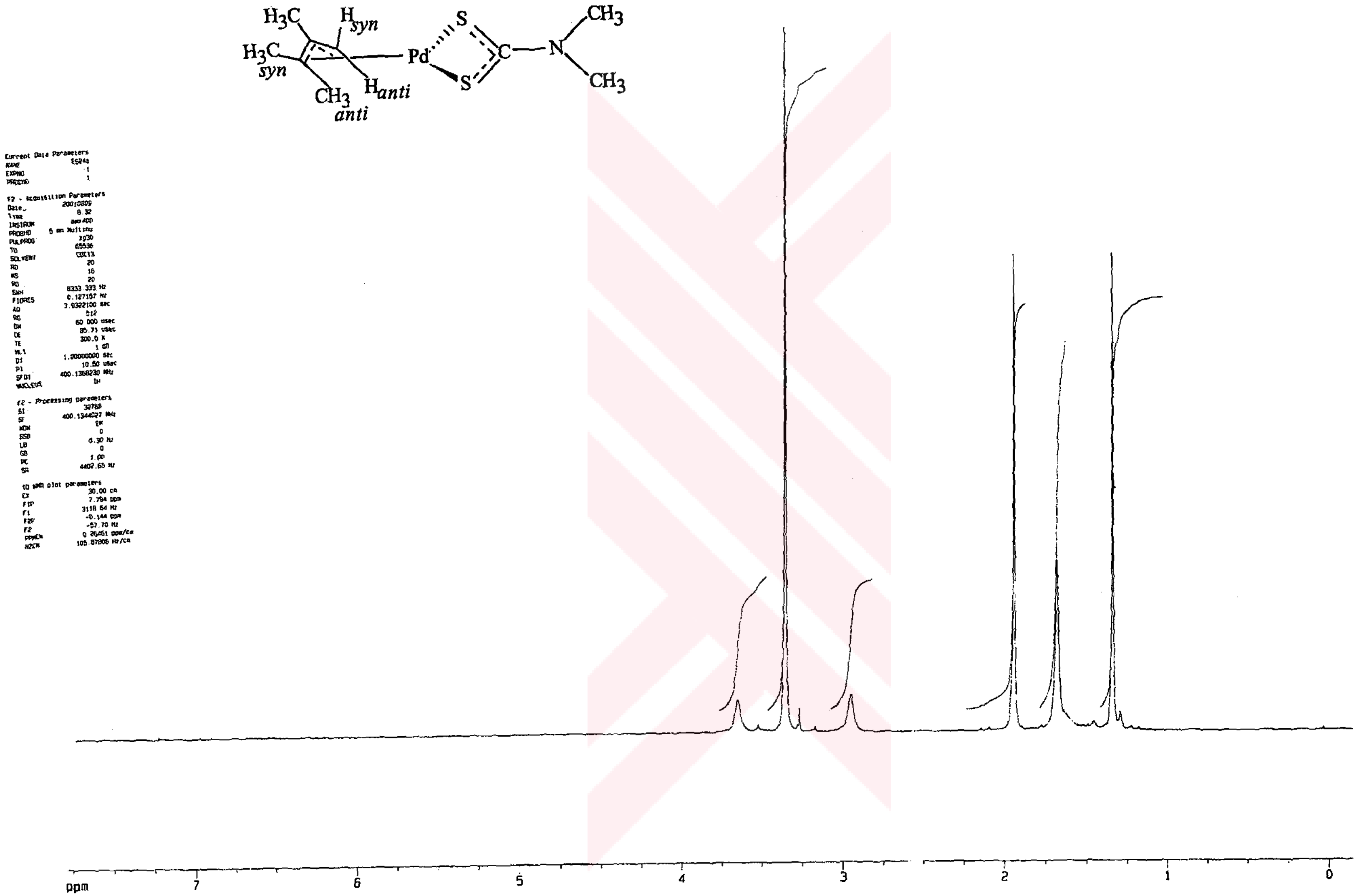


Fig. 3.33 ^{1}H NMR Spectrum of [(η^3-CMe$_2$CMeCH$_2$)Pd(S$_2$CNMe$_2$)] 4a

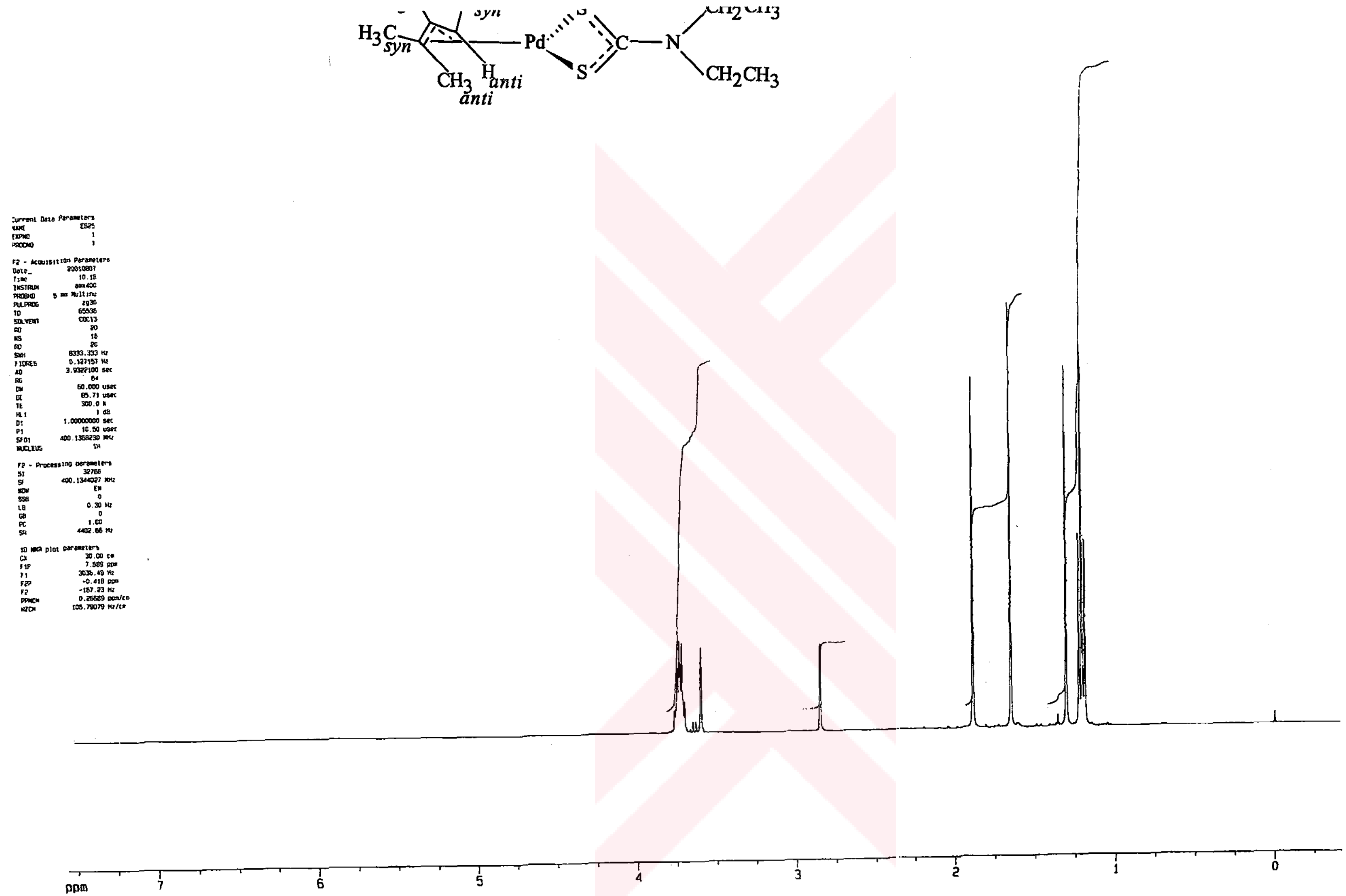
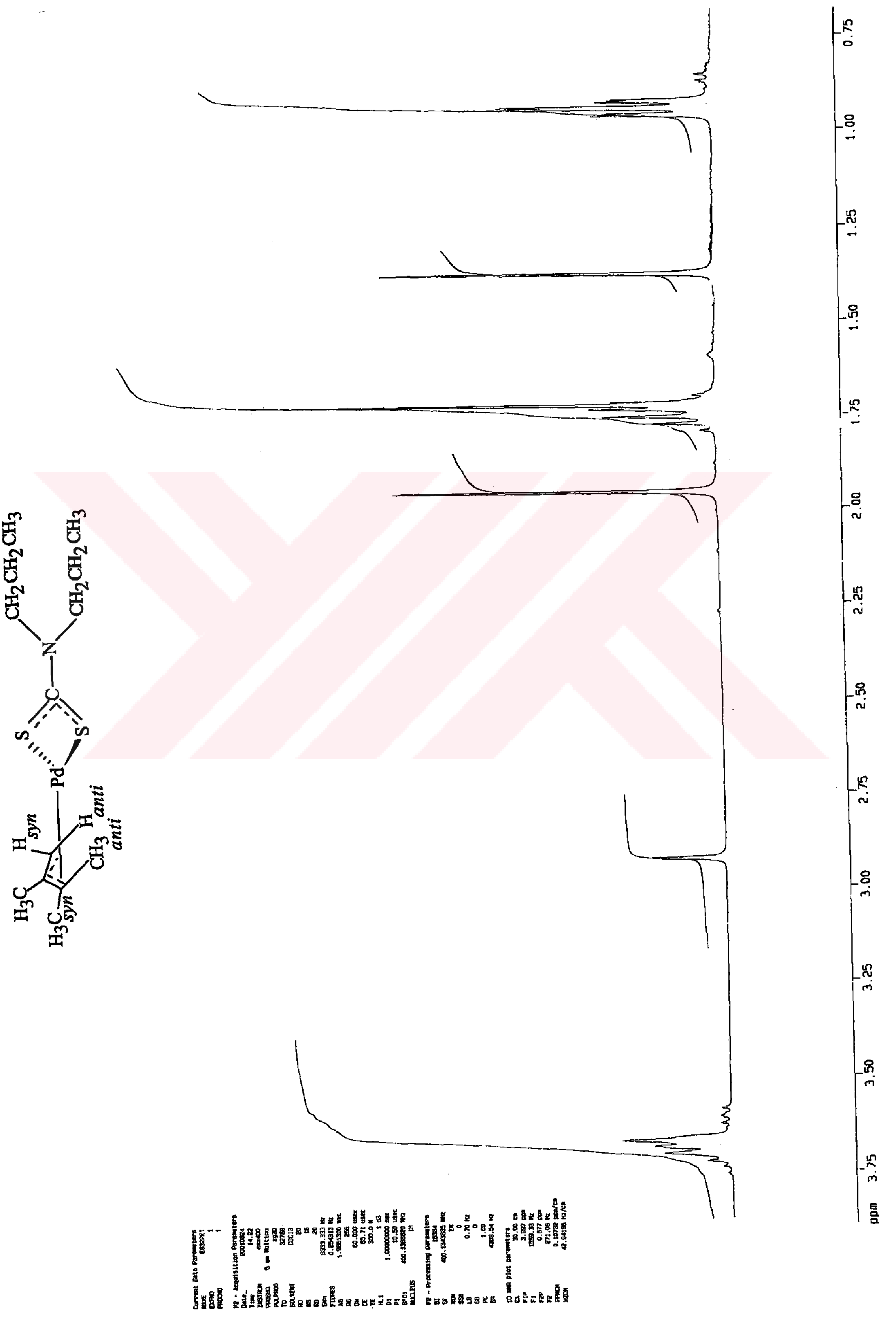


Fig. 3.23 ^{1}H NMR Spectrum of $[(\eta^3\text{-}CMe_2CMeCH_2)Pd(S_2CNEt_2)]$, **4b**



CH2CH2CH3
CH2CH2CH3
N
C
S
S
Pd
H syn
H anti
H3C
H3C syn
CH3 anti
0.75
1.00
1.25
1.50
1.75
2.00
2.25
2.50
2.75
3.00
3.25
3.50
3.75
ppm

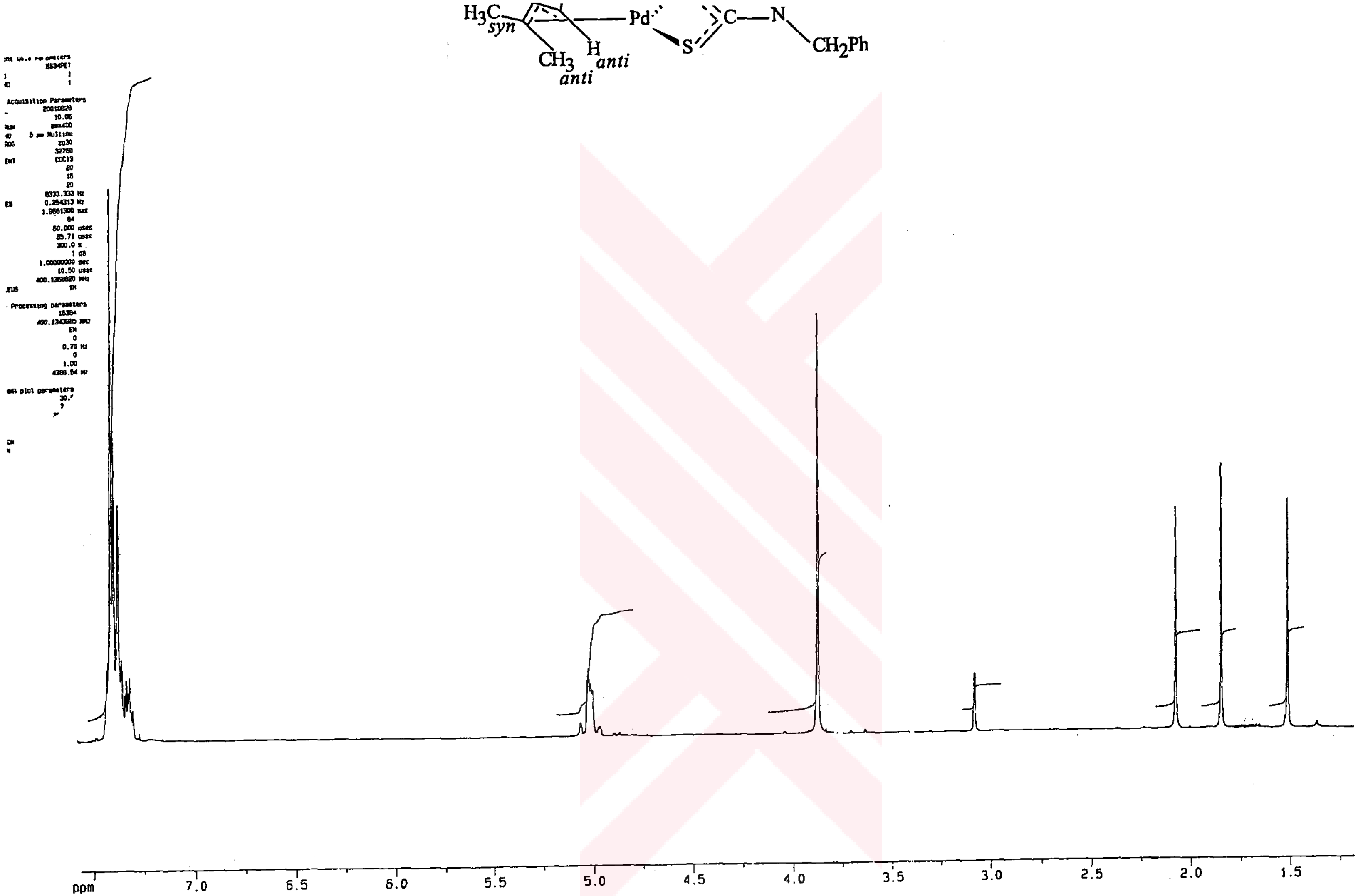


Fig. 3.25 ^{1}H NMR Spectrum of $[(\eta^3\text{-}CMe_2CMeCH_2)Pd(S_2CNBz_2)]$, 4d

3.5 FAB-Mass Spectral Data of Complexes

The method of choice for mass spectrometry of organometallic compounds of low volatility is positive ion Fast Atom Bombardment (FAB+). The compound is placed in a liquid matrix, and ionisation of the compound is brought about by impact of a beam of atoms from an ion gun onto the matrix. There is a subsequent transfer of energy from the matrix to the compound. This is a low impact procedure, so very often the molecular ion can be observed.

Palladium has six naturally occurring isotopes: ^{106}Pd (27.5%), ^{108}Pd (26.5%), ^{105}Pd (22%), ^{110}Pd (12%), ^{104}Pd (11%) and ^{102}Pd (1% abundance). Consequently all monomeric palladium-containing species show six lines in the mass spectrum, in the relative intensities.

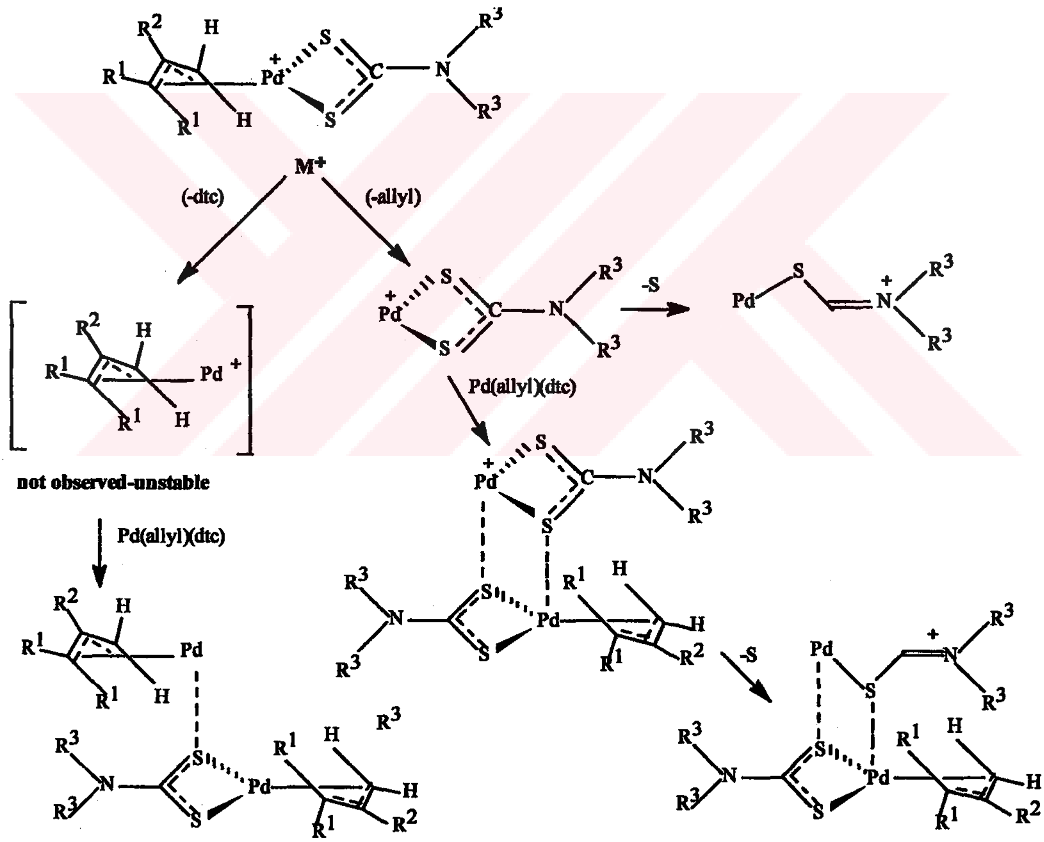
FAB-Mass spectral data for the complexes are listed in (Table 3.11). Relative intensities of the ions are given in parentheses after the weight of the fragments. Many of the complexes show peaks for the bridged species [Pd_2(allyl)$_2$dtc] and [Pd_2(allyl)dtc$_2$], showing the bridging ability of the dithiocarbamate ligand as demonstrated previously (Blake and Kathirgamanathan, 2000).

All of the molecules showed molecular ion peaks. An indication of the lability of the allyl-palladium bond in these complexes, suggest that they should prove useful as CVD precursors.

Table 3.11 FAB-Mass spectral data for the complexes (2a-2d; 3a-3b; 4a-4d)

Complex	M.W.	Relative intensities of the Ions m/e
$[(\eta^3\text{-}CH_2CMeCH_2)Pd(S_2CNMe_2)]$ (2a)	281	509(12), $[Pd_2(dtc)_2(allyl)]$; 444(50), $[Pd_2(dtc)(allyl)_2]$; 281(25), $[M^+]$, [Pd(dtc)(allyl)]); 228(42), [Pd(dtc)]; 194(18); 161(13), [Pd(allyl)]; 88(78); 57(100), $[CNMe_2]$.
$[(\eta^3\text{-}CH_2CMeCH_2)Pd(S_2CNEt_2)]$ (2b)	311	565(64), [Pd(dtc)]; 472(72), $[Pd_2(dtc)(allyl)_2]$; 311(30), $[M^+]$, [Pd(dtc)(allyl)]; 254(100), $[Pd_2(dtc)_2(allyl)]$; 222(42), $[Pd(\eta^1\text{-}SCN(CH_3)_2)]$; 161(32), [Pd(allyl)]; 116(62); 88(40).
$[(\eta^3\text{-}CH_2CMeCH_2)Pd(S_2CN^nPr_2)]$ (2c)	337	621(60), $[Pd_2(dtc)_2(allyl)]$; 500(52), $[Pd_2(dtc)(allyl)_2]$; 337(27), $[M^+]$, [Pd(dtc)(allyl)]; 282(97), [Pd(dtc)]; 250(45), $[Pd(\eta^1\text{-}SCN(C_3H_7)_2)]$; 161(22), [Pd(allyl)]; 144(52); 112(62); 60(26); 43(100).
$[(\eta^3\text{-}CH_2CMeCH_2)Pd(S_2CNBz_2)]$ (2d)	433	433(3), $[M^+]$, [Pd(dtc)(allyl)]; 814(2), $[Pd_2(dtc)_2(allyl)]$; 595(10), $[Pd_2(dtc)(allyl)_2]$; 377(9), [Pd(dtc)]; 221(15); 133(38); 91(100).
$[(\eta^3\text{-}C_6H_9)Pd(S_2CNMe_2)]$ (3a)	307	307(6), $[M^+]$, [Pd(dtc)(allyl)]; 289(6), 165(4), 154(100), 136(65), 120(10), 107(17).
$[(\eta^3\text{-}C_6H_9)Pd(S_2CNEt_2)]$ (3b)	335	591(7), $[Pd_2(dtc)_2(allyl)]$; 402(12), $[Pd(dtc)_2]$; 335(3), $[M^+]$, [Pd(dtc)(allyl)]; 254(12), [Pd(dtc)]; 187(3), [Pd(allyl)]; 116(95), 86(100), (allyl); 57(25), (CNEt).
$[(\eta^3\text{-}CMe_2CMeCH_2)Pd(S_2CNMe_2)]$ (4a)	311	537(13), $[Pd_2(dtc)_2(allyl)]$; 500(100), $[Pd_2(dtc)(allyl)_2]$; 416(25), $[Pd_2(dtc)(allyl)]$; 311(10), $[M^+]$, [Pd(dtc)(allyl)]; 226(18), [Pd(dtc)]; 88(20); 58(48), $(CNMe_2)$.
$[(\eta^3\text{-}CMe_2CMeCH_2)Pd(S_2CNEt_2)]$ (4b)	337	528(100), $[Pd_2(dtc)(allyl)_2]$; 402(20), $[Pd(dtc)_2(allyl)]$; 337(21), $[M^+]$, [Pd(dtc)(allyl)]; 254(40), $[Pd(dtc)_2]$; 222(33), $[Pd(SCNEt_2)]$; 154(12).
$[(\eta^3\text{-}CMe_2CMeCH_2)Pd(S_2CN^nPr_2)]$ (4c)	365	649 (43), $[Pd_2(dtc)_2(allyl)_2]$; 556(47), $[Pd_2(dtc)(allyl)_2]$; 472(10); 365(22), $[M^+]$, [Pd(dtc)(allyl)]; 282(46), [Pd(dtc)]; 144(100), [Pd(S)(allyl)].
$[(\eta^3\text{-}CMe_2CMeCH_2)Pd(S_2CNBz_2)]$ (4d)	461	841(43), $[Pd_2(dtc)_2(allyl)]$; 652(20), $[Pd_2(dtc)(allyl)_2]$; 461(8), $[M^+]$, [Pd(dtc)(allyl)]; 346(37); 198(100), [Pd(allyl)].

As can be seen from fragmantation patterns of the complexes, (2a-d), (3a-b), (4a-d) rearrangements are most likely to be happen. Therefore, allylpalladium dithiocarbamate complexes have quite distinctive fragmentation patterns. Possible fragmentation patterns of the new series of the (η^3-allyl)dithiocarbamato palladium(II) complexes are suggested as illustrated in (Scheme 3.3).



Scheme 3.3. Possible way of formation of fragments

The FAB-Mass spectra of the complexes (2a-2d; 3a-3b; 4a-4d) are shown in from Figure 3.26 to 3.35.

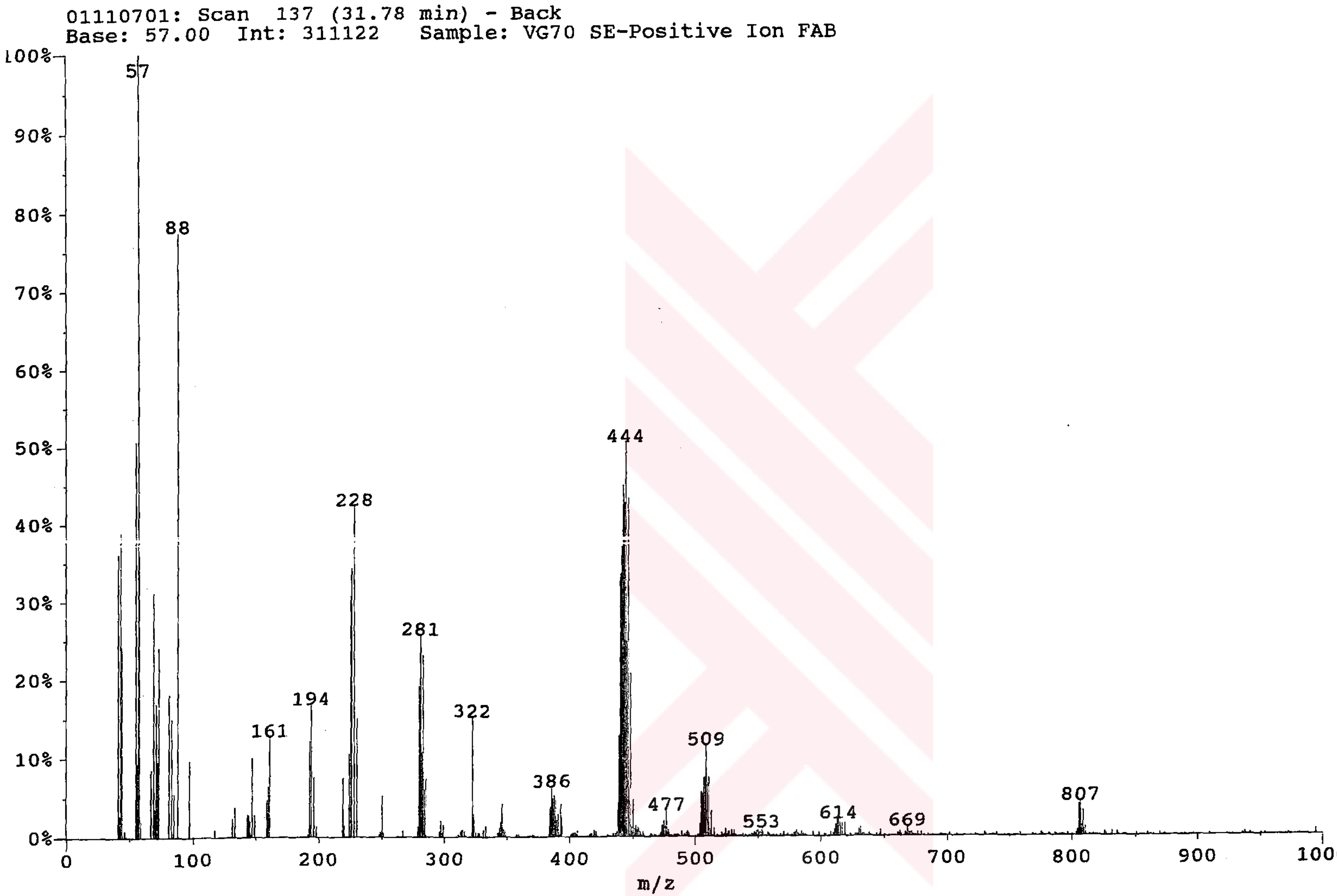


Fig. 3.26 The Mass Spectrum of $[(\eta^3\text{-}CH_2CMeCH_2)Pd(S_2CNMe_2)]$, 2a

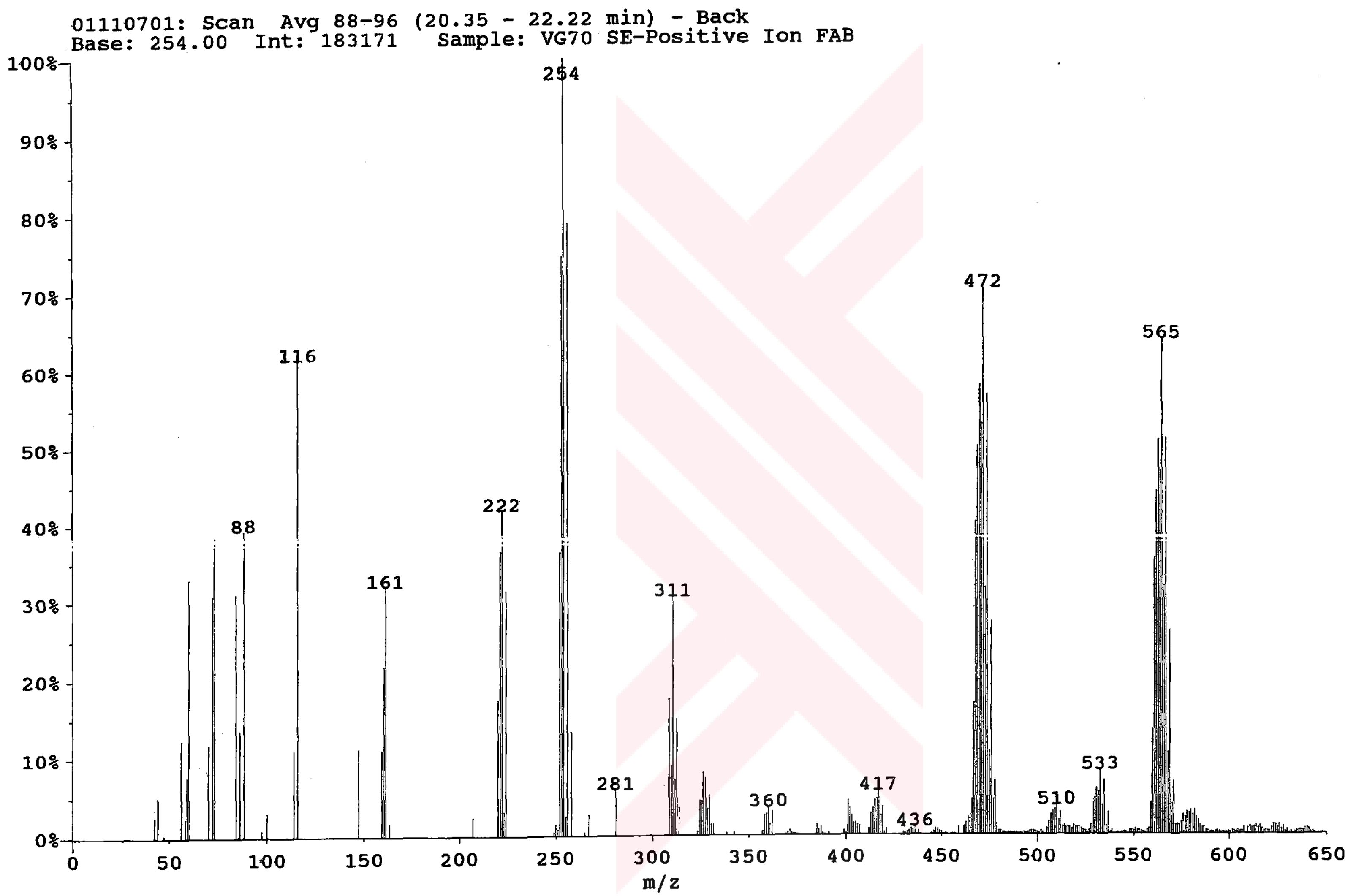


Fig. 3.27 The Mass Spectrum of $[(\eta^3\text{-}CH_2CMeCH_2)Pd(S_2CNEt_2)]$, 2b

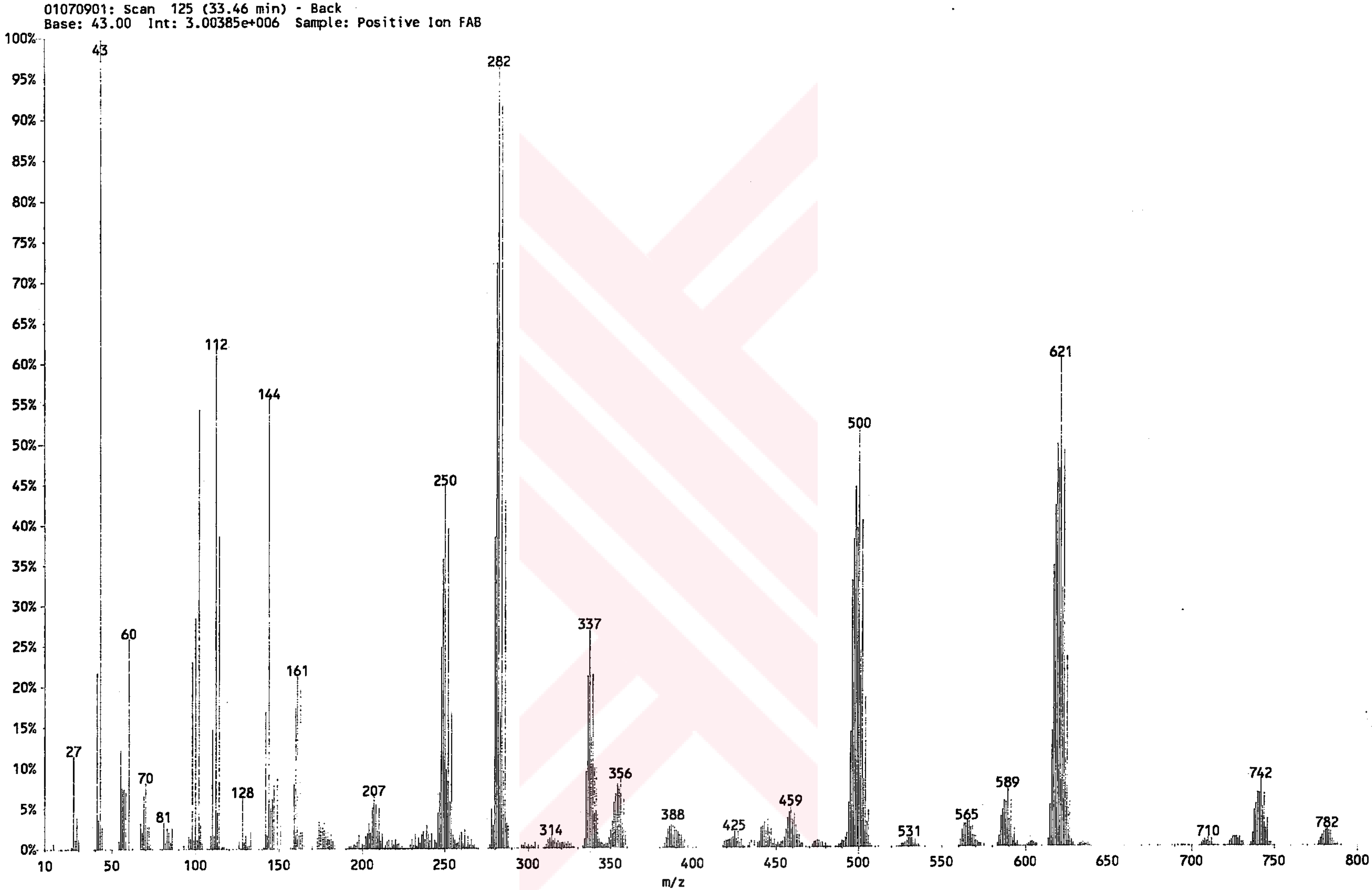


Fig. 3.28 The Mass Spectrum of [(η^3-CH_2CMeCH_2)Pd($S_2CN\,{}^nPr_2$)], 2c

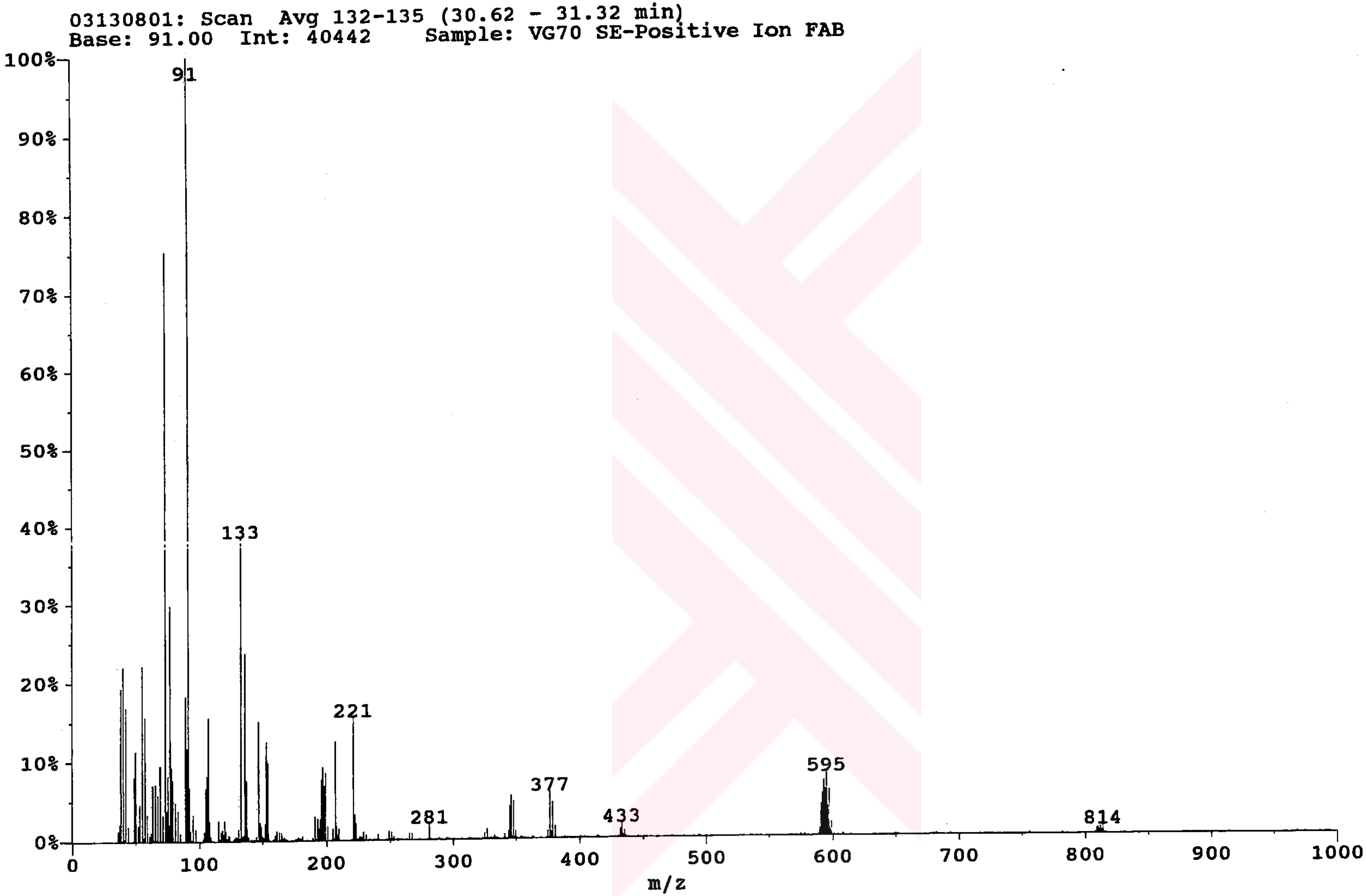


Fig. 3.20 The Mass Spectrum of [(η^3-CH_2CMeCH_2)Pd(S_2CNBz_2)], 2d

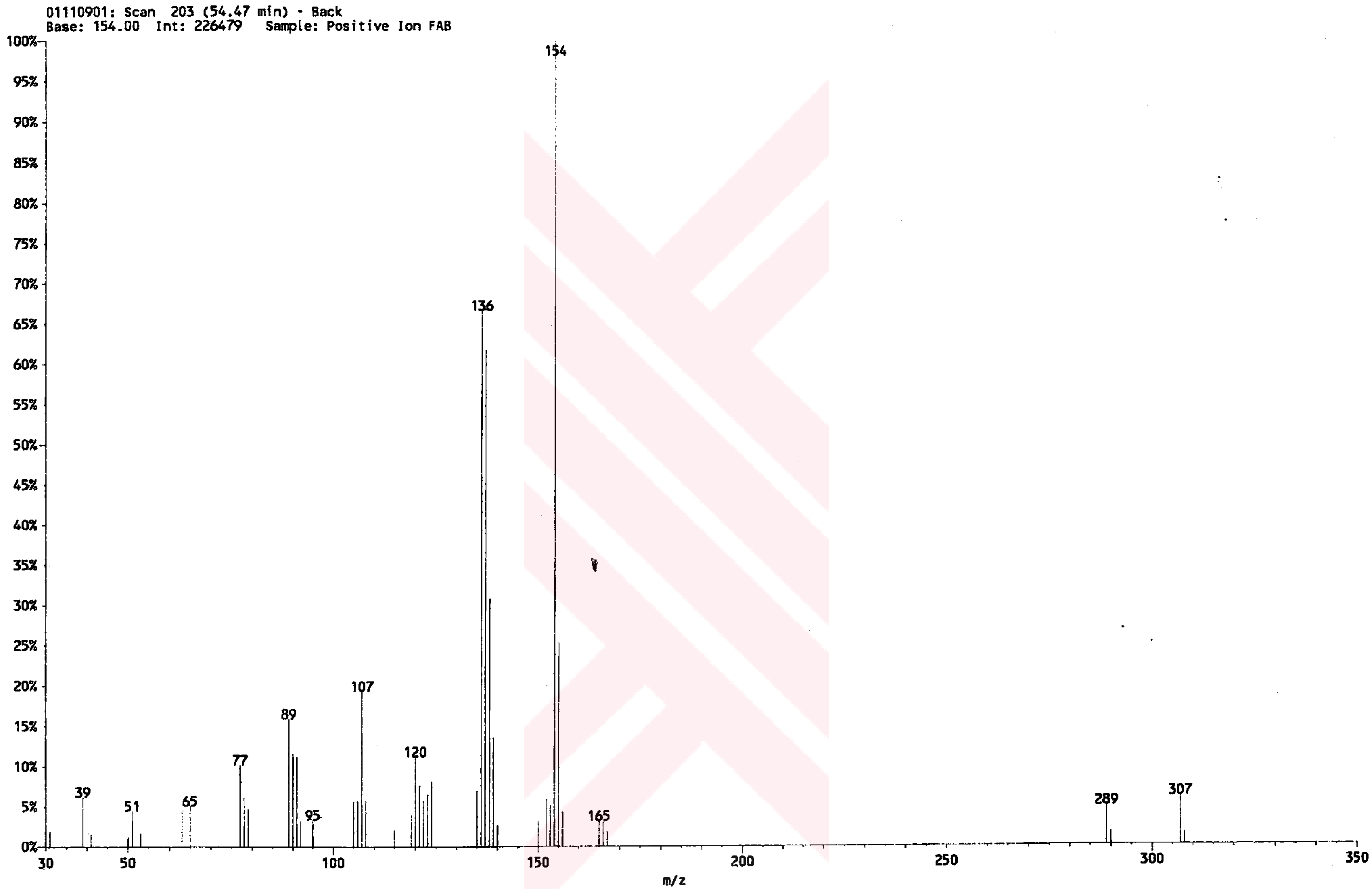


Fig. 3.30 The Mass Spectrum of [(η^3-C_6H_9)Pd(S_2CNMe_2)], 3a

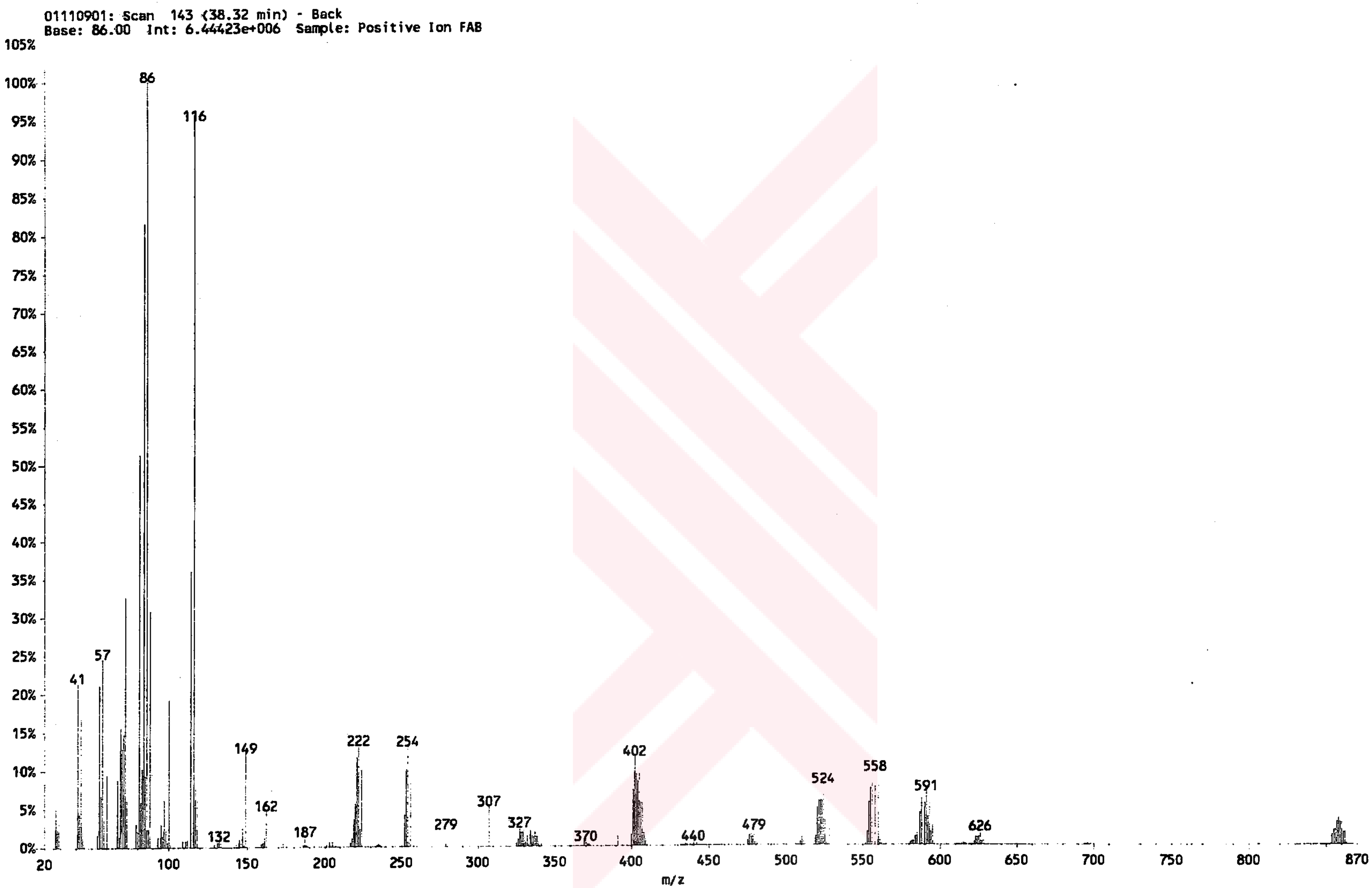


Fig. 3.31 The Mass Spectrum of $[(\eta^3\text{-}C_6H_9)Pd(S_2CNEt_2)]$, 3b

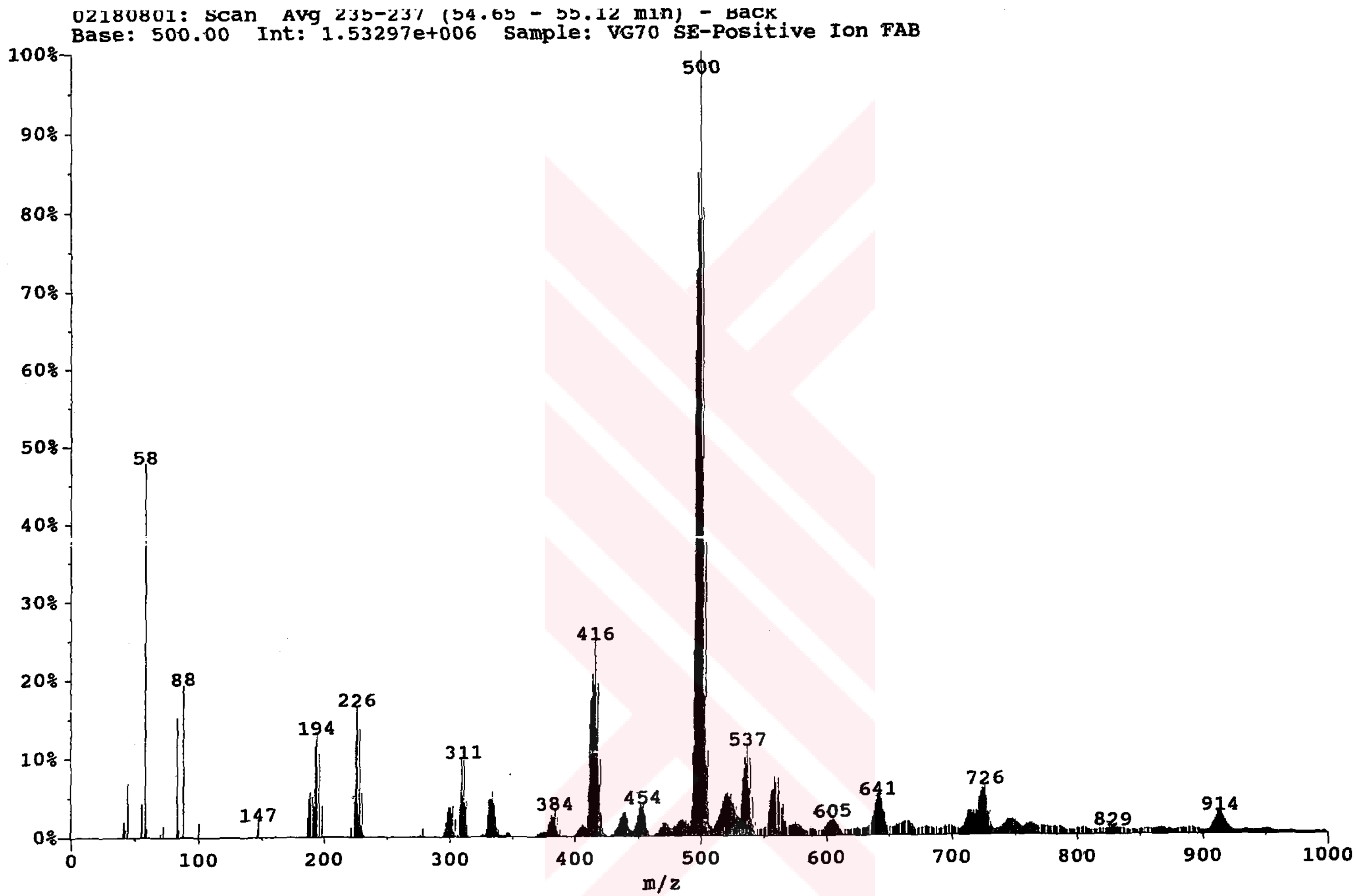


Fig. 3.32 The Mass Spectrum of $[(\eta^3\text{-}CMe_2CMeCH_2)Pd(S_2CNMe_2)]$, 4a

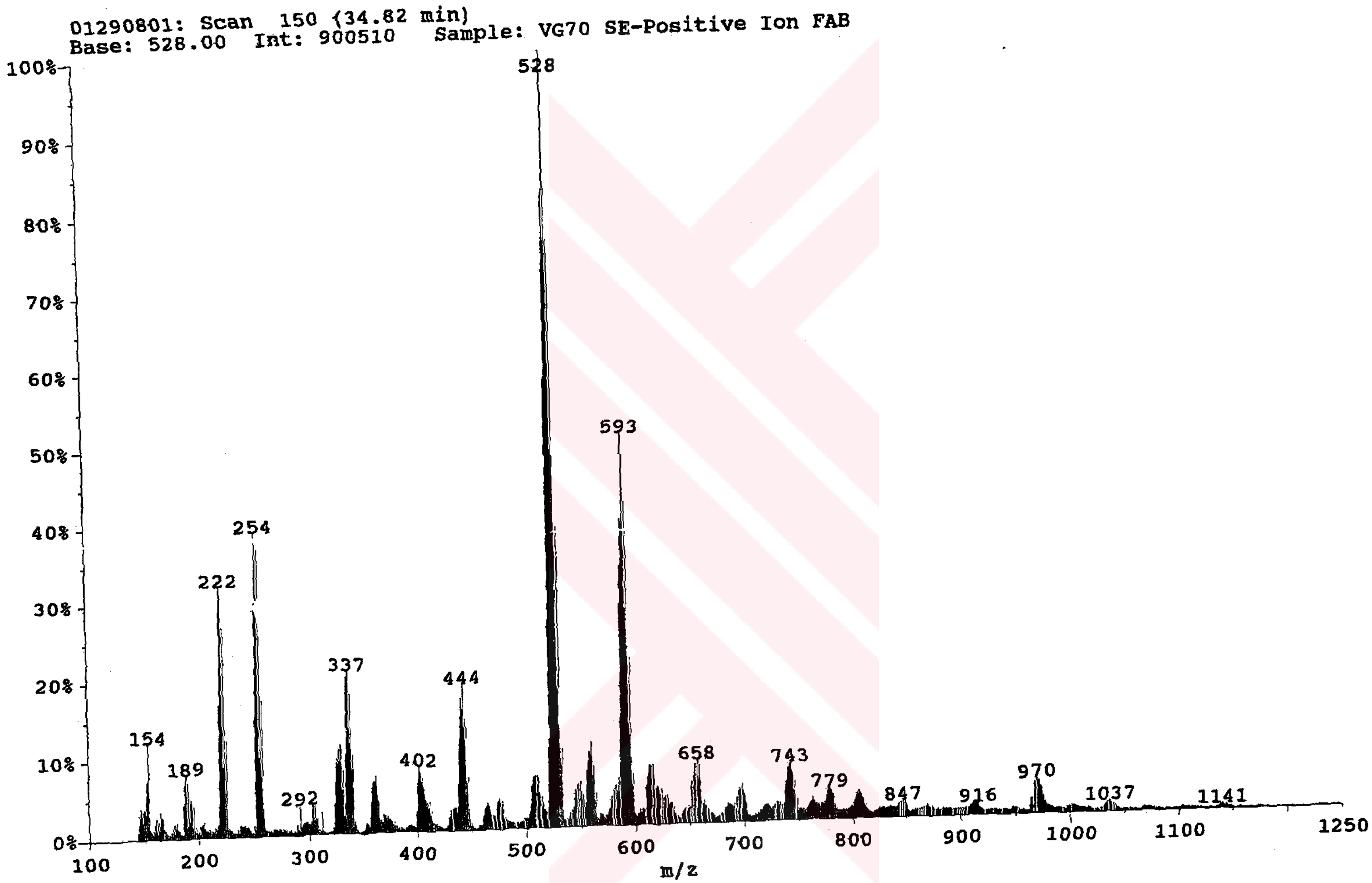


Fig. 3.33 The Mass Spectrum of $[(\eta^3\text{-CMe}_2\text{CMeCH}_2)\text{Pd}(\text{S}_2\text{CNEt}_2)]$, 4b

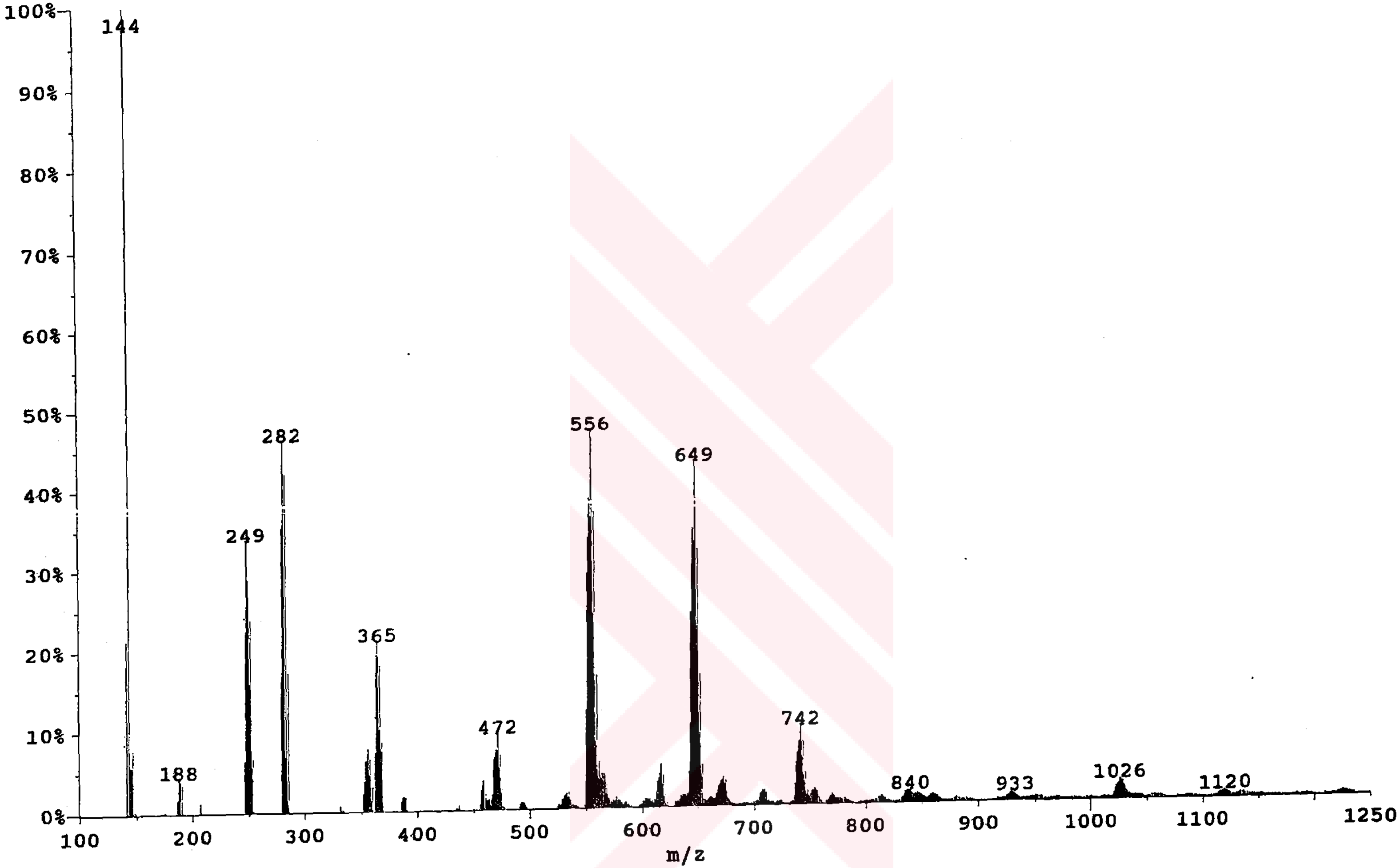
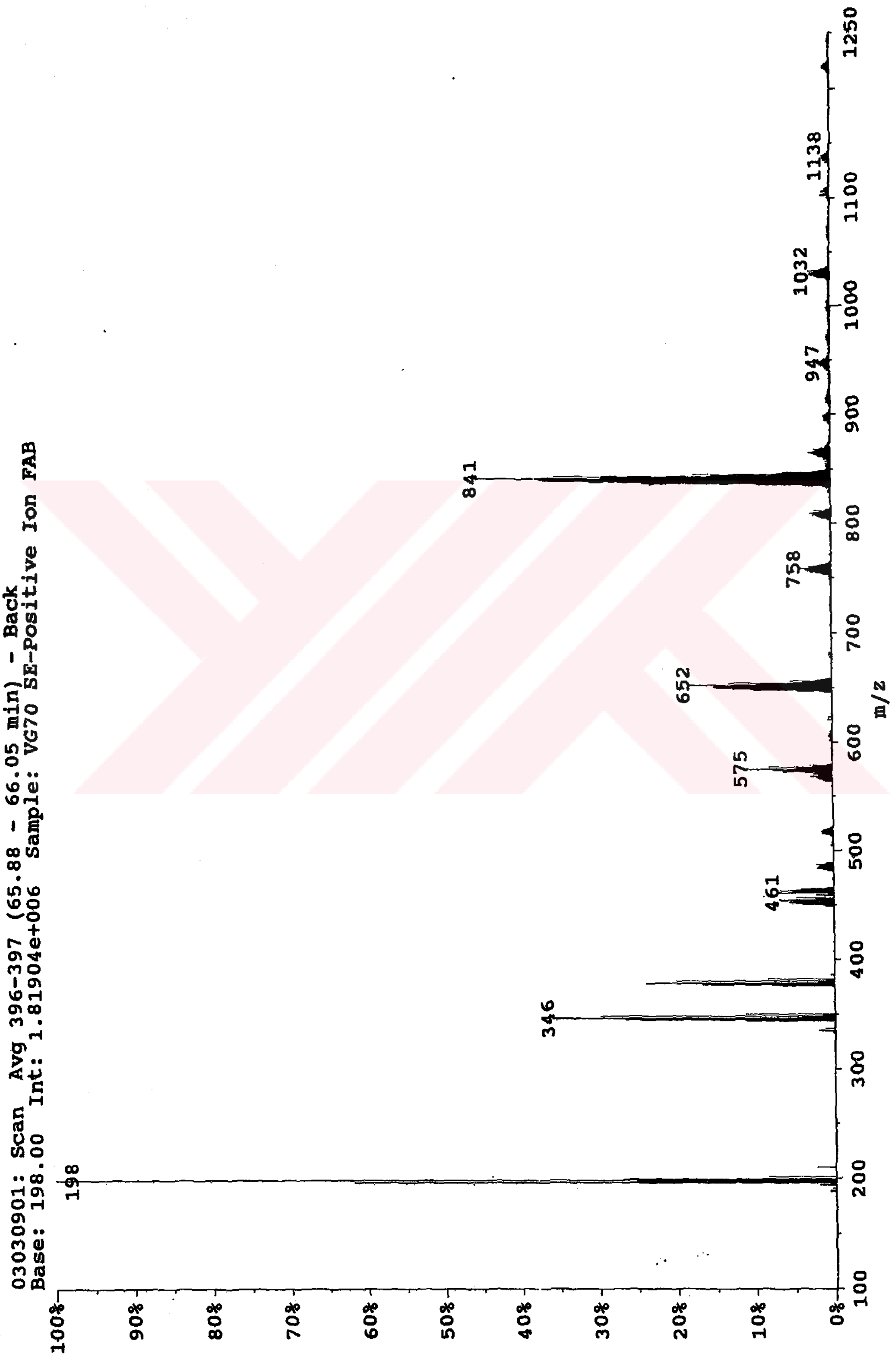


Fig. 3.34 The Mass Spectrum of $[(\eta^3\text{-}CMe_2CMeCH_2)Pd(S_2CN^nPr_2)]$, 4c


03030901: Scan Avg 396-397 (65.88 - 66.05 min) - Back
Base: 198.00 Int: 1.81904e+006 Sample: VG70 SE-Positive Ion FAB
198
346
461
575
652
758
841
947
1032
1138
m/z
100
200
300
400
500
600
700
800
900
1000
1100
1250
0%
10%
20%
30%
40%
50%
60%
70%
80%
90%
100%

3.6 X-ray Crystal Structure of [(η^3-$H_2CCMeCH_2$)Pd($S_2CN^nPr_2$)], 2c;

[(η^3-$H_2CCMeCH_2$)Pd($S_2CN^nPr_2$)], (2c) complex was structurally characterized by X-ray diffraction methods. Crystallographic data for compound 2c are listed in (Table 3.12). The atomic labelling scheme employed for the [(η^3-$H_2CCMeCH_2$)Pd($S_2CN^nPr_2$)] is given in Fig.3.36. Bond lengths and bond angles are also presented in Table 3.13.

This complex contains two molecules per unit cell which are shown in Figure 3.37. The geometry of the Pd complex cation is essentially a distorted square-planar, however, the bond angles subtended at the palladium atom reflect the narrow bites of the allyl and dipropyldithiocarbamate chelate ligands. The central coordination of the allyl and the S_2CN part of the dipropyl dithiocarbamate moiety are approximately co-planar with the palladium atom. The plane of C(5)-N(1)-C(2) is, however, twisted from the coordination plane, presumably, as a result of packing forces.

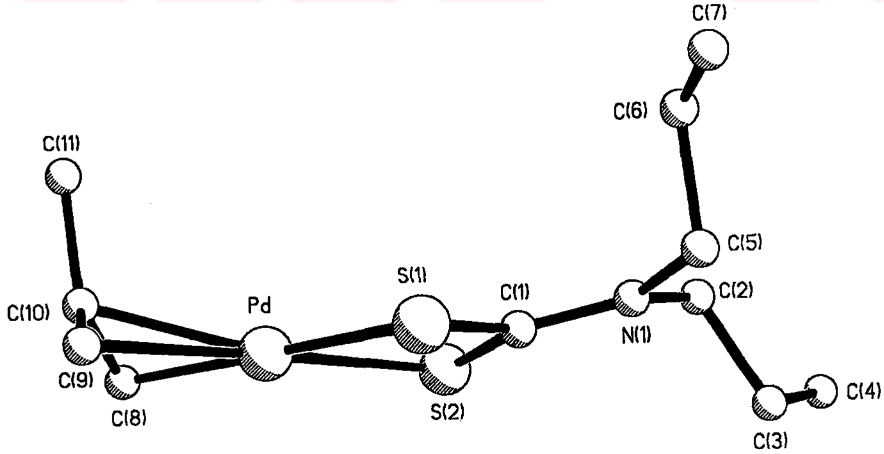


Figure 3.36 X-ray Crystal Structure of [(η^3-$H_2CCMeCH_2$)Pd($S_2CN^nPr_2$)], 2c.

Table 3.12 Crystal data and structure refinement for $[(\eta^3\text{-}H_2CCMeCH_2)Pd(S_2CN^nPr_2)]$, 2c;

Empirical formula	$C_{11}H_{21}NPdS_2$
Formula weight	337.81
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system	Triclinic
Space group	P1bar
Unit cell dimensions	a = 8.619(2) A alpha = 97.59(3) deg.
	b = 9.373(2) A beta = 109.10(3) deg.
	c = 9.800(2) A gamma = 89.86(3) deg.
Volume	740.9(3) A^3
Z	2
Density (calculated)	1.514 Mg/m^3
Absorption coefficient	1.507 mm^-1
F(000)	344
Crystal size	0.80x 0.24x 0.22 mm
Theta range for data collection	2.90 to 25.04 deg.
Index ranges	0<=h<=10, -11<=k<=11, -11<=l<=11
Reflections collected	2789
Independent reflections	2599 [R(int) = 0.0244]
Absorption correction	Psi
Max. and min. transmission	0.977 and 0.643
Refinement method	Full-matrix least-squares on F^2
Data/ restraints/ parameters	2594/ 0/136
Goodness-of-fit on F^2	1.076
Final R indices [I>2sigma(I)]	R1= 0.0357, wR2= 0.0884
R indices (all data)	R1= 0.0408, wR2= 0.1044
Largest diff. Peak and hole	0.481 and –0.825 e.A^-3

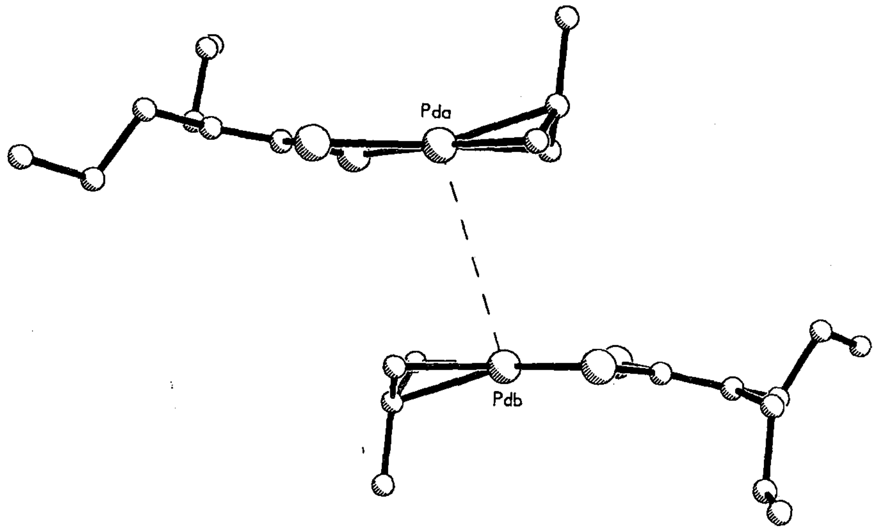


Figure 3.37 Complex, (2c), containing two molecules per unit cell.

Table 3.13 Bond lengths [A] and angles [deg] for 2c.

Pd-C(10)	2.138(4)	C(9)-Pd-S(2)	177.96(13)
Pd-C(9)	2.146(4)	C(8)-Pd-S(2)	111.11(14)
Pd-C(8)	2.158(4)	S(1)-Pd-S(2)	75.23(4)
Pd-S(1)	2.3622(12)	C(1)- S(1)-Pd	85.18(12)
Pd-S(2)	2.3787(13)	C(1)- S(2)-Pd	84.82(13)
S(1)-C(1)	1.732(4)	C(1)-N(1)-C(2)	121.9(3)
S(2)-C(1)	1.724(4)	C(1)-N(1)-C(5)	121.0(3)
N(1)-C(1)	1.335(5)	C(2)-N(1)-C(5)	116.9(3)
N(1)-C(2)	1.471(5)	N(1)- C(1)-S(2)	123.9(3)
N(1)-C(5)	1.476(4)	N(1)- C(1)-S(1)	122.4(3)
C(2)-C(3)	1.508(5)	S(2)-C(1)- S(1)	113.7(2)
C(3)-C(4)	1.509(7)	N(1)- C(2)-C(3)	114.2(3)
C(5)-C(6)	1.521(6)	C(2)- C(3)-C(4)	110.0(4)
C(6)-C(7)	1.511(7)	N(1)- C(5)-C(6)	111.9(3)
C(8)-C(10)	1.391(6)	C(7)- C(6)-C(5)	111.1(4)
C(9)-C(10)	1.404(6)	C(10)- C(8)-Pd	70.3(2)
C(10)-C(11)	1.510(6)	C(10)- C(9)-Pd	70.5(2)
C(10)-Pd-C(9)	38.3(2)	C(8)- C(10)-C(9)	117.2(4)
C(10)-Pd-C(8)	37.8(2)	C(8)- C(10)-C(11)	121.1(4)
C(9)-Pd-C(8)	67.3(2)	C(9)- C(10)-C(11)	120.6(4)
C(10)-Pd-S(1)	137.67(12)	C(8)- C(10)-Pd	71.9(2)
C(9)-Pd-S(1)	106.31(13)	C(9)- C(10)-Pd	71.2(2)
C(8)-Pd-S(1)	173.27(14)	C(11)- C(10)-Pd	116.9(3)
C(10)-Pd-S(2)	141.02(12)		

The molecular structure of all of these complexes; [(η^3-allyl)Pd(S_2CNR_2)] (allyl: 2-methylallyl, R: Me, Et, ^{n}Pr, Bz, (2a, 2b, 2c, 2d); allyl: 1,1,2-trimethylallyl, (4a, 4b, 4c and 4d); allyl: cyclohexadienyl, R: Me, Et, (3a, 3b)) confirms that dithiocarbamato ligand is *S,S*-bidentate, forming a Pd-S-C-S palladacycle with an (η^3-allyl) group completing the coordination sphere. In summary, cleavage of chloro-bridged bimetallic complexes; [(η^3-allyl)Pd(μ-Cl)]$_2$ (*allyl:* 2-methylallyl, 1,1,2-trimethylallyl, cyclohexenyl, (1b, 1c, 1d)) is readily accomplished using anions derived from *N,N*-dialkyldithiocarbamates with the formation of the four-membered chelate rings analogous to xanthate and dithiophosphinate ligands.

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