Transition Metal Centres Linked via Acetylide Ligands

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Abstract

This thesis consists of three closely related areas of study. The first chapter describes a brief history of organometallic chemistry which leads onto the use of phosphine/ diphosphine ligands in organometallic compounds.

The second chapter concerns the use of *para*-ethynylaniline as a building block towards the synthesis of large linear molecules in which transition metal centres are linked *via* a fully π-conjugated backbone. Two crystal structures were obtained, namely *trans*-$[Pt(PPh_3)_2(C\equiv CC_6H_4NH_2)_2]$ and $[(\mu\text{-}H)Ru_3(CO)_9(\mu^3\text{-}C\equiv CC_6H_4NH_2)]$.

The third chapter is about the synthesis of a range of supramolecular structures based on the use of functionalised acetylides, linked by silver ions. These have been probed by X-ray crystallography and three crystal structures, *trans*-$[PtAg(C\equiv CCH_2CH_2OH)_2(PMe_2Ph)_2]_n[ClO_4]_n(MeCN)_n$, *trans*-$[PtAg(C\equiv CPh)_2(PMe_2Ph)_2]_n[ClO_4]_n$ and *trans*-$[PtAg_2\{C\equiv CC(CH_3)_2OH\}_2(MeCN)_4(PPh_3)_2][ClO_4]_2$ were determined.

The final chapter describes the systematic synthesis of a number of small bite-angle diphosphine complexes and again X-ray crystallography has been used to probe the bite angle and its effect on the coordination sphere of the metal centre. A number of crystal structures of the type $[M(CO)_4\{\eta^2\text{-(o-tolyl)}_2PCHRP(\text{o-tolyl})_2\}]$ (R = H, Me, Et, CH_2Ph; M = Cr, Mo, W) were obtained.

Declaration

I confirm that the work presented in this thesis was carried out between September 1996 and December 2000 in the Chemistry Department of University College London and is my own except otherwise noted.

Acknowledgements

It is under God's grace that this thesis can be produced. May all the glory be to Him. I would like to thank my mother for her support and care. Many thanks to the brothers and sisters in the Chinese Church London (Finsbury Park Congregation) for their encouragement and prayers.

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Abbreviations

Me	methyl
Et	ethyl
^{n}Bu	butyl
^{t}Bu	tert-butyl
^{i}Pr	iso-propyl
Ph	phenyl
Ar	aryl
Cp	cyclopentadienyl
thf	tetrahydrofuran
pip	piperidine
dpepp	$Ph_2PCH_2CH_2P(Ph)CH_2CH_2PPh_2$
TMEDA	N, N, N', N'-teramethylethylenediiamine
NMP	1-methyl-2-pyrrolidinone

EI	electron ionisation
FAB	fast atom bombardment
ES	electrospray
M	molecular ion

With reference to Nuclear Magnetic Resonance Data

NMR	nuclear magnetic resonance
Hz	Hertz
J	Coupling constant
brs	broad singlet
ppm	parts per million

s	singlet
d	doublet
t	triplet
q	quartet
quin	quintet
sept	septet
m	mutiplet

With reference to infra-red data

IR	infra-red
s	strong
m	medium
w	weak

ν(CO)	carbonyl stretching frequency
br	broad

Chapter 1: General Introduction

Organometallic chemistry is the study of those compounds containing direct metal-carbon interactions. Although organometallic compounds have been known for over 200 years, it was only over the last 50 years where this field has grown rapidly. The first preparation of organometallic compound was by Cadet. In 1760, he reacted arsenic oxide with potassium acetate to produce cacodyloxide $[(CH_3)_2As]_2O$ known as "Cadet's fuming liquid". It was not until 1827 that a Danish pharmacist Zeise discovered the first transition metal organometallic compound, namely the platinum-ethylene complex $K[PtCl_3(C_2H_4)]$. About 20 years later, Frankland, a student of Bunsen's at Marburg, attempted to prepare an ethyl radical and reacted ethyl iodide with zinc and produced diethyl zinc, which is a pyrophoric liquid. In 1852, Frankland himself treated methyl halide with sodium amalgam and produced an alkyl transfer reagent, dimethyl mercury. He also introduced the concept of valency ("combining power") and the term organometallic.

After the discovery of the first metal carbonyl complex $[Pt(CO)Cl_2]_2$ by Schützenberger in 1868, Mond reacted nickel with carbon monoxide to produce nickel tetracarbonyl in 1890. This reaction became the first application of organometallic chemistry in which crude nickel is refined by Mond carbonylation-decarbonylation process for many decades.

The well known Grignard reagent was discovered by Grignard in 1899 who treated alkyl iodide with magnesium to produce RMgX. Although it is less sensitive than dialkyl zinc, it is a more potent alkyl transfer reagent. Subsequently in 1917, Schlenk discovered the alkyllithium reagent *via* transalkylation. In 1909, Pope prepared the first (-organo transition metal compound Me_3PtI.

After the birth of alkene (1827) and arene (1919) complexes, the first complex of a diene with a transition metal, butadienetricarbonyliron, was found in 1930 by the German chemist, Reihlen. In 1938, Roelen discovered the process, hydroformylation by transforming olefins into aldehydes through the addition of CO and H_2 to a double bond and in the following year, Reppe started his work on transition-metal catalysed reactions of acetylenes including the $Ni(CN)_2$ catalysed tetramerization of acetylene to cyclooctatetraene.

Transition metal molecular chemistry was dominated by German chemists up to the second world war. The British and then the Americans, however, took the lead in the1950s. In 1951, the chance synthesis of ferrocene simultaneously by Pauson and Miller was revolutionary as the simple idea of taking a transition metal in a 'sandwich' between two 'slices' of an organic aromatic molecule, established a year later by Wilkinson and Woodward, was totally unkown to classical organic chemistry.

In 1953, Wittig found that alkenes can be prepared from aldehydes and ketones *via* use of a phosphorus ylid. This well-known reaction is then named after Wittig. A significant discovery was made by Ziegler and Natta in the late 1950's. They found that it was possible to polymerise olefins from ethylene and propylene by a low pressure process employing soluble titanium and aluminium based catalysts. This reaction allows the production of plastic which is now part of our everyday life.

In 1964, Fischer discovered carbene complexes, which have a metal-carbon double bond. Carbyne complexes, having a metal-carbon triple bond, followed from the same laboratory in 1973. It was found later that complexes related to Fischer's carbenes are catalytic intermediates in metathesis reaction of olefins.

The famous Wilkinson catalyst $[RhCl(PPh_3)_3]$ which permits hydrogenation at low temperatures and pressures, was found as a homogeneous catalyst by Wilkinson and Coffey in 1965. Then in 1971, Monsanto presented a new industrial synthesis of acetic acid through carbonylation of methanol and the use of a rhodium catalyst.

Over the past 50 years, organometallic chemistry has become a mature area of science and is still an expanding area, being diverged from both organic and inorganic chemistry. Organometallic compounds have been utilised in creating new highly regioand stereo- selective reactions for the preparation of sophisticated organic molecules. Some of the organometallic compounds are good alkyl transfer reagents as discussed earlier, while others are important intermediates in catalytic cycles.

Ligands play a very important role in organometallic chemistry, since they can bring about drastic changes in the chemical and physical properties of transition metal complexes. Phosphines and diphosphines are common ligands used to fine-tune the properties of organometallic complexes. This can be achieved by having different substituents on the phosphines. For instance, long-chain alkyl groups on the phosphine can increase solubility of the complex while aromatic substituents on the phosphine can increase the crystallinity of the complex. Moreover, diphosphines such as bis(diphenylphosphino)methane (dppm) can act as a bridging ligand but can also sometimes chelate.

In this thesis, work in two general areas of organometallic chemistry is described. Firstly, the syntheses of long-chain, transition metal containing polymers and oligomers was investigated. The building of such polymers includes the binding of different metal centres with functionalised acetylides through (- bonds only and *via* (- and (- bonds. The structures of these polymers and oligomers were elucidated by X-ray crystallography. Some of these long-chain, metal containing molecules are conjugated and are potential conductors which may also exhibit optical properties. Secondly, synthesis of small bite angle diphosphine complexes was considered. By increasing the steric bulk of the substituent on the diphosphine, the bite angle should theoretically decrease. Therefore, investigation on the effect of having bulky diphosphines on metal centres and how this affects the bite angle was carried out by examining the structures of the complexes crystallographically.

Finally, each chapter in this thesis is self-contained and includes an introduction, results and discussion, a conclusion, an experimental section and references.

1.1 General Experimental

All manipulations were carried out under an atmosphere of dinitrogen using standard vacuum line and glove box techniques unless otherwise stated. The glove box used was a Vacuum Atmosphere HE-493 box in which the atmosphere was continuously circulated through R311 catalyst and 5Å molecular sieves to remove oxygen and moisture. The atmosphere was monitored using a toluene solution of $[(Cp_2TiCl_2)_2Zn]$ which remained green in the absence of oxygen. *para*-Iodoaniline, *para*-bromo-2,6-dimethyl-aniline, platinum dichloride, cyclohexanone, ferrocene, benzoyl chloride, terephthaloyl chloride, PPh_3Br_2, prop-2-yn-1-ol, 3-butyn-1-ol, 4-pentyn-1-ol, phenylacetylene, 2-methyl-3-butyn-2-ol, silver perchlorate, o-bromotoluene and 2-bromo-m-xylene were purchased from the usual suppliers. $[MoOCl_2((^2\text{-}S_2CNEt_2)_2]^1$, $[Os_3(CO)_{10}(MeCN)_2]^2$ and *cis*-$[PdCl_2(PhCN)_2]^3$ was prepared by Drs. Simon Redmond, Shahbano Ali and Romano Giorgi respectively following literature methods. All *trans*-$[Ru(CO)_2(PEt_3)_2Cl_2]^4$, *cis*-$[W(CO)_4(pip)_2]^5$, *cis*-$[Mo(CO)_4(pip)_2]^5$, $[Cr(CO)_5Cl][NEt_4]^6$ were prepared by Dr. Hogarth also following literature methods.

Apart from those used for crystallisations in air, all solvents were stored over activated 4(molecular sieves or sodium films in ampoules having been distilled under dinitrogen from the drying agents as below and thoroughly degassed. Toluene was distilled from sodium, THF from potassium/benzophenone, diethyl ether, petroleum ether (b.p.40-60^{0}C), pentane and heptane from a 1:3 alloy of sodium/potassium, methanol and ethanol from calcium oxide and dichloromethane, TMEDA from calcium hydride. Diethylamine was distilled over potassium hydroxide pellets.

Instrumental

Infrared Spectra

Infrared spectra were recorded between 4000 and 400 cm^{-1} or 2200 and 1800 cm^{-1} on a Nicolet 205 FTIR spectrometer or Shimadzu 8700 FTIR spectrometer. The solid state spectra were recorded as potassium bromide discs and the solution spectra using a cell fitted with calcium fluoride plates, subtraction of the solvent absorptions being achieved by computation. The solvent used was dichloromethane unless otherwise stated. Data reported in cm^{-1}.

Nuclear Magnetic Resonance Spectra

All NMR spectra were recorded on Brüker 300 (^1H) or VXR-400 (^1H, ^{13}C, ^{31}P) spectrometers at University College London and are internally referenced to residual chloroform in the case of ^1H and ^{13}C and H_3PO_4 in the case of ^{31}P. Data given as (x.xx (multiplicity, J, assignment).

Mass Spectra

The fast atom bombardment and electron impact mass spectra were recorded on a VG ZAB-SE high resolution mass spectrometer in the Chemistry department of University College London. The electrospray (positive ion) mass spectra were recorded on a MICROMASS QUATTRO LC high resolution mass spectrometer in the same department. Parent ion is recorded as M^+.

Microanalysis

Elemental analyses were performed by the staff of the analytical laboratory in the Chemistry department of University College London. Elemental analytical data are presented as % calculated, % found.

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Chapter 2: Transition metal bis(acetylide) complexes as building blocks to fully π-conjugated molecular systems

Last year's Nobel Prize in chemistry was awarded to Heeger, MacDiarmid and Shirakawa for their discovery of polyacetylene as conducting polymer in the late 1970's. The physical properties of polyacetylene are directly related to the π-conjugation along the polymer chain. Transition metals can be incorporated into these conducting polymers in order to modify their physical properties. The first polymetallaynes were isolated in 1977 by Sonogashira, Hagihara and Takahashi. In this chapter, we shall describe attempts to link electronically diverse metal centres together with fully π-conjugated systems. *para*-Ethynylaniline was chosen as a building block as it has the potential to bind a variety of low valent metal centres to form acetylide complexes and high valent metal centres to form imido linkages. A number of σ-acetylide complexes were prepared and used to extend the chain length *via* amide and imine linkages. Attempts were made to bind the σ-acetylide complex with high valent metal centres *via* an imido linkage.

Introduction

2.1 π-Conjugated systems

A π-conjugated unsaturated system is one that has p-orbital on an atom adjacent to a double bond, hence a molecule with delocalised π-bonds.[1] The term 'π-conjugation' arises in the chemistry of carbon where the disputed structure of benzene led Kekulé to propose resonance structures. This in turn led on to the ideas of aromaticity and conjugation.[2]

A significant example of π-conjugated system is polyacetylene. Heeger, MacDiarmid and Shirakawa were awarded Nobel Prize in chemistry in 2000 for a discovery made in Japan in the late 1970's of polyacetylene, a shiny black material which has an unexpectedly high conductivity that increases up to $1000\Omega cm^{-1}$ when doped with iodine. The building of long conjugated systems at a molecular level from diynes, through oligomers to polyacetylenes gave rise to linear chain molecules and the concept of molecular wires. More recently, ring opening metathesis polymerisation (ROMP) has been utilised as a synthetic route to functionalised polyacetylenes and other novel polymers.[3]

Polyaniline is another example of π-conjugated conducting polymer which was discovered by MacDiarmid and co-workers in 1983. It is air-stable and has a conductivity in the range of 1-10 Ωcm^{-1} when it undergoes a non-oxidative proton doping process.[4] However, it is only slightly soluble in polar solvents such as dimethyl formamide (DMF) and dimethyl sulphoxide (DMSO). In fact, a lot of organic conjugated polymers suffer from poor solubility in common organic solvents and thus poor processability. One solution to this problem is to incorporate metals into the polymer, where by the ancillary ligands on the metal can be tuned to give the polymer different properties. For example, to improve the solubility of the polymer. This incorporation of metals into the polymer led to the idea of rigid-rod organometallic polymer.

The first polymetallaynes containing nickel, palladium, or platinum atoms in the main chain were isolated in 1977 by Sonogashira, Hagihara and Takahashi as yellow, film-forming materials,[5] *trans*-$[M(P^nBu_3)_2\{C{\equiv}CC_6H_4C{\equiv}C\}]_n$. These were prepared by coupling reaction of *trans*-$[MCl_2(P^nBu_3)_2]$ with $HC{\equiv}CC_6H_4C{\equiv}CH$ in the presence of copper halide and amine solvent and have estimated molecular weights between 10^4 and 10^5 More recently, Lewis and co-workers reported a new route to *trans*-$[M(P^nBu_3)_2\{C{\equiv}CC_6H_4C{\equiv}C\}]_n$ based on the reaction of *trans*-$[PtCl_2(P^nBu_3)_2]$ with bis(trimethylstannyl)diynes, $Me_3SnC{\equiv}CC_6H_4C{\equiv}CSnMe_3$.[6] These rigid-rod polymers possessed estimated average molecular weights up to 10^5.

Metal containing π-conjugated polymers have attracted considerable attention due to their potential applications in materials science, as conductors and liquid crystals. They may also exhibit magnetic and non-linear optical properties. Such physical properties are expected to be directly related to the extended delocalisation along the polymeric chain and this motivates the design of new monomeric models in order to evaluate the capability of communication between metal centres.

2.2 σ-Acetylide transition metal complexes

The first acetylide complexes namely anionic $[M(C{\equiv}CR)_4]^{2-}$ were prepared in 1953.[7] They are very sensitive to protonation and this seems to depend on the electron configuration of the central metal atom. The action of acids on the complexes of the high-spin d^5-manganese (II) and on the d^{10}-metals of groups 11 and 12 quantitatively liberates the acetylene RC≡CH, whereas the protonation of all the other complexes yields unidentified organic products by side reactions. The anionic acetylides of transition metals are mostly insoluble in common organic solvents and explode on impact unless their central atom possess filled or half-filled d-orbitals.

Acetylides ($RC{\equiv}C^-$) are not only σ-donor ligands, but are also π-acceptors, especially in zero valent transition metal acetylide complexes. The high electron density on the low-valent metal atoms may be diminished by partial electron transfer from filled d-orbitals into vacant anti-bonding π*-orbitals of the acetylides. Such a transfer must reduce the bond order of the C≡C system which is reflected by a decrease of the ν(C≡C) frequencies. Indeed, the ν(C≡C) values of the phenylethynyl metal (0) complexes of palladium and platinum are markedly less than those of the corresponding metal (II) species.[8] However, the π-acceptor property of acetylide is very weak as compared with ligands such as carbon monoxide. Such a property is so small that it is not measurable by covalent radii measurement which is discussed later in this chapter.

Since 1959 an increasing number of uncharged acetylide complexes of transition metals have been prepared, for example, $[Ni(PPh_3)_2(C{\equiv}CPh)_2]$.[9] They are mostly non-explosive and are soluble in organic solvents. The vast majority of the first row transition metal acetylides are low-spin complexes indicating the strong field nature of the terminal acetylene ligands. In general, acetylides bind to low valent metal centres as they are soft ligands. In 1972 and during the following years, acetylides compounds of transition metal clusters were discovered and structurally characterised. In this chapter, we have chosen σ-bis(acetylide) transition metal complexes as our monomer units in building long chain molecules as there are many advantages in making these compounds. For example, Gladysz [10] and others[11] have shown that when metal centres are linked *via* π-conjugated acetylide based groups a high degree of electronic communication between them can be achieved.

The acetylide anion, $RC\equiv C^-$, is essentially linear due to the sp-hybridisation of both carbons. That is, the 2s and one 2p orbital on a carbon mix to form two new sp hybrid orbitals which are 180° apart. The two remaining unhybridized p-orbitals lie orthogonal to each other and to the sp hybrid orbitals. In a carbon-carbon triple bond, the σ-bond is formed by the overlapping of one sp hybrid orbital from each carbon. This bonding molecular orbital contains two electrons. The two π-bonds are formed by the side-to-side overlap of p-orbitals. These bonding π-molecular orbitals are orthogonal to each other and each contains two electrons, yielding a carbon-carbon triple bond.

Since the carbon atoms in the carbon-carbon triple bond are sp-hybridised and the geometry of the metals is usually either square planar or octahedral, and the M-C bonds in the *trans*-bis(acetylide) complexes are linear giving the complexes a rigid-rod structure.

Carbon-carbon triple bonds (1.20 Å) are shorter than carbon-carbon double (1.33 Å) or single (1.54 Å) bonds.[2] Carbon-hydrogen bond lengths also decrease along the series: ethane (1.11 Å), ethylene (1.08 Å) and acetylene (1.06 Å). This is because the acetylene C-H bond is derived from the overlap of a carbon sp orbital with a hydrogen 1s orbital, whereas the alkane C-H bond is derived from the overlap of a carbon sp^3 orbital with a hydrogen 1s orbital. Since electrons in the sp orbital are on average closer to the positive carbon nucleus than those in an sp^3 orbital, the C-H bond of the acetylene is shorter.

In a metal acetylide complex such as *trans*-$[PtCl(C\equiv CPh)(PPhMe_2)_2]$, the Pt-C bond length is 1.98 Å, whereas the covalent radius of Pt (II) is 1.31 Å and that of C (sp) is 0.60 Å.[12] Thus, the Pt-C length is not shorter than the sum of the covalent radii of Pt (II) and C (sp); suggesting that there is no indication of π bonding between the platinum (II) and carbon centres. If considerable back bonding were present, i.e. Pt (dπ) → C (p*π), the C≡C bond would lengthen but this is not observed.

Since σ-bonds between a transition metal and carbon are, in general, thermodynamically and kinetically unstable, many transition metal alkyl complexes decompose by abstraction of a β-hydrogen atom. However, σ-acetylide transition metal complexes have stable M-C σ bonds as they are lacking β-hydrogens. In addition, the interaction between the metal d-orbital (e.g. in platinum (0) complexes) and the π-orbitals of acetylenic carbon is favourable which strengthens the M-C σ bond. It should be noted that such interaction is small and there is no experimental evidence to support this argument so far. Therefore, transition metal acetylides are thermodynamically stable with respect to transition metal alkyl complexes.

Acetylides are easily identified by spectroscopic methods as they normally have a C≡C stretching absorption in the 2100-2200 cm^{-1} region of the infrared spectrum.[2] The ≡C-H stretching absorption of terminal acetylenes which occurs at about 3300 cm^{-1}, is also very useful in characterising such species,[13] as it is usually well-separated from other C-H absorptions. This occurs because ≡C-H have higher stretching frequencies than =C-H, which in turn have higher stretching frequencies than –C-H due to the decreasing bond strength from ≡C-H to –C-H. Further, typical chemical shifts of acetylenic protons occur at δ 1.7-2.5 in ^1H NMR spectrum, and this provides a powerful tool in distinguishing terminal acetylenes and their acetylides.

There are many ways to prepare σ-acetylide transition metal complexes, most being prepared from transition metal halides. A base is often required to remove the acetylenic hydrogen, hence to generate an acetylide anion which in turn react with a metal halide to produce a metal acetylide. Since the acetylenic hydrogen is relatively acidic (pKa = 25)[2] it is easily deprotonated. The acetylide anion is isoelectronic to CN^-, CO and N_2. However, unlike CN^- and CO, it is strongly basic and is easily hydrolysed. The preparation of acetylide complexes thus requires anhydrous solvents like liquid ammonia. One base commonly used to substitute the acetylenic hydrogen of an acetylene is sodium amide, formed by dissolving sodium metal in liquid ammonia. The amide ion has a pKa of 35,[2] and since it is a much stronger base than an acetylide, results in formation of sodium acetylide. Nowadays, organolithium reagents are used to prepare group 1 metal acetylide as they are more convenient to use than liquid ammonia.

$$HC\equiv CR \quad + \quad {}^{n}BuLi \longrightarrow LiC\equiv CR \quad + \quad {}^{n}BuH$$

Group 1 metal acetylides are commonly prepared *in situ* in order to synthesise other σ-acetylide complexes, such as trimethyl stannyl acetylide, *via* a metathesis reaction.

$$Me_3SnCl \quad + \quad LiC\equiv CR \longrightarrow Me_3SnC\equiv CR \quad + \quad LiCl$$

The relative acidity of acetylene is also reflected in the method usually used to prepare acetylenic Grignard reagents.

$$RC\equiv CH \quad + \quad R'MgX \longrightarrow RC\equiv CMgX \quad + \quad R'H$$

(R and R' = alkyl or aryl, X = halide)

Hagihara and co-workers[14] had synthesised cuprous acetylides *in situ* by reaction of acetylene with cuprous halide in amines. These in turn can couple with a group 10 metal halide *via* a metathesis reaction to form group 10 σ-acetylide complexes. Indeed, there are far more examples of group 10 metal σ-acetylide complexes than σ-acetylides of other groups. This is because amines are required as solvent in which many of the other transition metal halides are unstable. As highlighted earlier, a recent method for preparing metal σ-acetylide complexes, derived from Lewis and co-workers[6], is the reaction of a metal halide with trimethyl stannyl acetylide. No amine solvent was necessary. This provides a route in the preparation of σ-acetylide of other transition metals.

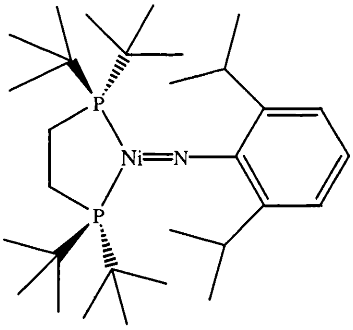
$$MX \quad + \quad Me_3SnC\equiv CR \longrightarrow MC\equiv CR \quad + \quad Me_3SnX$$

(R = alkyl or aryl, X = halide)

2.3 Imido complexes

In contrast to acetylide ligands, imido ligands (NR^{2-}) bind preferentially to high valent metal centres to produce stable complexes.[15] As the imido ligand is a good π-donor, the interactions between the metal d-orbitals and p-orbitals on nitrogen are strong. The imido ligand can be considered to bind to a transition metal *via* one σ and either one or two π interactions. The nitrogen on the imido ligand can be sp^2 hybridized and binds with a metal atom *via* a M=N double bond (1σ, 1π) giving a bent M-N-R linkage. The imido ligand in this case acts as a four-electron donor. However, most M-N-R linkages are linear suggesting sp hybridization about the nitrogen and a M≡NR bond order of 3. In this case, the imido dianion $(NR)^{2-}$ is a formal six electron, 1σ, 2π donor to the metal. In this chapter, we will consider only linear imido complexes.

The first imido complex, $[OsO_3(N^tBu)]$, was synthesised by Clifford and Kobayashi in 1956,[16] and since then a vast number have been prepared.[17] There are examples of imido complexes from groups (4 – 10) transition metals. The group 10 transition metal imido complex was prepared by Hillhouse *et al.* this year.[18] The nickel imido complex is bent and the nickel atom is three-coordinate.



The preparation of imido complexes have been covered extensively in reviews by Wigley[17] and Nugent and Haymore[19]. The most common method is the cleavage of N-H bond in amines and amides.[20]

$$[ReOCl_3(PEt_2Ph)_2] \quad + \quad H_2NPh \quad \longrightarrow \quad [Re(NPh)Cl_3(PEt_2Ph)_2] \quad + \quad H_2O$$

Isocyanates (RN=C=O), phosphinimines ($R_3P=NR$), sulfinylamines

(RN=S=O), carbodiimides (RN=C=NR) and organoimines (RN=CHR) have all been observed to react with M=O to introduce an imido complex in which the oxidation state of the metal is unchanged.[21]

$$[ReO_3(OSiPh_3)] + 3ArN{=}C{=}O \longrightarrow [Re(NAr)_3(OSiPh_3)] + 3CO_2$$

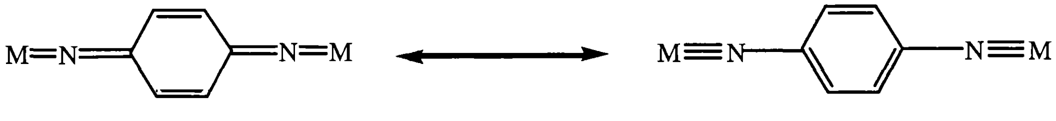
$$[^nBu_4N]_2[Mo_6O_{19}] + Ph_3P{=}Ntol \longrightarrow [^nBu_4N]_2[Mo_6O_{18}(Ntol)] + Ph_3P{=}O$$

There are many other ways of preparing imido complexes but those highlighted above are most relevant to this thesis.

The imido linkage (M=N-R) is not easily identified by vibrational spectroscopy. This is because most metal nitrogen ν(M=N) stretches appear to be strongly coupled to other metal-ligand vibrations in the molecule. Thus, imido ligands are generally characterised by two IR active modes, one between 1100-1350 cm^{-1} and the other around 900-1000 cm^{-1}. Although Dehnicke and Strähle[22] suggested that the ν(M=N) stretch was of the two modes, at the higher energy, from studies on a series of compounds $[Cl_3V(NX)]$ (X = Cl, Br, I), Osborne and Trogler[23] suggested the opposite according to their study of isotopic substitution of nitrogen on vanadium imides. Therefore, it is still unclear as to which band is associated with the ν(M=N) versus ν(NC) modes.

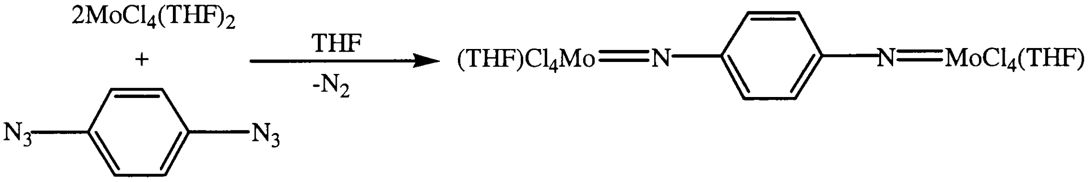
2.4 Diimido complexes

Since we are concerned with linking transition metals together by π-conjugated organic fragments, diimido ligands will be considered here as they can form a diimido bridge between metal centers as shown below:

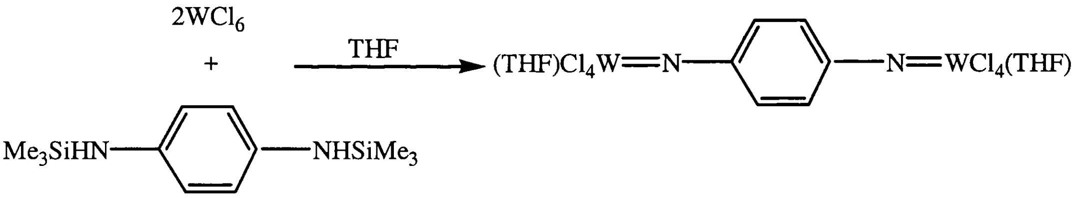


It is important to realise that only the *ortho* and *para-* arrangements of the diimido linkages give rise to π-conjugation of the system and the *ortho*-arrangement is often sterically disfavoured.

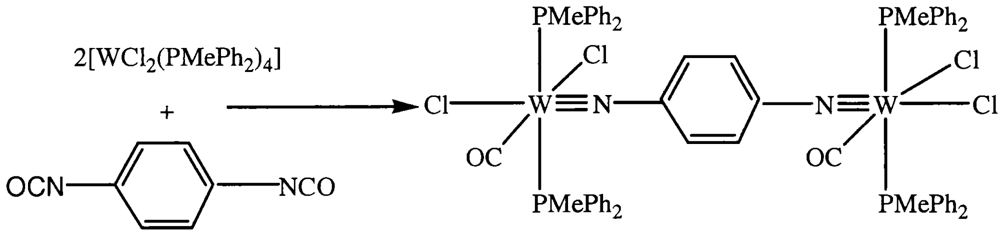
A limited amount of work has been reported concerning bimetallic diimido systems. It is known that molybdenum[24-26], rhenium[27], tungsten[28-30], niobium[31], vanadium[32] and uranium metals[33] have been linked *via* a *para*-phenylene diimido ligand. For example, Maatta *et al.*[24] treated [$MoCl_4(THF)_2$] with 1,4-phenylenediazide to give [{(THF)$MoCl_4$}$_2$(μ-NC_6H_4N)], while Errington[34] had used the same method to form [{(THF)WCl_4}$_2$(μ-NC_6H_4N)] from [$WCl_4(THF)_2$].



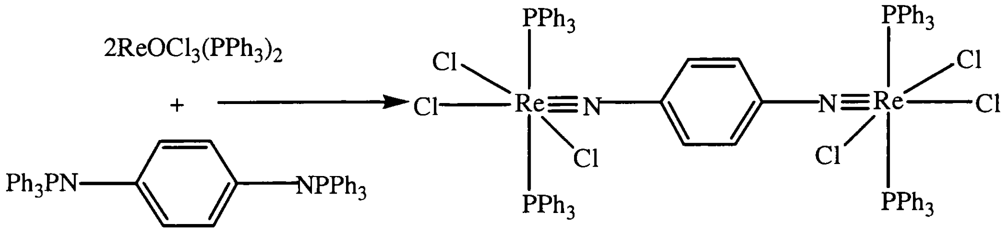
The same tungsten complexes had been prepared by the reaction of 1,4-phenylenediisocyanates and 1,4-phenylenedisulphinylimines with [$WOCl_4$][35] and the reaction of [WCl_6] with 1,4-bis(trimethylsilyl)phenylenediamine also afforded the same tungsten diimido complex.[36]



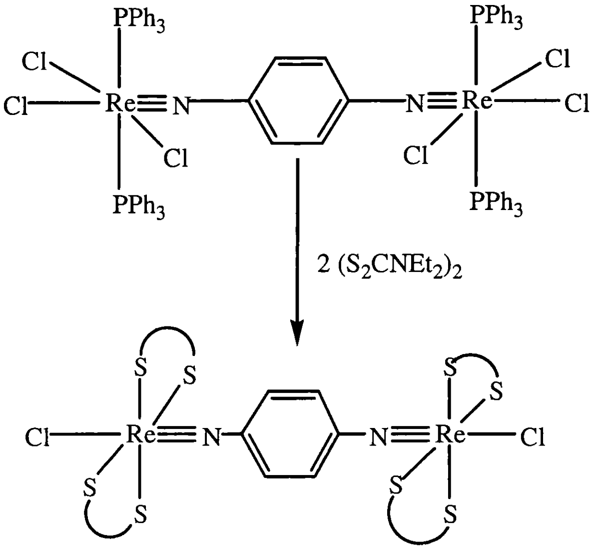
Hogarth *et al*[28] have prepared diimido complexes from diisocynates employing Mayer's route[37]. For example, air-stable, readily soluble green [{$(PMePh_2)_2WCl_2(CO)$}$_2$(μ-NC_6H_4N)] is formed cleanly and in high yield by the reaction of 1,4-phenylenediisocynate with [$WCl_2(PMePh_2)_4$] *via* oxidative addition. A number of tungsten diimido complexes [{$WCl_2(Ph_2PMe)_2(CO)$}$_2$(μ-N-X-N)] (NXN = *p*-N-*o*-MeC_6H_3N, *p*-N(*o*-$MeOC_6H_3C_6H_3OMe$-*o*)N, 1,5-$NC_{10}H_6N$ or *m*-NC_6H_4N) were prepared by the same method.[38]



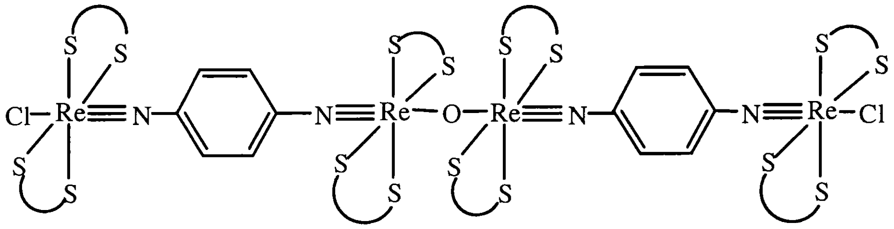
A bimetallic rhenium species $[\{ReCl_3(PPh_3)_2\}_2(\mu\text{-}NC_6H_4N)]$ was formed by treatment of $[ReOCl_3(PPh_3)_2]$ with 1,4-phenylenebis(triphenylphosphoranimine), $Ph_3P{=}NC_6H_4N{=}PPh_3$.[27] Here, phosphine oxide is lost and the oxidation state of the metal remains unchanged.



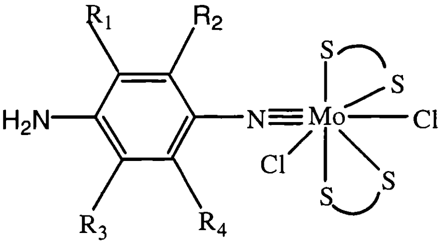
Two chloride and two phosphine ligands at each rhenium centre can be substituted by treatment under reflux with tetraethylthiuram sulphide to give a tetrakis(diethyldithiocarbamate) species.



Further treatment under reflux in the presence of NaOH afforded an insoluble oxo-bridged complex.



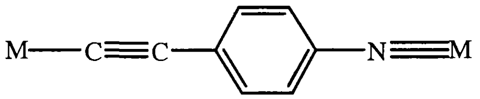
Hogarth *et al.* have prepared [{Mo(η^2-S_2CNEt_2)$_2$$Cl_2$}$_2$($\mu$-1,5-$NC_{10}H_6N$)] and [{Mo($S_2$)($\eta^2$-$S_2CNEt_2$)$_2$}$_2$($\mu$-*p*-$NC_6H_4N$)] by reaction of the appropriate diamine and diisocynate with two equivalents of [$MoOCl_2$(η^2-S_2CNEt_2)$_2$].[37] A number of imido complexes were also prepared by direct reaction of amine with [$MoOCl_2$(η^2-$SCNEt_2$)$_2$].



It is found that the amine lone pair is delocalised *via* the π-conjugated aryl group onto the electron deficient molybdenum (VI) centre. This deactivates the free amine in binding with the second molybdenum centre and seems to suggest that if a diimido molybdenum complex was made the high valent metal centres are strongly communicating *via* the π-conjugated linking unit. This phenomenon was found in 1964 by Chatt and co-workers during their studies on the synthesis of rhenium (V) imido complexes. Only *para*-amino-substituted imido complex [Re(*p*-$NC_6H_4NH_2$)Cl_3(PEt_2Ph)$_2$] was prepared by reaction of *para*-phenylene diamine with [$ReOCl_3$(PEt_2Ph)$_2$].[40] However, a marked contrast is observed to the oxidative addition of isocyanates to the tungsten (II) centre, where the second isocyanate is activated upon coordination of the first to a tungsten (IV) centre.[38] For molybdenum diimido complexes, only [{$MoCl_2$(η^2-S_2CNEt_2)$_2$}(μ-1,5-$NC_{10}H_6N$)] was isolated and this probably suggests that little deactivation occurs through this organic spacer group.

2.5 Our strategy

The aim of this project was to link low and high valent metal centres together *via* acetylide and imido linkages as shown below:



The simplest spacer group would be for example, a benzene ring. Therefore, *para*-ethynylaniline was chosen as our building block in linking both low and high valent metal centres. There are many ways in preparing this organic molecule. We have chosen an economical synthetic route derived by Melissaris and Litt[39] in the preparation of *para*-ethynylaniline. It involves a three-step synthesis starting from *para*-iodoaniline, namely the protection of amine with two-fold excess of trifluoroacetic anhydride, the coupling reaction of aryl iodide with 2-methyl-3-butyn-2-ol using $[Pd(PPh_3)_2Cl_2]$ and CuI in an amine solvent and the deprotection of the acetylene and the amine under distillation conditions in the presence of KOH pellets in iso-propyl alcohol.

para-Ethynylaniline can potentially bind to a low valent metal centre such as platinum to give platinum σ-bis(acetylide) complexes in both *cis*- and *trans*-fashion. This in turn can bind to high valent metal centres such as molybdenum and rhenium. The bis(acetylide) complexes have amines on each end and can be linked *via* imine and amide linkages. Metal fragments such as ferrocene can be incorporated, for example *via* imine linkages.

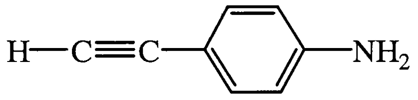
Results and Discussion

2.6 Synthesis of *para*-amino acetylenes

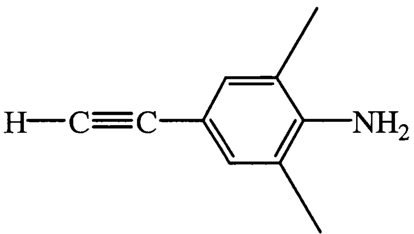
para-Ethynylaniline **1** can be synthesised in a number of ways, however, in most laboratories two methods are commonly empolyed. The first requires two steps, namely; the coupling of *para*-iodoaniline and trimethylsilylacetylene in the presence of [$PdCl_2(PPh_3)_2$] and CuI followed by removal of the silyl group upon treatment with dilute aqueous potassium hydroxide. However, trimethylsilylacetylene is expensive and the highest obtainable yield is 79%.[40]

As highlighted in the introduction, the second method developed by Melissaris and Litt[39] is a three-step reaction starting from *para*-iodoaniline. This involves the use of 2-methyl-3-butyn-2-ol which is cheap and the highest obtainable yield is 98%.

We chose the second method for the preparation of *para*-ethynylaniline **1** but in our experience, it was synthesised in around 50% overall yield. The most problematic step was the flash chromatography at 0°C after deprotection. As the product was only slightly soluble in dichloromethane, it was poured into the column as a suspension and this blocked the column. Compound **1** filtered through silica very slowly and the colour changed from pale yellow to brown suggesting hydrolysis or self-polymerisation. *para*-Ethynylaniline **1** was obtained as a yellow crystalline powder which was stored in the freezer. It was easily identified by spectroscopic methods. The $\nu(C{\equiv}C)$ stretch appeared at 2098 cm^{-1} in the IR spectrum, while the acetylenic proton appeared at δ 2.95 as a sharp singlet and the amine appeared as a broad singlet at δ 3.8 in ^1H NMR spectrum. It was recrystallised from hot toluene to afford pale brown block-shaped crystals.



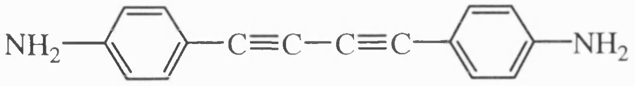
1



2

We attempted to prepare *para*-ethynyl-2,6-dimethylaniline **2** by the same method. This synthesis also involved a three-step reaction. The first two steps which involve the protection of amine and the coupling of aryl bromide with 2-methyl-3-butyn-2-ol were very successful. N-trifluoroacetyl-4-iodo-2,6-dimethylaniline **2a** was obtained as a tan powder in 99% yield. In the ^1H NMR spectrum, a broad singlet at δ 7.42 was assigned to the protected amine. 4-{N-(Trifluoroacetyl)-2,6-dimethylanilin-4-yl}-2-methyl-3-butyn-2-ol **2b** was then obtained as a yellow solid in 99% yield. In ^1H NMR spectrum, a broad singlet appearing at δ 7.60 was assigned to the protected amine, another broad singlet at δ 2.09 to the hydroxyl group and a sharp singlet at δ 1.61 to the methyl group on the acetylene. However, the last step, namely the deprotection of the amine and acetylene, was always incomplete. A 1:1 ratio of **2** and $HC{\equiv}CC_6H_2(CH_3)_2NHCOCF_3$ was found in ^1H NMR spectrum. There were two singlets at δ 3.10 and δ 2.95 which means that there were two terminal acetylenes. A broad singlet at δ 7.42 was assigned to the protected amine while another broad singlet at δ 3.57 corresponded to the free amine. The mass spectrum showed the molecular ion at *m/z* 145. Higher temperatures may be required to fully deprotect both ends of **2b** as the amine proton is now hindered by the methyl groups *ortho* to it. However at these elevated temperatures the risk of self-polymerisation is high and thus this synthesis was not pursued further.

The homo-coupling of *para*-ethynylaniline **1** to produce a diyne was not straight-forward. We attempted this using copper (II) acetate in a methanol-pyridine mixture[41] and also *via* use of a catalytic amount of copper (I) salt.[42] However, under both conditions, a mixture of **1** and a second compound (presumed to be the diyne) was produced. Since water might have poisoned the copper catalyst, we carried out the reaction in dry pyridine in the presence of copper (I) chloride. Diyne **3** was produced as an orange powder in 14% yield. Schaefer and Marsh have prepared $O_2NC_6H_4(C{\equiv}C)_nC_6H_4NH_2$ (n = 0-3) as orange/red solids in 36-53% yield *via* the use of the Hay catalyst[43] (Cu (I) chloride and dry pyridine) while Chang *et al*[44] have coupled **1** with 4-(octyloxy)phenylacetylene or 1-octyne in the presence of Eglinton's copper (II) acetate-pyrindine/methanol mixture to produce unsymmetrical diyne. Diyne **3** gave a molecular ion in the mass spectrum and the aryl protons *ortho* to the amine appeared at a higher field δ 6.70-6.60, in ^{1}H NMR spectrum.



3

2.7 Synthesis of σ-acetylide transition metal complexes

Our aim was to synthesise a number of transition metal σ-acetylide complexes by incorporation of low valent metal centres onto *para*-ethynylaniline **1**. Collamati and Furlani[45] had prepared *cis*- and *trans*-$[Pt(PPh_3)_2(C{\equiv}CPh)_2]$ using sodium metal and liquid ammonia, while Nagihara *et al.*[46] have produced *cis*- and *trans*-$[Pt(P^nBu_3)_2(C{\equiv}CPh)_2]$ using CuI and NEt_2H. We chose the latter method which produced *trans*-$[Pt(PR_3)_2(C{\equiv}CC_6H_4NH_2)_2]$ (R = Ph **4**, ^{n}Bu **5**) in good yield. These phosphines were chosen because it was easier to crystallise the complex containing triphenylphosphine and to examine its structure whereas tributylphosphine helped to increase the solubility of the complex in most organic solvents. In both **4** and **5**, the ν(C≡C) stretch appeared at a higher wavenumber 2105 and 2100 cm^{-1} respectively in the IR spectrum which is typical for metal acetylide. In ^{1}H NMR spectrum, the doublets assigned to the aromatic protons on the acetylide became closer to each other and were shifted upfield with respect to the free ligand in both complexes. Complex **4** was recrystallised from a saturated chlorobenzene solution to give brown block-shaped crystals. The X-ray crystal structure was carried out by Hirihattaya (Taya) Phetmung and Professor A. G. Orpen of the University of Bristol, the results of which are summarised in Figure 2-1.

Pt(1)-P(1)	2.310(1) Å
C(1)-C(2)	1.206(6) Å
Pt(1)-C(1)-C(2)	177.00(37)°
C(1)-C(2)-C(3)	175.24(46)°
P(1)-Pt(1)-C(1)	88.83(12)°

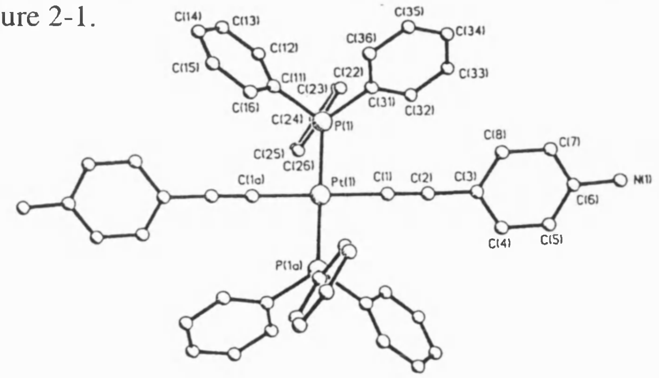
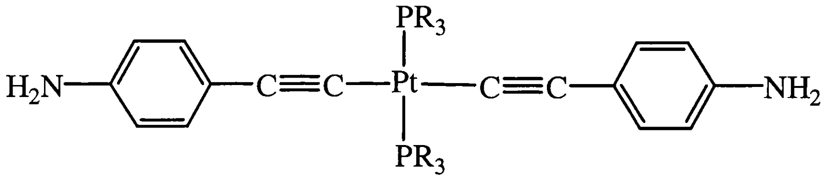


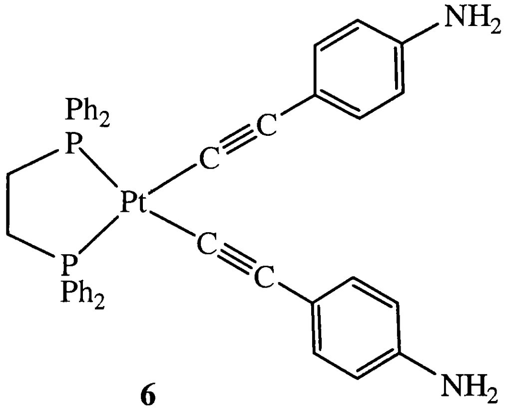
Fig.2-1 The crystal structure of *trans*-$[Pt(C{\equiv}CC_6H_4NH_2)_2(PPh_3)_2]$ **4** with selected bond lengths and angles.

The complex has an inversion centre and shows the expected *trans* arrangement of acetylides. The short C(1)-C(2) bond 1.206(6)Å is within the range found in related platinum (II) acetylide complexes[46-49] and the Pt(1)-P(1) bond is 2.310(1)Å. The acetylide ligand is essentially linear [Pt(1)-C(1)-C(2) 177.00(37), C(1)-C(2)-C(3) 175.24(46)°] and the bond angle between the phosphine and acetylide ligands [P(1)-Pt(1)-C(1) 88.83(12)°], is as expected for a square planar Pt(II) centre. The molecule co-crystallises with chlorobenzene but there are no short intermolecular contacts. As far as we are aware, the unsubstituted phenylacetylide complex *trans*-$[Pt(PPh_3)_2(C{\equiv}CPh)_2]$ has not been crystallographically characterised, although its *cis*-isomer has been analysed by an X-ray study[46] and there appear to be no significant differences in the structural parameters of this and **4**.



4, R=Ph; **5**, R=^{n}Bu

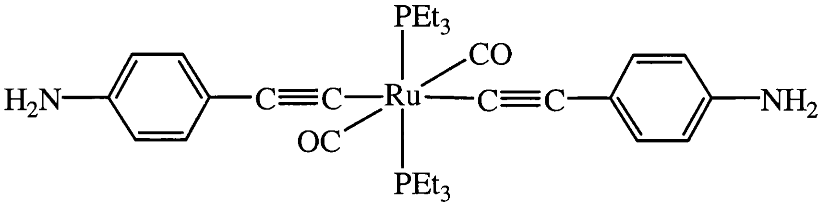
In the preparation of **4** and **5**, even though the starting material was *cis*-$[PtCl_2(PR_3)_2]$, the product was always a *trans*-complex. This is because *trans*-bis(acetylide) complexes are thermodynamically more stable than the *cis*-isomers. Therefore, if we want to prepare a *cis*-platinum bis(acetylide) complex, we need to "lock" the geometry around the metal centre by introducing a chelating ligand such as bis(diphenylphosphino) ethane (dppe). We tried preparing *cis*-$[Pt(\eta^2\text{-dppe})(C{\equiv}CC_6H_4NH_2)_2]$ **6** by the same method as we used to for **4** and **5**, however, the reaction was incomplete even when higher temperatures were used. An orange solid was obtained and the FAB mass spectrum showed an ion at *m/z* 887 consistent with the incorporation of Cu^+. The binding of copper (I) to bis(acetylide) units is well known[50] and in order to produce **6** cleanly, more forcing conditions were required. We chose the Hackett and Whitesides'[51] method, treating **1** with ^{n}butyllithium followed by a metathesis reaction between the lithium acetylide and *cis*-$[PtCl_2(\eta^2\text{-dppe})]$. This afforded **6** as a yellow powder in 36% yield. In the IR specrtum, the $\nu(C{\equiv}C)$ stretch appeared at 2108 cm^{-1} and in ^1H NMR spectrum the aromatic protons appeared as two doublets at δ 6.61 and δ 6.46, being shifted upfield with respect to **1**. The mass spectrum showed a molecular ion at *m/z* 826.



6

The ^{31}P NMR spectra of *cis*-[$PtCl_2(PPh_3)_2$], *cis*-[$PtCl_2(\eta^2$-dppe)] and complexes **4-6**, each show a singlet and a small doublet (Pt satellites). The latter arises as 33.3% of the platinum is ^{195}Pt which has a spin of 1/2 and thus couples with the two phosphorus atoms to give a doublet. The coupling constant (J_{Pt-P}) is very dependent upon the *trans* ligand. Since *cis*-[$PtCl_2(PPh_3)_2$] (J_{Pt-P} 3672 Hz) and *cis*-[$PtCl_2(\eta^2$-dppe)] (J_{Pt-P} 3617 Hz) have large values, the *trans* ligand (chlorides) must have a low *trans*-influence and therefore a short Pt-P bond. Similarly, the coupling constants for complexes **4-6** were smaller (J_{Pt-P} 2257 – 2660 Hz) which suggests that the *trans* ligand (phosphine or acetylide) has a stronger *trans*-influence and leading to a longer Pt-P bond.

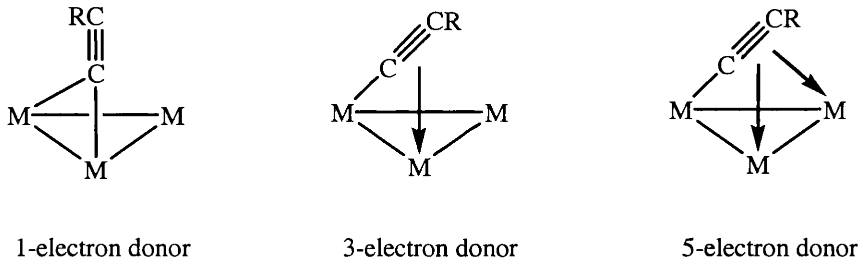
The ruthenium bis(acetylide) complexes *trans*-[$Ru(CO)_2(PEt_3)_2(C{\equiv}CPh)_2$] and *trans*-[$Ru(CO)_2(PEt_3)_2(C{\equiv}CH)_2$] have been synthesised by Sun, Taylor and Carty[52]. They were prepared by reacting HC≡CPh or HC≡CH respectively with ^{n}butyllithium to form lithium acetylide followed by a metathesis reaction with *trans*-[$RuCl_2(CO)_2(PEt_3)_2$]. We adopted this method in order to prepare *trans*-[$Ru(CO)_2(PEt_3)_2(C{\equiv}CC_6H_4NH_2)_2$] **7**. It was obtained as a sticky orange mass in *ca.*25% yield after chromatography. We were unable to produce an analytically pure sample, however, strong C≡C and CO bands at 2035 and 1972 cm^{-1} respectively in the IR spectrum were observed which are characteristic of this type of complex. For example, the C≡C and CO bands of *trans*-[$Ru(CO)_2(PEt_3)_2(C{\equiv}CPh)_2$] appear at 2093 and 1987 cm^{-1}.



7

2.8 Reaction of *para*-ethynylaniline and trinuclear metal cluster

We have carried out the reaction of **1** and $[Ru_3(CO)_{12}]$. This allows us to investigate the relative reactivity of the different metal binding sites of **1** as an acetylide[53], amide and imido[54], acetylene[55] and arene.[56] An acetylide can bind to a trinuclear metal cluster *via* three different modes as it can act as 1, 3 (1σ, 1π) or 5 (1σ, 2π) electron donor as shown below[57]:-



When $[Ru_3(CO)_{12}]$ and **1** were heated in heptane for 8 hours chromatography on alumina gave a number of products the major one being $[(\mu\text{-H})Ru_3(CO)_9(\mu^3\text{-}C{\equiv}CC_6H_4NH_2)]$ **8** in 24% yield. There were four ν(CO) stretches in the IR spectrum. The aromatic protons on the acetylide shifted downfield slightly in the ^1H NMR spectrum, as were the protons on the amine. A signal also appeared at δ -20.41 and was assigned to the bridging hydride. The mass spectrum showed the molecular ion at *m/z* 673. Complex **8** was crystallised from a saturated solution of hexane. An X-ray crystallographic study was carried out the results of which are summarised in figure 2-2.

Ru(1)-C(10)	1.969(4) Å
Ru(2)-C(10)	2.221(4) Å
Ru(3)-C(10)	2.224(4) Å
Ru(2)-C(11)	2.318(4) Å
Ru(3)-C(11)	2.297(4) Å
C(10)-C(11)	1.314(6) Å
C(1)-C(2)	1.206(6) Å
C(10)-C(11)-C(12)	145.5(4)°
C(1)-C(2)-C(3)	175.24(46)°

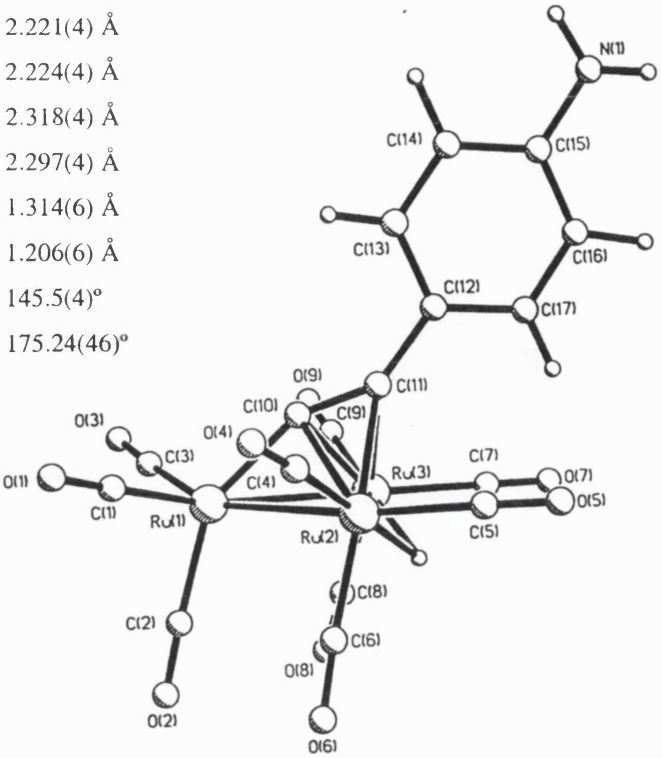
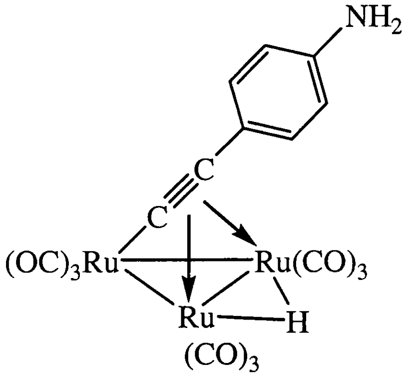


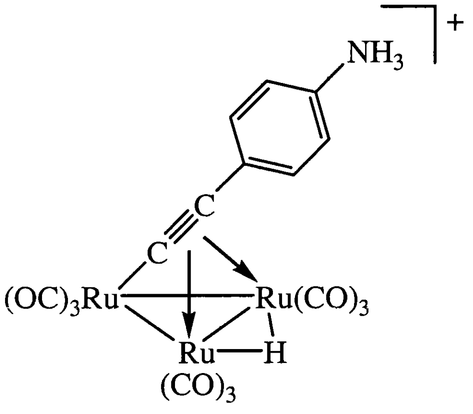
Fig.2-2 The crystal structure of $[(\mu\text{-H})Ru_3(CO)_9(\mu^3\text{-C}{\equiv}CC_6H_4NH_2)]$ **8** with selected bond lengths and angles.

The ruthenium triangle is capped by the 5-electron acetylide ligand, the α-carbon of which binds to all three metal centres [Ru(1)-C(10) 1.969(4), Ru(2)-C(10) 2.221(4), Ru(3)-C(10) 2.224(4) Å], while the β-carbon spans the Ru(2)-Ru(3) vector [Ru(2)-C(11) 2.318(4), Ru(3)-C(11) 2.297(4) Å]. The latter is also bridged by a hydride which lies approximately *trans-* to the α-carbon of the acetylide. As expected, the acetylenic bond is elongated upon π-coordination [**8**, C(10)-C(11) 1.314(6); **4**, C(1)-C(2) 1.206(6) Å] and also deviates significantly from linearity [**8**, C(10)-C(11)-C(12) 145.5(4); **4**, C(1)-C(2)-C(3) 175.24(46)°]. The *para*-aminophenyl substituent lies approximately perpendicular to a plane which includes Ru(1)-C(10) and C(11) and bisects Ru(2) and Ru(3) and the nitrogen is pyramidal as expected. General structural features of the $M_3(\mu^3\text{-}\eta^2\text{-perpendicular})$ acetylide ligand are as found in related trinuclear group 8 complexes[58] and the parent acetylide complex $[(\mu\text{-H})Ru_3(CO)_9(\mu^3\text{-C}{\equiv}CH)]$.[50]

Cluster **8** can potentially be protonated across the metal-metal bonds or at the amine functionality. A protonation study was carried out in order to investigate the preferred protonation site. Addition of CF_3CO_2H to a $CDCl_3$ solution or HBF_4 to a CH_2Cl_2 solution of cluster **8** afforded the ammonium salt $[(\mu\text{-H})Ru_3(CO)_9(\mu^3\text{-}C{\equiv}CC_6H_4NH_3)][X]$ **9**. In the ^1H NMR spectrum, the amine protons shifted downfield from δ 3.89 to 6.20 and integrated as three protons. The hydride resonance also shifted downfield from δ -20.41 to –6.47.



8

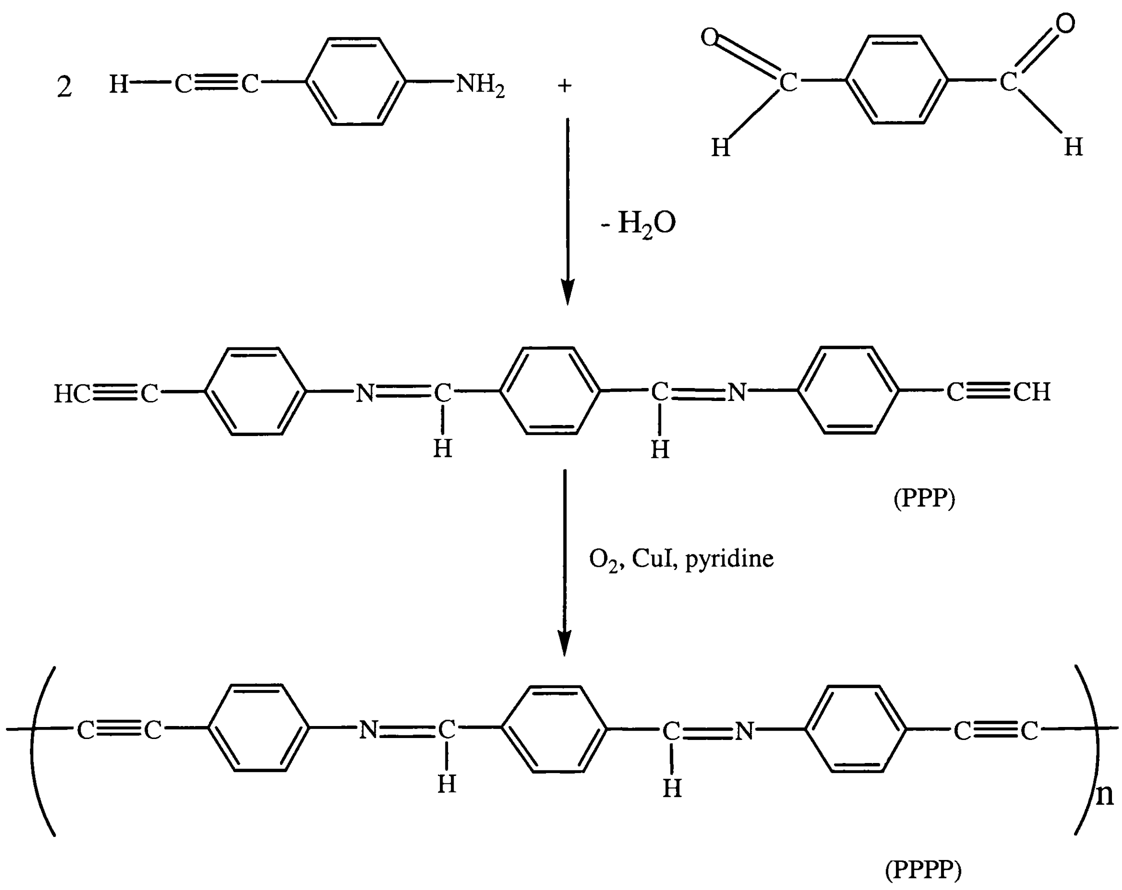


9

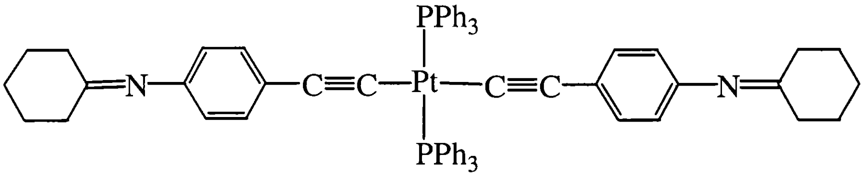
As far as we are aware, compounds **4-8** are the first examples where *para*-ethynylaniline **1** was bound to a metal or a cluster although soon after this was published, Paul and Lapinte[59] reported the series of iron complexes $[(\eta^2\text{-dppe})(\eta^5\text{-}C_5Me_5)Fe(C{\equiv}CC_6H_4X)]$ ($X = NO_2$, CN, CF_3, F, Br, H, Me, ^tBu, OMe, NH_2, NMe_2) which include the use of ligand **1**. Adams, Raithby and Yellowlees *et al.*[60] have also synthesised a series of related platinum complexes $[Pt(C{\equiv}CR)_2(^tBu_2bipy)]$ (bipy = bipyridyl; $R = C_6H_4NO_2\text{-p}$, C_6H_5, $C_6H_4CH_3\text{-p}$, $SiMe_3$).

2.9 Synthesis of imine linkages

As discussed earlier, following the preparation of metal σ-aryl acetylide complexes with an amino functionality, we went on to investigate ways of extending the chain length. Imines are formed by a reaction between an amine and an aldehyde or a ketone. Wei *et al.* [61] had produced a monomer, N,N'-(1,4-phenylenedimethylidyne)-bis-(4-ethynylaniline) (PPP) by reaction of **1** with terephthaldehyde and polymerising it using O_2 and CuI in pyridine to produce a new polymer (PPPP).

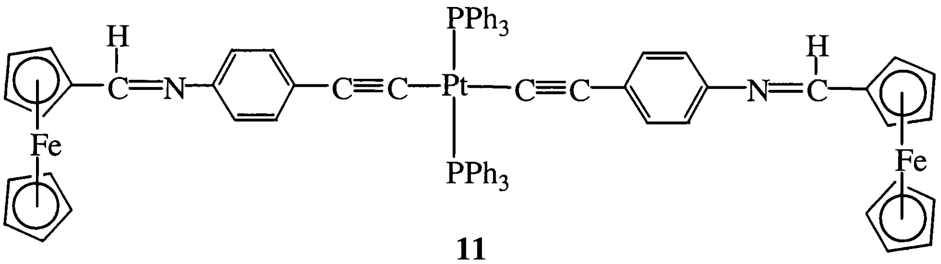


Water is produced as a side product in the preparation of imines. It is important to remove this as this increases the rate of reaction and prevents the reverse reaction (i.e. the reaction between the imine and water to produce amine and aldehyde or ketone). There are several ways to remove water from the reaction. For example, dehydration with potassium hydroxide, heat treatment under pressure, and water azeotrope in low boiling or high-boiling solvent.[62] Weingarten, Chupp and White[62] used $TiCl_4$ to remove water from the reaction effectively in the preparation of ketimines. However, this generates HCl which can react with carbon-carbon triple bond, and this cannot be employed in our reactions. Silver *et al.*[63] refluxed ferrocenecarbaldehyde with a base in toluene using Dean-Stark apparatus to form imine. Therefore, we reacted *trans*-$[Pt(PPh_3)_2(C{\equiv}CC_6H_4NH_2)_2]$ **4** and cyclohexanone as a test reaction in refluxing toluene in the presence of anhydrous $MgSO_4$. These reaction conditions are very mild and $MgSO_4$ is a good drying reagent. Reaction of **4** with cyclohexanone afforded an orange-brown solid *trans*-$[Pt(PPh_3)_2(C{\equiv}CC_6H_4N{=}C_6H_{10})_2]$ **10** in moderate yield. There are three ν(C=N) stretches in the IR spectrum and the ^{31}P NMR spectrum showed two sets of signals but in a 4:1 ratio suggesting that the 'up-down' configuration may be preferable to the 'up-up' configuration on steric grounds. The inversion of the nitrogen in imines is slow compared to the NMR timescale due to the restricted rotation at the double bond. Therefore, two sets of signals appeared even though there was only one type of compound in the NMR sample. In the mass spectrum a molecular ion was observed at *m/z* 1112.



10

One target was the incorporation of ferrocene into our compounds as we wanted to link electronically different metal centres together. Therefore, two equivalents of ferrocenecarboxaldehyde were added to **4** in refluxing toluene in the presence of $MgSO_4$ to produce *trans*-$[Pt(PPh_3)_2(C{\equiv}CC_6H_4N{=}CH\text{-}Fc)_2]$ **11** as an orange solid in 63% yield. There were again three ν(C=N) stretches in the IR spectrum and in ^{1}H NMR spectrum the imine protons appeared at δ 8.22. The aromatic protons on the acetylide appeared as two doublets at δ 6.75 and δ 6.29. The protons on the cyclopentadienyl ring attached to the imines appeared as triplets at δ 4.75 and δ 4.46, the free cyclopentadienyl rings, containing ten protons, appeared as a singlet at δ 4.22. In the mass spectrum a molecular ion was observed at *m/z* 1344.

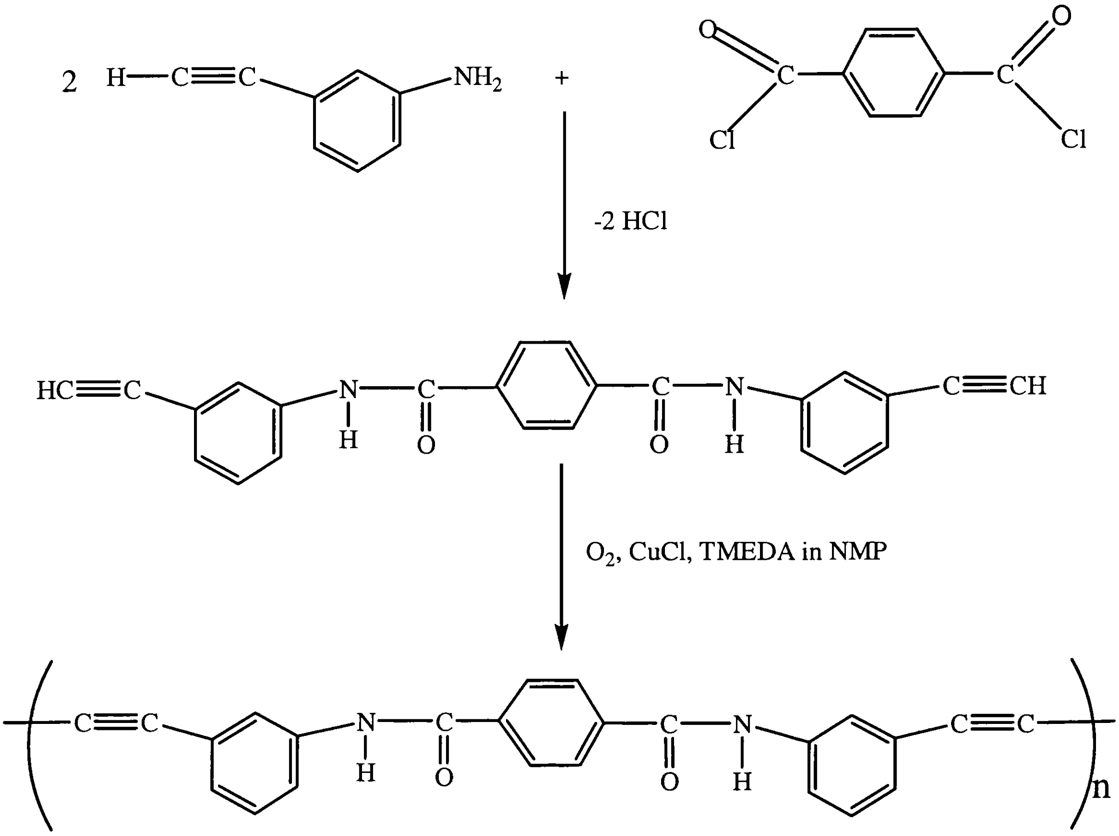


11

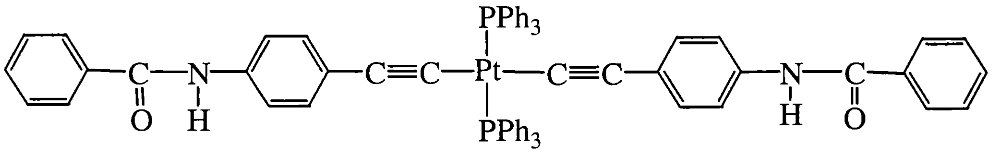
2.10 Synthesis of the amide linkages

The formation of amide allows the linking of metal fragments together by organic linkages. Amides can be easily produced by a condensation reaction between an amine and an acid halide or a carboxylic acid. Recently, Ogawa[64] *et al.*

have produced some cross-polymerised polymer which included acetylene group and amide linkage as shown below:

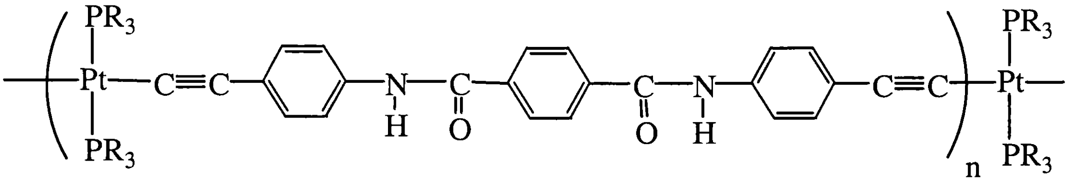


Dembek *et al.*[65] reacted (*p*-phenylenediamine)Cr(CO)$_3$ with terephthaloyl chloride in *N*,*N*-dimethylacetamide to afford an amide-linked polymer with molecular weight of 78,000. We adopted this idea and reacted *trans*-[Pt(PPh$_3$)$_2$(C≡CC$_6$H$_4$NH$_2$)$_2$] **4** with two equivalents of benzoyl chloride in the presence of base to produce *trans*-[Pt(PPh$_3$)$_2${C≡CC$_6$H$_4$NHC(O)Ph}$_2$] **12** in 92% yield. A base was required as HCl was produced in the reaction which would react with the carbon-carbon triple bond. In the ^{31}P NMR spectrum two signals of approximately equal intensity were observed at 28.2 ($J_{\text{Pt-P}}$ 2651) and 27.7 ($J_{\text{Pt-P}}$ 3000 Hz) ppm and these are attributed to *rac* (+ +) and *meso* (+ -) conformations at nitrogen. Similarly, there were two ν(CO) stretches in the IR spectrum. However, only one pair of aromatic doublets was observed in the ^{1}H NMR spectrum. This is probably due to accidental coincidence of the signals.



12

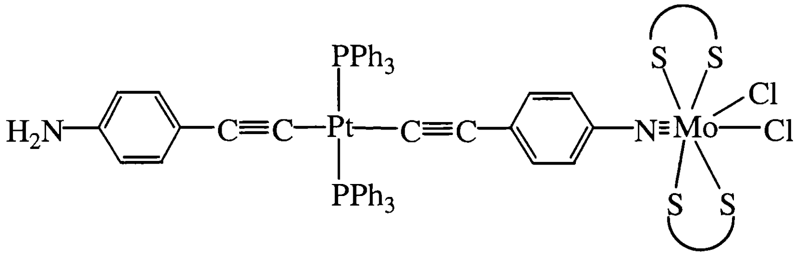
Reaction of terephthaloyl chloride and **4** afforded an insoluble yellow powder *trans*-$[Pt(PPh_3)_2\{C{\equiv}CC_6H_4NHC(O)C_6H_4C(O)NHC_6H_4C{\equiv}C\}]_2$ **13** in 65% yield. Due to the insolubility of **13**, we were unable to obtain meaningful NMR spectra. Further, the mass spectrum was not helpful in characterising the compound. Elemental analysis showed 2.09% of chlorine and based on the assumption that the ends of all molecules have a chlorine atom then the average molecular weight is *ca.* 3400 g, i.e.two monomer units (1443 g). Thus, we believe that **13** is an oligomer, produced by preciptation due to its insolubility. In order to produce soluble polymers, *trans*-$[Pt(P^nBu_3)_2(C{\equiv}CC_6H_4NH_2)_2]$ **5** was reacted with terephthaloyl chloride in the same manner to produce *trans*-$[Pt(P^nBu_3)_2\{C{\equiv}CC_6H_4NHC(O)C_6H_4C(O)\text{-}NHC_6H_4C{\equiv}C\}]_3$ **14** in 95% yield. Now, elemental analysis showed 1.86% of chlorine and based on the same assumption as above, the average molecular weight is *ca.* 3800 g, i.e. three and a half monomer units (961 g). This reaction was rather disappointing as **14** was still insoluble in common organic solvents and was precipitated out as oligomers. **14** was however, slightly soluble in DMF and a ^{31}P NMR spectrum showed a singlet and a small doublet (Pt satellites) at 4.02 ($J_{Pt\text{-}P}$ 2361 Hz) ppm implying a *trans*-arrangement around the platinum centre.



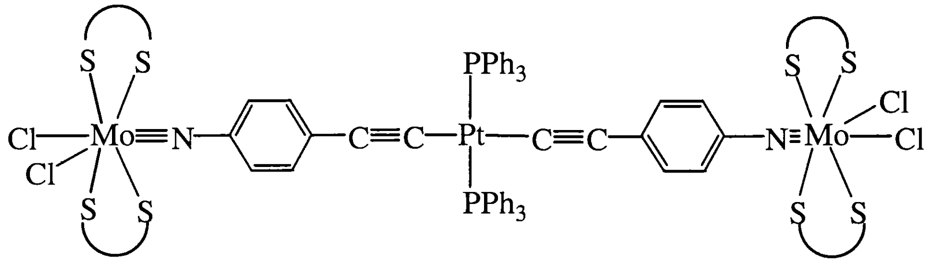
13, PPh_3; **14**, P^nBu_3

2.11 Attempted synthesis of imido and diimido complexes

As highlighted earlier, there are many ways of preparing imido complexes. We have utilised two of the methods in the preparation of molybdenum and rhenium imido complexes. Minelli *et al.*[66] first reported the synthesis of a molybdenum (VI) imido complex using an amine as starting material. Refluxing [MoOCl$_2$(η^2-S$_2$CNEt$_2$)$_2$] with 1,2-phenylene diamine in the presence of triethylamine in methanol produced [Mo(*ortho*-NC$_6$H$_4$NH$_2$)Cl$_2$(η^2-S$_2$CNEt$_2$)$_2$]. We adopted this method in order to prepare imido complexes. Reaction of **4** and two equivalents of [MoOCl$_2$(η^2-S$_2$CNEt$_2$)$_2$] in methanol afforded an orange-brown powder **I**. In the IR spectrum an imido stretch ν(Mo≡N) or ν(N-C) was observed at 1278 cm^{-1}. In the ^{31}P NMR spectrum two sets of peaks, which were not the starting material, were observed. This suggests that **(I)** is composed of two compounds **Ia** and **Ib** at 21.24 and 28.36 ppm in a ratio of 3:1. The J_{Pt-P} values of **Ia** and **Ib** in the ^{31}P NMR were large (J_{Pt-P} 3266 and 3026 Hz) respectively. These large values suggest that the imido linked acetylide ligands have a low *trans*-influence effect and the Pt-P distance is short. The high-valent molybdenum centre(s) are now highly electron-withdrawing whereas the acetylide ligands on their own are electron-donating. This changes the *trans*-influence of the ligand from high to low and therefore the J_{Pt-P} values change from small to large. This is important evidence to show that imido complexes were made. **Ia** and **Ib** are probably mono- and di-imido complexes formed in the reaction. In the mass spectrum, [Mo(NC$_6$H$_4$C≡C)(η^2-S$_2$CNEt$_2$)$_3$Cl]$^+$ and [Mo(NC$_6$H$_4$C≡C)(η^2-S$_2$CNEt$_2$)$_2$Cl]$^+$ ions were observed at *m/z* 690 and 542. However, ^{1}H NMR and analytical data proved confusing and this was not pursued further.

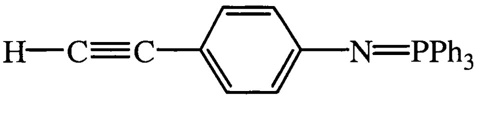


Ia



Ib

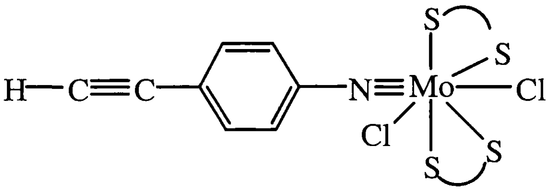
Since it was difficult to separate **Ia** and **Ib**, we attempted the reaction of **1** and $[MoOCl_2(\eta^2\text{-}S_2CNEt_2)_2]$. Addition in methanol afforded a sticky red solid **IIa**. However, spectral data was confusing and we were unable to conclude whether imido complex was made or not. Haymore, Wentworth and Maatta[67] refluxed $[MoOCl_2(S_2CNEt_2)_2]$ and $PhNPPh_3$ in toluene for 3 hours to produce $[Mo(NPh)Cl_2(S_2CNEt_2)_2]$. In order to obtain the desired product, the phosphorimine $Ph_3P{=}NC_6H_4C{\equiv}CH$ **15** was prepared as a yellow powder in quantitative yield from the reaction of **1** and Ph_3PBr_2 in toluene in the presence of NEt_3.



15

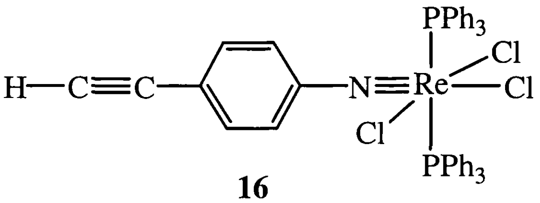
In the IR spectrum a strong peak at 1327 cm^{-1} was assigned to $\nu(P{=}N)$ stretch. In ^1H NMR spectrum the amine protons had disappeared and the phenyl protons appeared at the aromatic region (δ 7.77-7.43). In ^{31}P NMR a broad singlet appeared at 10.6 ppm showing that there is only one product from the reaction, while the mass spectrum showed a molecular ion at *m/z* 377. Reaction of **15** and $[MoOCl_2(\eta^2\text{-}S_2CNEt_2)_2]$ in refluxing toluene afforded a sticky red solid **IIb**. Attempts to remove the side-product $PPh_3{=}O$ were unsuccessful and we were unable to interpret the

NMR spectra. In the IR spectrum a strong peak at 1277 cm^{-1} again suggested formation of an imido ligand. However, this is the only evidence we have that an imido complex was made. We believe that imido complexes were made in both attempts to prepare **II** as the molybdenum oxo stretch was not observed in the IR spectrum. Further, the starting material $[MoOCl_2(\eta^2\text{-}S_2CNEt_2)_2]$ is an insoluble yellow solid and in both cases the reaction changed from yellow to red solutions, the majority of $[Mo(NAr)Cl_2(\eta^2\text{-}S_2CNEt_2)_2]$ are obtained as oily red solids[26] and it seems that **II** was probably produced in both reactions.



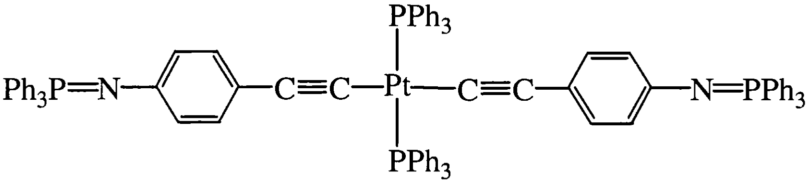
II

Rhenium (V) imido complexes are easily prepared from *mer,trans*-$[ReOCl_3(PPh_3)_2]$ and amine or phosphorimine.[68] Heating a toluene solution of *mer,trans*-$[ReOCl_3(PPh_3)_2]$ and **1** in the presence of PPh_3 afforded a brown precipitate, believed to be $[ReCl_3(PPh_3)_2(NC_6H_4C{\equiv}CH)]$ **16** in 81% yield. Due to the insolubility of this compound it was impossible to obtain meaningful NMR spectra. The mass spectrum showed the molecular ion at *m/z* 932 and the elemental analysis was in good agreement with the theoretical values.



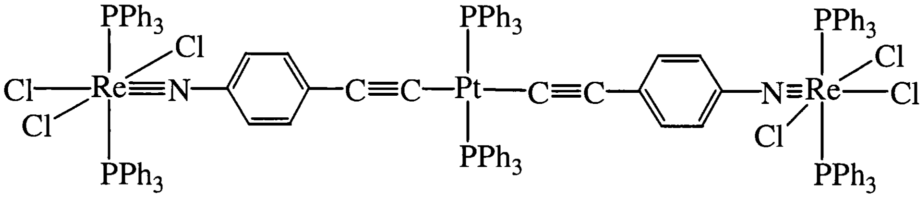
16

Haymore *et al.*[69] refluxed *mer,trans*-$[ReOCl_3(PPh_3)_2]$ and p-$CH_3C_6H_4N{=}PPh_3$ in benzene for 10 minutes to produce $[Re(NC_6H_4p\text{-}CH_3)Cl_3(PPh_3)_2]$. Therefore, the phosphorimine *trans*-$[Pt(PPh_3)_2(C{\equiv}CC_6H_4N{=}PPh_3)_2]$ **17** was prepared in 65% yield in order to prepare imido complex. Reaction of **4** and two equivalents of Ph_3PBr_2 in refluxing toluene afforded **17** as a yellow-orange solid. In ^1H NMR spectrum, there was no amine signal but more phenyl protons instead which appeared at the aromatic region δ 7.80-7.28. In the ^{31}P NMR spectrum, a broad singlet was observed at 7.3 ppm which suggests that only one compound was made. The mass spectrum showed the molecular ion at *m/z* 1473.



17

Reaction of **17** with two equivalents of *mer,trans*-[$ReOCl_3(PPh_3)_2$] afforded a sparingly soluble orange solid believed to be *trans*-[$Pt(PPh_3)_2\{C{\equiv}CC_6H_4N{\equiv}ReCl_3(PPh_3)_2\}_2$] **18** in 89% yield. Due to the low solubility of this compound we were unable to get meaningful NMR data. In the mass spectrum the heaviest ion was seen at *m/z* 2547 and corresponds to loss of chloride. Elemental analysis was in good agreement with the theoretical values. Complex **18** contains two Re(V) centres linked *via* a diimido ligand which includes a Pt(II) centre. A number of related diimido linked compounds have shown that the two high-valent metal centres can communicate electronically through the π-conjugated ligand by electrochemical measurements.[37] Unfortunately, due to the low solubility of **18** in common organic solvents, electrochemical measurements were not possible and therefore we are unable to investigate whether there is communication between the metal centres. As mentioned in the introduction, one way to improve the solubility of these rhenium imido complexes was to substitute two chloride and two phosphine ligands at each rhenium centre by diethyldithiocarbamate ligands. This should help characterising the species formed and electrochemical measurements may be possible



18

Since imido complexes can be easily hydrolysed one way to prevent this is to have a system where two methyl groups are *ortho* to the imido linkage. Therefore, attempts to prepare *para*-ethynyl-2,6-dimethylaniline **2** were made. However, since we were unable to isolate **2** pure, we were unable to incorporate this ligand.

2.12 Conclusions

We have shown that *para*-ethynylaniline can successfully be bound to low valent metal centres to form acetylide complexes. However, coordination of high valent transition metals to the amino groups *via* imido linkages was more problematic. Such complexes have poor solubility and stability which made full characterisation difficult. Attempts to prepare stable imido complexes by inserting methyl groups *ortho* to the imido linkages were unsuccessful as such amine precursor could not be isolated in high yield. Attempts to link the acetylide complexes *via* amide linkages were also unfavourable due to the insolubility of the compound and the precipitation of oligomers. Changing the ancillary ligands from PPh_3 to P^nBu_3 in order to improve the solubility of the compounds was disappointing. Oligomerisation still occurred through precipitation. Therefore, we abandoned this line of work. On a positive side, the extension of the chain length of a platinum (II) complex by incorporation of electrochemically important ferrocene units through imine linkages was favourable giving a soluble and stable complex. This suggests that organometallic polymers may be achieved based on this approach.

2.13 Experimental

Purification of para-Iodoaniline

para-Iodoaniline(25.0 g) was dissolved in a minimum amount of diethyl ether and was poured onto a chromatography column packed with silica and a 4:1 ratio of light petroleum(40-60)/diethyl ether eluent. The column was eluted with the same eluent until a yellow band and a colourless band were collected leaving the pink and purple impurities behind. The fractions were evaporated to dryness on a rotary evaporator. Pure *para*-iodoaniline (24.98 g, 99.9%) was obtained.

Synthesis of N-trifluoroacetyl-4-iodoaniline (1a)

para-Iodoaniline (24.98 g, 0.114 mol) was placed into a Schlenk tube under nitrogen. THF (150 cm^3) was added to form a clear dark red solution. Trifluoroacetic anhydride (31.87 cm^3, 0.228 mol) was added dropwise via a syringe at 0°C over 20 minutes. The reaction mixture was left stirring at room temperature overnight. The solvent was evaporated under reduced pressure until an off-white solid was obtained. The solid was washed with distilled water, filtered, and then dried under vacuum. Compound **1a** was obtained as off-white flakes (36.97 g, 99%). ^{1}H NMR ($CDCl_3$): δ 7.84 (bs, 1H, NH); 7.76 (d, J_{H-H} = 8.6 Hz, 2H, Ar); 7.34 (d, J_{H-H} = 8.6 Hz, 2H, Ar).

Synthesis of 4-{N-(trifluoroacetyl)anilin-4-yl}-2-methyl-3-butyn-2-ol (1b)

1a (36.97 g, 0.117 mol), copper(I)iodide (0.19 g, 1.02 mmol), triphenylphosphine (0.74 g, 2.82 mmol) and 2-methyl-3-butyn-2-ol (25.04 g, 0.298 mol) were placed into a two-necked 500 cm^3 round bottom flask with dried triethylamine (250 cm^3). The reaction mixture was stirred under nitrogen at 50°C. Dichlorobis(triphenylphosphine)palladium (0.195 g, 0.277 mmol) was then added and was left to stir at 50°C for 20 minutes under nitrogen. After that, it was further refluxed for another 20 minutes. It was then cooled to room temperature and a yellow solution with a lot of precipitate was obtained. Diethyl ether was added to the mixture for further precipitation. The mixture was then filtered leaving a white residue behind. The solid was washed with diethyl ether again and the filtrates were combined. The filtrate was evaporated to dryness under reduced pressure. Since the product came out fairly viscous, acetic acid (100 cm^3) was added to the solid in an ice bath. The mixture smoked immediately. It was left stirring at room temperature and a brown solution was obtained very slowly. The solution was pumped under reduced pressure to give a sticky reddish brown solid. Distilled water (300 cm^3) was then added and the mixture was stirred and scraped. An orange powder in a yellow solution was formed which was filtered and air-dried leaving **1b** (31.83 g, 99%) behind. ^{1}H NMR ($CDCl_3$): δ 7.53 (d, J_{H-H} = 8.6 Hz, 2H, Ar), 7.42 (d, J_{H-H} = 8.6 Hz, 2H, Ar); 1.60 (s, 6H, Me).

Synthesis of para-ethynylaniline (1)

KOH pellets (16.44 g, 0.294 mol) were added to ^{i}PrOH (200 cm^3) in a two-necked round bottom flask connected to a water-condenser. The mixture was refluxed and **1b** (31.83 g, 0.117 mol) was added to the refluxing solution. The mixture was refluxed for 2.5 hours. It was then cooled to room temperature and pumped to dryness under reduced pressure. The brown solid obtained was washed with cold hexane, filtered and air-dried. It was then stirred in dichloromethane (400 cm^3) for an hour and filtered. The filtrate was poured onto a water jacket chromatography column that was packed with silica and eluted with dichloromethane. The yellow band was collected at 0°C and the solvent was pumped to dryness under reduced pressure. A fine yellow powder of *para*-ethynylaniline **1** (7.44 g, 54%) was obtained. IR (KBr): 3486s (NH), 3389s, 3260s, 2098m (C≡C) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.30 (d, J_{H-H} = 9.0 Hz, 2H, Ar), 6.60 (d, J_{H-H} = 9.0 Hz, 2H, Ar), 3.79 (brs, 2H, NH_2), 2.95 (s, 1H, HC≡C); mass spectrum (EI): m/z 117 (M^+). Single crystals suitable for X-ray diffraction were grown upon slow cooling of a saturated warm toluene solution.

Synthesis of N-trifluoroacetyl-4-iodo-2,6-dimethylaniline (2a)

para-Bromo-2,6-dimethyl-aniline (20 g, 0.1 mol) was placed in a 250 cm^3 round bottom flask and this was flushed with nitrogen and dried THF (80 cm^3) was added by syringe. The mixture was stirred in a nitrogen atmosphere until all the solid had dissolved. Trifluoroacetic anhydride (42 g, 0.2 mol) was added dropwise *via* syringe at 0°C over 20 minutes and the mixture stirred overnight at room temperature. Removal of volatiles under reduced pressure gave an off-white solid which was washed thoroughly with distilled water, filtered and dried under vacuum. A tan shiny powder **2a** (29.28 g, 99%) was obtained. ^{1}H NMR ($CDCl_3$): δ 7.42 (bs, 1H, NH); 7.29 (s, 2H, Ar); 2.22 (s, 6H, Me).

Synthesis of 4-{N-(trifluoroacetyl)-2,6-dimethylanilin-4-yl}-2-methyl-3-butyn-2ol (2b)

2a (29.28 g, 0.1 mol), PPh_3 (0.62 g, 2.37 mmol), copper(I)iodide (0.16 g, 0.86 mmol) and 2-methyl-3-butyn-2-ol (21.11 g, 0.25 mol) were placed into a two-necked 500 cm^3 round bottom flask and 250 cm^3 of dry Et_3N was added. An air-condenser was fitted and the mixture heated to 50°C under a nitrogen atmosphere. Solid $[PdCl_2(PPh_3)_2]$ (0.16 g, 0.23 mmol) was added and the reaction heated at 50°C for 20 minutes and at reflux for a further 20 minutes. Cooling to room temperature gave a yellow solution with a copious precipitate. Diethyl ether (75 cm^3) was added and the mixture filtered to leave a white solid. The solid was washed with a further 75 cm^3 of diethyl ether and the filtrates were combined. Removal of volatiles under reduced pressure gave a viscous oil which was dried further under vacuum overnight. Acetic acid (100 cm^3) was added in an ice bath and the mixture left to stir at room temperature producing a brown solution. This was evaporated to produce a sticky red-brown solid. Distilled water (300 cm^3) was added and the mixture stirred to give an orange solid and the yellow solution which was filtered. The product was crystallised from hot toluene to give a yellow solid which was dissolved in dichloromethane (400 cm^3) (after ca. 3 hours stirring). This was then extracted with copious quantites of distilled water and the organic layer was dried with $MgSO_4$ and evaporated to dryness to afford **2b** as a yellow solid (29.58 g, 99%). ^{1}H NMR ($CDCl_3$): δ 7.60 (bs, 1H, NH); 7.18 (s, 2H, Ar); 2.20 (s, 6H, Me); 2.09 (bs, 1H, OH); 1.61 (s, 6H, Me).

Attempted synthesis of para-ethynyl-2,6-dimethylaniline (2)

KOH pellets (15.52 g, 0.28 mol) were added to 200 cm^3 of ^{i}PrOH in a flask connected to a water condenser and brought to reflux. **2b** (29.58 g, 0.1 mol) was added to the refluxing solution and the mixture heated for 2.5 hours. After cooling to room temperature the solvent was removed under reduced preesure to give a brown solid which was washed with 2 × 80 cm^3 of cold hexane. The resulting brown solid was taken up in dichloromethane (400 cm^3) and stirred for 1 hour although all solids did not dissolve. The resulting slurry was poured onto a short (ca. 2cm) ice-cooled silica column made up with dichloromethane and eluted with more dichloromethane until the eluent was colourless. Yellow band was collected and solvent removed to afford a yellow sticky mass. We were unable to isolate **2** since it was mixed with $HC{\equiv}CC_6H_2(CH_3)_2NHCOCF_3$ in a 1:1 ratio. ^1H NMR ($CDCl_3$) δ 7.42 (brs, 1H, NH), 7.30 (s, 2H, Ar), 7.07 (s, 2H, Ar), 3.57 (brs, 2H, NH_2), 3.10 (s, 1H, C≡CH), 2.95 (s, 1H, C≡CH), 2.23 (s, Me), 2.16 (s,Me); mass spectrum (E.I.): m/z 145 (M^+).

Synthesis of $H_2NC_6H_4C{\equiv}CC{\equiv}CC_6H_4NH_2$ (3)

CuCl (0.54 g, 2.73 mmol) was weighed out in a glove box and was placed into a three-necked round bottom flask equipped with a water condenser and a adaptor connected to an oxygen source. Pyridine (50 cm^3) was transferred into the same flask. The mixture was then warmed in a water bath at 40°C while oxygen was bubbled through the mixture very vigorously for 20 minutes until a dark green solution was observed. *para*-Ethynylaniline (0.89 g, 7.57 mmol) was added to the dark green solution and the reaction mixture was stirred for 1.5 hours at 40°C with oxygen bubbling through. After 15-20 minutes, the reaction mixture turned from dark green to black and the solution became more and more viscous. After another hour, the reaction mixture became a black solid. Dilute ammonium hydroxide (ca. 200 cm^3) was added in several portions to the black solid, and the mixture was stirred and filtered. The filtrate that came out was firstly a dirty-blue colour, then a bright royal blue. The solid was washed thoroughly with dilute ammonium hydroxide until no more blue filtrate was observed. The residue was air-dried and then redissolved in dichloromethane (ca.200 cm^3) to extract the product. An orange filtrate was collected which was dried by $MgSO_4$. The mixture was filtered again and the filtrate was pumped to dryness under reduced pressure to give **3** as an orange-red solid (0.07 g, 14%). IR (KBr): 2135w (C≡C) 2202w cm^{-1}; ^1H NMR ($CDCl_3$): δ 3.87 (brs, 4H, NH_2), 6.59 (d, $J_{H\text{-}H}$ = 8.61 Hz, 4H, Ar), 7.32 (d, $J_{H\text{-}H}$ = 8.52 Hz, 4H, Ar); mass spectrum (E.I.): m/z 232 (M^+); elemental analysis calc. for $C_{16}H_{12}N_2.CH_2Cl_2$: C, 64.35; H, 4.42; N, 8.83. Found C, 62.40; H, 5.94; N, 6.50.

Preparation of cis-$[Pt(PhCN)_2Cl_2]$[70]

$PtCl_2$ (8.38 g, 0.03 mol) was dissolved in minimum amount of hot benzonitrile (250 cm^3). The yellow solution was cooled to room temperature to afford a heavy precipitation of cis-$[Pt(PhCN)_2Cl_2]$ as yellow crystals. The mixture was filtered and the crystals were washed with hexane. Cold hexane was also added to the filtrate to precipitate more crystals of cis-$[Pt(PPhCN)_2Cl_2]$ (13.29 g, 89%). IR (KBr): 2284 (C≡N) cm^{-1}; mass spectrum (FAB): m/z 472 (M^+); elemantal analysis calc. for $PtCl_2N_2C_{14}H_{10}$: C, 35.59; H, 2.12; N, 5.93; Cl, 15.04. Found C, 36.59; H, 2.16; N, 6.15; Cl, 15.27.

Preparation of cis-$[Pt(PPh_3)_2Cl_2]$[70]

cis-$[PtCl_2(PhCN)_2]$ (1.20 g, 2.54 mmol) and PPh_3 (1.33 g, 5.08 mmol) were dissolved in benzene (110 cm^3) under nitrogen. A cloudy white solution was formed which was stirred at room temperature for 18 hours. The mixture was then filtered and the residue was washed with hexane and air-dried. A white powder of *cis*-$[Pt(PPh_3)_2Cl_2]$ (1.93 g, 96%) was obtained. ^{31}P-$\{^1H\}$ NMR ($CDCl_3$): δ 22.69 (s + ^{195}Pt satellites, $J_{Pt\text{-}P}$ = 3672 Hz); mass spectrum (FAB): m/z 790 (M^+); elemental analysis calc. for $PtP_2Cl_2C_{36}H_{30}$: C, 54.68; H, 3.80; Cl, 8.99; P, 7.85. Found C, 56.13; H, 3.74; Cl, 9.12; P, 6.68.

Synthesis of trans-$[Pt(PPh_3)_2(C{\equiv}CC_6H_4NH_2)_2]$ (4)

cis-platinum-bis(triphenylphosphine)dichloride (0.50 g, 0.64 mmol), *para*-ethynylaniline (0.15 g, 1.28 mmol) and copper(I) iodide (10 mg) were placed into a Schlenk tube. Diethylamine (40 cm^3) was then added and the mixture was left to stir under nitrogen at room temperature for 18 hours. A yellow precipitate was produced gradually. After 24 hours, the solvent was pumped to dryness under reduced pressure to yield a yellow solid which was then washed with distilled water, filtered and air-dried giving a fine yellow powder (0.53 g, 88%). The yellow powder was recrystallised from hot dichloromethane to give **4** as shiny, flake-liked, yellow crystals. IR (KBr): 3325m (NH) 3432m (NH) 2105m (C≡C) cm^{-1}, ^1H NMR ($CDCl_3$): δ 7.83 - 7.81 (m, 12H, Ph), 7.39 – 7.34 (m, 18H, Ph), 6.26 (d, $J_{H\text{-}H}$ = 8.5 Hz, 4H, Ar), 6.10 (d, $J_{H\text{-}H}$ = 8.5 Hz, 4H, Ar), 3.42 (brs, 4H, NH_2); ^{31}P-$\{^1H\}$ NMR ($CDCl_3$): δ 19.6 (s + ^{195}Pt satellites, $J_{Pt\text{-}P}$ = 2660 Hz); mass spectrum (FAB): m/z

952 (M^++1); elemental analysis calc. for $PtP_2N_2C_{52}H_{42}$: C, 65.62; H, 4.42; N, 2.94. Found C, 64.80; H, 4.27; N, 2.81. The yellow powder was recrystallised again in chlorobenzene to give some dark brown, block-shape crystals for X-rays analysis.

Preparation of cis-[Pt(P^nBu_3)$_2$$I_2$][71]

[Pt(COD)I_2] (0.65 g, 1.17 mmol) was placed into a Schlenk tube. Dichloromethane (40 cm^3) was added and tri-n-butylphosphine (0.57 cm^3, 2.34 mmol) was syringed slowly. The original bright yellow solution immediately turned orange. After stirring at room temperature for 4 hours, the solution was pumped dry under reduced pressure to yield an orange oil. This was washed with hexane and dried under reduced pressure until an orange powder was obtained. This was redissolved in dichloromethane and a creamy solid was precipitated upon addition of hexane. The mixture was filtered and dried under reduced pressure. The total mass of the orange and off-white solids *cis*-[Pt(P^nBu_3)$_2$$I_2$] was (0.84 g, 84%). IR (KBr): 2850s (CH), 2920s, 2955s cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.99-1.94 (q, $J_{H\text{-}H}$ = 6.1 Hz, 12H, CH_2), 1.53-1.38 (m, 18H, CH_2CH_2), 0.94 (t, $J_{H\text{-}H}$ = 7.1 Hz, 12H, Me); ^{31}P-{^{1}H} NMR ($CDCl_3$): δ 7.54 (s + ^{195}Pt satellites, $J_{Pt\text{-}P}$ = 3519 Hz).

Synthesis of trans-[Pt(P^nBu_3)$_2$($C\equiv CC_6H_4NH_2$)$_2$] (5)

para-Ethynylaniline (0.23 g, 1.97 mmol) and CuI (10mg) were placed into a Schlenk tube. *cis*-[Pt(P^nBu_3)$_2$$I_2$] (0.84 g, 0.99 mmol) was placed into a round bottom flask. Diethylamine (20 cm^3) was added to give an orange solution which was then transferred to the Schlenk tube. The mixture immediately turned cloudy yellow. It was left to stir under nitrogen at room temperature for 96 hours. The solution was then pumped to dryness under reduced pressure to give a sticky brown solid which was redissolved in dichloromethane. This dark red clear solution was extracted from distilled water. The organic layer was dried by $MgSO_4$ and filtered. The filtrate was pumped to dryness under reduced pressure to give a viscous brown oil. This was washed with diethyl ether and dried to give a sticky brown solid. The solid was redissolved in 1:1 mixture of benzene/hexane. It was columned with silica and eluted with 1:1 mixture of benzene/hexane. A yellow solution was collected which gave **5** as an orange oil (0.80 g, 78%) when dried under reduced pressure. IR (KBr): 3347w (NH), 3343w (NH), 2100m ($C\equiv C$) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.09 (d, $J_{H\text{-}H}$ = 8.4 Hz, 4H, Ar), 6.56 (d, $J_{H\text{-}H}$ = 8.4 Hz, 4H, Ar), 3.60 (brs, 4H, NH_2), 2.18-

2.15 (m, 12H, CH_2), 1.42-1.46 (m, 24H, CH_2), 0.94-0.90 (m, 18H, Me); $^{31}P-\{^1H\}$ NMR ($CDCl_3/CH_2Cl_2$): δ 9.22 (s + ^{195}Pt satellites, J_{Pt-P} = 2376 Hz); mass spectrum (FAB): m/z 831 (M^+); elemental analysis calc. for $PtP_2C_{40}H_{66}N_2$: C, 57.76; H, 7.94; N, 3.37. Found C, 57.88; H, 7.99; N, 3.43.

Preparation of cis-[Pt(η^2-dppe)Cl_2][72]

cis-[Pt(COD)Cl_2] (0.80 g, 2.14 mmol) was placed into a Schlenk tube. Dichloromethane (40 cm^3) was transferred into the same Schlenk tube. Bis(diphenylphosphino)ethane (0.96 g, 2.37 mmol) was placed into a two-necked round bottom flask and dichloromethane (40 cm^3) was transferred into the same flask. This colourless solution was then added to the Schlenk tube dropwise for 15 minutes while the reaction mixture was stirred at room temperature. The mixture turned slightly pale yellow but was still clear. After 20 minutes, it turned milky and a white precipitate was formed in a cloudy solution. The precipitate was filtered, washed by dichloromethane and air-dried. The filtrate was pumped to dryness under reduced pressure to give a creamy solid. This was washed with hexane, filtered and air-dried. It was then recrystallised from dichloromethane to give white crystals. The total mass of *cis*-[Pt(η^2-dppe)Cl_2] was (1.17 g, 82%). ^1H NMR ($CDCl_3$): δ 7.89-7.84 (m, 8H, Ar), 7.53-7.48 (m, 12H, Ar), 2.37-2.28 (m, 4H, CH_2); $^{31}P-\{^1H\}$ NMR ($CDCl_3$): δ 47.71 (s + ^{195}Pt satellites, J_{Pt-P} = 3617 Hz); mass spectrum (FAB): m/z 629 (M^+-Cl); elemental analysis calc. for $PtP_2Cl_2C_{26}H_{24}.0.5CH_2Cl_2$: C, 44.98; H, 3.54; Cl, 12.55; P, 8.77. Found C, 43.95; H, 3.16; Cl, 12.71; P, 7.28.

Synthesis of cis-[Pt(η^2-dppe)($C{\equiv}CC_6H_4NH_2)_2$] (6)

para-Ethynylaniline (0.65 g, 4.79 mmol) was placed into a three-necked flask equipped with a condenser and a bubbler. Diethyl ether (20 cm^3) was added to the same flask and a clear yellow solution was formed. Butyllithium (1.2 cm^3, 2.99 mmol) was added to the ether solution dropwise at 0°C. A yellow solid was formed immediately and a gas was given off rapidly. The mixture was then stirred at room temperature and it stayed as a cloudy yellow solution. *cis*-[Pt(η^2-dppe)Cl_2] (0.20 g, 0.301 mmol) was placed into a three-necked round bottom flask equipped with a take-off adaptor connected to a nitrogen source. THF (40 cm^3) was added to the three-necked round bottom flask and the mixture was stirred rapidly to give a cloudy white solution. This was then transferred to the ether solution at –78°C under nitrogen. The reaction mixture was warmed gradually to room temperature under nitrogen and left to stir for 60 hours. Aqueous NH_4Cl (ca.10ml) was added and the mixture was then transferred to a separating funnel. The orange layer was collected, washed with distilled water and brine, dried with $MgSO_4$ and pumped to dryness under reduced pressure. A sticky yellow solid was obtained. Dissolution in the minimum amount of dichloromethane followed by addition of light petroleum gave a yellow precipitate which was dried under vacuum to yield **6** as a dry yellow powder (0.09 g, 36%). IR (KBr): 3424s (NH), 3332s (NH), 2108m (C≡C) cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.00-6.97 (m, 20H, Ph), 6.61 (d, $J_{H\text{-}H}$ = 8.5 Hz, 4H, Ar), 6.46 (d, $J_{H\text{-}H}$ = 8.5 Hz, 4H, Ar), 3.6 (brs, 4H, NH_2), 2.63-2.37 (m, 4H, CH_2); $^{31}P\text{-}\{^1H\}$ NMR ($CDCl_3$): δ 46.3 (s + ^{195}Pt satellites, $J_{Pt\text{-}P}$ = 2257 Hz); mass spectrum (EI) m/z 826 (M^+); elemental analysis calc. for $PtP_2C_{42}H_{36}N_2$: C, 61.09; H, 4.36; N, 3.39; P, 7.52. Found C, 60.90; H, 4.65; N, 3.46; P, 8.16.

Synthesis of all trans-[$Ru(CO)_2(PEt_3)_2(C{\equiv}CC_6H_4NH_2)_2$] (7)

para-Ethynylaniline (0.38 g, 3.28 mmol) was placed into a three-necked round bottom flask equipped with a take-off adaptor connected to a nitrogen source. Diethyl ether (10 cm^3) was added to the same flask and a clear yellow solution was formed. Butyllithium (2.2 ml, 23 mmol) was then added dropwise to the ether solution at –78°C. The solution immediately turned to a clear orange solution. All trans-[$Ru(CO)_2(PEt_3)_2Cl_2$] (0.76 g, 1.64 mmol) was placed into a two-necked round bottom flask also equipped with a take-off adaptor connected to a nitrogen source. THF (40 cm^3) was added to the Schlenk and a clear yellow solution was formed. This was added dropwise to the ether solution at –78°C under nitrogen. The reaction mixture was stirred at room temperature for 18 hours and then pumped to dryness under reduced pressure to give a sticky orange solid. The solid was redissolved in dichloromethane and was chromatographed with silica and dichloromethane/hexane (1:1). A yellow solution was collected which gave **7** as an orange solid (0.50 g, 49%) when pumped to dryness under reduced pressure. All attempts at recrystallisation proved fruitless and thus we were unable to obtain satisfactory analytical data. IR (CH_2Cl_2): 2035s (C≡C), 1972vs (CO) cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.06 (d, $J_{H\text{-}H}$ = 8.1 Hz, 4H, Ar), 6.51 (d, $J_{H\text{-}H}$ = 8.1 Hz, 4H, Ar), 3.55 (s, 4H, NH_2), 2.13-2.07 (m, 12H, CH_2), 1.21 (quin, $J_{H\text{-}H}$ = 7.6 Hz, 18H, CH_3); $^{31}P\text{-}\{^1H\}$ NMR ($CDCl_3$): δ 24.3 (s); mass spectrum: m/z 481 (M^+-L-CO-H).

Synthesis of [(μ-H)$Ru_3(CO)_9$(μ_3-C≡$CC_6H_4NH_2$)] (8)

A heptane solution (30 cm^3) of [$Ru_3(CO)_{12}$] (0.25 g, 0.39 mmol) and *para*-ethynyl aniline (91 mg, 0.77 mmol) was heated at 95°C for 8 hours resulting in the formation of an orange solution and a yellow precipitate. After cooling to room temperature, volatiles were removed under reduced pressure to give a mustard solid. Chromatography on silica eluting with hexane gave a yellow band which afforded unreacted [$Ru_3(CO)_{12}$] (30 mg). Elution with hexane-diethyl ether (3:2) gave a yellow band which afforded 8 as a yellow solid (73 mg, 32%). Crystals suitable for X-ray crystallography were grown upon cooling a saturated hexane solution to –20°C. IR (C_6H_{14}): 2096w (CO), 2071s (CO), 2053vs (CO), 1989w (CO) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.39 (d, 2H, $J_{H\text{-}H}$ = 8.4 Hz, Ar), 6.64 (d, 2H, $J_{H\text{-}H}$ = 8.4 Hz, Ar), 3.89 (s, 2H, NH_2), -20.41 (s, 1H, μ-H); mass spectrum (FAB): m/z 673 (M^++1); elemental analysis calc. for $Ru_3C_{17}H_7N_1O_9$: C, 30.36; H, 1.04; N, 2.08. Found C, 29.71; H, 0.90; N, 1.95. Elution with diethyl ether-acetone (9:1) gave a second yellow band which afforded 103 mg of an orange-yellow solid as a mixture of isomers and as yet not fully characterised. IR (C_6H_{14}): 2078s (CO), 2049vs (CO), 2016m (CO), 2008s (CO), 1995s (CO), 1929m (CO) cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.02 (s, NH, 0.6H), 8.88 (s, NH, 0.4H), 7.45-6.45 (m, 10H, Ph + C≡CH), 3.92-3.70 (m); mass spectrum (FAB): m/z 606, 578, 550, 522, 494, 466, 438.

Synthesis of [(μ-H)$Ru_3(CO)_9$(μ_3-C≡$CC_6H_4NH_3$)][X] (9)

Addition of a drop of $HBF_4.Et_2O$ to a hexane solution of [(μ-H)$Ru_3(CO)_9$(μ_3-C≡$CC_6H_4NH_2$)] resulted in a distinct lightening of the solution and complete loss of [(μ-H)$Ru_3(CO)_9$(μ_3-C≡$CC_6H_4NH_2$)] as shown by IR spectroscopy. Similarly, addition of CF_3CO_2H to a $CDCl_3$ solution of [(μ-H)$Ru_3(CO)_9$(μ_3-C≡$CC_6H_4NH_2$)] resulted in rapid protonation as shown by ^1H NMR spectroscopy to give [(μ-H)$Ru_3(CO)_9$(μ_3-C≡$CC_6H_4NH_3$)][X]. IR (C_6H_{14}): 2134m (CO), 2100s (CO), 2075vs (CO), 2056s (CO), 2026s (CO), 1993sh cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.58 (d, 2H, $J_{H\text{-}H}$ = 8.0 Hz, Ar), 7.18 (d, 2H, $J_{H\text{-}H}$ = 8.0 Hz, Ar), 6.20 (brs, 3H, NH_3), -6.47 (s, 1H, μ-H).

Synthesis of trans-[Pt(PPh$_3$)$_2$(C≡CC$_6$H$_4$N=C$_6$H$_{10}$)$_2$] (10)

trans-[Pt(PPh$_3$)$_2$(C≡CC$_6$H$_4$NH$_2$)$_2$] (0.10 g, 0.11 mmol) and MgSO$_4$ (0.10 g, 0.84 mmol) were placed into a three-necked round bottom flask equipped with a water condenser and a bubbler. Toluene (20 cm^3) was added to the same flask. Cyclohexanone (0.06 cm^3, 0.63 mmol) was added via syringe to the toluene mixture which was refluxed under nitrogen for 18 hours giving a clear yellow-orange solution with MgSO$_4$ at the bottom of the flask. This was filtered and volatiles were removed under reduced pressure to give **10** as an orange solid (0.10 g, 86%). All attempts to recrystallise this were unsuccessful. IR (KBr): 2950w (CH), 2104w (C≡C), 1702m (C=N), 1619m (C=N), 1603m (C=N), 1510s, 1481m, 1430m, 1261s, 1096vs, 1018s, 802s, 750m, 710m, 694s, 525m cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 7.82-7.15 (m, 30H, Ph), 6.25 (d, J_{H-H} = 8.6 Hz, 4H, Ar), 6.09 (d, J_{H-H} = 8.6 Hz, 4H, Ar), 2.36 (m, 8H, CH$_2$), 1.88 (m, 8H, CH$_2$), 1.72 (m, 4H, CH$_2$); ^{31}P-{^{1}H} NMR (CDCl$_3$): 29.2 (s + ^{195}Pt satellites, J_{Pt-P} = 2689 Hz, 20%), 26.4 (s + ^{195}Pt satellites, J_{Pt-P} = 2686 Hz, 80%); mass spectrum (FAB): m/z 1112 (M$^+$+1).

Preparation of ferrocenecarbaldehyde[73]

Ph(Me)NCHO (3.87 g, 17.92 mmol) and POCl$_3$ (4.40 g, 28.67 mmol) were placed into a three-necked round bottom flask giving a clear orange solution. Ferrocene (2.00 g, 10.75 mmol) was added in small portions and the mixture immediately turned red and then purple and became more viscous. The mixture was stirred at room temperature under nitrogen for 1 hour. It was then heated to 65-70°C for 2 hours. After 2 hours, the mixture was cooled to room temperature. Sodium acetate (14.1 g, 172 mmol) was dissolved in distilled water (120 cm^3). This was then added to the reaction mixture in small portions at 0°C. A dark red solution was formed which was stirred for 18 hours. After 18 hours, diethyl ether (100 cm^3) was added to the solution and extracted from water three times. Then 1M HCl (100 cm^3) was added to the ether extract followed by saturated brine (100 cm^3). Saturated sodium bicarbonate (100 cm^3) and saturated brine (100 cm^3) were added to the ether extract respectively. The ether extract was collected and was reduced to a volume of 10ml. Sodium bisulfite (40 g) was dissolved in distilled water (100 cm^3). This solution was added to the viscous ether solution. A heavy precipitate was deposited. It was filtered, washed with cold saturated sodium bisulfite and diethyl ether and was air-dried. A yellow solid was obtained. NaOH (16 g) was dissolved in distilled water (200 cm^3). This was added to the yellow solid to give an orange–red solution. Diethyl ether was added to extract the product. The ether extract was reduced to a volume of 100 cm^3 before it was washed with saturated sodium chloride and dried with $MgSO_4$. Removal of volatiles afford ferrocenecarbaldehyde as a deep red powder (1.36 g, 59%). IR (KBr): 1681 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$): δ 9.96 (s, 1H, CHO), 4.80 (t, 2H, J_{H-H} = 1.83 Hz, C_5H_4), 4.62 (t, 2H, J_{H-H} = 1.83 Hz, C_5H_4), 4.29 (s, 5H, C_5H_5); mass spectrum (FAB): m/z 214 (M^+); elemental analysis calc. for $FeC_{11}H_{10}O$: C, 61.68; H, 4.67. Found C, 61.57; H, 4.60.

Synthesis of trans-[Pt(PPh$_3$)$_2$(C≡CC$_6$H$_4$N=CH-Fc)$_2$] (11)

trans-[Pt(PPh_3)$_2$(C≡C$C_6H_4NH_2$)$_2$] **4** (0.17 g, 0.18 mmol), ferrocenecarbaldehyde (0.08 g, 0.36 mmol) and $MgSO_4$ (0.09 g, 0.72 mmol) were placed in a two-necked round bottom flask equipped with a water condenser and a bubbler. Toluene (50 cm^3) was added and the mixture was refluxed under nitrogen for 60 hours. After that, the mixture was filtered and the filtrate was pumped to dryness under reduced pressure to afford **11** as a red sticky solid (0.01 g, 6%). All attempts at recrystallisation proved fruitless and thus we were unable to obtain satisfactory analytical data. IR (KBr): 2964m (CH), 2102w (C≡C), 1638s (C=N), 1627s (C=N), 1607s (C=N) cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.22 (s, 2H, CH=N), 7.83 (m, 12H, Ph), 7.39 (m, 18H, Ph), 6.75 (d, J_{H-H} = 8.2 Hz, 4H, Ar), 6.29 (d, J_{H-H} = 8.2 Hz, 4H, Ar), 4.75 (s, 4H, C_5H_4), 4.46 (s, 4H, C_5H_4), 4.22 (s, 10H, C_5H_5); ^{31}P-{^1H} NMR ($CDCl_3$): δ 21.91 (s + ^{195}Pt satellites, J_{Pt-P} = 2707 Hz); mass spectrum (FAB): m/z 1344 (M^+).

Synthesis of trans-[Pt(PPh$_3$)$_2${C≡CC$_6$H$_4$NHC(O)Ph}$_2$] (12)

trans-[Pt(PPh_3)$_2$(C≡C$C_6H_4NH_2$)$_2$] **4** (0.10 g, 0.11 mmol) was placed into a three-necked round bottom flask equipped with a take-off adaptor connected to a nitrogen source. Dichloromethane (70 cm^3) was transferred into the same flask. Triethylamine (0.03 cm^3, 0.21 mmol) and benzoyl chloride (0.03 cm^3, 0.21 mmol) were added to the dichloromethane solution via syringes. The mixture was stirred under nitrogen at room temperature for 18 hours. The solution was pumped to dryness under reduced pressure to afford a sticky brown solid. It was redissolved in dichloromethane and washed thoroughly with distilled water. The organic layer was collected and was dried by $MgSO_4$. The filtrate was pumped to dryness under reduced pressure. A sticky brown solid **12** was obtained (0.11 g, 92%). IR (KBr): 3560vs (NH), 3480vs (NH), 3416vs (NH), 2105w (C≡C), 1640s (C=O), 1618s (C=O), 1506s, 1481m, 1433m, 1392w, 1310w, 1261s, 1096vs, 1020s, 802s, 690s, 669m, 524m cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 8.10 (d, $J_{H\text{-}H}$ = 8.5 Hz, 4H, Ar), 7.90-7.29 (m, 40H, Ph), 6.15 (d, $J_{H\text{-}H}$ = 8.5 Hz, 4H, Ar); $^{31}P\text{-}\{^{1}H\}$ NMR ($CDCl_3$): δ 28.2 (s + ^{195}Pt satellites, $J_{Pt\text{-}P}$ = 2651 Hz), 27.7 (s + ^{195}Pt satellites, $J_{Pt\text{-}P}$ = 3000 Hz); mass spectrum (FAB): m/z 1160 (M^+); elemental analysis calc. for $PtP_2N_2O_2C_{66}H_{50}.1.5CH_2Cl_2$: C, 62.91; H, 4.12; N, 2.17. Found C, 62.89; H, 4.45; N, 1.73.

Synthesis of trans-[$Pt(PPh_3)_2\{C{\equiv}CC_6H_4NHC(O)C_6H_4C(O)NHC_6H_4C{\equiv}C\}]_2$ (13)

trans-[$Pt(PPh_3)_2(C{\equiv}CC_6H_4NH_2)_2$] **4** (0.17 g, 0.18 mmol) was placed into a two-necked round bottom flask equipped with a take-off adaptor connected to a nitrogen source. Dichloromethane (40 cm^3) was transferred into the same flask and a clear yellow solution was formed. Triethylamine (0.1 cm^3) and terephthaloyl chloride (0.04 g, 0.18 mmol) were added to the yellow solution. The mixture turned into a cloudy yellow solution. It was left to stir under nitrogen at room temperature for 60 hours. After 60 hours, a yellow precipitate was deposited. After filtration the yellow solid was washed thoroughly with water to remove salts and dried to afford **13** as a yellow powder (0.13 g, 65%). IR (KBr): 3050w (NH), 2105m (C≡C), 1696w (C=O), 1667m (C=O), 1587m, 1520m, 1506s, 1483m, 1435m, 1315m, 1099m, 835w, 740w, 700w, 693s, 520s cm^{-1}; mass spectrum (FAB): m/z 919, 764, 720, 613; mass spectrum (TOFSPEC): m/z 1101, 1050, 984, 916, 718; elemental analysis calc. for $Pt_3P_6N_6O_8C_{188}H_{136}$: C, 65.47; H, 3.95; N, 2.44; Cl, 2.06. Found C, 64.94; H, 4.18; N, 2.63; Cl, 2.09. Due to the extreme insolubility of this compound in common organic solvents we have been unable to get any meaningful NMR spectra.

Synthesis of trans-[$Pt(P^{n}Bu_3)_2\{C{\equiv}CC_6H_4NHC(O)C_6H_4C(O)NHC_6H_4C{\equiv}C\}]_3$ (14)

trans-[$Pt(P^{n}Bu_3)_2(C{\equiv}CC_6H_4NH_2)_2$] **5** (0.30 g, 0.36 mmol) was dissolved in dichloromethane (50 cm^3) to give a yellow solution under nitrogen. Triethylamine (0.05 cm^3, 0.36 mmol) and terephthaloyl chloride (0.07 g, 0.36 mmol) were added to the yellow solution. The reaction was stirred at room temperature for 18 hours and yellow precipitate was deposited. After filtration, the yellow solid was washed thoroughly with water to remove salts and dried to afford **14** as a yellow powder (0.33 g, 95%). ^{31}P-{^{1}H} NMR (DMF/CDCl$_3$): δ 4.02 (s + ^{195}Pt satellites, $J_{Pt\text{-}P}$ = 2361 Hz); mass spectrum (FAB): m/z 1469, 984, 893, 597; mass spectrum (TOFSPEC): m/z 2041, 1832, 1718, 1443, 1340, 1233, 1134, 1016, 902; elemental analysis calc. for $Pt_4P_8N_8O_{10}C_{200}H_{276}$: C, 59.30; H, 6.82; N, 2.77; Cl, 1.75; P, 6.13. Found C, 58.56; H, 7.00; N, 3.23; Cl, 1.86; P, 7.36. Due to the extreme insolubility of this compound in common organic solvents we have been unable to get any meaningful NMR spectra.

Attempted synthesis of trans-[Pt(PPh$_3$)$_2${C≡CC$_6$H$_4$NMoCl$_2$(η^2-S$_2$CNEt$_2$)}$_2$] (I)

[MoOCl$_2$(η^2-S$_2$CNEt$_2$)$_2$] (0.1 g, 0.21 mmol) and *trans*-[Pt(PPh$_3$)$_2$(C≡CC$_6$H$_4$NH$_2$)$_2$] **4** (0.1 g, 0.11 mmol) were placed into a Schlenk tube. Methanol (30 cm^3) was transferred into the same Schlenk tube. The reaction mixture gradually turned into a clear orange solution. It was left to stir under nitrogen at room temperature for 18 hours giving a clear red solution. The solution was pumped to dryness under reduced pressure to give an oily solid. This was redissolved in dichloromethane and precipitated with hexane. The mixture was filtered and the residue was dried under reduced pressure. An orange-brown powder (0.12 g) was obtained. Further purification was not made. IR (KBr): 2966w (CH), 2929w, 2869w, 2851w, 2100vw (C≡C), 1278m (Mo≡N) cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 7.55-7.24 (m, Ar), 3.94-3.82 (m, CH$_2$); ^{31}P-{^{1}H} NMR (methanol/CDCl$_3$): δ 21.24 (s + ^{195}Pt satellites, $J_{Pt\text{-}P}$ = 3266 Hz, a), 28.36 (s + ^{195}Pt satellites, $J_{Pt\text{-}P}$ = 3026 Hz, b). The ratio of the peaks a:b was 3:1; mass spectrum (FAB): m/z 867 (M$^+$ = [Pt(PPh$_3$)$_2$(η^2-S$_2$CNEt$_2$)]$^+$), 719 (M$^+$ = [Pt(PPh$_3$)$_2$]$^+$), 690 (M$^+$ = [Mo(NC$_6$H$_4$C≡C)(η^2-S$_2$CNEt$_2$)$_3$Cl]).

Synthesis of Ph$_3$P=NC$_6$H$_4$C≡CH (15)

para-Ethynylaniline **1** (1.00 g, 8.55 mmol) was dissolved in toluene (60 cm^3) under nitrogen to give a yellow solution. Triethylamine (4.8 cm^3, 0.03 mol) was added to the yellow solution *via* a syringe. PPh$_3$Br$_2$ (3.61 g, 8.55 mmol) was dissolved in toluene (40 cm^3) under nitrogen to give a cloudy solution. The yellow solution was added to this solution dropwise under nitrogen. It was then stirred at room temperature for 18 hours. The mixture was filtered and the residue was washed with toluene and diethyl ether. The filtrate was pumped to dryness under reduced pressure to afford **15** as a yellow powder (3.22 g, 100%). IR (KBr): 2092w (C≡C), 1596s, 1496vs, 1436s, 1327vs (P=N), 1259m, 1169m, 1104s, 1017m, 997m, 827m, 719s, 693s, 554m, 525s cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.77-7.43 (m, 15H, Ph), 7.16 (d, J_{H-H} = 8.6 Hz, 2H, Ar), 6.71 (d, J_{H-H} = 8.6 Hz, 2H, Ar), 2.95 (s, 1H, C≡CH); ^{31}P-{^{1}H} NMR ($CDCl_3$): δ 10.6 (s); mass spectrum (EI): m/z 377 (M^+); elemental analysis calc. for $PC_{26}H_{20}N$: C, 82.76; H, 5.31; N, 3.71. Found C, 82.59; H, 5.30; N, 4.58.

Attempted synthesis of [MoCl$_2$(η^2-S$_2$CNEt$_2$)$_2$(NC$_6$H$_4$C≡CH)] (II)

[$MoOCl_2$(η^2-S_2CNEt_2)$_2$] (0.82 g, 1.71 mmol) and **1** (0.20 g, 1.71 mmol) were dissolved in methanol (50 cm^3) under nitrogen. The mixture was stirred at room temperature for 18 hours. It was then filtered and the red filtrate was pumped to dryness to afford a sticky red solid (0.99 g, 86%). IR (KBr) 2098w (C≡C), 1594w, 1526vs, 1457m, 1440m, 1380w, 1355m, 1277s, 1204m, 1150m, 1095m, 1075m, 945m, 847m cm^{-1}; ^{1}H NMR (acetone-d^6): δ 7.74 (d, J_{H-H} = 8.8 Hz, Ar, a), 7.53 (d, J_{H-H} = 8.7 Hz, Ar, b), 7.44 (d, J_{H-H} = 8.7 Hz, Ar, b), 6.68 (d, J_{H-H} = 8.8 Hz, Ar, a), 4.05-3.87 (m, CH_2), 2.57 (s, ≡CH, a), 2.40 (s, ≡CH, b), 1.50-1.30 (m, CH_3). The ratio of peaks a:b was 3:5; mass spectrum (FAB): m/z 690 {Mo(η^2-S_2CNEt_2)$_3$($NC_6H_4C_2H$)+1}, 544.

[$MoOCl_2$(η^2-S_2CNEt_2)$_2$] (0.64 g, 1.33 mmol) and HC≡CC_6H_4N=PPh_3 **15** (0.76 g, 2.00 mmol) were dissolved in toluene (50 cm^3) under nitrogen. The mixture was refluxed for 24 hours. The mixture was then filtered and the volume of the red filtrate was reduced to ca. 15 cm^3 and light petroleum (ca. 20 cm^3) was added which resulted in the precipitation of Ph_3P=O. This was filtered and the filtrate was pumped to dryness under reduced pressure to afford a red oily solid (ca. 0.56g). IR (KBr) 2094w (C≡C), 1594w, 1520s, 1498vs, 1457m, 1437m, 1380w, 1341m, 1277s, 1204m, 1168m, 1150m, 1107s, 1074m, 998w, 837m cm^{-1}; mass spectrum (FAB): m/z 657, 544, 509.

Preparation of [ReOCl$_3$(PPh$_3$)$_2$][74]

Rhenium metal (1.00 g, 5.37 mmol) was placed into a round bottom flask. Hydrogen peroxide (17 cm^3) was added to the metal at 0°C. The mixture was heated on a water bath until the volume was reduced to 2 cm^3. Concentrated hydrochloric acid (10 cm^3) was added to acetone (70 cm^3). This solution was added to the rhenium mixture to give a pale yellow solution. Triphenylphosphine (10.00 g, 38.1 mmol) was added and the mixture immediately turned bright green. The mixture was refluxed for 2 hours. It was then filtered, washed with ethanol and air-dried. A green powder (5.71 g, 99%) was obtained. It was recrystallised from benzene to give green crystals. IR (KBr): 969s (Re=O) cm^{-1}; ^{31}P-{^{1}H} NMR (CDCl$_3$/benzene): δ -11.95 (s); elemental analysis calc. for $ReOCl_3P_2C_{36}H_{30}$: C, 51.89; H, 3.60. Found C, 51.83; H, 3.48.

Attempted synthesis of [ReCl$_3$(PPh$_3$)$_2$(NC$_6$H$_4$C≡CH)] (16)

[ReOCl$_3$(PPh$_3$)$_2$] (1.10 g, 1.33 mmol), *para*-ethynylaniline **1** (0.50 g, 1.33 mmol) and triphenylphosphine (0.09 g, 0.34 mmol) were refluxed in toluene (80 cm^3) for 18 hours under nitrogen. The reaction mixture was cooled to room temperature and was filtered. The brown residue (0.12 g, 81%) was air-dried. Mass spectrum (FAB): m/z 1049 (M$^+$+1), 932 (M$^+$); elemental analysis calc. for $ReP_2C_{44}H_{35}NCl_3.1.5CH_2Cl_2$: C, 51.56; H, 3.59; N, 1.32; P, 5.85. Found C, 50.99; H, 3.58; N, 1.15; P, 5.70. Due to the extreme insolubility of this compound in common organic solvents we have been unable to obtain any meaningful NMR spectra.

Preparation of trans-[Pt(PPh$_3$)$_2$(C≡CC$_6$H$_4$N=PPh$_3$)$_2$] (17)

trans-[Pt(PPh$_3$)$_2$(C≡CC$_6$H$_4$NH$_2$)$_2$] **4** (0.30 g, 0.32 mmol) was placed into a three-necked round bottom flask equipped with a water condenser and a bubbler. Toluene (70 cm^3) was transferred into the same flask. Triethylamine (0.32 g, 3.15 mmol) was added to the flask. The mixture was refluxed under nitrogen until it became a clear yellow solution. PPh$_3$Br$_2$ (0.27 g, 0.63 mmol) was put into a Schlenk tube. Toluene (30 cm^3) was transferred into the Schlenk tube followed by the yellow solution under nitrogen.. White fumes were given off. The solution gradually changed from yellow to orange. The reaction mixture was stirred at room temperature under nitrogen for 18 hours turning an intense orange colour. After 18 hours, there was some fine precipitate in the orange solution. The reaction was cooled and the mixture was filtered. The filtrate was pumped to dryness under reduced pressure to give **17** as a yellow-orange solid (0.30 g, 65%). Recrystallisation from dichloromethane-light petroleum gave yellow needles. IR (KBr): 2104w (C≡C), 1595m, 1496s, 1482m, 1435s, 1400w, 1352m (P=N), 1335m (P=N), 1261m, 1173w, 1162m, 1101vs, 1035s, 802s, 720m, 692s, 548m, 528m, 525m cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.80-7.28 (m, Ph), 6.36 (d, J_{H-H} = 8.0 Hz, 4H, Ar), 5.97 (d, J_{H-H} = 8.0 Hz, 4H, Ar); ^{31}P-{^{1}H} NMR ($CDCl_3/CH_2Cl_2$): δ 26.3 (s + ^{195}Pt satellites, J_{Pt-P} = 2705 Hz), 7.3 (s, P=N); mass spectrum (FAB): m/z 1473 (M^++2); elemental analysis calc. for $PtP_4N_2C_{88}H_{68}.CH_2Cl_2$: C, 68.64; H, 4.24; N, 1.80. Found C, 68.73; H, 4.50; N, 1.70.

Attempted synthesis of trans-[Pt(PPh$_3$)$_2${C≡CC$_6$H$_4$N≡ReCl$_3$(PPh$_3$)$_2$}$_2$] (18)

trans-[Pt(PPh$_3$)$_2$(C≡CC$_6$H$_4$NPPh$_3$)$_2$] **4** (0.07 g, 0.05 mmol) and [ReOCl$_3$(PPh$_3$)$_2$] (0.08 g, 0.10 mmol) were placed into a three-necked round bottom flask equipped with a water condenser and a bubbler. Benzene (70 cm^{3}) was transferred to the same flask. The mixture was refluxed under nitrogen for 18 hours. Upon cooling to room temperature, the mixture was filtered and the red filtrate was pumped to dryness under reduced pressure to give **18** as an orange powder (0.11 g, 89% yield). The black residue was dried to give a brown powder. The brown powder was washed with dichloromethane, filtered and dried. The orange powder was recrystallised from dichloromethane and methanol which gave yellow-orange needles. IR (KBr): 2096w (C≡C), 1638m, 1618s, 1578m, 1485w, 1436s, 1262s, 1118vs, 1095vs, 1026vs, 803s, 739w, 715m, 693s, 542m cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.80-7.10 (m, Ph), 6.62 (d, 2H, J_{H-H} = 6.9 Hz, Ar), 5.86 (d, 2H, J_{H-H} = 6.9 Hz, Ar); mass spectrum (FAB): m/z 2546 (M^+-Cl), 1651, 1389; elemental analysis calc. for $PtRe_2P_6Cl_6N_2C_{124}H_{98}$: C, 57.7; H, 3.80; N, 1.09. Found C, 59.62; H, 3.77; N, 0.58.

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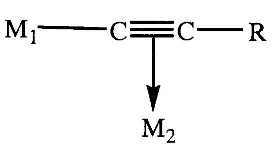
Chapter 3: Synthesis of heterometallic aggregates and polymers *via* transition metal acetylide systems

The last chapter focused on our attempts to make large molecules linking high and low-valent metal centres via use of substituted acetylides. In this chapter, we will focus on *trans*-platinum bis(acetylide) complexes being linked by coinage metals, mainly silver ions. The acetylides are usually σ-bonded to platinum and π-bonded to coinage metals. These polynuclear acetylide complexes are of considerable interest because of their unusual structural features, and polymers and oligomers are synthesised in different shapes and geometries. In order to investigate whether differently substituted acetylides have any effect on the overall shape of the silver adduct, and as perchlorate ions were found to bind silver ions, functionalised acetylides with a hydroxyl group on the ends were prepared in order to examine whether the oxygen on the hydroxyl group would bind to silver ions. It is also of our interest to explore the ratio between the platinum bis(acetylide) complexes and the silver perchlorate in the adduct.

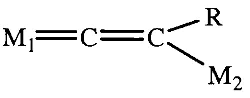
Introduction

3.1 Binding of metals to metal-acetylides

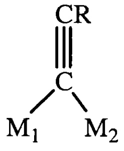
We have discussed transition metal σ-acetylide complexes earlier in Chapter 2. Generally, the carbon-carbon triple bond in those complexes was uncoordinated. In this chapter, we will describe the binding of a hetero-metal atom to transition metal σ-acetylide complexes *via* the alkyne function, in particular, the binding of coinage metals (Cu^+, Ag^+) to platinum acetylide complexes which form the basis of our studies. In general, there are four different binding modes of a metal acetylide towards another electrophilic metal centre.[1,2]



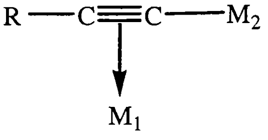
(A)



(B)



(C)



(D)

In (A), (B) and (D) the acetylide acts as a three-electron donor, while in (C) it is a one-electron donor. There are also more complex modes of coordination involving more than two metal atoms but these will not be discussed further.

3.2 Simple copper(I) and silver(I) acetylide complexes

There has been considerable interest in organocopper chemistry over the last 20 years primarily since organocopper complexes have found widespread use in organic synthesis. However, organo-copper and –silver compounds are susceptible to hydrolysis, oxidation and reactions with CO, CO_2 and H_2. Therefore, an inert atmosphere must generally be maintained during their preparation, isolation and handling. In addition, the organosilver compounds are often light sensitive. The solubility of organo-copper and –silver compounds of type MR in common organic solvents is low since they are polymeric. They are usually prepared without isolation in most organic syntheses. Thus, it was not until 1923 when the first organocopper compound was actually isolated.

In general, organocopper compounds of the type RCu are prepared by transmetallation reaction of a copper(I) salt with an organolithium, -magnesium or –zinc reagent. This method has been successfully used for the preparation and isolation in the pure state of copper acetylide.[3]

$$\mathrm{CuX} + \mathrm{LiR} \longrightarrow \mathrm{CuR} + \mathrm{LiX}$$

Copper acetylides can be also prepared by the reaction of a terminal acetylene with an ammoniacal solution of copper(I) halide.[4-6] Copper *t*-butoxide complex, being soluble in common organic solvents, is a useful reagent in preparing copper acetylide under mild conditions at –78 °C.[7,8]

$$\mathrm{RC{\equiv}CH} + \mathrm{Cu(NH_3)_2^+} \longrightarrow \mathrm{CuC{\equiv}CR} + \mathrm{NH_3} + \mathrm{NH_4^+}$$

$$\mathrm{PhC{\equiv}CH} + \mathrm{Cu(^tBuO)} \longrightarrow \mathrm{CuC{\equiv}CPh} + \mathrm{^tBuOH}$$

Organosilver compounds in general are less thermally stable than their copper analogues. They can be prepared by the reaction of silver nitrate with tetraalkyllead in methanol or ethanol at low temperatures (usually –80 °C) and are stable for several hours. However, upon warming to room temperature, decomposition takes place with the formation of metallic silver and a mixture of alkanes and alkenes.

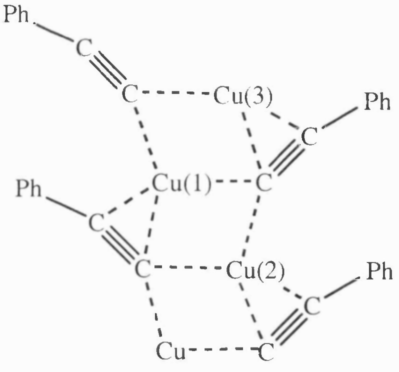
$$\mathrm{AgNO_3} \quad + \quad \mathrm{R_4Pb} \xrightarrow{-80\,^{\circ}\mathrm{C}} \mathrm{AgR} \quad + \quad \mathrm{R_3PbNO_3}$$

In general, the order of thermal stability is alkyl- < aryl- ~ alkenyl- < acetylenic-copper or silver compounds. Silver acetylides (e.g. propynylsilver, which decompose above 150 °C) were obtained in the second part of the nineteenth century and they can be prepared *via* metallation in the presence of an auxiliary base. Subsequently, aryllithium[9,10] and arylzinc[11] have been found to be more convenient arylating reagents.

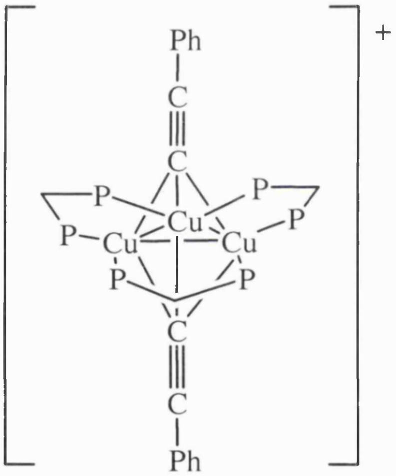
$$\mathrm{RC{\equiv}CH} \quad + \quad \mathrm{AgNO_3} \quad + \quad \mathrm{NH_3} \longrightarrow \mathrm{AgC{\equiv}CR} \quad + \quad \mathrm{NH_4NO_3}$$

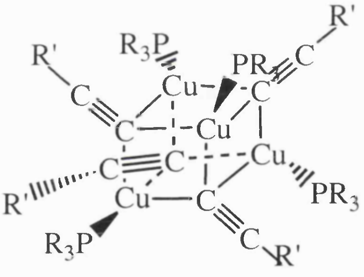
Compound	Decomposition/ °C	Degree of Association
$\mathrm{CuC{\equiv}CR}$	200	Polymer
$\mathrm{AgC{\equiv}CR}$	100-200	Polymer

The structures of copper and silver acetylides are polymeric. X-ray analysis of $[\mathrm{CuC{\equiv}CPh}]_n$ reveals infinite zig-zag chains of copper atoms lying roughly in one plane. Superficially, the phenylethynyl group is σ-bonded to one copper atom, and symmetrically π-bonded to a second and a third copper atom.[12] However, the structure may be explained equally well in terms of the acetylide group being two electron-three centre bonded to Cu-(1) and Cu-(2) and π-bonded to Cu-(3).

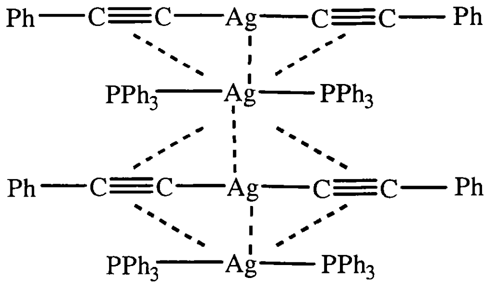


Recently, trinuclear and tetranuclear copper(I) acetylide complexes, $[Cu_3(\mu\text{-dppm})_3(\mu^3\text{-}\eta^1\text{-}C{\equiv}CPh)_2]^+$ and $[Cu_4(PR_3)_4(C{\equiv}CR')_4]$ were prepared and shown to exhibit rich photo-physical properties.[13] They have very different structures from $[CuC{\equiv}CPh]_n$. The acetylides are σ-bonded to three copper atoms and the electrons are delocalised between the carbon and the copper atoms.



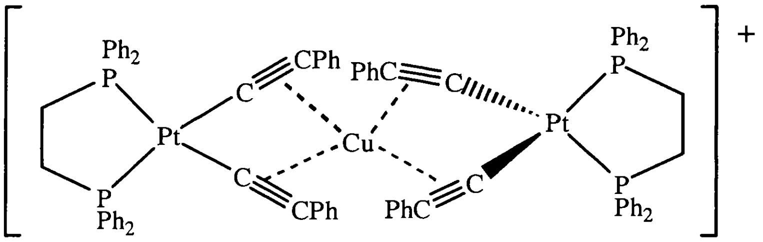


In the solid state, $[Ag(C{\equiv}CPh)(PMe_3)]_n$ was found to consist of almost straight chains of silver atoms.[14] The silver atoms in the chain alternate between being bonded to two σ-phenylethynyl groups or to two phosphine ligands with two additional weak π-ethynyl interactions.

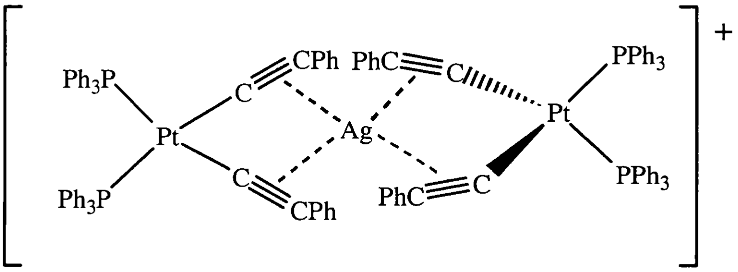


3.3 π-Bonded metal acetylide compounds

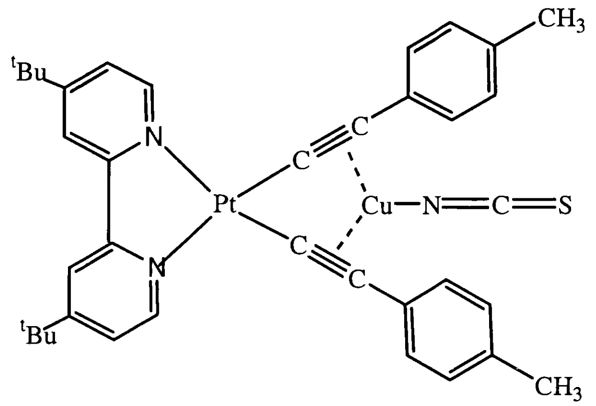
We have discussed copper- and silver- acetylides which are σ-bonded, now we shall look at examples where copper and silver form π-interaction with acetylides. For example, Deeming and Yamazaki treated *cis*-[Pt(C≡CPh)$_2$(η^2-dppe)] with [Cu(MeCN$_4$)][BF$_4$] to afford a 1:1 complex [PtCu(MeCN)(C≡CPh)$_2$(η^2-dppe)][BF$_4$]. An acetone-acetonitrile solution of this complex produced crystals of [Pt$_2$Cu(C$_2$Ph)$_4$(dppe)$_2$][BF$_4$].[15]



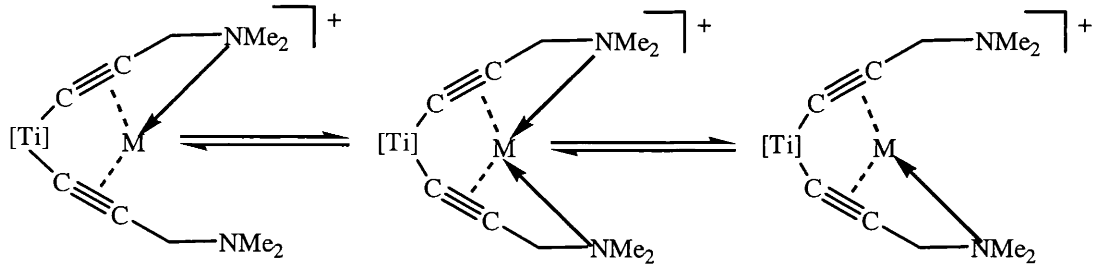
Similarly, Forniés *et al.* treated *cis*-[Pt(C≡CPh)$_2$(PPh$_3$)$_2$] with silver perchlorate in 2:1 ratio to give [Pt$_2$Ag(C≡CPh)$_4$(PPh$_3$)$_4$][ClO$_4$].[16] This complex showed a weak ν(C≡C) absorption in the IR spectrum at lower frequencies than the starting platinum bis(acetylide), suggesting the side-on π coordination of the C≡CR ligands.



Recently, Raithby *et al.* treated (4,4'-bis-*tert*-butyl-2,2'-dipyridyl) bis(alkynyl)platinum [($^tBu_2$bipy)Pt(C≡CR)$_2$] (R = C_6H_4Me, $SiMe_3$) with group 11 metal thiocyanate salts (M = Cu, Ag) to afford 1:1 mixed-metal complexes [($^tBu_2$bipy)Pt(C≡CR)$_2$M(SCN)].[17] Each coinage metal ion is bonded in an η^2 fashion to two carbon-carbon triple bonds so that the co-ordination geometry is trigonal planar.

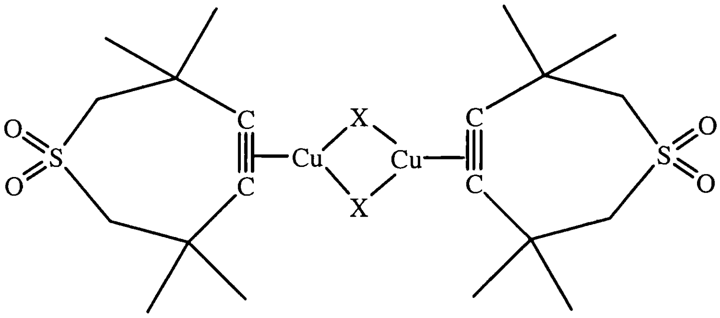


This year, Lang *et al.* have reported the synthesis of heterobimetallic complexes [(η^5-$C_5H_4SiMe_3$)$_2$Ti(C≡CCH$_2$NMe$_2$)$_2$ML] (ML = $CuPF_6$ and $AgBF_4$) upon treatment of [(η^5-$C_5H_4SiMe_3$)$_2$Ti(C≡CCH$_2$NMe$_2$)$_2$] with [Cu(CH$_3$CN)$_4$][PF$_6$] and $AgBF_4$ in THF.[18] In all the above examples, the coinage metal is trapped in between the acetylides and forms tweezer complexes. In this case, the lone pair of electrons on the amine is bonded to the coinage metal and gives structures in which the NMe$_2$ groups can exchange.

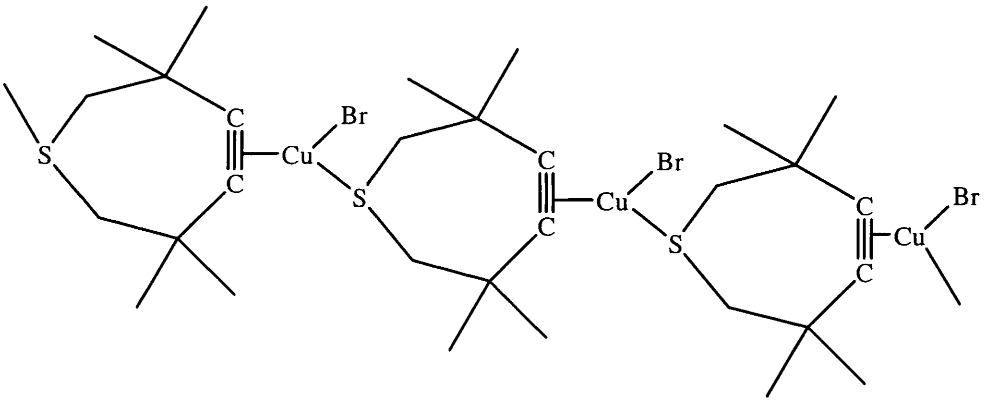


[Ti] = (η^5-$C_5H_4SiMe_3$)$_2$Ti; M = Ag, Cu

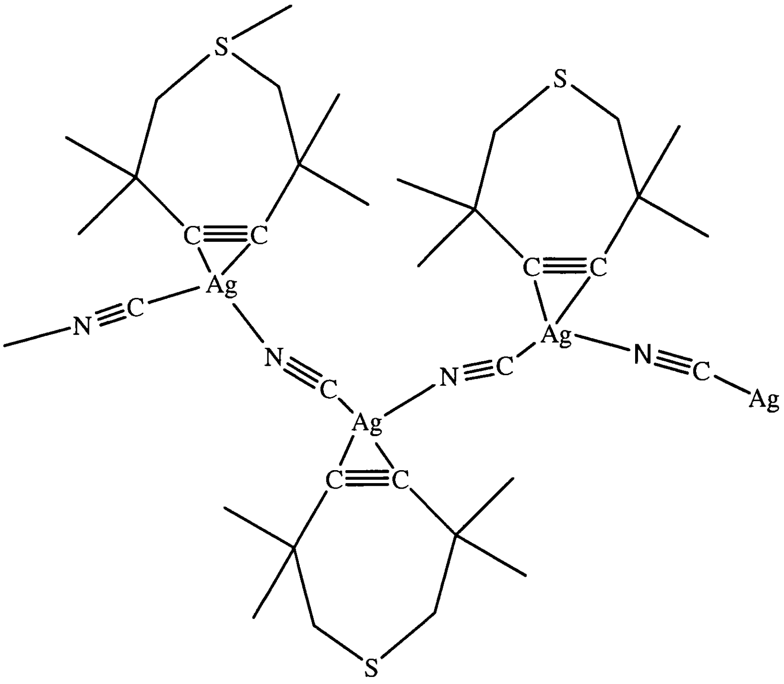
Coinage metal ions can also link acetylenes, acetylides or other functional groups together to form polymers or oligomers. For instance, Behrens *et al.* treated 3,3,6,6-tetramethyl-1-thiacyclohept-4-yne-1,1-dioxide (SO$_2$-alkyne) with copper(I) halides to form the dinuclear complexes [CuX(SO_2-alkyne)]$_2$.[19] It was found by X-ray diffraction studies that the strength of the copper-alkyne bond decreased from X = Cl to X = I. The complexes [CuX(S-alkyne)] (X = Cl, Br) form a simple polymeric chain in the solid-state when crystallised from dimethylsulfide/*n*-hexane whereas [CuI(S-alkyne)] forms another more complex polymer when crystallised from tetrahydrofuran/cyclopentane.



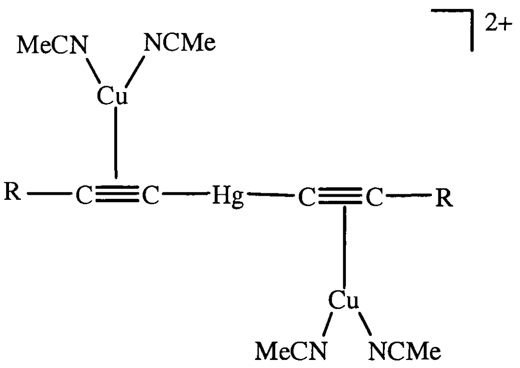
X = Cl, Br, I

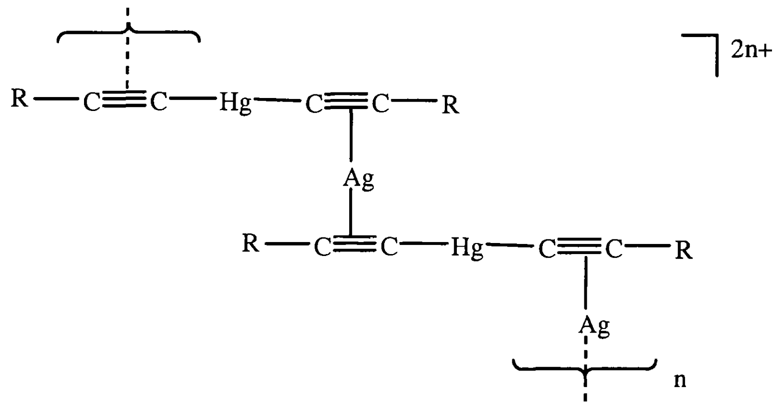


Similarly, Behrens *et al.* treated (S-alkyne) with silver(I) salts to form complex [Ag(MeCN)(S-alkyne)] which was studied by X-ray diffraction and was found to be polymeric. In addition, a copper(I) complex [Cu(BF_4)(CH_3CN)(S-alkyne)] was characterised by crystal structure analysis and was also found to be polymeric in the solid state. It was discovered that the interaction between the silver(I) ion and the C≡C bond is much weaker than the corresponding copper(I)-alkyne interaction.

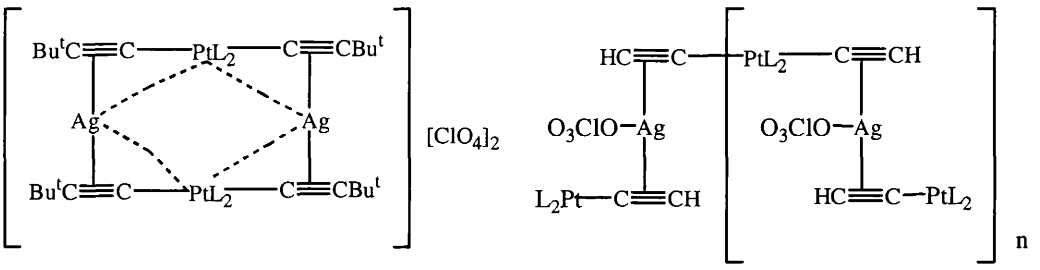


Recently, Vilar *et al.* reported that treatment of [Hg(C≡CR)$_2$] (R = C_6H_5, p-MeC_6H_4 and C^{t}Bu) with two equivalents of [Cu(CH$_3$CN)$_4$][PF$_6$] or [Ag(CH$_3$CN)$_4$][BF$_4$] afforded compounds with the general formula [Hg(C≡CR)$_2$Cu$_2$(CH$_3$CN)$_4$][PF$_6$]$_2$ and {[Hg(C≡CR)$_2$Ag][BF$_4$]}$_n$.[21] The IR spectra showed a shift of the ν(C≡C) stretch toward lower frequencies when compared to the starting materials, suggesting a π-bonding mode of the copper or silver ions to the C-C triple bond. The larger shift of the ν(C≡C) bond stretch to lower frequencies in the copper derivatives compared to those of the silver complexes suggested a stronger coordination of the copper ion to the alkynyl bonds. In all these complexes, the coinage metal ions are coordinated at the opposite sides of each mercury bis(acetylides) plane. Although these experiments were carried out under similar conditions, each copper ion is coordinated with one triple bond and two acetonitrile molecules forming an oligomer, whereas each silver ion is coordinated with two triple bonds forming a zig-zag Ag...Hg chain polymer.





3.4 Our strategy for the use of platinum acetylide complexes with silver



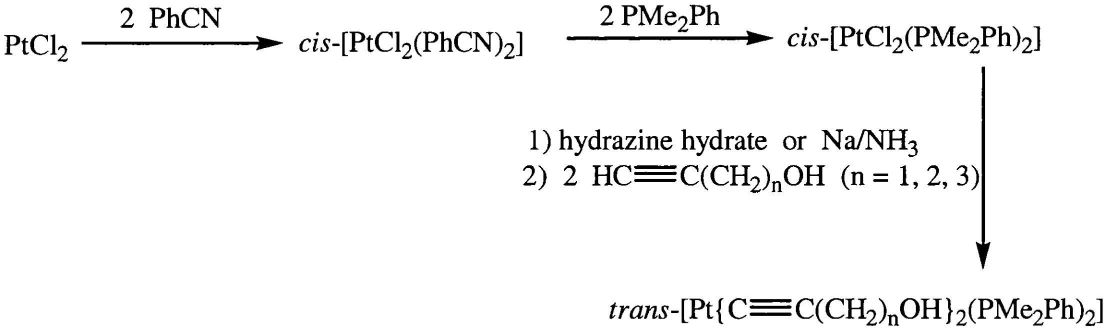
L = PMe_2Ph

Deeming and Yamazaki[22] treated *trans*-[$Pt(C{\equiv}CR)_2(PMe_2Ph)_2$] (R = Bu^t, H) with $AgClO_4$ to give the 1:1 adducts *trans*-[$PtAg(ClO_4)(\mu\text{-}C{\equiv}CR)_2(PMe_2Ph)_2$]. When R = Bu^t, the complex is a cyclic dimer with no coordinated perchlorate. However, when R = H, the adduct is a linear polymer with perchlorate coordinated to the silver atoms. We can conclude that changing the substituent R can alter the structure of the silver adduct. Therefore, *trans*-[$Pt(C{\equiv}CR)_2L_2$] {R = Ph, $C(CH_3)_2OH$; L = PMe_2Ph, PPh_3} were prepared in order to compare their behaviour with that of *trans*-

$[Pt(C{\equiv}CR)_2(PMe_2Ph)_2]$ (R = H, ^{t}Bu) in the reaction with $AgClO_4$. We shall explore the relationship between the substituent R and the shapes of the silver adducts. We also decided to synthesise *trans*-$[Pt\{C{\equiv}C(CH_2)_nOH\}_2(PMe_2Ph)_2]$ (n = 1, 2 and 3) in order to investigate whether the oxygen on the OH group would coordinate intramolecularly to the silver atom, whether the silver adducts of these complexes would give rings or linear polymers and also to see if the silver atom would substitute the hydrogen on the OH group. We have also studied the stoichiometry of the reactions between $AgClO_4$ and the platinum compounds in an exploratory manner by studying mixtures of the reagents at different molar ratios. We have used combined ^1H NMR and electrospray mass spectrometry methods to monitor these reactions.

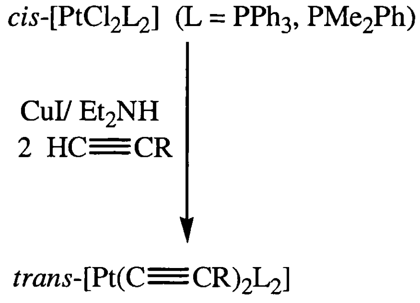
3.5 Synthesis of neutral platinum acetylide complexes

The complexes *trans*-$[Pt\{C\equiv C(CH_2)_nOH\}_2(PMe_2Ph)_2]$ (n = 1, 2 and 3) were prepared in three steps starting from $PtCl_2$. Dissolving $PtCl_2$ in hot benzonitrile and cooling the yellow solution gave a yellow crystal of *cis*-$[PtCl_2(PhCN)_2]$. Addition of PMe_2Ph to a benzene solution of *cis*-$[PtCl_2(PhCN)_2]$ gave colourless precipitate of *cis*-$[PtCl_2(PMe_2Ph)_2]$. The complexes *trans*-$[Pt\{C\equiv C(CH_2)_nOH\}_2\text{-}(PMe_2Ph)_2]$ (n = 1 and 2) had previously been prepared by Shaw *et al.*[23] in different ways. Reaction of *cis*-$[PtCl_2(PMe_2Ph)_2]$ with hydrazine hydrate in refluxing ethanol afforded a yellow solution. Addition of prop-2-yn-1-ol to the refluxing mixture gave yellow crystals of *trans*-$[Pt(C\equiv CCH_2OH)_2(PMe_2Ph)_2]$ **19** in 17% yield. The low yield was due to the difficulty in obtaining a yellow solution from the treatment of the refluxing ethanol solution of *cis*-$[PtCl_2(PMe_2Ph)_2]$ with hydrazine hydrate. Often a blue solution was obtained. We prepared compounds *trans*-$[Pt(C\equiv CCH_2CH_2OH)_2(PMe_2Ph)_2]$ **20** (57%) and *trans*-$[Pt(C\equiv CCH_2CH_2CH_2OH)_2(PMe_2Ph)_2]$ **21** (43%) by addition of 3-butyn-1-ol and 4-pentyn-1-ol respectively to a solution of sodium in liquid ammonia to form a yellow solution. *Cis*-$[PtCl_2(PMe_2Ph)_2]$ was then added to give **20** and **21** respectively.



19-21

The complexes *trans*-$[Pt(C\equiv CCH_2CH_2CH_2OH)_2(PPh_3)_2]$ **22**, *trans*-$[Pt(C\equiv CPh)_2(PMe_2Ph)_2]$ **23** and *trans*-$[Pt\{C\equiv CC(CH_3)_2OH\}_2(PPh_3)_2]$ **24** were prepared by Hagihara's method.[24] Compound **22** was synthesised in addition to the PMe_2Ph complex because we could not obtain suitable crystals for X-ray analysis of the product from the 1:1 reaction between **21** and $AgClO_4$. Therefore, we changed the ancillary ligand in the hope of more successful crystallisation. Compound **23** was prepared since the phenyl group is planar and bulky and the reactivity with $AgClO_4$ might be compared with other related alkynyl complexes, in particular those of $C\equiv CH$ and $C\equiv C^tBu$ studied by Deeming and Yamazaki. Compound **24** was studied because it is similar to *trans*-$[Pt(PMe_2Ph)_2(C\equiv CBu^t)_2]$ but with OH group replacing a Me group on the end of the acetylide. Since *trans*-$[Pt(PMe_2Ph)_2(C\equiv CBu^t)_2]$ gave a cyclic dimer on the addition of $AgClO_4$, we would like to compare **23** and **24** with *trans*-$[Pt(PMe_2Ph)_2(C\equiv CBu^t)_2]$ in order to investigate whether a cyclic dimer or polymer will form when reacted with $AgClO_4$. Thus we used a range of different compounds of the type $[Pt(alkynyl)_2L_2]$ ($L = PPh_3$, PMe_2Ph) to study the effects of the different acetylides and L ligands. Compounds **22-24** were prepared by reaction of *cis*-$[PtCl_2L_2]$ with 4-pentyn-1-ol, phenylacetylene and 2-methyl-3-butyn-2-ol respectively in the presence of catalytic amounts of CuI in diethylamine. All were obtained as yellow solids in 90%, 63% and 88% yield respectively.



22-24

R = Ph, $CH_2CH_2CH_2OH$, $C(CH_3)_2OH$

We also attempted to prepare *cis*-$[Pt\{C\equiv C(CH_2)_nOH\}_2(\eta^2\text{-dppe})]$ (n = 1, 2 and 3) by the same methods used for the *trans*-platinum bis(acetylide) complexes **19-21**. However, a mixture was obtained in each case and separation by chromatography was unsuccessful. Spectroscopic data were too complicated to assign any product peaks and this approach was not continued.

The complexes *trans*-$[Pt\{C\equiv C(CH_2)_nOH\}_2(PMe_2Ph)_2]$ (n = 1, 2 and 3) **19-21** were easily identified by spectroscopic methods. In the IR spectra $\nu(OH)$ bands appeared between 3422 and 3392 cm^{-1}, the $\nu(C\equiv C)$ stretch appeared between 2118 and 2109, while the $\nu(CH)$ absorptions appeared between 3043 and 2838 cm^{-1}. In the ^1H NMR spectrum of **19**, a triplet with ^{195}Pt satellites at δ 4.17 ($J_{P\text{-}H} = 1.4$ Hz, $J_{Pt\text{-}H} =$

12.6 Hz) was assigned to the CH_2OH group. For **20**, a triplet and another triplet with ^{195}Pt satellites, appeared at δ 3.41 (J_{H-H} = 6 Hz) and δ 2.38 (J_{H-H} = 6 Hz) were assigned to CH_2OH and CH_2 respectively, while for **21**, a triplet, a triplet of triplets and a quintet at δ 3.51 (J_{H-H} = 5.5 Hz), δ 2.18 (J_{H-H} = 2 Hz, J_{H-H} = 6.5 Hz) and δ 1.51 (J_{H-H} = 6.1 Hz) respectively were assigned to CH_2OH, CH_2 and CH_2 groups. Virtual triplets appearing between δ 2.00-1.92 (J_{P-H} = 7.6-7.0 Hz, J_{Pt-H} = 32.2-31.0 Hz) in **19-21** were assigned to the methyl groups of PMe_2Ph showing that they all are *trans* complexes. Moreover, in the ^{31}P NMR spectra, singlets with platinum satellites at δ – 5.90 (J_{Pt-P} = 2401 Hz), -5.21 (J_{Pt-P} = 2427 Hz) and –5.42 (J_{Pt-P} = 2434 Hz) were apparent for **19-21** respectively. The relatively small coupling constants suggest that the phosphine ligands are experiencing a large *trans*-influence and therefore lie *trans* to one another in all compounds. The values are consistent with mutually *trans*-phosphines. In the ^{13}C NMR spectrum of **19**, a singlet at δ 106.94 was assigned to C_β ($Pt-C_\alpha\equiv C_\beta$) whereas a triplet appeared at δ 101.38 (J_{P-C} = 44 Hz) was assigned to C_α. (with Pt satellites being too weak to be observed). Similarly, a singlet with ^{195}Pt satellites at δ 103.33 (J_{Pt-C} = 265 Hz) and a triplet with ^{195}Pt satellites at δ 95.32 (J_{P-C} = 30 Hz, J_{Pt-C} = 951 Hz) were assigned to C_β and C_α in **20**. Corresponding signals at δ 107.61 (J_{Pt-C} = 264 Hz) and δ 93.25 (J_{Pt-C} = 948 Hz, J_{P-C} = 30 Hz) were observed for **21**. The mass spectra of **19-21** gave parent molecular ions at *m/z* 581, 610 and 637 respectively. Compounds **19** and **20** have been prepared by Shaw *et al.* and our results are compatible with theirs.[22]

The complex *trans*-[$Pt(C\equiv CCH_2CH_2CH_2OH)_2(PPh_3)_2$] **22** was also easily identified spectroscopically. In the IR spectrum, the ν(C≡C) stretch appeared at 2131 cm^{-1}, while in ^{1}H NMR spectrum, two multiplets at δ 7.75 and δ 7.38 were observed for the phenyl protons. A singlet and two multiplets at δ 3.09, δ 1.62 and δ 0.99 were assigned to CH_2OH, CH_2 and CH_2 respectively. In ^{31}P NMR spectrum, a singlet with platinum satellites appeared at δ 2.65 (J_{Pt-P} = 2673 Hz), the small coupling constant again being consistent with the phosphines is *trans* to one another. The mass spectrum gave the peak for [M + Cu] ion at *m/z* 949 since CuI was involved in the synthesis and copper(I) probably contaminates the product.

Characterisation of *trans*-[$Pt(C\equiv CPh)_2(PMe_2Ph)_2$] **23** was very simple. The IR spectrum showed ν(C≡C) at 2107 cm^{-1}, while in the ^{1}H NMR spectrum, three multiplets at δ 7.81, δ 7.34 and δ 7.07 were observed for the phenyl protons. A virtual triplet at δ 2.02 (apparent $J_{P\text{-}H}$ = 7 Hz, $J_{Pt\text{-}H}$ = 32 Hz) was assigned to the methyl groups. In ^{31}P NMR spectrum, a singlet with platinum satellites appeared at δ −11.30 ($J_{Pt\text{-}P}$ = 2395 Hz), while the mass spectrum gave the parent molecular ion at *m/z* 674.

Trans-$[Pt\{C{\equiv}CC(CH_3)_2OH\}_2(PPh_3)_2]$ **24** was also characterised straightforwardly. The IR spectrum showed ν(OH) at 3415 cm^{-1}, ν(C≡C) at 2115 cm^{-1} and ν(CH) between 2962 and 2858 cm^{-1}. In ^{1}H NMR spectrum, signals at δ 7.74 ($J_{H\text{-}H}$ = 5.8 Hz) and δ 7.38 corresponded to the phenyl protons. A singlet with Pt satellites at δ 0.77 ($J_{Pt\text{-}H}$ = 94.3 Hz) was assigned to the methyl groups. In the ^{31}P NMR spectrum, a singlet with platinum satellites at δ 2.41 ($J_{Pt\text{-}P}$ = 2666 Hz) confirmed the phosphines were *trans* to each other. As with **23**, the mass spectrum gave the [M + Cu] ion at *m/z* 949, suggesting contamination with Cu(I).

3.6 Synthesis of cationic platinum/silver complexes

Addition of $AgClO_4$ to the *trans*-platinum acetylides **20**, **23** and **24** in 1:1 ratio in acetonitrile and crystallisation from acetonitrile and benzene afforded the polymers *trans*-$[PtAg(C{\equiv}CCH_2CH_2OH)_2(PMe_2Ph)_2]_n[ClO_4]_n(MeCN)_n$ **25,** *trans*-$[PtAg(C{\equiv}CPh)_2(PMe_2Ph)_2]_n[ClO_4]_n$ **27** and the oligomer *trans*-$[PtAg_2\{C{\equiv}CC(CH_3)_2OH\}_2(MeCN)_4(PPh_3)_2][ClO_4]_2$ **28** in moderate yields. It is important to realise that these compounds in the solid state may have different structures from those in solution as the polymers or oligomer may fragment in this medium. Spectroscopic studies would not easily lead to information on the state of aggregation of the compounds.

$$\textit{trans}\text{-}[Pt(C{\equiv}CR)_2L_2] \xrightarrow[CH_3CN]{AgClO_4} \mathbf{25, 27, 28}$$

$\{L = PPh_3, PMe_2Ph; R = CH_2CH_2OH, Ph, C(CH_3)_2OH\}$

The reaction between *trans*-$[Pt(C{\equiv}CCH_2CH_2CH_2OH)_2(PMe_2Ph)_2]$ **21** and $AgClO_4$, afforded the silver adduct **26**. However, we could not produce good quality crystals, so we were unable to give a definite formula of **26**. We believe that it has a polymeric structure since its spectroscopic data were very similar to those of *trans*-$[PtAg(C{\equiv}CCH_2CH_2OH)_2(PMe_2Ph)_2]_n[ClO_4]_n(MeCN)_n$ **25** which has been fully characterised by crystallographic techniques. In IR spectra, ν(OH) absorptions appeared between 3428 and 3401 cm^{-1}, while three or four ν(C≡C) appeared between 2119 and 2011 cm^{-1}. This shows that different types of acetylide groups were present in both compounds. Most of the ν(C≡C) absorptions appeared at lower frequencies than in the starting materials indicating that the silver ions were coordinated to all the carbon-carbon triple bonds. There were three or four ν(ClO_4) between 1119 and 1048 cm^{-1} indicating a symmetry lower than tetrahedral for these ions. Since the ^1H NMR spectra of all reactions with silver perchlorate were run in d^6-acetone, while the ^1H NMR spectra of the starting materials were run in $CDCl_3$, it is difficult to compare the two types of spectra directly and therefore, the ^1H NMR results will not be discussed here. In ^{31}P NMR spectra of **25** and **26**, the singlet with platinum satellites was shifted upfield to between δ -11.86 and –11.41 ($J_{Pt\text{-}P}$ = 2171-2166 Hz) on addition of electropositive Ag^+ ion to **20** and **21**. The small value of $J_{Pt\text{-}P}$ indicated a *trans*-arrangement of the phosphines. The electrospray mass spectrum of **25** gave $[M_2Ag]^+$ (M = compound **20**) ion at *m/z* 1327 and $[MAg]^+$ ion at *m/z* 717. In ^{13}C NMR spectrum of **26**, the separation between the C_α and C_β signals of 35.9 ppm was greater than in **21**, 14.36 ppm. The mass spectrum of **26** gave $M_2Ag_2ClO_4^+$ (M = compound **21**) at *m/z* 1590, M_2Ag^+ at *m/z* 1383, $MAg_2ClO_4^+$ at *m/z* 953 and MAg^+ at *m/z* 745.

For compounds **25** and **26**, the proton in the OH group can still be observed in ^1H NMR spectra, showing that substitution of hydrogen in the OH group by Ag^+ ion has not occurred.

Analysis of *trans*-$[PtAg(C{\equiv}CPh)_2(PMePh)_2]_n[ClO_4]_n$ **27** was unambiguous. In the IR spectrum, two ν(C≡C) bands appeared at 2108 and 2034 cm^{-1}. The higher frequency stretch is probably due to contamination with **23**, while the lower absorption is indicative of coordinated silver ions. In ^{31}P NMR spectrum, a singlet with platinum satellites at δ –10.37 ($J_{Pt\text{-}P}$ = 2138 Hz) confirmed the *trans*-arrangement of phosphines and the mass spectrum showed ions M_2Ag^+ {M = compound **23**} at *m/z* 1455, $MAg_2ClO_4^+$ at *m/z* 989 and MAg^+ at *m/z* 781.

The compound *trans*-$[PtAg_2(MeCN)_4(PPh_3)_2\{C{\equiv}CC(CH_3)_2OH\}_2][ClO_4]_2$ **28** was obtained as crystals from addition of $AgClO_4$ to **24** in acetonitrile and identified by solid state IR and solution studies. In the IR spectrum, a ν(OH) band at 3397 cm^{-1}, two ν(CH) bands at 2977, 2929 cm^{-1}, a ν(C≡C) band at 2028 cm^{-1} and a ν(ClO_4) band at 1097 cm^{-1} were observed. The lower value of the ν(C≡C) indicates that the silver ions were coordinated to the carbon-carbon triple bonds. In the ^{31}P NMR spectrum, the singlet with platinum satellites had shifted upfield to δ –0.45 (J_{Pt-P} = 2402 Hz) on coordination of electropositive Ag^+ ion. The mass spectrum gave ions $MAg_2ClO_4^+$ (M = compound **24**) at *m/z* 1201 and MAg^+ at *m/z* 993.

We also treated the amines *trans*-$[Pt(C{\equiv}CC_6H_4NH_2)_2(PPh_3)_2]$ **4**, *trans*-$[Pt(C{\equiv}CC_6H_4NH_2)_2(P^nBu_3)_2]$ **5** and *cis*-$[Pt(C{\equiv}CC_6H_4NH_2)_2(\eta^2\text{-dppe})]$ **6** (See Chapter 2) with $AgClO_4$, but we were unable to obtain any meaningful spectroscopic data and attempted crystallisation of products was unsuccessful. Finally, we reacted *trans*-$[Pt(C{\equiv}CCH_2OH)_2(PMe_2Ph)_2]$ **19** with $AgClO_4$ and *trans*-$[Pt(C{\equiv}CCH_2CH_2OH)_2(PMe_2Ph)_2]$ **20** with $[Os_3(CO)_{10}(MeCN)_2]$ but again we were unable to obtain crystalline products or meaningful spectroscopic data.

3.7 Exploratory work using electrospray and ^1H NMR solution studies

Electrospray mass spectrometry (ESMS) is a relatively new ionisation method introduced in the mid-1980's by Fenn and co-workers.[25,26] It involves spraying a solution of the sample into the source of a mass spectrometer and stripping away the solvent. Solubility rather than volatility becomes the critical factor and since the ionisation occurs under very mild conditions, molecular ions of fragile molecules can be observed. Thus, ESMS is a softer technique than electron impact (EI) and fast atom bombardment (FAB). It avoids fragmentation of molecules and therefore it gives a higher abundance of parent ions or heavier ions since these are formed by processes such as protonation rather than removal of electrons.

Ag^+ ions have been used previously for the ESMS analysis of phosphines[27,28], arsines[29], thioethers[30], arenes[31] and metal carbonyls.[32,33] For example, neutral metal carbonyl compounds generally do not give any ESMS signals as they do not undergo protonation reactions to yield cationic species due to the low basicity of CO groups.[34] However, if small quantities of Ag^+ ions are added to a solution of $[Ru_3(CO)_{12}]$ in MeCN, a spectrum of an adduct $[Ru_3(CO)_{12} + Ag(MeCN)]^+$ consisting of a single envelope at *m/z* 789 is observed.[35] Identification of adducts is straightforward and is helped by the distinctive isotope pattern for silver [^{107}Ag (52%), ^{109}Ag (48%)] combination with those for Ru. Ag^+ ions can also coordinate to carbon-carbon double or triple bonds, therefore adducts of polyalkyne compounds such as $[\{Cp(CO)_3W\}_2C_8]$ are readily observed by ESMS.[36]

Henderson *et al.* have used ESMS to investigate the relative ligating properties of triphenylpnictogen ligands EPh_3 (E = P, As, Sb and Bi) towards silver(I) and copper(I) ions.[37] Samples for ESMS analysis were prepared by dissolving 5 mg of either silver nitrate or $[Cu(MeCN)_4][BF_4]$ together with appropriate molar amounts of the EPh_3 ligands in MeCN (20 cm^3). ESMS spectra were recorded for mixtures of $AgNO_3$ with 1:1, 2:1, 3:1 or 4:1 molar ratios of either PPh_3, $AsPh_3$, $SbPh_3$ or $BiPh_3$ to measure the extent of complexation.

We adopted the Henderson method to investigate the ratio between *trans*-$[Pt(C{\equiv}CCH_2CH_2OH)_2(PMe_2Ph)_2]$ **20** and $AgClO_4$. Firstly, 15 mg of **20** was dissolved in 1.5 cm^3 of methanol. The mixture was shaken until all solids dissolved and this was then divided into six samples, each containing 0.25 cm^3 of the yellow solution. Secondly, 425 mg of $AgClO_4$ was completely dissolved in 5 cm^3 of methanol with shaking. 100 μl of this solution was mixed with 0.25 cm^3 of the yellow solution followed by the addition of 0.15 cm^3 of methanol. The first sample was made up to a volume of 0.5 cm^3 in which the molar ratio of $AgClO_4$: **20** was 10:1. This solution darkened immediately and a grey precipitate was formed. Solutions were prepared similarly with molar ratio of $AgClO_4$: **20** with values 2:1, 1:1, and 0.5:1. These solutions all darkened and some grey precipitate formed. These solutions were filtered before injecting into the mass spectrometer. Samples were used within 1 hour after being prepared.

It was found that spectra for solutions (1-3) were almost the same. In spectra of solutions (1-4), peaks corresponded to $[M_2Ag]^+$ (where M = compound **20**), $[MAg]^+$

and M^+ ions were observed. Since the same peaks were observed in a spectrum of crystals of *trans*-$[PtAg(C{\equiv}CCH_2CH_2OH)_2(PMe_2Ph)_2]_n[ClO_4]_n(MeCN)_n$ **25**, we concluded that 1:1 adduct was formed in all four solutions even when there is an excess of Ag^+ present. However, we cannot tell the accuracy of this experiment since the formation of grey precipitate was unexpected and made the experiment non-quantitative. We have not analysed the grey precipitate so its identity remains unknown. This experiment could have been repeated by using MeCN as the solvent which might have avoided the formation of precipitate with conditions more similar to those used in preparing compound **25**.

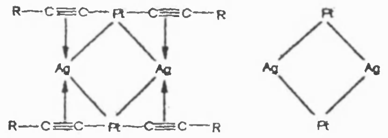
Four NMR samples in d^6-acetone were prepared in different ratios, for instance, $AgClO_4$: **20** in 1:1 (sample 1) and 0.5 :1 (sample 2), $AgClO_4$: *trans*-$[Pt(C{\equiv}CCH_2CH_2CH_2OH)_2(PMe_2Ph)_2]$ **21** in 1:1 (sample 3) and 0.5 :1 (sample 4) and ^1H NMR spectra were recorded. It was found that spectra of samples 1 and 2 were similar especially in the phenyl region. In the aliphatic region, the peaks from sample 2 were shifted slightly upfield as compare with the signals from sample 1. It is difficult to conclude whether the major upfield signals corrresponded to **20** or they were the same signals as the 1:1 adduct. There were some small signals next to the major ones and they were difficult to assign. In general, sample 1 gave a clean spectrum with the correct integrals, whereas the spectrum for sample 2 was more complicated. These were also true of samples 3 and 4. However, after the spectra were recorded, crystals were formed inside all NMR tubes. These crystals were the 1:1 adducts confirmed by redissolving and running ^1H NMR spectra.

In general, we seem to get the 1:1 adduct even when different ratios of $AgClO_4$ were added to the platinum bis(acetylide) complexes. Therefore, we decided to use this ratio in the preparation of polymers or oligomers.

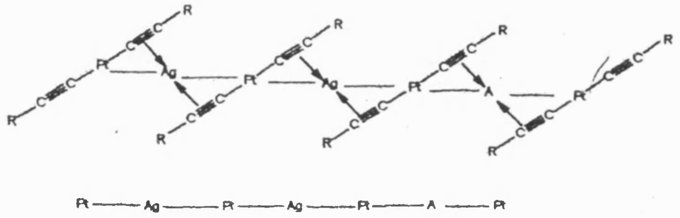
3.8 Studies on crystals obtained from $AgClO_4$ and platinum acetylides

Three crystal structures were obtained, those of *trans*-$[PtAg(C{\equiv}CCH_2CH_2OH)_2(PMe_2Ph)_2]_n[ClO_4]_n(MeCN)_n$ (**25**), *trans*-$[PtAg(C{\equiv}CPh)_2(PMe_2Ph)_2]_n[ClO_4]_n$ (**27**) and *trans*-$[PtAg\{C{\equiv}CC(CH_3)_2OH\}_2(MeCN)_4(PPh_3)_2][ClO_4]_2$ (**28**). These were determined by Dr. J. Steed of King's College, London. They are all quite different types of polymers or oligomers and will be discussed in detail below.

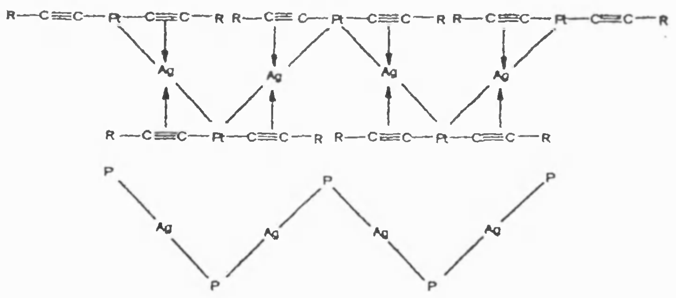
RING II



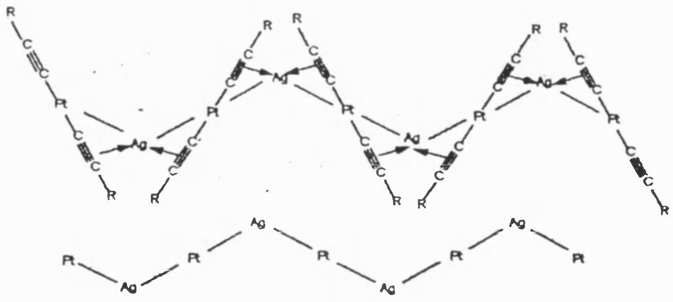
STRAIGHT LINEAR POLYMER 27



ZIG-ZAG LINEAR POLYMER **Pt at bends** I



ZIG-ZAG LINEAR POLYMER **Ag at bends** 25



In all three crystal structures that we have produced, the *trans*-platinum bis(acetylide) complexes are linked by Ag^+ ions. The silver atoms are coordinated on opposite faces of each platinum square plane in the compounds **25**, **27** and **28** whereas in *trans*-$[PtAg(ClO_4)(\mu\text{-}C{\equiv}CH)_2(PMe_2Ph)_2]_n$ **I** and *trans*-$[Pt(C{\equiv}C^tBu)_2(PMe_2Ph)_2AgClO_4]_n$ **II**, the silver atoms are coordinated at the same face of each square plane. In **I**, the acetylides are unsubstituted, and thus there is no steric problem having the silver atoms coordinated on the same side of each square plane. As the substituent R changes from H to CH_2CH_2OH, Ph and $C(CH_3)_2OH$ adverse steric interactions arise if the silver atoms are coordinated at the same side of each platinum square plane. Therefore, the silver atoms are coordinated at the opposite side of each platinum square plane and a polymer is formed. As R changes from CH_2CH_2OH, Ph and $C(CH_3)_2OH$ to ^{t}Bu, the silver atoms are coordinated at the same face of each platinum square plane again. In this case, a polymer is not formed but rather a cyclic dimer **II** results. Here the acetylides are bent away from the silver atoms. Therefore, compounds **I** and **II** are probably the extreme cases where the silver atoms are coordinated at the same side of the platinum square plane. It would be interesting to synthesise *trans*-$[Pt(C{\equiv}CCH_3)_2(PMe_2Ph)_2]$ and to react it with $AgClO_4$ in a 1:1 ratio in order to investigate the shape of the silver adduct and the coordination of silver atoms to the carbon-carbon triple bonds. This intermediate case between **I** and **II** has not been studied.

Compounds **25**, **27** and **I** are polymers in the solid state, all containing a zig-zag chain of ...PtAgPtAgPtAg... atoms. Polymer **I** has platinum atoms at the bends of the zig-zag chain, while silver atoms are at the bends of the chain in **25**. The platinum and silver atoms are approximately in a straight line in **27**. The Pt...Ag distances in these compounds below vary considerably. (Table 3-1)

Table 3-1

Compounds	**25**	**27**	**28**	**I**	**II**
Pt...Ag distances/Å	3.401(7) 3.314(7) 3.408(7) 3.477(7)	3.089(8) 3.488(8)	3.477(7) 3.506(7)	3.689(6) 3.778(6)	3.1960(10) 3.2161(9) 3.2080(9) 3.2683(10)

In all three structures **25, 27-28**, the perchlorate ions are not coordinated, unlike polymer **I** in which the perchlorate ions are coordinated to the silver ions. In **25**, only one of the OH groups from each platinum bis(acetylide) fragment is bound to each silver atom and the Ag-O distances vary. From the table below, the Ag...O distance in **I** is shorter than those in **25**. In **28**, the Ag...O distances are too long for covalent bonds and two acetonitrile molecules are bound to each silver atom. The Ag-N distances are different. [Ag(1)-N(1) 2.194(16) Å, Ag(1)-N(2) 2.282(18) Å, Ag(2)-N(3) 2.284(16) Å and Ag(2)-N(4) 2.295(19) Å]. We conclude that the coordination of hydroxyl groups to silver ions is in preference to acetonitrile and perchlorate ions. The coordination of perchlorate ions to silver atoms is the least preferable among the three different groups.

Table 3-2

Compounds	**25**	**28**	**I**
Ag...O distances/Å	2.911(1) 4.944(1) 3.865(1) 2.922(2) 4.043(2) 2.704(2)	3.529(1) 3.663(1) 4.508(1)	2.65(1)

Compound **25** is a fairly complicated polymer and the results of the X-ray study are summarised in Figures 3-1 and 3-2.

Ag(1)-C(1)	2.286(8) Å
Ag(1)-C(2)	2.379(9) Å
Ag(1)-C(13)	2.273(8) Å
Ag(1)-C(14)	2.346(9) Å
C(17)-Pt(2)-C(13)	178.4(3)°
P(3)-Pt(2)-P(2)	178.59(8)°
C(41)-Pt(3)-C(37)	178.8(4)°
P(4)-Pt(3)-P(5)	177.49(8)°

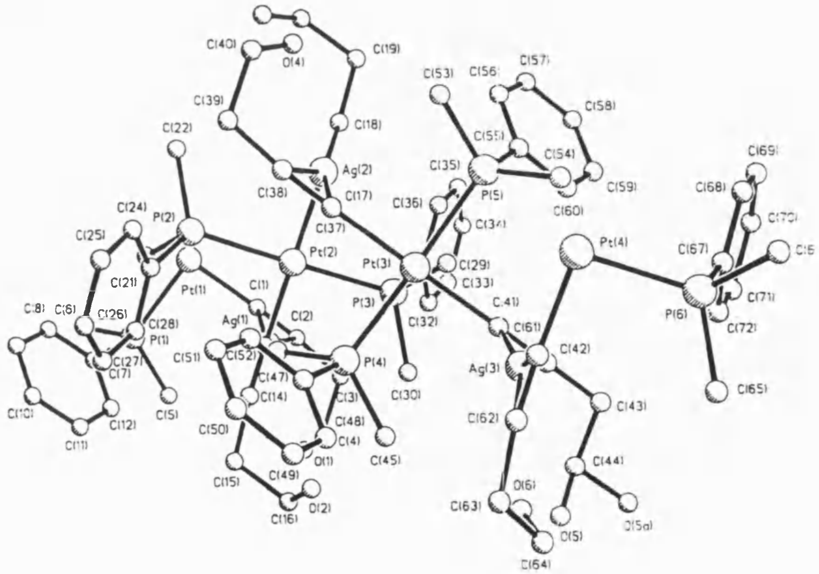


Fig 3-1 The structure of *trans*-$[PtAg(C{\equiv}CCH_2CH_2OH)_2(PMe_2Ph)_2]_n[ClO_4]_n$-$(MeCN)_n$ **25** with selected bond lengths and angles. Only part of the polymeric chain is shown.

Ag(1)-O(1) 2.911 Å
Ag(1)-O(2) 4.944 Å
Ag(2)-O(3) 3.865 Å
Ag(2)-O(4) 2.922 Å
Ag(3)-O(5) 4.043 Å
Ag(3)-O(6) 2.704 Å

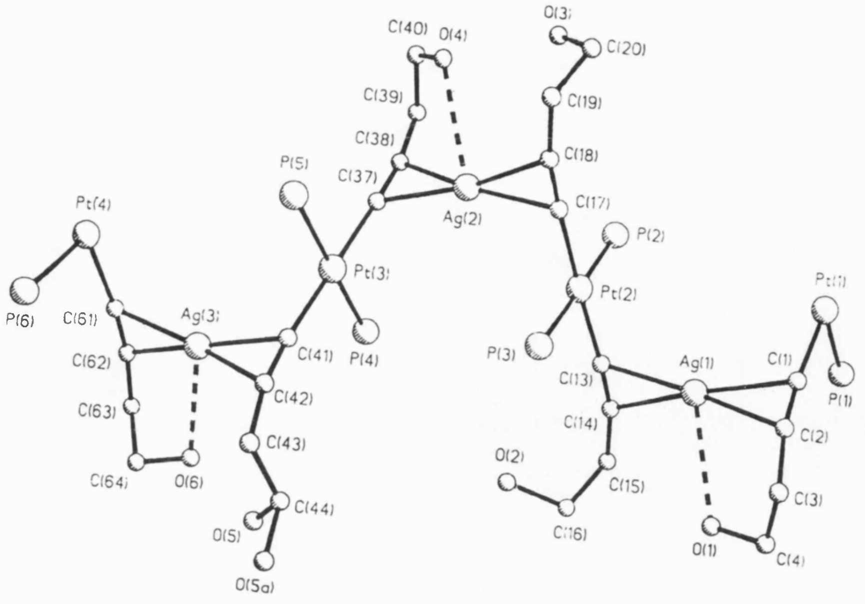


Fig.3-2 A diagram showing the distances between the Ag^+ ion and the oxygen on the OH group in **25**.

The geometry around the platinum centres in **25** is approximately square-planar as shown by the angles between ligands: [C(17)-Pt(2)-C(13) 178.4(3)° and P(3)-Pt(2)-P(2) 178.59(8)°; C(41)-Pt(3)-C(37) 178.8(4)° and P(4)-Pt(3)-P(5) 177.49(8)°]. Each silver ion is bound to two carbon-carbon triple bonds and one of the two OH groups on the platinum bis(acetylide) complexes. The phosphines and acetylides are pseudo-staggered. The phenyl ring on the phosphines is pointing away from the platinum.

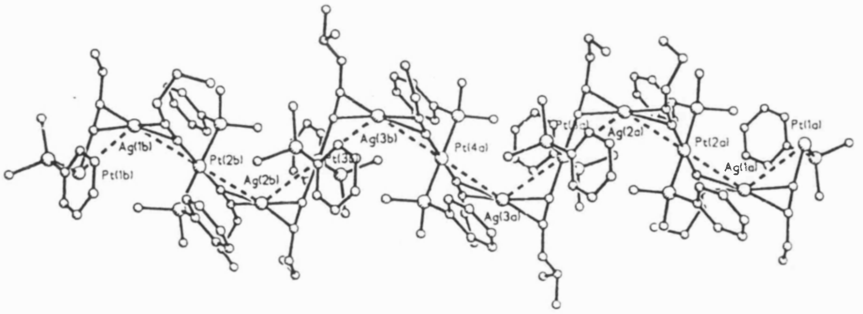


Fig 3-3 A diagram showing the Pt...Ag distances and the shape of the ...PtAgPtAgPtAg... chain for **25**.

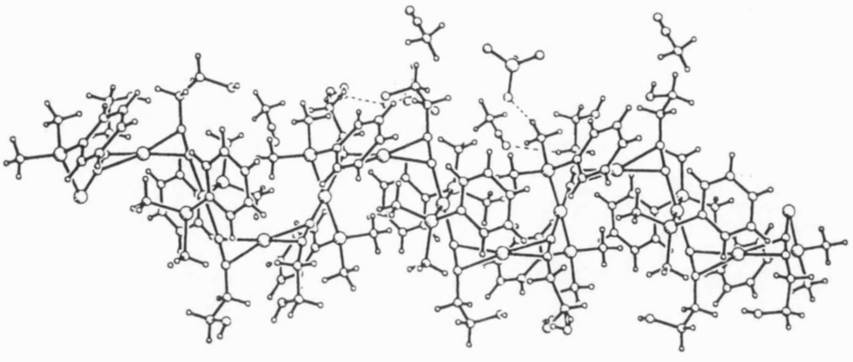


Fig.3-4 A packing diagram of the polymer **25**.

In all three compounds, each silver ion is bound to at least one carbon-carbon triple bond. The silver ion is closer to C_α than C_β. (Table 3-3)

Table 3-3

Compounds	**25**	**27**	**28**
Ag...C_α distance/Å	2.286(8) 2.273(8)	2.293(7) 2.262(6)	2.317(14) 2.257(13)
Ag...C_β distance/Å	2.379(9) 2.346(9)	2.348(7) 2.470(6)	2.336(17) 2.270(16)

It is believed that the distance between the Ag^+ ion and C_β might correlate with the C_α-C_β-C angle in both **27** and **28**. The shorter the distance between Ag^+ and C_β, the greater the bending at C_β. (Table 3-4)

Table 3-4

Compounds	Ag...C_β distance/Å	C_α-C_β-C angle/°
27	2.348(7) 2.470(6)	165.4(7) 176.8(7)
28	2.336(17) 2.270(16)	164.0(19) 163.4(19)

Compound **27** is also a polymer in which the *trans*-platinum bis(acetylide) complexes were linked by Ag^+ ions. The results of the X-ray study of **27** are summarised in Fig.3-5 which shows the repeat unit in the polymer..

C(1)-C(2)	1.229(9) Å	C(1)-Pt(1)-C(9)	175.7(3)°
Pt(1)-C(1)	1.999(7) Å	P(2)-Pt(1)-P(1)	175.40(6)°
Ag(1)-C(1)	2.293(7) Å	C(1)-C(2)-C(3)	165.4(7)°
Ag(1)-C(2)	2.348(7) Å	C(9)-C(10)-C(11)	176.8(7)°
Ag(1)-C(9)#2	2.262(6) Å		
Ag(1)-C(10)#2	2.470(6) Å		

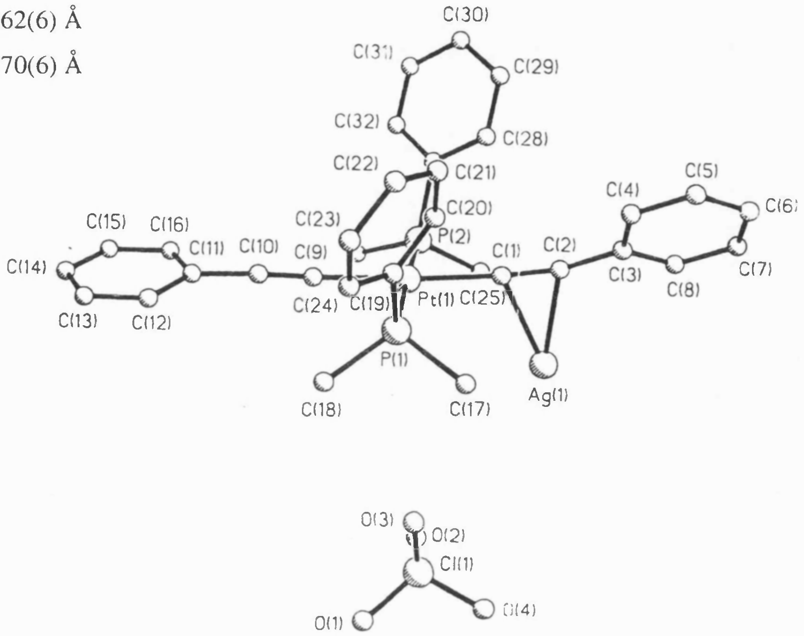


Fig 3-5 The structure of *trans*-$[\mathrm{PtAg(C{\equiv}CPh)_2(PMe_2Ph)_2}]_n[\mathrm{ClO_4}]_n$ **27** with selected bond lengths and angles.

In this polymer, the geometry around the platinum centres is approximately square-planar: C(1)-Pt(1)-C(9) 175.7(3)° and P(2)-Pt(1)-P(1) 175.40(6)°. Crystal structure of *trans*-$[\mathrm{Pt(C{\equiv}CPh)_2(PMe_2Ph)_2}]$ **III** has been determined at UCL but is unpublished. Comparing the geometry around the platinum centre of **III** and **27**, **III** is closer to a square- planar geometry around the platinum than **27**: C(1)-Pt(1)-C(1A) 180.0(1)° and P(1)-Pt(1)-P(1A) 180.0(1)°. Indeed, one acetylide is more bent than the other within the bis(acetylide) complex in **27**: C(1)-C(2)-C(3) 165.4(7)° and C(9)-C(10)-C(11) 176.8(7)°. In **III**, the phenyl ring of each phosphine is pointing away from the platinum so that one phenyl ring is pointing up and the other is pointing down. However, this is not the case for **27**. In **27**, the phenyl rings of both phosphines are closer to the bent acetylide whereas the methyl groups of both phosphines are closer to the linear acetylide. Such orientations of the phenyl rings and the methyl groups are probably affected by sterically and this explains why one of the acetylide is more bent than the other.

In **27**, each silver ion is only bound to two alkyne triple bonds. The phosphine and the bis(acetylides) are pseudo-eclipsed to each other. All the Pt atoms are crystallographically equivalent and there is no solvent in the crystal.

Ag...Pt distances:
3.089 Å
3.488 Å

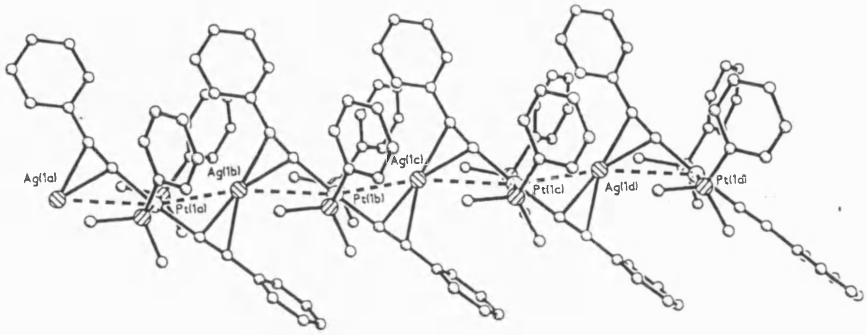


Fig.3-6 A diagram showing the Pt...Ag distances and the shape of the ...PtAgPtAgPtAg... chain in **27**.

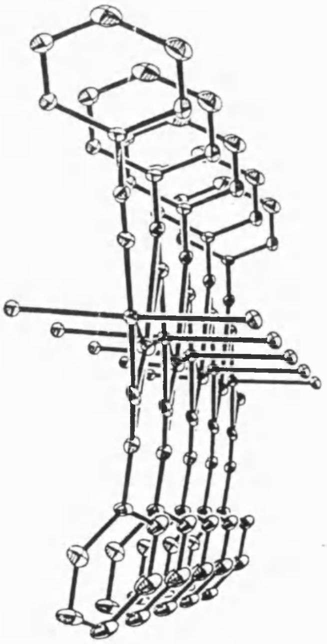


Fig. 3-7 A side-view of the polymer **27** showing the eclipsing of the phosphines and acetylides..

Compound **28** is an oligomer in which the platinum bis(acetylide) complex is coordinated to two silver ions. The results of thé X-ray study are summarised in Fig.3-8.

Ag(1)-C(1)	2.317(14) Å	P(1)-Pt(1)-P(2)	179.71(14)°
Ag(1)-C(2)	2.336(17) Å	C(1)-Pt(1)-C(6)	177.8(7)°
Ag(2)-C(6)	2.257(13) Å	C(1)-C(2)-C(3)	164.0(19)°
Ag(2)-C(7)	2.270(16) Å	C(6)-C(7)-C(8)	163.4(19)°
Ag(1)-N(1)	2.194(16) Å		
Ag(1)-N(2)	2.282(18) Å		
Ag(2)-N(3)	2.284(16) Å		
Ag(2)-N(4)	2.295(19) Å		

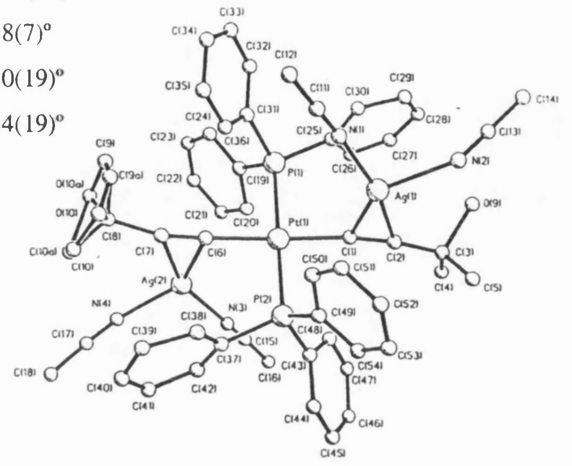


Fig.3-8 The structure of *trans*-$[PtAg\{C{\equiv}CC(CH_3)_2OH\}_2(MeCN)_4(PPh_3)_2]$-$[ClO_4]_2$ **28** with selected bond lengths and angles.

In this oligomer, the geometry around the platinum centre is approximately square planar. [P(1)-Pt(1)-P(2) 179.71(14)° and C(1)-Pt(1)-C(6) 177.8(7)°] The bis(acetylides) on both sides of the platinum are slightly bent.

Although in **28**, the $C(CH_3)_2OH$ group is very similar to a ^{t}Bu group, a cyclic dimer is not formed as with compound **II**. The coordination of acetonitrile molecules to silver atoms prevents the formation of a polymer. We are uncertain whether the bulkier PPh_3 group has any effect on the shape of compound **28** compare with the smaller PMe_2Ph ligand.

Ag(1)-Pt(1)	3.477 Å
Ag(2)-Pt(1)	3.506 Å
Ag(1)-O(9)	3.529 Å
Ag(2)-O(10)	4.508 Å
Ag(2)-O(10a)	3.663 Å

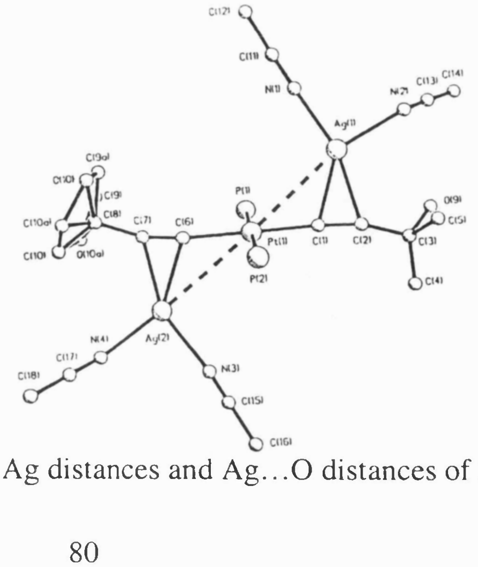


Fig.3-9 A diagram showing the Pt...Ag distances and Ag...O distances of **28**.

3.9 Conclusions

We have successfully built large molecular chains by linking platinum bis(acetylide) complexes together *via* silver ions and three crystal structures were obtained in which two of them are polymers **25** and **27** and one of them is oligomer **28**. Both polymers are 1:1 platinum-silver adduct whereas the oligomer is a 1:2 platinum-silver adduct even though the reaction between platinum bis(acetylide) complex and silver perchlorate was carried out in 1:1 ratio. In all three structures, the silver atoms are coordinated at the opposite faces of each Pt square plane. We postulate that **I** and **II** are the extreme cases where the silver atoms are coordinated at the same side of the Pt square plane. It would be of interest to synthesise the silver adduct of *trans*-$[Pt(C{\equiv}CCH_3)_2(PMe_2Ph)_2]$ and to examine its structure because this would lie sterically between the $C{\equiv}CH$ and $C{\equiv}C^tBu$ complexes and might either form a ring as in **II** or a chain as in **I**. In **25**, we have successfully proved that one of the hydroxyl group from the bis(acetylide) can bend round and bind to the silver atom, in preference to acetonitrile or perchlorate ions. Substitution of hydrogen in the hydroxyl groups by Ag is not observed. Since the coordination of acetonitrile to silver ions is in preference to perchlorate ions, silver adduct of bis(acetylide) with cyano or amino groups at the end could be prepared and to investigate whether the functional groups can bend round and bind to the silver atom analogous to the behaviour of the hydroxyl group in **25**.

3.10 Experimental

Preparation of *cis*-[PtCl$_2$(PPhMe$_2$)$_2$][38]

cis-[Pt(PhCN$_2$)$_2$Cl$_2$] (3.17 g, 6.71 mmol) was dissolved in benzene (50 cm^3) under nitrogen. PPhMe$_2$ (1.9 cm^3, 13.43 mmol) was added to the solution *via* a syringe. The reaction mixture was stirred at room temperature under nitrogen for 18 hours. The precipitate formed was then filtered, washed with hexane and air-dried. A white solid (3.39 g, 93%) was obtained. IR (KBr): 2913m (CH) cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 7.43-7.25 (m, 10H, Ph), 1.76 (d + ^{195}Pt satellites, 12H, $J_{P\text{-}H}$ = 11 Hz, $J_{Pt\text{-}H}$ = 35 Hz, Me); ^{31}P-{^{1}H} NMR (CDCl$_3$/CH$_2$Cl$_2$): δ -8.62 (s + ^{195}Pt satellites, $J_{Pt\text{-}P}$ = 3549 Hz); mass spectrum (FAB): *m/z* 542 (M$^+$).

Preparation of *trans*-[Pt(C≡CCH$_2$OH)$_2$(PPhMe$_2$)$_2$] (19)

A solution of *cis*-[Pt(PPhMe$_2$)$_2$Cl$_2$] (0.66 g, 1.22 mmol) in ethanol (5 cm^3) was heated under reflux. Hydrazine hydrate (0.23 cm^3, 4.8 mmol) was syringed into the solution. After 2 minutes, the solution turned yellow. Prop-2-yn-1-ol (0.55 cm^3, 9.44 mmol) was added *via* a syringe. The reaction mixture was refluxed for 30 minutes and then cooled in an ice-bath. Yellow crystals (0.12 g, 17%) were filtered off. IR (KBr): 3422s (OH), 3043w (CH), 2976w (CH), 2915w (CH), 2858w (CH), 2117m (C≡C) cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 7.80-7.75 (m, 4H, Ph), 7.44-7.42 (m, 6H, Ph), 4.17 (t + ^{195}Pt satellites, 4H, $J_{P\text{-}H}$ = 1.4 Hz, $J_{Pt\text{-}H}$ = 12.6 Hz, CH$_2$), 2.00 (t + ^{195}Pt satellites, 12H, $J_{P\text{-}H}$ = 7.6 Hz, $J_{Pt\text{-}H}$ = 32.2 Hz, Me); ^{31}P-{^{1}H} NMR (CDCl$_3$): δ -5.90 (s + ^{195}Pt satellites, $J_{Pt\text{-}P}$ = 2401 Hz); ^{13}C-{^{1}H} NMR (CDCl$_3$): δ 134.37 (t, $J_{P\text{-}C}$ = 69 Hz, P-C), 131.56 (t, $J_{P\text{-}C}$ = 16 Hz, o-C), 130.16 (s, p-C), 128.24 (t, $J_{P\text{-}C}$ = 12 Hz, m-C), 106.94 (s, Pt-C≡C), 101.38 (t, $J_{P\text{-}C}$ = 44 Hz, Pt-C), 53.37 (s, CH$_2$), 14.67 (t, $J_{P\text{-}C}$ = 40 Hz, Me); mass spectrum (FAB): *m/z* 581 (M$^+$).

Preparation of *trans*-[Pt(C≡CCH$_2$CH$_2$OH)$_2$(PPhMe$_2$)$_2$] (20)

Liquid ammonia (50 cm^3) was condensed into a three-necked round-bottomed flask at –78 °C which was equipped with a water condenser and a bubbler under nitrogen. Sodium (0.17 g, 7.38 mmol) was added to the ammonia and the liquid immediately turned dark blue. 3-Butyn-1-ol (0.30 cm^3, 3.69 mmol) was added *via* a syringe and the solution turned yellow. Then *cis*-[PtCl$_2$(PPhMe$_2$)$_2$] (1.00 g, 1.85 mmol) was added to the yellow solution and the reaction mixture in liquid ammonia was stirred at –78°C under nitrogen for 3 hours. Volatiles were evaporated at room temperature leaving a yellow solid behind which was washed with hexane and air-dried. A dry yellow powder (0.57 g, 51%) was obtained. IR (KBr): 3392s (OH), 2971w (CH), 2944w (CH), 2923w (CH), 2888w (CH), 2860w (CH), 2109w (C≡C) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.78 (m, 4H, Ph), 7.40 (m, 6H, Ph), 3.41 (t, J_{H-H} = 6 Hz, CH_2), 2.38 (tt, J_{H-H} = 6 Hz, CH_2), 1.96 (tt, J_{P-H} = 7 Hz, J_{Pt-H} = 32 Hz, Me); ^{31}P-{^{1}H} NMR ($CDCl_3$): δ -5.21 (s + ^{195}Pt satellites, J_{Pt-P} = 2427 Hz); ^{13}C-{^{1}H} NMR ($CDCl_3$): δ 134.47 (t, J_{P-C} = 56 Hz, P-C), 131.51 (t, J_{P-C} = 12 Hz, o-C), 130.13 (s, p-C), 128.23 (t, J_{P-C} = 10 Hz, m-C), 103.33 (t, J_{Pt-C} = 265 Hz, Pt-C≡C), 95.32 (tt, J_{P-C} = 30 Hz, J_{Pt-C} = 951 Hz , Pt-C), 61.54 (s, CH_2), 25.68 (s, CH_2), 14.81 (t, J_{P-C} = 39 Hz, Me); mass spectrum (FAB): *m/z* 610 (MH^+); elemental analysis calc. for $PtP_2O_2C_{24}H_{32}$: C, 47.29; H, 5.25; P, 10.18. Found C, 46.32; H, 5.19; P, 9.81.

Preparation of *trans*-$[Pt(C\equiv CCH_2CH_2CH_2OH)_2(PPhMe_2)_2]$ (21)

Liquid ammonia (50 cm^3) was condensed into a three-necked round-bottomed flask at –78 °C which was equipped with a water condenser and a bubbler under nitrogen. Sodium (0.17 g, 7.38 mmol) was added to the ammonia and the liquid immediately turned dark blue. 4-Pentyn-1-ol (0.21 cm^3, 2.21 mmol) was added *via* a syringe and the solution turned yellow. Then *cis*-$[PtCl_2(PPhMe_2)_2]$ (0.48 g, 0.88 mmol) was added to the yellow solution and the reaction mixture in liquid ammonia was stirred at –78°C under nitrogen for 3 hours. Volatiles were evaporated at room temperature leaving a yellow solid behind which was washed with hexane and air-dried. A sticky brown solid was obtained (0.37 g, 43%). IR (KBr): 3418br,s (OH), 2963w (CH), 2934w (CH), 2909w (CH), 2885w (CH), 2875w (CH), 2864w (CH), 2838w (CH), 2118w (C≡C) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.74 (m, 4H, Ph), 7.31 (m, 6H, Ph), 3.51 (t, J_{H-H} = 5.5 Hz, CH_2), 2.18 (tt, J_{H-H} = 2 Hz, J_{H-H} = 6.5 Hz, CH_2), 1.92 (J_{P-H} = 7 Hz, J_{Pt-H} = 31 Hz, Me), 1.51 (quin, J_{H-H} = 6.1 Hz, CH_2); ^{31}P-{^{1}H} NMR ($CDCl_3$) δ -5.42 (s + ^{195}Pt satellites, J_{Pt-P} = 2434 Hz); ^{13}C-{^{1}H} NMR ($CDCl_3$): δ 134.59 (t, J_{P-C} = 56 Hz, P-C), 131.50 (t, J_{P-C} = 12 Hz, o-C), 129.83 (s, p-C); 128.07 (t, J_{P-C} = 10 Hz, m-C), 107.61 (t, J_{Pt-C} = 264 Hz, Pt-C≡C), 93.25 (tt, J_{Pt-C} = 948 Hz, J_{P-C} = 30 Hz, Pt-C), 62.80 (s, CH_2), 32.14 (s, CH_2), 18.55 (s, CH_2), 14.76 (t, J_{P-C} = 40 Hz, Me); mass spectrum (FAB): *m/z* 637 (M^+); elemental analysis calc. for $PtP_2O_2C_{26}H_{36}$: C, 48.98; H, 5.65; P, 9.73. Found C, 46.03; H, 5.62; P, 8.98.

Preparation of *trans*-[Pt(C≡CCH$_2$CH$_2$CH$_2$OH)$_2$(PPh$_3$)$_2$] (22)

The compound *cis*-[PtCl$_2$(PPh$_3$)$_2$] (0.20 g, 0.25 mmol) and CuI (10 mg) were added to dry diethylamine (10 cm^3) under nitrogen. 4-Pentyn-1-ol (0.05 cm^3, 0.49 mmol) was added to the mixture. The reaction mixture was stirred at room temperature under nitrogen for 18 hours. It was then pumped to dryness under reduced pressure to yield a brown solid. This was redissolved in dichloromethane and filtered thorough silica. The brown solution was pumped to dryness under reduced pressure to give a brown powder (0.20 g, 90%). IR (KBr): 2970w (CH), 2927w (CH), 2835w (CH), 2131w (C≡C) cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 7.75 (m, 12H, Ar), 7.38 (m, 18H, Ar), 3.09 (s, 2H, CH$_2$OH), 1.62 (m, 2H, C≡CCH$_2$), 0.99 (m, 2H, CH$_2$); ^{31}P-{^{1}H} NMR (CDCl$_3$): δ 2.65 (s + ^{195}Pt satellites, J_{Pt-P} = 2673 Hz); mass spectrum (FAB): *m/z* 949 (M$^+$+Cu); elemental analysis calc.for PtP$_2$O$_2$C$_{46}$H$_{44}$.CuCl: C, 56.06; H, 4.47; P, 6.30. Found C, 55.47; H, 5.60; P, 5.48.

Preparation of *trans*-[Pt(C≡CC$_6$H$_5$)$_2$(PPhMe$_2$)$_2$] (23)

The compound *cis*-[PtCl$_2$(PPhMe$_2$)$_2$] (0.59 g, 1.09 mmol) and CuI (10mg) were added to dry diethylamine (10 cm^3) under nitrogen. Phenylacetylene (0.24 cm^3, 2.18 mmol) was added to the mixture *via* a syringe. The reaction mixture was stirred at room temperature under nitrogen for 18 hours. It was then pumped to dryness under reduced pressure, redissolved in dichloromethane and filtered thorough silica. A yellow solution was obtained which was pumped to dryness under reduced pressure to afford a yellow powder (0.46 g, 63%). IR (KBr): 2107s (C≡C) cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 7.84-7.78 (m, 4H, Ph), 7.34-7.33 (m, 6H, Ph), 7.08-7.06 (m, 10H, Ar), 2.02 (tt, J_{P-H} = 7 Hz, J_{Pt-H} = 32 Hz, Me); ^{31}P-{^{1}H} NMR (CDCl$_3$): δ -11.30 (s + ^{195}Pt satellites, J_{Pt-P} = 2395 Hz); mass spectrum (ESP): *m/z* 674 (MH$^+$); elemental analysis calc. for PtP$_2$C$_{32}$H$_{32}$: C, 57.06; H, 4.75; P, 9.21. Found C, 55.45; H, 4.76; P, 8.13.

Preparation of *trans*-[Pt{C≡CC(CH$_3$)$_2$OH}$_2$(PPh$_3$)$_2$] (24)

The compound *cis*-[PtCl$_2$(PPh$_3$)$_2$] (0.23 g, 0.29 mmol) and CuI (10mg) were added to dry diethylamine (20 cm^3) under nitrogen. 2-methyl-3-butyn-2-ol (0.06 cm^3, 0.58 mmol) was added to the mixture and the reaction mixture was stirred under nitrogen at room temperature for 18 hours. It was pumped to dryness under reduced pressure to give a solid. This was redissolved in dichloromethane and was filtered thorough silica. The filtrate was pumped to dryness under reduced pressure to afford a yellow powder (0.23 g, 88%). IR (KBr): 3415m (OH), 2962w (CH), 2922w (CH), 2858w (CH), 2115w (C≡C) cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 7.74 (q, 12H, $J_{H\text{-}H}$ = 5.8 Hz, Ar), 7.38 (m, 18H, Ar), 0.77 (s, 12H, $J_{Pt\text{-}H}$ = 94.3 Hz, Me); ^{31}P-{^{1}H} NMR (CDCl$_3$): δ 2.41 (s, $J_{Pt\text{-}P}$ = 2666 Hz); mass spectrum (FAB): *m/z* 949 (M$^+$+Cu); elemental analysis calc.for $PtP_2O_2C_{46}H_{44}.CuCl$: C, 56.07; H, 4.47; P, 6.30. Found C, 55.24; H, 5.93; P, 5.27.

Preparation of *trans*-[PtAg(C≡CCH$_2$CH$_2$OH)$_2$(PMe$_2$Ph)$_2$]$_n$.[ClO$_4$]$_n$.(MeCN)$_n$ (25)

trans-[Pt(PPhMe$_2$)$_2$(C≡CCH$_2$CH$_2$OH)$_2$] (0.05 g, 0.08 mmol) and AgClO$_4$ (0.02 g, 0.08 mmol) were dissolved in acetonitrile (20 cm^3) under nitrogen. The reaction mixture was stirred at room temperature for 18 hours. The solution was reduced to 3 cm^3 and benzene was added until the solution was cloudy. Colourless needles and block-shape crystals (0.09 g, 82%) were obtained. IR (KBr): 3428s (OH), 2957w (CH), 2930w (CH), 2911w (CH), 2878w (CH), 2119w (C≡C), 2062w (C≡C), 2055w (C≡C), 2023w (C≡C), 1119s (ClO$_4$), 1108s (ClO$_4$), 1093s (ClO$_4$), 1048s (ClO$_4$) cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 7.78-7.77 (m, 4H, Ph), 7.52-7.48 (m, 6H, Ph), 4.53 (s, 2H, OH), 3.62 (q, 4H, $J_{H\text{-}H}$ = 16 Hz, CH$_2$), 2.68 (t, 4H, $J_{H\text{-}H}$ = 5.5 Hz, CH$_2$), 2.18 (tt, 12H, $J_{P\text{-}H}$ = 7 Hz, $J_{Pt\text{-}H}$ = 11 Hz, Me); ^{31}P-{^{1}H} NMR (d^6-acetone) δ -11.86 (s + ^{195}Pt satellites, $J_{Pt\text{-}P}$ = 2171 Hz); mass spectrum (+ ion ES): *m/z* 1327 (M$_2$Ag$^+$), 717 (MAg$^+$); elemental analysis calc.for $PtAgP_2ClO_6C_{24}H_{32}$: C, 35.27; H, 3.92; Cl, 4.35; P, 7.59. Found C, 35.83; H, 4.22; Cl, 4.47; P, 7.01.

Treatment of *trans*-[Pt(C≡CCH$_2$CH$_2$CH$_2$OH)$_2$(PPhMe$_2$)$_2$] with silver chlorate (26)

trans-[Pt(PPhMe$_2$)$_2$(C≡CCH$_2$CH$_2$CH$_2$OH)$_2$] (0.05 g, 0.08 mmol) and AgClO$_4$ (0.02 g, 0.08 mmol) were dissolved in acetonitrile (20 cm^3) under nitrogen. The reaction mixture was stirred at room temperature for 18 hours. The solution was reduced to 3 cm^3 and benzene was added until the solution was cloudy. Yellow crystals (0.03 g, 29%) were obtained. IR (KBr): 3401s (OH), 2934w (CH), 2911w (CH), 2881w (CH), 2876w (CH), 2840w (CH), 2116w (C≡C), 2040w (C≡C), 2011w (C≡C), 1141s (ClO$_4$), 1106s (ClO$_4$), 1092s (ClO$_4$) cm^{-1}; ^{1}H NMR (d^6-acetone): δ 7.82-7.80 (m, 4H, Ph), 7.54-7.50 (m, 6H, Ph), 3.83 (s, 2H, OH), 3.60 (s, 4H, CH_2), 2.55 (s, 4H, CH_2), 2.04 (t, 12H, J_{H-H} = 2 Hz, Me), 1.70 (t, 4H, J_{H-H} = 6 Hz, CH_2); $^{31}P-\{^1H\}$ NMR (d^6-acetone): δ -11.41 (s + ^{195}Pt satellites, J_{Pt-P} = 2166 Hz); $^{13}C-\{^1H\}$ NMR (d^6-acetone): δ 133.80 (t, J_{P-C} = 58 Hz, P-C), 131.21 (s, o-C), 129.26 (s, p-C), 114.43 (t, J_{Pt-C} = 296 Hz, Pt-C≡C), 78.53 (t, J_{Pt-C} = 949 Hz, Pt-C), 61.30 (s, CH_2), 33.06 (s, CH_2), 18.62 (s, CH_2), 14.66 (t, J_{P-C} = 38 Hz, Me); mass spectrum (+ ion ES): *m/z* 1590 ($M_2Ag_2ClO_4^+$), 1383 (M_2Ag^+), 953 ($MAg_2ClO_4^+$), 745 (MAg^+); elemental analysis calc. for $PtP_2AgClO_6C_{26}H_{36}$: C, 36.94; H, 4.26; Cl, 4.20; P, 7.34. Found C, 36.19; H, 3.99; Cl, 4.94; P, 7.60.

Preparation of *trans*-[PtAg(C≡CPh)$_2$(PMePh)$_2$]$_n$.[ClO$_4$]$_n$ (27)

trans-[Pt($PPhMe_2$)$_2$(C≡CPh)$_2$] (0.07 g, 0.10 mmol) and $AgClO_4$ (0.02 g, 0.10 mmol) were dissolved in acetonitrile (20 cm^3) under nitrogen. The reaction mixture was stirred at room temperature for 18 hours. The solution was reduced to 3 cm^3 and benzene was added until the solution was cloudy. Yellow crystals (0.04 g, 42%) were obtained. IR (KBr): 2108w (C≡C), 2034 (C≡C) cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.03-7.98 (m, 4H, Ph), 7.59-7.53 (m, 6H, Ph), 7.31 (s, 10H, Ar), 2.30 (tt, 12H, J_{P-H} = 7.8 Hz, J_{Pt-H} = 27.3 Hz, Me); $^{31}P-\{^1H\}$ NMR ($CDCl_3$): δ -10.37 (s + ^{195}Pt satellites, J_{Pt-P} = 2138 Hz); mass spectrum (+ ion ES): *m/z* 1455 (M_2Ag^+), 989 ($MAg_2ClO_4^+$), 781 (MAg^+); elemental analysis calc. for $PtAgClO_4P_2C_{32}H_{32}$: C, 43.61; H, 3.63; Cl, 4.03; P, 7.04. Found C, 42.53; H, 3.42; Cl, 5.58; P, 5.46.

Preparation of *trans*-[PtAg$_2$(MeCN)$_4${C≡CC(CH$_3$)$_2$OH}$_2$(PPh$_3$)$_2$][ClO$_4$]$_2$ (28)

trans-[Pt(PPh_3)$_2${C≡CC(CH_3)$_2$OH}$_2$] (0.16 g, 0.18 mmol) and $AgClO_4$ (0.04 g, 0.18 mmol) were dissolved in acetonitrile (20 cm^3) under nitrogen. The reaction mixture was stirred at room temperature for 18 hours. The solution was reduced to 3 cm^3 and benzene was added until the solution was cloudy. Yellow crystals (0.10 g, 51%) were obtained. IR (KBr): 3397m (OH), 2977w (CH), 2929w (CH), 2028w (C≡C), 1097s (ClO_4) cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.75 (m, 12H, Ar), 7.55 (m, 18H, Ar), 2.14 (s, 12H, Me), 0.84 (s, 12H, Me); $^{31}P-\{^1H\}$ NMR ($CDCl_3$): δ -0.54 (s + ^{195}Pt satellites, J_{Pt-P} = 2402 Hz); mass spectrum (+ ion ES): *m/z* 1201 (M^++Ag_2ClO_4), 993 (M^++Ag); elemental analysis calc.for $PtAg_2P_2O_{10}Cl_2N_4C_{54}H_{56}$: C, 44.26; H, 3.83; N, 3.83; Cl, 4.85; P, 4.23. Found C, 44.97; H, 3.74; N, 3.60; Cl, 3.40; P, 4.46.

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Chapter 4: The synthesis of small bite angle diphosphine complexes

The development of new homogeneous catalysts is an ever expanding area in chemistry. Catalysts that are chirally active, such as some optically active phosphines, are particularly useful as they speed up the production of one form of chiral molecules only. Indeed, this year's Nobel Prize for chemistry was awarded to Knowles, Noyori and Sharpless for their work on chirally catalysed hydrogenation and oxidation reactions. In this chapter, an alternative way of preparing homogeneous catalysts is considered. Bis(diphenylphosphino)-methane (dppm) can be a bridging or a chelating ligand, although the latter is rare. A chelating dppm ligand creates a bite angle (P-M-P angle) which is ver small. The advantage of achieving small bite angle complexes is that, excluding the diphosphine, a large vacant coordination site results and this is potentially good for homogeneous catalysis. For example, if the energy of this reactant complex is raised to a value close to the transition state of the reaction. Then, the activation energy will be low and the catalytic reaction will run smoothly and fast. Bis(di-o-tolylphosphino)methane (dotpm) is chosen to chelate low valent metal centres as it is bulkier than dppm. We investigated whether increasing the steric bulk of both the phenyl rings of dppm, and its backbone substituents, decreases the bite angle.

Introduction

4.1 Phosphines

Phosphines, first prepared by Thénard in 1847, are classfied as primary (PH_2R), secondary (PHR_2) or tertiary (PR_3) and have three covalently bonded groups at a phosphorus (III) centre, which also has a lone pair of electrons. The chemistry of phosphines is growing rapidly as tertiary phosphines, when coordinated to a metal, are useful catalysts in many industrial processes such as hydroformylation, olefin hydrogenation and olefin polymerisation.[1] Moreover, the preparation of optically active phosphines by Horner and co-workers[2] greatly stimulated the entire field of phosphine chemistry resulting in the award of the Nobel Prize in Chemistry this year to Knowles, Noyori and Sharpless. The properties of a phosphine depend markedly on the substituents at phosphorus and can be discussed in terms of steric properties, which are controlled by the size of the ligand, and the electronic properties which depend on the donor properties of the substituents.

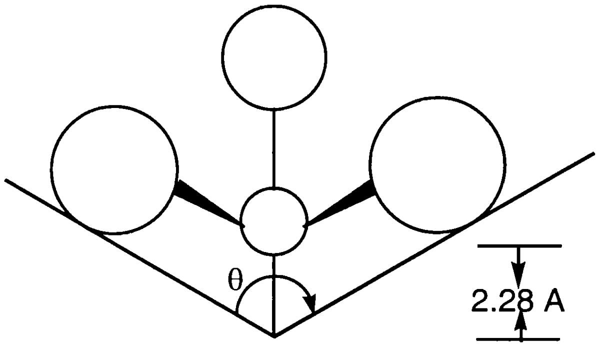
4.2 Cone angle

The steric properties of a phosphine ligand can be discussed in terms of its cone angle. This concept was initially proposed by Tolman[3] in 1970 when he replaced CO from the zerovalent complex, $Ni(CO)_4$, by bulky phosphine ligands (L) in order to see how many phosphines can fit around the nickel atom.

$$Ni(CO)_4 \quad + \quad nL \quad \rightleftharpoons \quad Ni(CO)_{4-n}L_n \quad + \quad n\,CO$$

The degree of substitution was estimated from the relative intensities of the carbonyl infrared bands. For instance, the A_1 band of $[Ni(CO)_3(PCy_3)]$ and the B_1 band of $[Ni(CO)_2(PCy_3)_2]$ were of about the same intensity, so that the degree of substitution was estimated at 1.5. The estimates were probably reliable to ±0.2. Under such experimental conditions, Tolman found that the extent of displacement of CO decreased as the size of the ligand increased and concluded that the binding ability of a ligand depended strongly on its steric requirement. Therefore, a quantitative means of measuring the size of a ligand was needed.

By convention, the metal is placed at 2.28 Å from the phosphorus atom (a typical Ni-P distance). A cone is then drawn which just touches the outermost atoms of the groups bound to phosphorus and comes to an apex at the metal. The angle at the apex of the cone is the Tolman's cone angle (θ) which gives an indication of the steric demand of the phosphine. For instance, two P^nBu_3 ligands (cone angle 130°) was estimated by Tolman to give $[Ni(CO)_2(P^nBu_3)_2]$ whereas only one P^tBu_3 ligand (cone angle 182°) was substituted to afford $[Ni(CO)_3(P^tBu_3)]$ under the same experimental conditions.



There are drawbacks of Tolman's cone angle definition as it does not take into account variations in cone angle from complex to complex due to changes in ligand conformation and ligand meshing effects. Despite this limitation, however, Tolman's cone angle has become the standard parameter for discussing ligand sizes. It can be derived directly from crystallographic data which defines the centres of the atoms. A knowledge of the van der Waals surface of the ligand (and in particular, the surface generated by the peripheral hydrogen atoms) being required for the calculation.

4.3 The electronic parameter

The electronic properties of a phosphine ligand is measured by the electronic parameter (ν). Strohmeier and Müller[4] first showed that phosphorus ligands could be ranked in an electronic series for a variety of monosubstituted transition metal carbonyls. A CO ligand was displaced from $Ni(CO)_4$ by a phosphine (L) and this changed the CO stretching frequencies of the remaining carbonyls by an amount depending on the donor-acceptor properties of the phosphine.

$$Ni(CO)_4 \quad + \quad L \quad \rightleftharpoons \quad Ni(CO)_3L \quad + \quad CO$$

The infrared spectrum of $[Ni(CO)_3L]$ therefore provides a simple method to estimate this combined donor-acceptor character of a phosphine. The C_{3v} symmetric $Ni(CO)_3$ fragment shows two CO bands in the infrared spectrum, namely the A_1 and E modes. The position of the higher frequency A_1 mode was used to rank the overall donor-acceptor properties of a variety of phosphorus ligands.

Phosphine	ν(cm^{-1})	Phosphine	ν(cm^{-1})
$^{t}Bu_3P$	2056.1	Me_3P	2064.1
$^{n}Bu_3P$	2060.3	Ph_3P	2068.9
Et_3P	2061.7	F_3P	2111.0
Et_2PPh	2063.7		

It was found that the more electron-withdrawing the phosphine is (a good π acceptor), the higher the frequency of the A_1 carbonyl band. Conventionally, the π acceptor properties of a phosphine ligand were thought to involve the vacant 3d orbitals of the phosphorus atom.[5] However, theoretical calculations of LUMO energies of the M-P bond show that the unoccupied σ* orbitals of the P-R bonds are the principal back-acceptors.[6] Thus, removal of an electron from a metal-phosphine orbital containing σ* character would increase the M-P bond length and the strength of the P-R bonds.

4.4 PPh_3 vs $P(o\text{-tolyl})_3$

Although the only difference between PPh_3 and $P(o\text{-tolyl})_3$ is the methyl groups *ortho* to the benzene ring, the steric properties of the two phosphines are remarkably different. The cone angle is 50° discrepant between the two phosphines. Thus, two PPh_3 ligands (cone angle 145°) can fit around nickel to give $[Ni(CO)_2(PPh_3)_2]$, only one $P(o\text{-tolyl})_3$ (cone angle 194°) can substitute to afford $[Ni(CO)_3\{P(o\text{-tolyl})_3\}]$.

Howell and co-workers[7] have synthesised a number of $[L(CO)_2Cr(arene)]$ complexes (L = PPh_3 and $P(o\text{-tolyl})_3$) in order to investigate their structures and stereodynamic properties. The major finding of this work is the much greater steric demands of $P(o\text{-tolyl})_3$ when compared to PPh_3. For example, it was found that NMR spectra of $[(PPh_3)(CO)_2Cr(arene)]$ were temperature independent down to -110 °C indicating that the metal-arene, metal-phosphorus and phosphorus-carbon bond rotations were fast on the NMR timescale.[8] On the other hand, ^{1}H and ^{13}C NMR spectra of $[\{P(o\text{-tolyl})_3\}(CO)_2Cr(\eta^6\text{-}C_6H_6)]$ showed a decoalescence of both methyl and aryl resonances of the $P(o\text{-tolyl})_3$ ligand, while the benzene and the ^{31}P resonances were temperatureinvariant. These results were most consistent with hindered rotation of the P-C_{ipso} bonds, while both metal-benzene and metal phosphorus rotation remained rapid on the NMR timescale even at low temperature. The restricted rotation of the P-C_{ipso} bonds of the P(o-tolyl)$_3$ is clearly a steric effect. In fact, the cone angle of P(o-tolyl)$_3$ ligand in [{P(o-tolyl)$_3$}(CO)$_2$Cr(p-xylene)] is 160°, whereas the cone angle of PPh$_3$ in [(PPh$_3$)(CO)$_2$Cr(1,4-^{t}Bu$_2$C$_6$H$_4$)] is 145°. The smaller cone angle of P(o-tolyl)$_3$ in [{P(o-tolyl)$_3$}(CO)$_2$Cr(p-xylene)] indicates an increase in intraphosphine interactions.

In contrast, the difference in electronic properties between the two phosphines is small. The stretching frequencies of the carbonyls on [Ni(CO)$_3$L] (L = PPh$_3$ or P(o-tolyl)$_3$) complexes being close to one another.

Ligand	$\nu_{CO}(A_1)cm^{-1}$	$\nu_{CO}(E)cm^{-1}$
P(o-tolyl)$_3$	2066.6	1986
PPh$_3$	2068.9	1990

4.5 Diphosphines

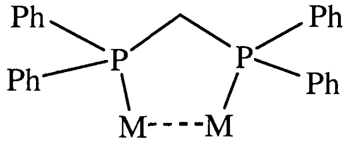
Diphosphines are a special class of tertiary phosphines which have two phosphorus binding sites. They are four electron-donor, bidentate ligands in which the two phosphorus atoms are kept at a specific distance depending on the ligand backbone. The distance between the phosphorus atoms and the flexibility of the backbone are the important characteristics of a diphosphine ligand.

The P-M-P, bite, angle of a transition metal diphosphine complex is the compromise between the ligand's preferred bite angle and that preferred by the metal centre.[9] The former is mainly determined by constraints imposed by the ligand backbone and by the steric repulsion between substituents on the phosphorus and backbone atoms. The metal's preferred bite angle, on the other hand, is mainly determined by electronic requirements, that is the nature and number of d-orbitals involved in forming the molecular orbitals.

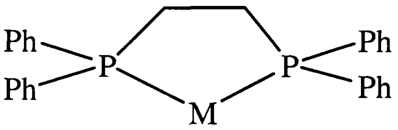
In a catalytic reaction, the metal preferred bite angle changes as the reaction proceeds. If the diphosphine is a flexible ligand, the ligand preferred bite angle will also vary in order to maximise orbital overlap between the ligand and metal, keeping the activation barrier low. On the other hand, if the ligand preferred bite angle is constrained to a value close to the transition state of the reaction, the energy of the reactant complex is higher than that of the unrestrained complex. The metal preferred bite angle in the transition state will have to alter to a value near the ligand preferred bite angle in order to gain satisfactory orbitals overlap between the diphosphine and the metal. Since the energy of the reactant complex is raised to a value close to the transition state of the reaction, the activation energy is low. The catalytic reaction therefore runs smoothly and fast.

4.6 Bridging vs chelating diphosphine ligation

When a diphosphine ligand binds to transition metal, it can act as a bridge between two metal atoms forming a binuclear complex, or it can chelate to a single metal atom to afford a monomeric product. In general, the optimum ring size for a diphosphine ligand to chelate is five and bis(diphenylphosphino)ethane, dppe, is known as an excellent chelating ligand.[10] Bis(diphenylphosphino)methane, dppm, can also chelate to form a strained four-membered ring. However, it is known better as a monodentate ligand or a bridging bidentate ligand. For diphosphine ligands $Ph_2P(CH_2)_nPPh_2$, the tendency to chelation is greatest for n = 2. As the length of the diphosphine backbone increases, the chelating tendency decreases. For instance, $[RhCl(CO)\{Ph_2P(CH_2)_2PPh_2\}]$ is a monomer in which the dppe is a chelating ligand, whereas $[RhCl(CO)\{Ph_2P(CH_2)_nPPh_2\}]$ (n = 1, 3 and 4) are dimers in which the diphosphines are bridging ligands.[11]



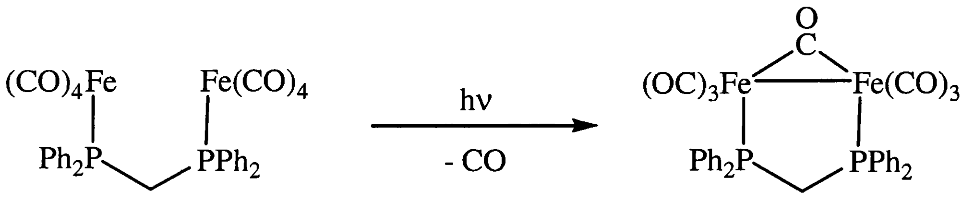
bridging



chelating

4.7 Bis(diphenylphosphino)methane (dppm) as a bridging ligand

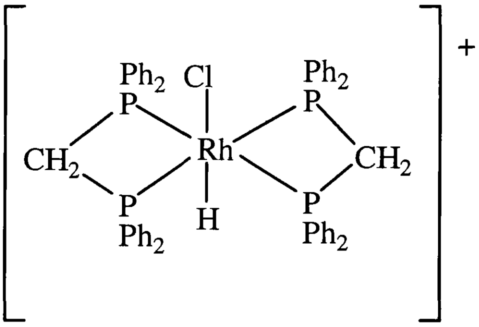
As discussed earlier, bis(diphenylphosphino)methane, dppm, is an efficient bridging ligand due to its geometric ability to form closed or open five-membered ring with metal atoms. It can therefore lock together two metal atoms in close proximity and hence encourages reactions involving two metal centres. The role of the bridging dppm ligand is to prevent dissociation of dimer to monomer, to assist bridging by other groups and to aid binuclear reactions involving formation and cleavage of metal-metal bonds. For instance, photolysis of $[(CO)_4Fe(\mu\text{-}\eta^1,\eta^1\text{-dppm})Fe(CO)_4]$ causes the loss of a carbonyl group and the formation of the metal-metal bond to afford $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-dppm})]$.[12,13] The latter has a carbonyl group bridging between the iron centres and it is believed that the reaction is facilitated by the proximity of the two metal centres.



There are many further examples of reactions involving bridging dppm ligands highlighted in reviews by Puddephatt[10], and Chaudret, Delavaux and Poilblanc.[14] The chemistry of bridging dppm complexes is growing rapidly due to the potential of these binuclear complexes to act as catalysts. For instance, $[Rh_2(CO)_2(\mu\text{-dppm})_2]$ can add acetylene in the bridging position and this complex is a good catalyst for hydrogenation of acetylene to ethylene.[15]

4.8 Dppm as a chelating ligand

Although relatively rare, dppm, can chelate to form complexes with strained four-membered ring, where the MP_2C fragment is essentially planar. For instance, in *trans*-$[RhHCl(\eta^2\text{-dppm})_2]^+$, the bite angles (PMP angles) are low (67-74°)[16] and the PCP angles are approximately 95°. Steric effects are likely to assist chelation. For instance, in *trans*-$[RhHCl(\eta^2\text{-dppm})_2]^+$ and $[Rh(\eta^2\text{-dppm})_2]^+$, the ratio of dppm:Rh is 2:1. However, when the ratio of dppm:Rh is 1:1, the dppm acts as a bridging ligand.[17] It is likely that the "Rh_2(μ-dppm)$_4$" fragment would be very congested and hence is not formed, whereas the "Rh_2(μ-dppm)$_2$" fragment is not too crowded.

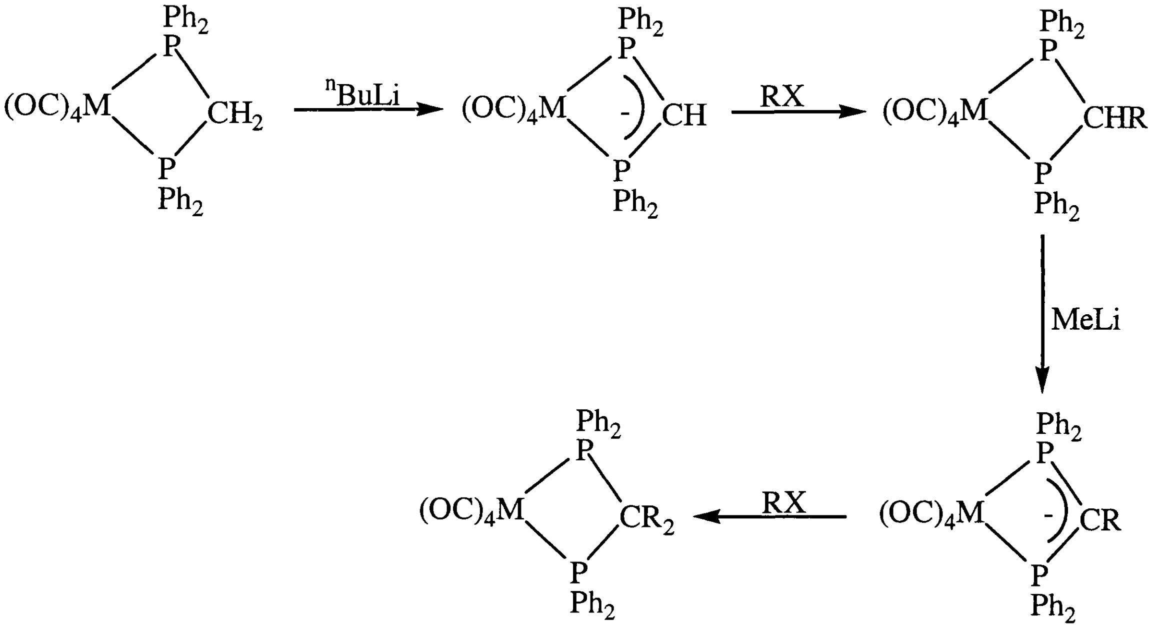


There are an increasing number of complexes with chelating dppm ligands, the series of Group 6 carbonyl derivatives being remarkable for its completeness. Indeed, the interaction of zerovalent carbonyl complexes of Group 6 with dppm usually gives rise to mononuclear complexes. For example, *cis*-[Mo(CO)$_4$(η^2-dppm)], *cis*-[Mo(CO)$_2$(η^2-dppm)$_2$] and [Mo(η^2-dppm)$_3$] are all known.[18-21]

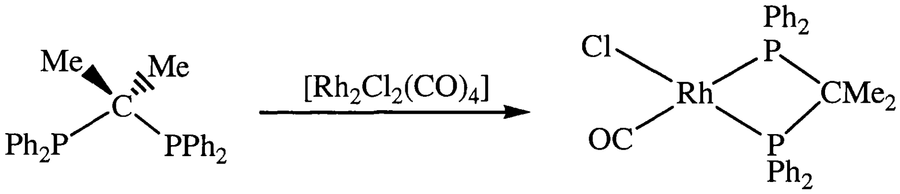
4.9 Backbone functionalisation

The chemistry of diphosphines with two or more backbone atoms has been extensively studied. In contrast, studies on the effect of varying the steric and electronic properties of dppm are limited. Such properties of dppm can be fine-tuned in a systematic way by varying the aryl substituents on phosphorus and by changing the substituents on the backbone. In general, the more sterically crowded the substituents on the dppm derivatives, the smaller the bite angles of these ligands and the stronger their tendency to chelate due to the Thorpe-Ingold effect.[22]

The hydrogens on the backbone carbon of dppm are relatively acidic. Shaw *et al.* deprotonated dppm using strong bases ^{n}BuLi or MeLi to afford carbanions *cis*-[M(CO)$_4$(η^2-$Ph_2PCHPPh_2$)]$^-$ which were subsequently alkylated by RX (X = halogen, R = Me, Et, $PhCH_2$, CH_2=$CHCH_2$ or Me_3Si) to give *cis*-[M(CO)$_4$(η^2-$Ph_2PCHRPPh_2$)].[23] Indeed, in the presence of excess MeLi and MeI, further deprotonation occurred and *cis*-[M(CO)$_4${η^2-Ph$_2$PC(Me)$_2$PPh$_2$}] was obtained.

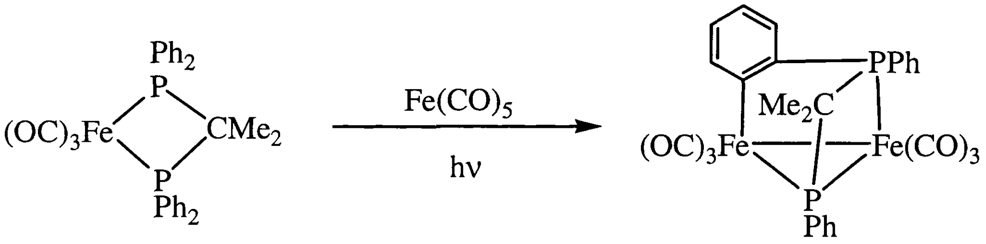


Similarly, the same group attempted to deprotonate and to alkylate square planar complexes of platinum(II) or palladium(II) of the type *cis*-[MX$_2$(η^2-dppm)] (X = halogen).[24] However, MeLi or ^{n}BuLi could not be used as they alkylated the platinum or palladium centre. A non-coordinating base, [LiN(SiMe$_3$)$_2$], was employed for deprotonation and *cis*-[MX$_2$(η^2-Ph$_2$PCHRPPh$_2$)] (M = Pt, Pd, X = halogen, R = Me, Et, CH$_2$Ph) and *cis*-[MI$_2$(η^2-Ph$_2$CMe$_2$PPh$_2$)] were successfully synthesised. The chemistry of this latter ligand, 2,2-bis(diphenylphosphino)propane, (2,2-dppp), is very different to that of dppm. Higgins *et al.* has shown that 2,2-dppp is very effective at chelating Rh(I).[25] Thus, reaction of 2,2-dppp with [Rh$_2$Cl$_2$(CO)$_4$] affords only [RhCl(CO)(η^2-2,2-dppp)], in marked contrast with dppm.



The substitution of hydrogens at the backbone carbon atom of dppm by methyl groups therefore strengthened the stability of four-membered chelate rings. Indeed, 2,2-dppp can form stable chelate complexes with Ni(II) and Pt(II) centres. Since nickel-phosphine complexes can catalyse cross-coupling of Grignard reagents with aryl halides (Kumada coupling), it was found that nickel-2,2-dppp complexes are active catalysts in these coupling reactions, while related dppm complexes are inactive.[26]

While dppm acts as a bridging ligand in the binuclear complex [$Fe_2(CO)_6(\mu$-CO)(μ-dppm)], 2,2-dppp, on the other hand, forms exclusively, and in high yields, the chelate complex [$Fe(CO)_3(\eta^2$-2,2-dppp)]. It is noteworthy, however, that attempts to force 2,2-dppp to bridge the diiron centre *via* UV irradiation in the presence of excess $Fe(CO)_5$ resulted in benzene loss and formation of [$Fe_2(CO)_6\{\mu$-$\eta^2(P),\eta^1(P),\eta^1(C)$-$PhPCMe_2P(Ph)C_6H_4\}$].[27]

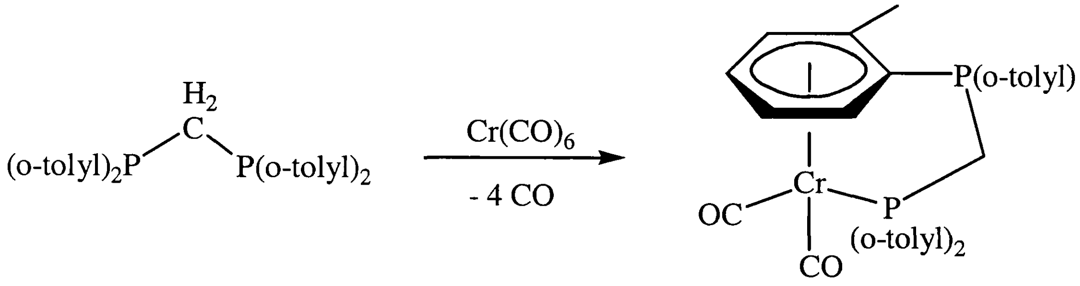


4.10 Aryl ring functionalisation

Alterations to the aryl rings of dppm can vary both steric and electronic properties of the diphosphine. In general, placing substituents in the *meta* and *para* positions can influence electronic effects, while at the *ortho* positions also result in steric effects. At present, research on substitution at the aryl rings of dppm is very limited and only a few of these dppm derivatives have been prepared. For instance, bis(di(4-*tert*-butylphenyl)phosphino)methane, dtbppm, was prepared by Nocera and co-workers[28] in order to overcome the problem of $[Mo_2X_6(\mu\text{-dppm})_2]$ compounds (X = halogen) being virtually insoluble. The introduction of *tert*-butyl groups at the *para* position of the phenyl rings of dppm significantly enhancing the solubility. Thus, $[Mo_2X_6(\mu\text{-dtbppm})_2]$ complexes can dissolve in THF and this has allowed photoreactivity when irradiated with near-UV light, cleanly producing the corresponding quadruple metal-metal bonded complexes, $[Mo_2X_4(\mu\text{-dtbppm})_2]$.

Schmidbaur *et al.*[29] has prepared bis(di-o-tolylphosphino)methane, dotpm, and bis(bis(2,6-dimethylphenyl)phosphino)methane, dmppm, and reacted these ligands with [(CO)AuCl] in different ratios to afford $[Au_2Cl_2(\mu\text{-dotpm})]$, $[Au_2Cl_2(\mu\text{-dmppm})]$, and the eight-membered ring complexes $[Au_2Cl_2(\mu\text{-dotpm})_2]$ and $[Au_2Cl_2(\mu\text{-dmppm})_2]$. Further treatment of the eight-membered ring complexes with $AgBF_4$ gave $[Au_2(\mu\text{-dotpm})_2][BF_4]_2$ and $[Au_2(\mu\text{-dmppm})_2][BF_4]_2$. Moreover, reactions of ligands dotpm and dmppm with MeLi and $ClAuPMe_3$ formed neutral eight-membered ring complexes $[Au_2(\mu\text{-dotpm})_2]$ and $[Au_2(\mu\text{-dmppm})_2]$ respectively.

In addition, thermal reaction of dotpm with $Cr(CO)_6$ produces $[Cr(CO)_2(dotpm)]$ in which one phosphorus atom binds directly to the metal together with an aryl ring on the second, affording an unusual η^6-arene complex.[30] In contrast, the thermal reaction of dppm with $Cr(CO)_6$ under the same conditions produces a simple chelate complex.

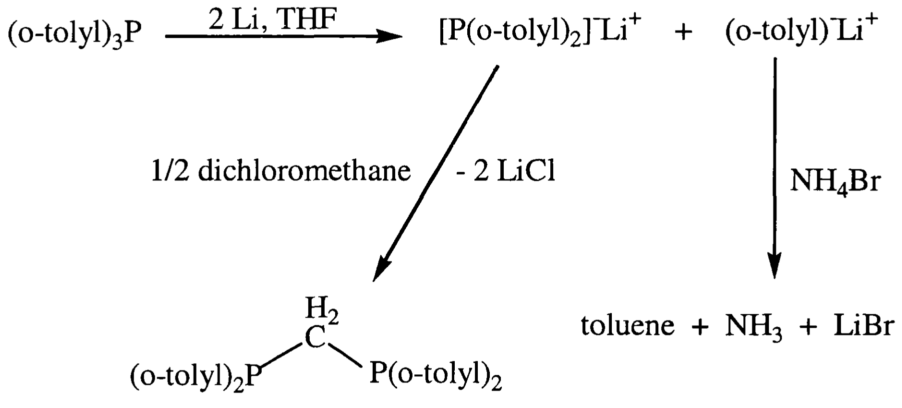


4.11 Our approach

The aim of this project was to increase the steric bulk of both the phenyl rings of dppm and its backbone substituents. By doing so, the bite angle (P-M-P angles) of these dppm derivatives when bonded to metal centres, will decrease. It is hoped that these small bite angle dppm derivatives may act as homogeneous catalysts. This is an alternative way to synthesise catalysts with small bite angles. As the ligand preferred bite angle is constrained to a small value, the energy of complex is raised to a value close to the transition state of the reaction, it is then a matter of finding a metal which has a metal preferred bite angle that can compromise with the one from the ligand. Since the activation energy is low, a good homogeneous catalyst is produced. Therefore, we would like to synthesise a number of ligands of the type (o-tolyl)$_2$PCHRP(o-tolyl)$_2$ in a systematic way and form complexes with a range of low valent metal centres. At this early stage, testing whether the complexes are good catalysts has not been attempted.

4.12 Ligand Synthesis

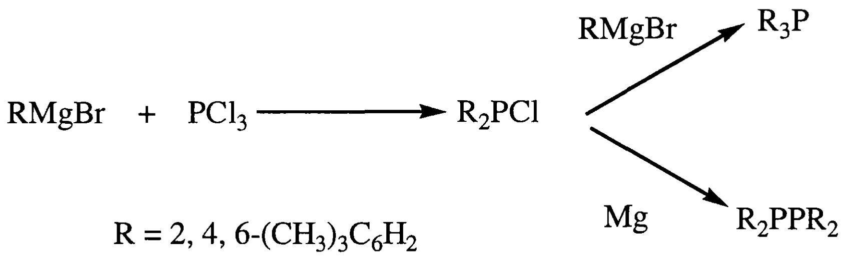
An undergraduate student at University College, Maria Cullen, previously synthesised bis(di-o-tolylphosphino) methane, dotpm, **30** in good yield using commercially available P(o-tolyl)$_3$ as a starting material. This tertiary phosphine was reacted with lithium metal in THF to generate lithium di-o-tolylphosphide, this reaction takes about 40 minutes to initiate, being dependent on the condition of the lithium metal. The lithium di-o-tolylphosphide generated was then reacted with dichloromethane to afford **30** smoothly and rapidly.



30

Since P(o-tolyl)$_3$ is relatively expensive, our initial idea was to synthesise this white crystalline solid *via* a Grignard reaction as it is easy to handle. Clark and Mulraney[31] have claimed that commercially available o-chlorotoluene and magnesium turnings could be used to prepare the Grignard. We therefore used the same reagents and found that the Grignard reaction could not be initiated either when iodine or ethylene dibromide was added. Therefore, o-bromotoluene was used instead (also commercially available) and the Grignard reaction ran smoothly in refluxing THF.

The molar ratio between the Grignard and PCl$_3$ is critical. Stepanov, Karpova and Bokanov have reported that treatment of mesitylmagnesium bromide with PCl$_3$ in 3:1 ratio afforded PAr_3, while reaction of the same reagents in 2:1 ratio gave the biphosphine Ar_2PPAr_2.[32]

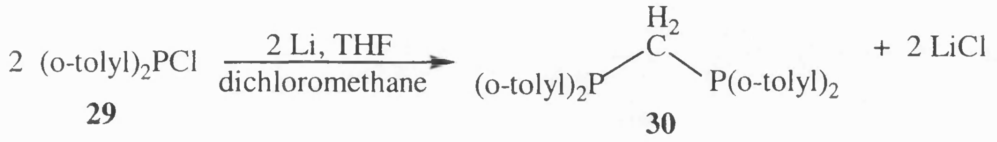


In contrast, we reacted (o-tolyl)MgBr with PCl_3 in 3:1 ratio and obtained tetra(o-tolyl)biphosphine, $(o\text{-tolyl})_2PP(o\text{-tolyl})_2$ **31**. We believe that this is probably due to the reaction between (o-tolyl)MgBr and the excess magnesium in the reaction mixture. We then adopted Clark and Mulraney's method and prepared chloro-di-o-tolylphosphine **29** as a precursor towards the synthesis of **30**.[31] Compound **29** was formed by the reaction between the Grignard, (o-tolyl)MgBr, and PCl_3 in 2:1 ratio. A small amount of $P(o\text{-tolyl})_3$ was detected as there is no control over the amount of product formed, i.e. Ar_2PCl or PAr_3. Clark and Mulraney reported that PAr_3 was usually the dominant product. However, if the aryl group was sterically hindered, then $ArPCl_2$ or Ar_2PCl could be formed. Compound **29** was best stored under nitrogen as it slowly oxidised in air.

$$2\,(o\text{-tolyl})MgBr + PCl_3 \longrightarrow \underset{\mathbf{29}}{(o\text{-tolyl})_2PCl} + 2\,MgBrCl$$

The ^1H NMR spectrum of **29** was particularly informative. The *ortho*-proton in the aryl ring appeared as a doublet of doublets at δ 7.42. It couples with the *meta*-proton (*para* to the methyl group) ($J_{H\text{-}H}$ = 7.6 Hz) and phosphorus ($J_{P\text{-}H}$ = 3.9 Hz). The *meta*-proton (*para* to the methyl group) appeared as a triplet at δ 7.23, coupling with the *ortho*- and *para*-protons ($J_{H\text{-}H}$ = 7.4 Hz), while the *para*-proton appeared as a triplet at δ 7.13 coupled to both *meta*-protons ($J_{H\text{-}H}$ = 7.3 Hz). The *meta*-proton (next to the methyl group) appeared as a triplet at δ 7.11. It couples with the *para* proton and the phosphoruses ($J_{H\text{-}H}$ = 5.7 Hz). These results agree with those reported by Clark and Mulraney. The ^{31}P NMR spectrum showed a singlet at δ 49.8 and the mass spectrum gave the PAr_3^+ ion at *m/z* 304 and the PAr_2^+ ion at *m/z* 215.

Compound **29** was then lithiated to give LiP(o-tolyl)$_2$ which was reacted with dichloromethane to afford **30** in 26% yield. The yield was possibly underestimated as the starting material, **29**, was mixed with a certain amount of MgBrCl. The latter proved difficult to remove as this led to a significant loss of product.



The ^{1}H NMR spectrum of **30** showed a multiplet for the aryl protons between δ 7.36-7.10, a triplet for the protons on the backbone at δ 2.60 ($J_{P\text{-}H}$ = 2.5 Hz) and a singlet for the methyl protons at δ 2.30. These results are in agreement with those reported in the literature.[31] The ^{31}P NMR spectrum showed a singlet at δ -60.5 and the mass spectrum gave the molecular ion at *m/z* 440. The elemental analysis was in good agreement with the theoretical values. Compound **30** was recrystallised from dichloromethane and methanol to afford white needles which was stable in air. The X-ray crystal structure was determined by Professor Todd Marder and Jacquie Burke of University of Durham. The results are summarised in Figure 4-1.

P(1)-C(1)	1.850(2) Å
P(1)-C(11)	1.839(2) Å
P(1)-C(31)	1.843(2) Å
P(2)-C(1)	1.854(2) Å
P(2)-C(21)	1.843(3) Å
P(2)-C(41)	1.836(3) Å
C(1)-P(1)-C(11)	103.53(10)°
C(1)-P(1)-C(31)	99.76(11)°
C(11)-P(1)-C(31)	101.40(10)°
C(1)-P(2)-C(21)	99.01(11)°
C(1)-P(2)-C(41)	103.89(12)°
C(21)-P(2)-C(41)	101.97(12)°
P(1)-C(1)-P(2)	108.11(12)°

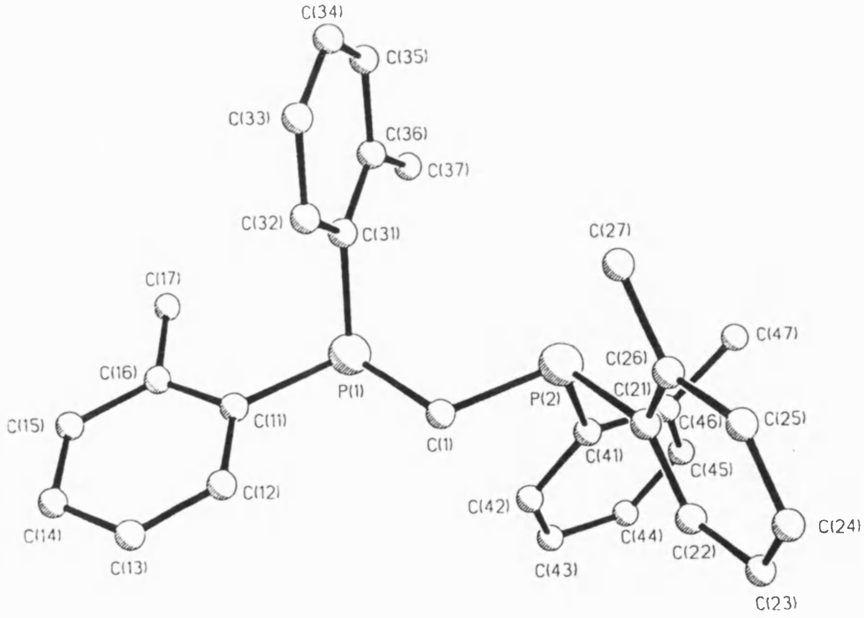


Fig.4-1 The crystal structure of bis(di-o-tolylphosphino)methane **30** with selected bond lengths and angles.

The crystal structure of **30** is very similar to bis(diphenylphosphino)methane.[33] It has no crystallographic symmetry and the lone pairs and the aryl rings at the two phosphorus atoms are staggered. The lone pairs are on the opposite side of the P(1)-C(1)-P(2) plane. Ignoring the relative orientations of the aryl rings, the "C_2PCPC_2" fragment has a C_2 symmetry. The phosphorus-carbon(*ipso*) bonds are shorter than the phosphorus-carbon(backbone) bonds. The P(1)-C(1)-P(2) angle in **30** [108.11(12)°] is slightly greater than the same angle in bis(diphenylphosphino)methane [106.2(3)°].

As discussed earlier, treatment of (o-tolyl)MgBr with PCl_3 in 3:1 ratio in the presence of excess magnesium afforded tetra(o-tolyl)biphosphine, $(o\text{-tolyl})_2PP(o\text{-tolyl})_2$, **31**, as a creamy solid in 71% yield. In ^1H NMR spectrum, the *meta* (next to the methyl group) and *para* protons appeared as a multiplet between δ 7.30-7.23. The *meta* proton (*para* to the methyl group) appeared as a triplet ($J_{H\text{-}H}$ = 6.9 Hz) and the *ortho* proton appeared as a doublet of doublet ($J_{P\text{-}H}$ = 2.7 Hz and $J_{H\text{-}H}$ = 7.0 Hz). The ^{31}P NMR spectrum showed a singlet at δ -45.8 and the mass spectrum gave the molecular ion at *m/z* 426.

Tetra(2,6-dimethylphenyl)biphosphine, **32** was synthesised in a similar way. Commercially available 2-bromo-m-xylene was used to prepare the Grignard. Compound **32** was obtained as a white powder in 58% yield. In ^1H NMR spectrum, two multiplets between δ 7.16-7.07 and δ 6.99-6.97 were assigned to the aryl protons. The methyl groups appeared as a doublet at δ 2.36 ($J_{P\text{-}H}$ = 2.3 Hz) and a singlet at δ 2.28. The ^{31}P NMR spectrum showed a singlet at δ -44.3 and the mass spectrum gave the molecular ion at *m/z* 482. The elemental analysis was in good agreement with the theoretical values.

Kuchen and Buchwald had successfully cleaved the phosphorus-phosphorus bond of tetraphenylbiphosphine, Ph_2PPPh_2, using sodium metal in THF or diethylether.[34] We adopted this method in order to attempt to cleave **32** under the same conditions. However, even though the colour of the solution changed from pale yellow to orange on stirring with sodium metal in THF, the reaction failed to cleave the phosphorus-phosphorus bond. The orange solution was left to stir with the sodium metal for 20 hours. Dichloromethane was then added to the filtered, orange solution and the mixture lightened its colour. However, the starting material, **32** was recovered at the end of the reaction. We therefore repeated the reaction again with potassium metal and the colour of the solution changed from pale yellow to dark red. Similarly, dichloromethane was added to the filtered, dark red solution and **32** was recovered at the end.

Kordosky, Cook, Cloyd and Meek had cleaved the phosphorus-phosphorus bond of tetramethyldiphosphine, Me_2PPMe_2, using sodium metal in liquid ammonia.[35] We carried out this reaction with **32** and after the addition of dichloromethane, a white powder $[Ar_2(CH_3)PNH_2]^+Cl^-$ **33** (Ar = 2,6-dimethylphenyl) was eventually obtained in 61% yield.

$$\underset{\mathbf{32}}{Ar_2PPAr_2} \xrightarrow[2)\ CH_2Cl_2]{1)\ Na/\ NH_3} \underset{\mathbf{33}}{[Ar_2(CH_3)PNH_2]^+Cl^-}$$

Ar = 2,6-dimethylphenyl

In the ^1H NMR spectrum of **33**, a doublet of triplets at δ 7.32 (J_{P-H} = 1.2 Hz, J_{H-H} = 7.8 Hz) was assigned to the *para* protons. A doublet of doublets at 7.07 (J_{P-H} = 2.9 Hz, J_{H-H} = 4.7 Hz) was assigned to the *meta* protons. The NH_2 group appeared as a doublet at δ 6.58 (J_{P-H} = 3.1 Hz) and the methyl group directly attached to the phosphorus atom appeared as a doublet at δ 2.72 (J_{P-H} = 13.2 Hz). The methyl groups on the aryl rings appeared as a singlet at δ 2.45. The ^{31}P NMR spectrum showed a singlet at δ 18.9 and the mass spectrum gave $[Ar_2PCH_3]^+$ ion at *m/z* 256. The elemental analysis was in good agreement with the theoretical values.

There are other methods to cleave the biphosphine which we have not attempted. Organometallic reagents[36] such as PhLi and halogens[37-41] can cleave the biphosphine to form Ar_2PLi and Ar_2PX (X = Cl, Br, I) respectively.

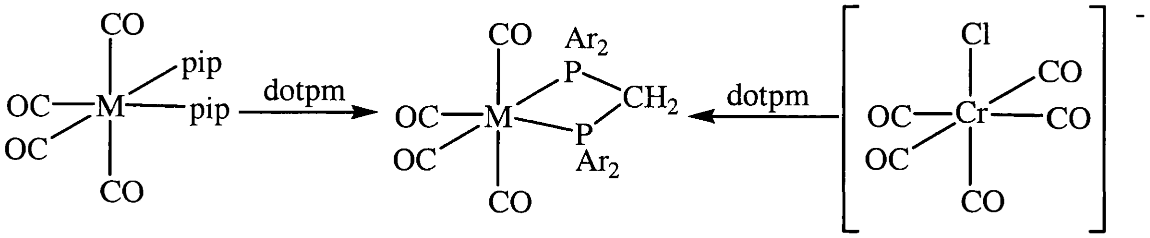
Since we were unable to cleave **32**, we prepared bis(2,6-dimethylphenyl) chlorophosphine **34** in order to synthesise bis(di-2,6-dimethylphenylphosphino) methane. The Grignard 2,6-dimethylphenylmagnesium bromide was prepared from commercially available 2-bromo-m-xylene. It was then reacted with PCl_3 in 2:1 ratio to afford a yellow mass which was a mixture of PAr_3 and **34**. In ^1H NMR spectrum, a triplet at δ 7.33 (J_{H-H} = 7.5 Hz) was assigned to the *para* protons. The *meta* protons appeared as a doublet of doublets at δ 7.05 ($J_{H\text{-}H}$ = 6.6 Hz, $J_{P\text{-}H}$ = 2.1 Hz) and the methyl protons appeared as a doublet at δ 2.33 ($J_{P\text{-}H}$ = 1.6 Hz). The ^{31}P NMR spectrum showed a singlet at δ 55.48 and the mass spectrum gave the molecular ion at *m/z* 277.

Reaction of lithium metal with a mixture of PAr_3 (Ar = 2,6-dimethylphenyl) and **34**, followed by addition of dichloromethane failed to give the desired product. A complicated mixture was obtained instead. Therefore, separation of PAr_3 and **34** by vacuum distillation is required before reacting **34** with lithium metal and dichloromethane. However, this was not pursued.

We also attempted to synthesise (o-tolyl)$_2$PCMe$_2$P(o-tolyl)$_2$ by reaction of **29** with lithium metal for 20 hours followed by the addition of 2,2-dichloropropane to the dark red solution. However, a complicated mixture was obtained but there was no sign of the anticipated product.

4.13 Synthesis of *cis*-[M(CO)$_4${η^2-(o-tolyl)$_2$PCH$_2$P(o-tolyl)$_2$}] (M = W, Mo, Cr) 35-37

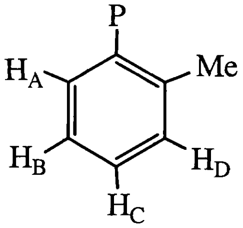
Cis-[M(CO)$_4${η^2-(o-tolyl)$_2$PCH$_2$P(o-tolyl)$_2$}] (M = W, Mo, Cr) **35-37** were synthesised from *cis*-[M(CO)$_4$(pip)$_2$] (M = W, Mo, pip = NHC_5H_{10}) and [Cr(CO)$_5$Cl][NEt$_4$], both being prepared following literature methods.[42,43] Treatment of *cis*-[M(CO)$_4$(pip)$_2$] or [Cr(CO)$_5$Cl][NEt$_4$] with **30** in refluxing dichloromethane under nitrogen for 2.5 hours to 5 hours afforded *cis*-[W(CO)$_4${η^2-(o-tolyl)$_2$PCH$_2$P(o-tolyl)$_2$}] **35** as a yellow solid (66% yield), *cis*-[Mo(CO)$_4${η^2-(o-tolyl)$_2$PCH$_2$P(o-tolyl)$_2$}] **36** as a tan solid (62 % yield) and *cis*-[Cr(CO)$_4${η^2-(o-tolyl)$_2$PCH$_2$P(o-tolyl)$_2$}] **37** as a yellow solid (73% yield). Compounds **35-37** were recrystallised from dichloromethane and methanol to afford yellow crystals. All have previously been synthesised by Clark and co-workers but by different methods.[30]



M = W, Mo

M = W, Mo, Cr (**35-37**)

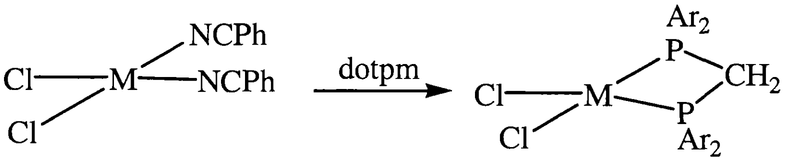
Spectroscopic data for **35-37** were similar. Solution IR spectra, each showed three strong carbonyl stretches between 2006-2019, 1896-1909 and 1866-1872 cm^{-1}. In ^1H NMR spectrum, all showed a doublet of doublets for H_A between δ 7.69-7.62 (J_{H-H} = 7.2-8.0 Hz, J_{P-H} = 12.4-13.9 Hz), and a triplet for H_B between δ 7.30-7.29 (J_{H-H} = 7.4-7.5 Hz).



A triplet and a doublet of doublets were assigned to H_C and H_D at δ 7.14-7.18 (J_{H-H} = 7.5-7.6 Hz) and δ 7.10-7.12 (J_{H-H} = 7.2-7.6 Hz, J_{P-H} = small or 1 Hz) respectively. A triplet between δ 4.91-4.38 (J_{P-H} = 8.5-7.9 Hz) was assigned to the methylene protons and a singlet between δ 2.04-2.00 to the methyl protons. The ^{31}P NMR spectra all showed singlets at δ -37.7 (J_{W-P} = 196 Hz) for **35**, δ -14.22 for **36** and δ 9.76 for **37**. In the mass spectra, molecular ions at *m/z* 736 for **35**, 650 for **36** and 604 for **37** were observed in each case and the elemental analyses were in good agreement with the theoretical values. Our results was compatible with those reported by Clark and co-workers.[30]

4.14 Synthesis of *cis*-[$MX_2\{\eta^2$-(o-tolyl)$_2PCH_2P$(o-tolyl$_2$)}] (M = Pd, Pt; X = Cl, Br, I) 38-41

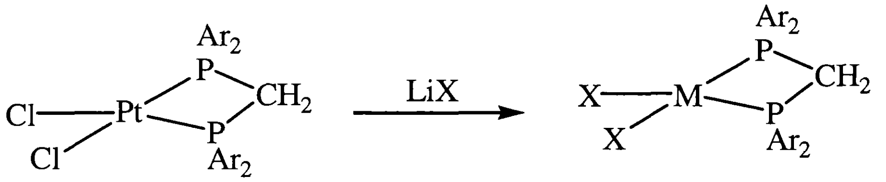
Syntheses of *cis*-[$MCl_2\{\eta^2$-(o-tolyl)$_2PCH_2P$(o-tolyl)$_2$}] (M = Pd, Pt) **38-39** were very simple and utilised *cis*-[M(PhCN)$_2Cl_2$] (M = Pd, Pt) following literature methods.[24] The bis-(benzonitrile) complexes were treated with **30** in refluxing dichloromethane under nitrogen for 10 to 20 hours to afford *cis*-[$PdCl_2\{\eta^2$-(o-tolyl)$_2PCH_2P$(o-tolyl)$_2\}$] **38** as a brown powder (75 % yield) and *cis*-[$PtCl_2\{\eta^2$-(o-tolyl)$_2PCH_2P$(o-tolyl)$_2\}$] **39** as a white powder (92% yield).



M = Pt, Pd M = Pt, Pd **(38-39)**

In the IR spectra, both showed ν(CH) bands between 3056-2856 cm^{-1}. In the ^{1}H NMR spectra, a doublet of doublets for H_A between δ 7.97-7.96 ($J_{H\text{-}H}$ – 8.2-7.5 Hz), a triplet for H_B between δ 7.45-7.43 ($J_{H\text{-}H}$ = 7.6-7.3 Hz), multiplets for H_C and H_D between δ 7.25-7.19 were observed, while a triplet for the methylene protons between δ 4.59-4.33 ($J_{P\text{-}H}$ = 10.0-9.9 Hz) and a singlet for the methyl protons between δ 2.32-2.26 were observed. The ^{31}P NMR spectra showed a singlet at δ -69.0 for **38** and a singlet with platinum satellites at –77.9 ($J_{Pt\text{-}P}$ = 3097 Hz) for **39**. The mass spectra gave M$^+$-Cl ion (M = molecular ion) at *m/z* 583 for **38** and 671 for **39**, and elemental analyses were in good agreement with the theoretical values.

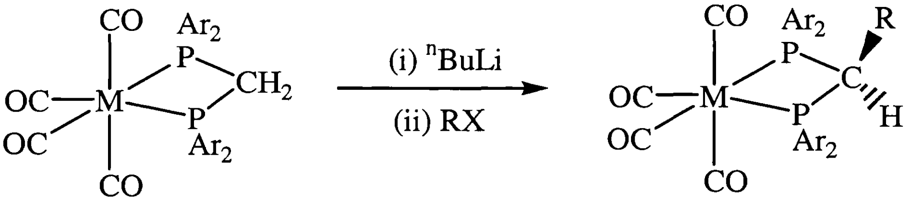
Interestingly, it was found that the chlorides in **38** and **39** could be substituted by bromide and iodide. Treatment of **39** with LiBr or LiI in THF under nitrogen for 20 hours afforded *cis*-[$PtBr_2\{\eta^2$-(o-tolyl)$_2PCH_2P$(o-tolyl)$_2\}$] **40** (78% yield) and *cis*-[$PtI_2\{\eta^2$-(o-tolyl)$_2PCH_2P$(o-tolyl)$_2\}$] **41** (62% yield) as yellow powders. The ^{31}P NMR spectra were particularly informative. They showed a singlet with platinum satellites for both **40** and **41** at δ -80.32 ($J_{Pt\text{-}P}$ = 7549 Hz) and δ -87.73 ($J_{Pt\text{-}P}$ = 2876 Hz) respectively. The mass spectra gave the M$^+$-Br ion (M = molecular ion) at *m/z* 715 for **40** and M$^+$ ion at *m/z* 889 for **41**, while elemental analyses were in good agreement with theoretical values.



X = Br, I **(40-41)**

4.15 Synthesis of *cis*-[M(CO)$_4${η^2-(o-tolyl)$_2$PCH(R)P(o-tolyl)$_2$}] (M =W, Mo, Cr; R = Me, Et, CH$_2$Ph) 42-48

As discussed in the introduction, alteration at the backbone carbon by bulky groups can lead to smaller bite angle of the diphosphine complex. We followed Shaw's method[23] in order to substitute one hydrogen at the methylene carbon in a systematic way. Compounds **35-37** were deprotonated by ^{n}BuLi, followed by alkylation using MeI to afford *cis*-[W(CO)$_4${η^2-(o-tolyl)$_2$PCH(Me)P(o-tolyl)$_2$}] **42** (62% yield), *cis*-[Mo(CO)$_4${η^2-(o-tolyl)$_2$PCH(Me)P(o-tolyl)$_2$}] **43** (59 % yield) and *cis*-[Cr(CO)$_4${η^2-(o-tolyl)$_2$PCH(Me)P(o-tolyl)$_2$}] **44** (99% yield). All were yellow powders which were recrystallised from dichloromethane and methanol to form yellow block-shaped crystals.



M = W, Mo, Cr; R = Me, Et, CH$_2$Ph **(42-48)**

Spectroscopic data followed a similar pattern. The ^{1}H and ^{31}P NMR spectra were most distinctive in showing the difference before and after substitution of a hydrogen on the backbone carbon atom. Compounds **42-44** all showed a quartet between δ 6.01-5.38 ($J_{H\text{-}H}$ = 7.7-7.2 Hz) for the methylene proton, two singlets between δ 2.14-2.09 and δ 2.09-2.04 for the methyl groups on the aryl rings and a doublet of triplets between δ 1.08-1.02 ($J_{H\text{-}H}$ = 7.7-7.3 Hz, $J_{P\text{-}H}$ = 15.9-14.8 Hz) for the methyl group on the backbone. The ^{31}P NMR spectra showed a singlet with tungsten satellites at δ -18.03 ($J_{W\text{-}P}$ = 199 Hz) for **42**, a singlet at δ 4.9

for **43** and a singlet at δ 27.8 for **44**. The mass spectra all gave molecular ions at *m/z* 750 for **42**, 664 for **43** and 618 for **44**.

Variable temperature ^{1}H NMR spectra were obtained for **42**. It was found that a multiplet between δ 8.17-8.11 for H_A and the quartet at δ 6.01 for the methylene proton were broad at room temperature. As the temperature increased to 318K, these signals together with the doublet of triplets at δ 1.02 for the methyl group on the backbone sharpened significantly. At this stage, the aryl rings on the diphosphine were rotating rapidly on the NMR timescale. As the temperature decreased to 278K, the peaks corresponding to H_A and the methylene proton broadened considerably, whereas the doublet of triplet for the methyl group on the backbone broadened slightly. At 260K, all three peaks coalescenced into broad singlets and the aryl rings on the diphosphine were rotating slowly on the NMR timescale.

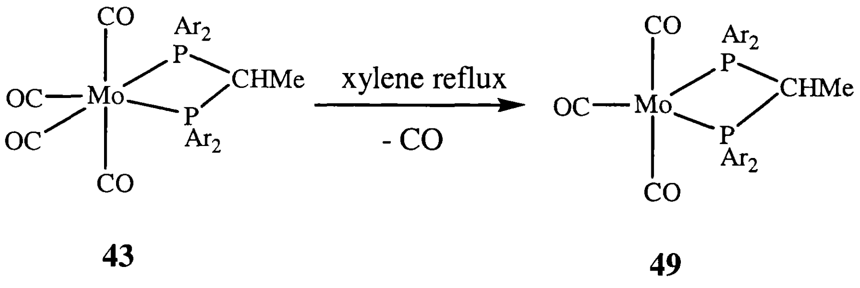
Following the same method as above, addition of ethyl iodide or benzyl bromide afforded *cis*-[Mo(CO)$_4${η^2-(o-tolyl)$_2$PCH(Et)P(o-tolyl)$_2$}] **45** (72% yield), *cis*-[W(CO)$_4${η^2-(o-tolyl)$_2$PCH(Et)P(o-tolyl)$_2$}] **46** (72% yield), *cis*-[Mo(CO)$_4${η^2-(o-tolyl)$_2$PCH(CH$_2$Ph)P(o-tolyl)$_2$}] **47** (34% yield) and *cis*-[W(CO)$_4${η^2-(o-tolyl)$_2$PCH(CH$_2$Ph)P(o-tolyl)$_2$}] **48** (40% yield). All were yellow solids which were recrystallised from dichloromethane and methanol to form yellow crystals.

In ^{1}H NMR spectrum of **45**, a triplet of triplets at δ 4.77 ($J_{P\text{-}H}$ = 4.8 Hz, $J_{H\text{-}H}$ = 9.7 Hz) was assigned to the methylene proton and two singlets at δ 2.18 and δ 2.05 to the methyl protons on the aryl rings. A doublet of multiplet at δ 1.87 ($J_{H\text{-}H}$ = 7.4 Hz) for the CH_2 group and a triplet at δ 0.77 ($J_{H\text{-}H}$ = 7.4 Hz) for the CH_3 in the ethyl group were observed. For **46**, a broad singlet at δ 5.29 was assigned to the methylene proton and two singlets at δ 2.13 and δ 2.01 were observed for the methyl groups on the aryl rings. A doublet of multiplet at δ 1.81 ($J_{P\text{-}H}$ = 2.1 Hz, $J_{H\text{-}H}$ = 7.4 Hz) was assigned to the CH_2 group and a triplet at δ 0.79 ($J_{H\text{-}H}$ 7.3 Hz) to the CH_3 in the ethyl group. The ^{31}P NMR spectra showed singlets at δ 5.90 for **45** and δ -15.75 for **46**. The mass spectra gave the molecular ion at *m/z* 678 for **45** and 764 for **46**.

In ^1H NMR spectra of **47** and **48**, both showed two broad singlets between δ 8.13-8.05 and δ 8.02-7.91 for the phenyl protons, while a broad singlet between δ 6.17-5.53 was assigned to the methylene proton. A doublet of triplets between δ 3.04-2.98 (J_{H-H} = 5.6-5.4 Hz, J_{P-H} = 15.0-14.2 Hz) was observed for the CH_2 protons and two singlets between δ 2.16-2.10 and δ 1.80-1.71 were assigned to the methyl protons on the aryl rings. The ^{31}P NMR spectra showed a singlet at δ 6.95 for **47** and a singlet at δ -15.62 for **48**. The mass spectra gave molecular ions at *m/z* 740 for **47** and 826 for **48**.

4.16 Attempted synthesis of [M(CO)$_2${η^6-C$_6$H$_4$MeP(o-tolyl)CHMeP(o-tolyl)$_2$}] (M = W, Mo)

Clark *et al.* reported that the thermal reaction of **30** with [M(CO)$_6$] (M = Cr, Mo) afforded [M(CO)$_2${η^6-C$_6$H$_4$MeP(o-tolyl)CHMeP(o-tolyl)$_2$}].[30] We adopted this method and refluxed **42** in decalin under nitrogen for 60 hours. The colour of the solution changed from yellow to green, then to blue. A blue powder was obtained which was only decomposition. Repeating the reaction with **43**, in refluxing xylene gave a black solid (62% yield) after 60 hours which was shown to have the formula [Mo(CO)$_3${η^2-(o-tolyl)$_2$PCH(Me)P(o-tolyl)$_2$}] **49**.



Spectroscopic data were very simple. In the IR spectrum, two strong ν(CO) bands were seen at 1901 and 1840 cm^{-1}, and in the ^1H NMR spectrum, a multiplet between δ 7.41-6.98 was assigned to the aryl protons. A quartet at δ 3.27 (J_{H-H} = 7.1 Hz) was assigned to the methylene proton and two singlets at δ 2.49 and δ 2.23 to the methyl groups. A doublet of triplet at δ 0.97 (J_{H-H} = 4.0 Hz, J_{P-H} = 11.1 Hz) was assigned to the methyl group on the backbone carbon atom. The ^{31}P NMR spectrum showed a singlet at δ -46.7. The mass spectrum was particularly informative, showing peaks due to successive loss of CO groups at *m/z* 606 (M^+-CO), 576 (M^+-2CO) and 552 (M^+-3CO).

We believe that **49** is a five-coordinate, 16-electron species, being coordinatively and electronically unsaturated. Such zero-valent molybdenum complexes are rare. A previous example of a 16-electron complex is $[Mo(CO)_3(PCy_3)_2]$, prepared by Kubas *et al.*[44] It is intensely coloured, nearly black in the solid state and deep purple in solution. The C-H bond of the cyclohexyl group of the phosphine has an "agostic" interaction with the metal centre. $[Mo(CO)_3(PR_3)_2]$ readily "add" another donor ligands, either reversibly or irreversibly, to give *mer,trans*-$[Mo(CO)_3(PR_3)_2L]$. The ability to bind additional ligands is strongly influenced by steric factors. Smaller phosphines, such as PPh_3, PPh_2Cy, or even o-tolyl give 18-electron species $[Mo(CO)_3(PR_3)_3]$. Comparing **49** with *mer*-$[Cr(CO)_3(\eta^1$-dppm$)(\eta^2$-dppm$)]$[45], the dppm (cone angle 145°) is too small and cannot stabilise an 16-electron species, so another dppm molecule binds with the metal in a η^1-fashion to produce an 18-electron complex. In contrast, the dotpm (cone angle 194°) is much bulkier and is stabilising **49** as a 16-electron complex.

From ^1H NMR studies of compounds **42-49** it is seen that the substituent R on the backbone causes the upper aryl rings to be different from the lower aryl rings. Thus, two singlets for the methyl group on the aryl rings and two sets of aromatic signals are in generally observed, although the aromatic protons always appeared as multiplets, being difficult to assign unambiguously.

4.17 Attempted synthesis of *cis*-$[M(CO)_4\{\eta^2$-(o-tolyl)$_2$PCMe$_2$P(o-tolyl)$_2\}]$ (M = W, Mo) and *cis*-$[Cr(CO)_4\{\eta^2$-(o-tolyl)$_2$PCMe(D)P(o-tolyl)$_2\}]$

Since substitution of one hydrogen on the backbone carbon atom of compounds **35-37** was successful, further substitution was attempted in order to increase the steric bulk on the backbone and consequently decrease the bite angle of the diphosphine. Compounds **42** and **43** were deprotonated by MeLi the colour changing from pale yellow to bright yellow or orange. Upon addition of MeI the solutions became pale yellow again, however, only starting materials were recovered. These reactions were repeated adding TMEDA, however, again the reactions failed to give the desired products. Similarly, attempted deprotonation of **44** by MeLi followed by the addition of D_2O, did not lead to deuterium incorporation into the product.

In these three reactions, we can conclude that the second hydrogen on the backbone carbon atom is now less acidic and also more sterically inaccessible (lower kinetic acidity). The change in colour from the reactions may due to attack of the CO groups in the molecule and such a process is probably reversible. Much more forcing conditions maybe required to remove the second hydrogen, however, further work on this problem was not pursued.

4.18 Solid state structures

Since the aim of this project was to synthesise a number of small bite angle diphosphine complexes by substituting bulky groups both on the backbone carbon atom and on the aryl rings from dppm, crystal structures are important in order to examine the bite angles, the orientation of the phenyl rings. Seven single crystal X-ray structures were obtained from the above experiments and they were all determined by Dr. G. Hogarth. The results will be discussed in detail below.

Compounds **35** (Fig.4-2) and **36** (Fig.4-3) have similar structures and both have no crystallographic symmetry and the aryl rings at the two phosphorus atoms are staggered. Ignoring the relative orientations of aryl rings, the "$M(CO)_4(C_2PCH_2PC_2)$" fragment has C_h symmetry. The M-C bonds of the *trans*-carbonyl groups are longer than that of the other two carbonyl groups. Since carbon is a better π-acceptor than phosphorus and since the carbonyl groups have a large *trans* effect, the two M-C bonds *trans* to phosphorus have a greater share of the d_π electron density leaving only a residue for the M-P π-back bonding. On the other hand, the two mutually *trans* M-C bonds have an equal share of the *d* electron density. It is, therefore, the different degree of π-bonding which accounts for the differences in the M-C bond lengths. The M-P distances are slightly longer than those in the literature.[46] The angles of the chelate ring are similar to those in the literature (Table 4-1).

W-P(1)	2.545(2) Å
W-P(2)	2.524(2) Å
W-C(1)	2.046(11) Å
W-C(2)	2.039(11) Å
W-C(3)	1.989(11) Å
W-C(4)	1.980(10) Å
P(1)-W-P(2)	67.00(7)°
W-P(1)-C(5)	94.0(3)°
W-P(2)-C(5)	95.3(3)°
P(1)-C(5)-P(2)	98.2(4)°

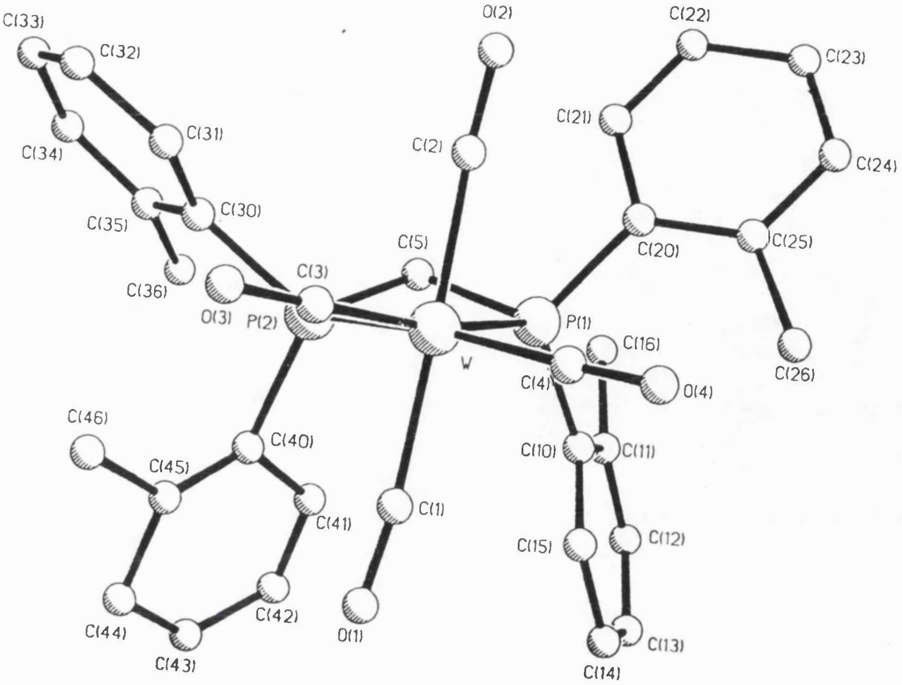


Fig 4-2 The crystal structure of *cis*-[W(CO)$_4${η^2-(o-tolyl)$_2$PCH$_2$P(o-tolyl)$_2$}] **35** with selected bond lengths and angles.

Mo-P(1)	2.5561(10) Å
Mo-P(2)	2.5338(11) Å
Mo-C(1)	2.028(5) Å
Mo-C(2)	2.051(5) Å
Mo-C(3)	1.979(4) Å
Mo-C(4)	1.981(5) Å
P(1)-Mo-P(2)	67.20(3)°
Mo-P(1)-C(5)	93.49(13)°
Mo-P(2)-C(5)	94.62(12)°
P(1)-C(5)-P(2)	99.2(2)°

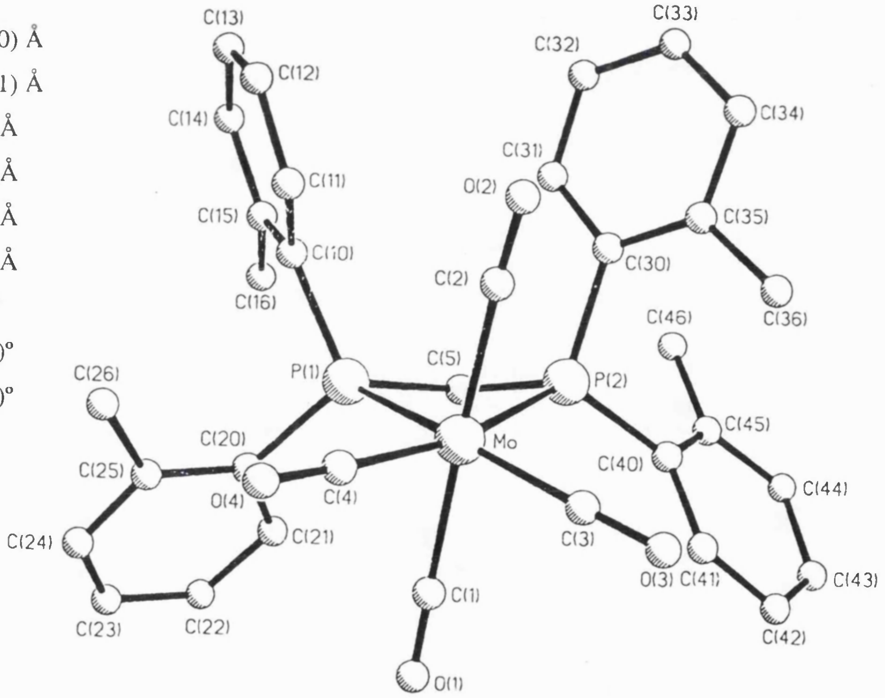


Fig.4-3 The crystal structure of *cis*-[Mo(CO)$_4${η^2-(o-tolyl)$_2$PCH$_2$P(o-tolyl)$_2$}] **36** with selected bond lengths and angles.

Table 4-1

Compound	Compound Number	M-C bond lengths/Å	M-P bond lengths/Å	PMP angle/°	PCP angle/°	M-P(1)-C angle/°	M-P(2)-C angle/°	M-C-O angle/°
fac-W$(CO)_3$(η^2-dppm)(CH_3CN)[46]		1.970(8)	2.514(2)	67.5(1)	98.1(3)	95.8(2)	95.7(2)	174.3(6)
		1.962(6)	2.512(2)					177.9(6)
		1.929(6)						178.6(4)
W-CH_2	34	2.046(11)	2.545(2)	67.00(7)	98.2(4)	94.0(3)	95.3(3)	177.1(10)
		2.039(11)	2.524(2)					177.0(10)
		1.989(11)						176.3(9)
		1.980(10)						179.1(10)
W-Me	41	1.979(14)	2.527(2)	67.68(8)	96.6(4)	95.5(2)	95.5(2)	177(2)
		2.012(14)	2.527(2)					179.8(11)
		1.978(10)						176.8(10)
		1.978(10)						
W-Et	45	2.00(2)	2.522(4)	67.65(13)	95.7(6)	95.9(5)	94.3(4)	176(2)
		2.00(2)	2.536(4)					175(2)
		2.00(2)						172(2)
		2.03(2)						176(2)
Mo$(CO)_4$(η^2-dppm)[18]		2.02(2)	2.535(3)	67.3(0.1)	95.6(0.4)	96.3(0.3)	97.5(0.3)	172.4(1.5)
		2.07(1)	2.501(2)					176.3(1.4)
		1.94(1)						177.4(1.2)
		1.92(1)						175.9(1.4)
Mo$(CO)_2$(η^2-dppm)(η^2-dppe)[47]		1.951(5)	2.522(2)	67.90(5)	98.4(3)	93.0(2)	96.8(2)	176.6(5)
		1.932(5)	2.421(2)					177.5(5)
			2.559(2)					
			2.449(2)					
Mo(CO)(η^2-dppm)(η^2-dpepp)[48]		1.940(3)	2.4970(9)	68.47(3)	98.24(15)	96.20(10)	97.07(10)	178.1(3)
			2.4788(10)					
			2.4237(10)					
			2.442(3)					

			2.5100(15)					
Mo-CH_2	35	2.028(5)	2.5561(10)	67.20(3)	99.2(2)	93.49(13)	94.62(12)	178.4(4)
		2.051(5)	2.5338(11)					176.1(4)
		1.979(4)						178.0(4)
		1.981(5)						178.3(5)
Mo-Me	42	2.042(8)	2.5502(12)	67.66(5)	97.6(3)	94.94(14)	94.94(14)	178.7(6)
		1.993(8)	2.5502(12)					177.4(9)
		1.972(5)						177.3(6)
		1.972(5)						
Mo-CH_2Ph	46	1.963(4)	2.5767(9)	66.58(3)	96.33(13)	93.45(9)	94.98(9)	178.4(3)
		1.990(3)	2.5378(8)					177.7(3)
		2.031(4)						175.3(3)
		2.021(3)						173.8(3)
Mer-Cr$(CO)_3$(η^1-dppm)(η^2-dppm)[45]		1.87(1)	2.395(4)	71.1(1)	94.0(5)	95.2(4)	98.8(4)	178.6(1.1)
		1.80(1)	2.298(4)					177.4(1.1)
		1.86(1)	2.332(4)					178.8(1.1)
Cr-Me	43	1.873(7)	2.3995(12)	70.96(5)	95.5(2)	94.45(12)	94.45(12)	176.6(7)
		1.903(7)	2.3995(12)					177.7(5)
		1.847(5)						176.9(5)
		1.847(5)						

W-C(1)	1.979(14) Å
W-C(2)	2.012(14) Å
W-C(3)	1.978(10) Å
W-C(3a)	1.978(10) Å
W-P(1)	2.527(2) Å
W-P(1a)	2.527(2) Å
P(1)-W-P(1a)	67.68(8)°
P(1)-C(4)-P(1a)	96.6(4)°
W-P(1)-C(4)	95.5(2)°
W-P(1a)-C(4)	95.5(2)°

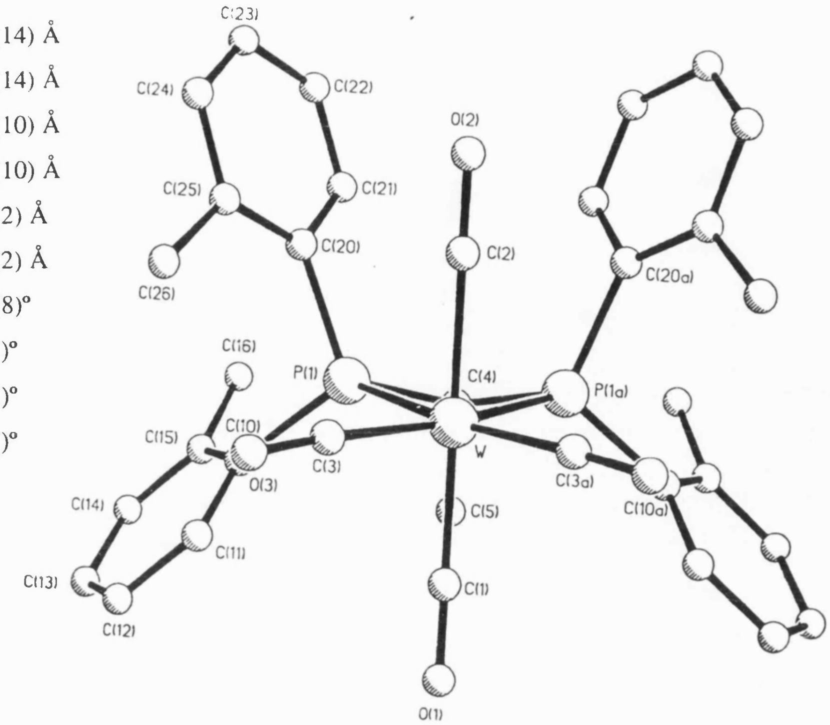


Fig.4-4 The crystal structure of *cis*-[W(CO)$_4${η^2-(o-tolyl)$_2$PCH(Me)P(o-tolyl)$_2$}] **42** with selected bond lengths and angles.

Mo-C(1)	2.042(8) Å
Mo-C(2)	1.993(8) Å
Mo-C(3)	1.972(5) Å
Mo-C(3a)	1.972(5) Å
Mo-P(1)	2.5502(12) Å
Mo-P(1a)	2.5502(12) Å
P(1)-Mo-P(1a)	67.66(5)°
P(1)-C(4)-P(1a)	97.6(3)°
Mo-P(1)-C(4)	94.94(14)°
Mo-P(1a)-C(4)	94.94(14)°

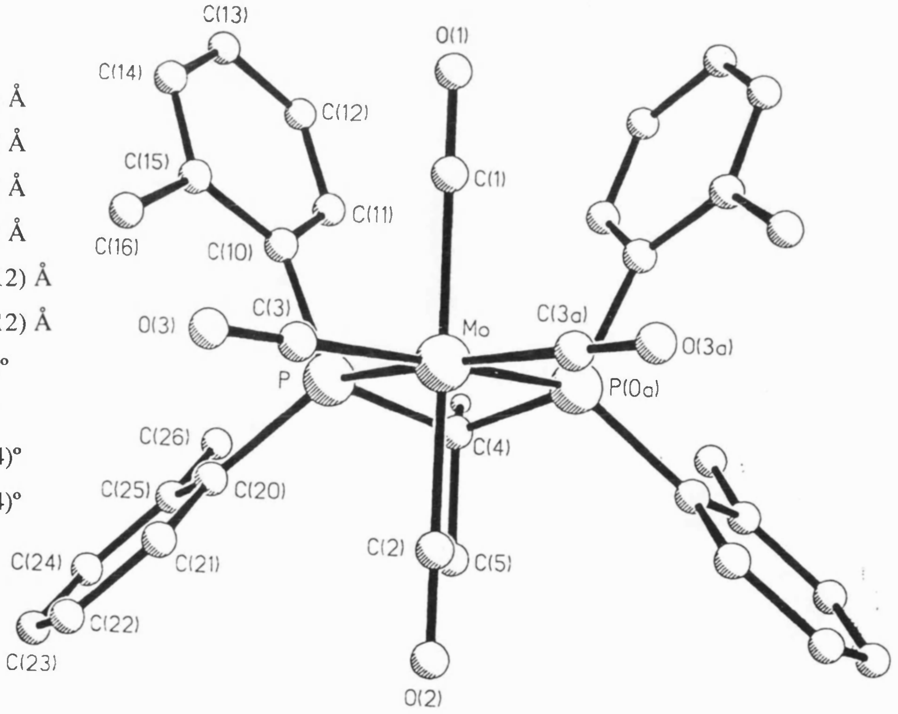


Fig. 4-5 The crystal structure of *cis*-[Mo(CO)$_4${η^2-(o-tolyl)$_2$PCH(Me)P(o-tolyl)$_2$}] **43** with selected bond lengths and angles.

Cr-C(1)	1.873(7) Å
Cr-C(2)	1.903(7) Å
Cr-C(3)	1.847(5) Å
Cr-C(3a)	1.847(5) Å
Cr-P(1)	2.3995(12) Å
Cr-P(1a)	2.3995(12) Å
P(1)-Cr-P(1a)	70.96(5)°
P(1)-C(4)-P(1a)	95.5(2)°
Cr-P(1)-C(4)	94.45(12)°
Cr-P(1a)-C(4)	94.45(12)°

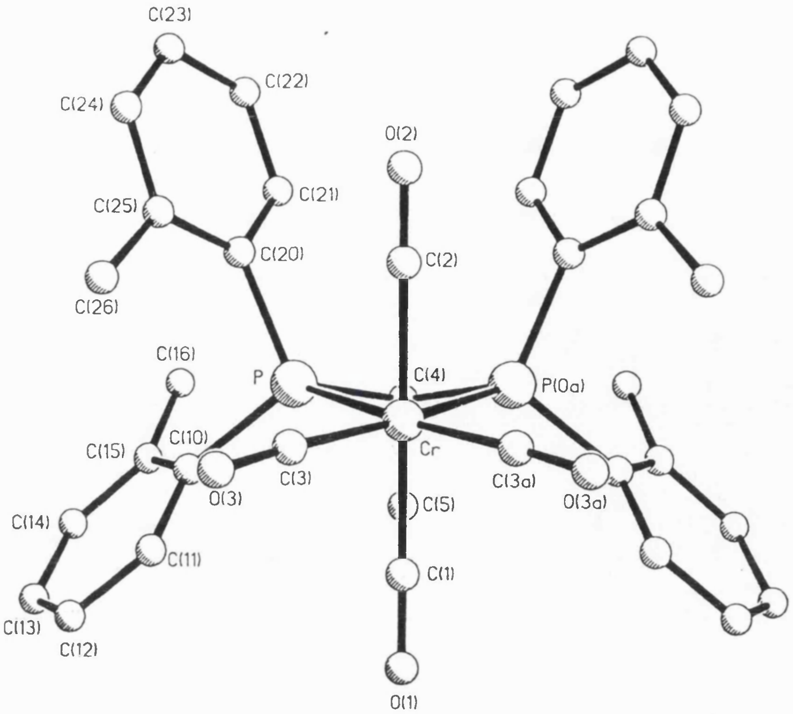


Fig.4-6 The crystal structure of *cis*-[Cr(CO)$_4${η^2-(o-tolyl)$_2$PCH(Me)P(o-tolyl)$_2$}] **44** with selected bond lengths and angles.

W-C(1)	2.00(2) Å
W-C(2)	2.00(2) Å
W-C(3)	2.00(2) Å
W-C(4)	2.03(2) Å
W-P(1)	2.522(4) Å
W-P(2)	2.536(4) Å
W-C(1)-O(1)	176(2)°
W-C(2)-O(2)	175(2)°
W-C(3)-O(3)	172(2)°
W-C(4)-O(4)	176(2)°
P(1)-W-P(2)	67.65(13)°
P(1)-C(5)-P(2)	95.7(6)°
W-P(1)-C(5)	95.9(5)°
W-P(2)-C(5)	94.3(4)°

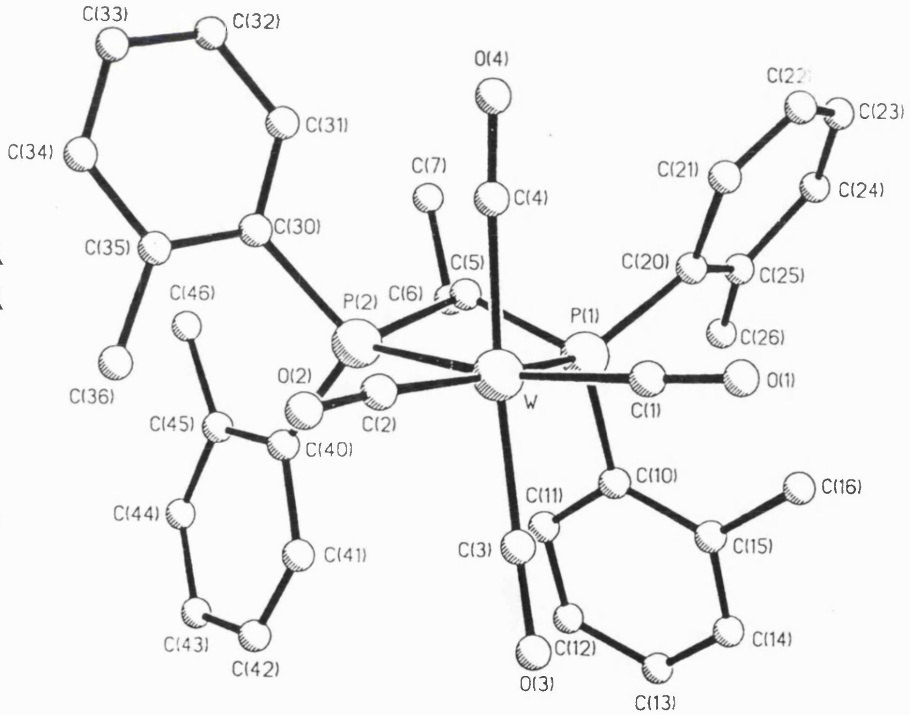


Fig.4-7 The crystal structure of *cis*-[W(CO)$_4${η^2-(o-tolyl)$_2$PCH(Et)P(o-tolyl)$_2$}] **46** with selected bond lengths and angles.

Mo-C(1)	1.963(4) Å
Mo-C(2)	1.990(3) Å
Mo-C(3)	2.031(4) Å
Mo-C(4)	2.021(3) Å
Mo-P(1)	2.5767(9) Å
Mo-P(2)	2.5378(8) Å
Mo-C(1)-O(1)	178.4(3)°
Mo-C(2)-O(2)	177.7(3)°
Mo-C(3)-O(3)	175.3(3)°
Mo-C(4)-O(4)	173.8(3)°
P(1)-Mo-P(2)	66.58(3)°
P(1)-C(5)-P(2)	96.33(13)°
Mo-P(1)-C(5)	93.45(9)°
Mo-P(2)-C(5)	94.98(9)°

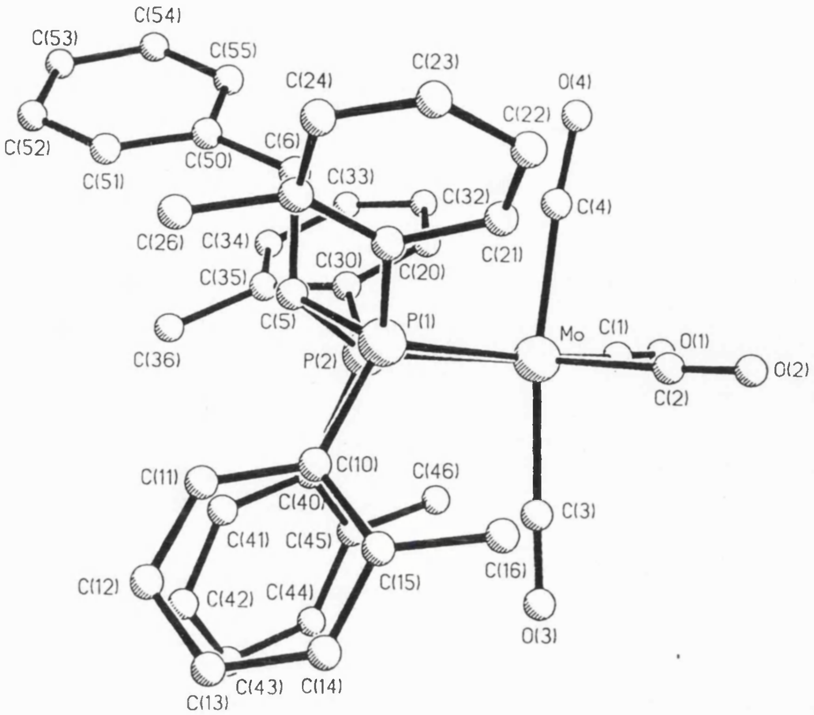


Fig.4-8 The crystal structure of *cis*-$[\mathrm{Mo(CO)_4\{\eta^2\text{-}(o\text{-}tolyl)_2PCH(CH_2Ph)P(o\text{-}tolyl)_2\}}]$ **47** with selected bond lengths and angles.

The three methyl substituted compounds **42-44** (Fig. 4-4 to 4-6) have similar crystal structures. They all have a mirror plane which contains the metal atom, the *trans* CO groups and the carbon atoms C(4) and C(5). The methyl group on the backbone is pointing in between the upper aryl rings. This causes the upper aryl rings to be in a fixed position and consequently leading the lower aryl rings to be geared into a position such that the methyl groups on the o-tolyl groups will not collide. Indeed, the methyl groups on the upper aryl rings are pointing in the opposite direction to those on the lower aryl rings. The M-C bonds of the *trans* CO groups are slightly longer than the other CO groups. For the M-P bonds, the W-P and the Mo-P bonds are slighly longer than those in the literature[18,47,48] while the Cr-P bonds are similar to those in the literature[45] (Table 4-1).

The ethyl substituted compound **46** (Fig. 4-7) and the benzyl substituted compound **47** (Fig. 4-8) have no crystallographic symmetry. The ethyl and benzyl groups are situated in between the upper aryl rings. The carbonyl groups on the metal (especially the *trans* ones) are slightly bending away from the aryl rings. The M-P bonds are longer than those in the literature[18,45-48] (Table 4-1).

The bite angles of our compounds are similar to those from the literature as shown. Theoretically, the bulkier the substituents on the diphosphine, the smaller the bite angle. This, however, is not always true as can be seen from the table above. The substituent R is always situated in between the upper aryl rings and these aryl groups are repelling away from the substituent R. Since the upper aryl rings are in a fixed position and causing the lower aryl rings to be geared into a position such that the methyl groups on the o-tolyl rings will not collide, the bite angle therefore may not necessarily become smaller depending on how the aryl rings and the substituent R occupy the space. However, as the substituents on the backbone changed from Me to Et and from Me to CH_2Ph, the bite angle of the diphosphine in general does become smaller. The smallest bite angle we have achieved is 66.58(3)° from compound **47**.

4.19 Conclusion

We have successfully synthesised a number of small bite angle diphosphine complexes by binding bis(di-o-tolylphosphino)methane (dotpm) with low valent metal centres and by increasing the steric bulk of the substituent R on the backbone carbon atom systematically. However, substituting the second hydrogen on the backbone of the diphosphine is problematic as the hydrogen atom is now both less acidic and less kinetically acidic.

A rare, five coordinate, 16-electron species, $[Mo(CO)_3\{\eta^2\text{-(o-tolyl)}_2PCH(Me)P(\text{o-tolyl})_2\}]$, **49**, is produced upon heating $[Mo(CO)_4\{\eta^2\text{-(o-tolyl)}_2PCH(Me)P(\text{o-tolyl})_2\}]$ **43** in xylene. This reaction proves that dotpm is sterically bulky enough to stabilise this coordinatively and electronically unsaturated complex.

Eight crystal structures were obtained in this project and dotpm is found to have similar structure to dppm. Increasing the steric bulk of the substituent R of dotpm complexes does not necessarily decrease the bite angle of the complex depending on how the substituent

R and the o-tolyl rings occupy the space.

4.20 Experimental

Preparation of (o-tolyl)$_2$PCl (29)

Ground magnesium (7.14 g, 0.30 mol) was placed into a three-necked round bottom flask equipped with a condenser, a bubbler, a mechanical stirrer and a pressure-equalising dropping funnel. Dry THF (200 cm^3) was transferred into the same flask and the mixture was purged with nitrogen. o-Bromotoluene (49.59 g, 0.29 mol) was diluted in dry THF (80 cm^3) and was poured into the pressure-equalising dropping funnel under a flow of nitrogen. o-Bromotoluene (1 g, 5.8 mmol) was added to the magnesium and the reaction was refluxed under nitrogen. A few drops of ethylene dibromide was added to initiate the reaction. When the reaction was under reflux, o-bromotoluene diluted in dry THF was added dropwise to the reaction mixture. After the addition was complete (1 hour), the reaction was refluxed under nitrogen for 2 hours. The reaction mixture was transferred into the pressure equalising dropping funnel. PCl$_3$ (12 cm^3, 0.13 mol) was diluted in dry THF (150 cm^3) and was cooled to 0°C. The Grignard was added to the PCl$_3$ dropwise under a flow of nitrogen. After the addition was complete (45 mins), the reaction mixture was refluxed under nitrogen for 1 hour. The THF was then distilled off and benzene (350 cm^3) was added. A white precipitate was filtered and the benzene solution was pumped to dryness under reduced pressure to give **29** as an orange paste (19.51 g). The orange paste was a mixture of PAr$_3$ and the product. ^{1}H NMR (CDCl$_3$): δ 7.42 (dd, 1H, J_{H-H} = 7.6 Hz, J_{P-H} = 3.89 Hz, Ar), 7.23 (t, 1H, J_{H-H} = 7.4 Hz, Ar), 7.13 (t, 1H, J_{H-H} = 7.3 Hz, Ar), 7.11 (t, 1H, J_{H-H} = 5.7 Hz, Ar), 2.41 (d, 3H, J_{P-H} 2.7 Hz, Me); ^{31}P-{^{1}H} NMR (CDCl$_3$): δ 49.8 (s); mass spectrum (FAB): *m/z* 304 (PAr$_3^+$), 289 (PAr$_3^+$-Me), 230 (M$^+$-Cl+Me), 215 (M$^+$-Cl); elemental analysis calc for ClPC$_{14}$H$_{14}$: C, 67.61; H, 5.63; Cl, 14.29; P, 12.47. Found C, 45.94; H, 5.01; Cl, 18.10; P, 6.52.

Preparation of bis(di-o-tolylphosphino)methane (30)

(o-tolyl)$_2$PCl **29** (13.17 g, 0.053 mol) was dissolved in dry THF (100 cm^3) under nitrogen. Lithium metal (2.10 g, 0.265 mol) was hammered and was cut into strips before adding to the pale yellow solution. The reaction mixture gradually turned into a blood red solution. This was left to stir at room temperature under nitrogen for 20 hours. Dry dichloromethane (1.7 cm^3, 0.027 mol) was added at 0°C. The solution immediately turned brown, and was stirred under nitrogen for 1 hour before it was refluxed for another hour. After removal of volatiles, yellow-brown solid was redissolved in dichloromethane. This was washed thoroughly with distilled water and the organic layer was dried by $MgSO_4$. The mixture was filtered and the filtrate was pumped to dryness under reduced pressure to give a creamy solid (3.02 g, 26%). It was recrystallised from dichloromethane and methanol to give **30** as white needles. ^{1}H NMR ($CDCl_3$): δ 7.36-7.10 (m, 16H, Ar), 2.60 (t, 2H, $J_{P\text{-}H}$ = 2.5 Hz, CH_2), 2.30 (s, 12H, Me); ^{31}P-{^{1}H} NMR ($CDCl_3$): δ -60.5 (s); mass spectrum (EI): *m/z* 440 (M^+), 425 (M^+-CH_3), 349 (M^+-$C_6H_5CH_3$), 304 {M^+-$C_6H_5(CH_3)_4$}; elemental analysis calc. for $C_{29}H_{30}P_2.0.5H_2O$: C, 77.51; H, 6.90; P, 13.81. Found C, 77.23; H, 6.88; P, 13.97.

Preparation of tetra(o-tolyl)biphosphine, Ar_2PPAr_2 (Ar = o-tolyl) (31)

Ground magnesium (7.02 g, 0.292 mol) was placed into a three-necked round bottom flask equipped with a water condenser, a bubbler, a mechanical stirrer and a pressure-equalising dropping funnel. Dry THF (200 cm^3) was added under a flow of nitrogen followed by o-bromotoluene (1 g, 5.85 mmol) and a few drops of ethylene dibromide. The reaction was refluxed under nitrogen. o-Bromotoluene (49 g, 0.287 mol) diluted with dry THF (80 cm^3) was poured into the pressure-equalising dropping funnel under a flow of nitrogen and was added to the refluxing mixture dropwise. After the addition was complete (ca. 1 hour), the reaction was continued to reflux for another 3 hours and the reaction mixture was cooled to 0°C. PCl_3 (8 cm^3, 0.097 mol) diluted in dry THF (150 cm^3) was added to the Grignard dropwise. After the addition was complete (ca. 0.5 hour), the reaction was refluxed under nitrogen for another hour. This was then pumped to dryness under reduced pressure to yield a white solid. This was redissolved in dichloromethane and was washed thoroughly with distilled water. The organic layer was dried by $MgSO_4$. The mixture was filtered and the filtrate was pumped to dryness under reduced pressure to give **31** as a creamy solid (19.88 g, 71%). ^{1}H NMR ($CDCl_3$): δ 7.30-7.23 (m, 8H, Ar), 7.09 (t, 4H, $J_{H\text{-}H}$ = 6.9 Hz, Ar), 6.77 (dd, 4H, $J_{P\text{-}H}$ = 2.7 Hz, $J_{H\text{-}H}$ = 7.0 Hz, Ar), 2.43 (s, 12H, Me); ^{31}P-{^{1}H} NMR ($CDCl_3$): δ -45.83 (s); mass spectrum (EI):

m/z 426 (M^+), 335 (M^+-o-tolyl), 319 (M^+-o-tolyl-Me), 304 (M^+-o-tolyl-2Me), 289 (M^+-o-tolyl-3Me); elemental analysis calc. for $P_2C_{28}H_{28}$.THF: C, 77.11; H, 7.23; P, 12.45. Found C, 77.39; H, 6.78; P, 9.89.

Preparation of tetra (2,6-dimethylphenyl) biphosphine, Ar_2PPAr_2 (Ar = 2,6-$Me_2C_6H_3$) (32)

Ground magnesium (7.15 g, 0.298 mol) was placed into a three-necked round bottom flask equipped with a water condenser, a bubbler, a mechanical stirrer and a pressure-equalising dropping funnel. Dry THF (200 cm^3) was added under a flow of nitrogen followed by 2-bromo-m-xylene (1 g, 5.41 mmol) and a few drops of ethylene dibromide. The reaction was refluxed under nitrogen. 2-bromo-m-xylene (50.70 g, 0.275 mol) was diluted with dry THF (80 cm^3) and was poured into the pressure equalising dropping funnel under a flow of nitrogen. This was added to the reaction mixture dropwise. After the addition was complete (ca. 1 hour), the reaction was refluxed for 3.5 hours. It was then cooled to 0°C and PCl_3 (8 cm^3, 0.09 mol) diluted with dry THF (150 cm^3) and was added dropwise. After the addition was complete (ca.0.5 hour), the reaction was continued to reflux for an hour. The mixture was pumped to dryness under reduced pressure to give a white solid which was washed thoroughly with distilled water. The mixture was filtered and the solid **32** (17.98 g, 58%) was air-dried. ^1H NMR ($CDCl_3$): δ 7.16-7.07 (m, 6H, Ar), 6.99-6.97 (m, 6H, Ar), 2.36 (d, 12H, J_{P-H} = 2.3 Hz, Me), 2.28 (s, 12H, Me); ^{31}P-{^1H} NMR ($CDCl_3$): δ -44.30 (s), mass spectrum (EI): *m/z* 482 (M^+), 377 (M^+-C_8H_9), 243 (M^+-$PC_{16}H_{18}$); elemental analysis calc. for $P_2C_{32}H_{36}$: C, 79.67; H, 7.47; P, 12.86. Found C, 79.14; H, 7.44; P, 12.69.

Preparation of bis(2,6-dimethylphenyl) chlorophosphine (34)

Ground magnesium (6.50 g, 0.271 mol) was placed into a three-necked round bottom flask equipped with a water condenser, a bubbler, a mechanical stirrer and a pressure equalising dropping funnel. Dry THF (200 cm^3) was added under a flow of nitrogen followed by 2-bromo-m-xylene (1 g, 5.41 mmol) and a few drops of ethylene dibromide. The reaction mixture was then refluxed under nitrogen. 2-bromo-m-xylene (47.20 g, 0.255 mol) diluted with dry THF (80 cm^3) was poured into the pressure equalising dropping funnel. This was added dropwise and after the addition was complete (ca. 1 hour), the reaction was refluxed for another 2.5 hours. The Grignard was then transferred into a pressure eqaulising dropping funnel. PCl_3 (9.9 cm^3, 0.114 mol) diluted with dry THF (150 cm^3) was poured into a three-necked round bottom flask equipped with a water condenser, a bubbler, a mechanical stirrer and a pressure equalising dropping funnel containing the Grignard. The Grignard was added dropwise under nitrogen to the PCl_3 at 0°C. After the addition was complete (ca.0.5 hour), the reaction was stirred under nitrogen at room temperature for another 20 hours and was refluxed for 1 hour. It was then pumped to dryness under reduced pressure. Copious quantities of benzene was added to the solid and the mixture was filtered. The filtrate was pumped to dryness under reduced pressure to obtain **33** as a yellow solid (23.59 g). The solid was a mixture of PAr_3 and product. ^{1}H NMR ($CDCl_3$): δ 7.33 (t, 2H, $J_{H\text{-}H}$ = 7.5 Hz, Ar), 7.05 (dd, 4H, $J_{H\text{-}H}$ = 6.6 Hz, $J_{P\text{-}H}$ = 2.1 Hz, Ar), 2.42 (s, 12H, Me), 2.33 (d, 12H, $J_{P\text{-}H}$ = 1.6 Hz, Me); ^{31}P-{^{1}H} NMR ($CDCl_3$): δ 55.48 (s); mass spectrum (EI): *m/z* 277 (M^+), 243 (M^+-Cl), 346 (M^+-Cl+C_8H_9); elemental analysis calc.for $PClC_{16}H_{18}$: C, 69.44; H, 6.51; Cl, 12.84; P, 11.21. Found C, 72.87; H, 7.64; Cl, 3.36; P, 11.17.

Attempted synthesis of bis(di-2,6-dimethylphenylphosphino)methane

Tetra(2,6-dimethylphenyl)bisphosphine (2.03 g, 4.2 mmol) was dissolved in dry THF (50 cm^3) under nitrogen to give a clear solution. Sodium metal (1 g, 8.4 mmol) was chopped into pieces before adding to the clear solution. This was left to stir under nitrogen at room temperature for 20 hours turning bright orange. The mixture was filtered and the orange solution was cooled to 0°C. Dry dichloromethane (0.3 cm^3, 4.2 mmol) was added dropwise to the orange solution. After the addition was complete, the solution was stirred at room temperature for 5 minutes. It was then warmed slightly turning pale yellow. After refluxing for 2 hours, no further change was observed. The solution was pumped to dryness under reduced pressure to give an oil which was redissolved in dichloromethane and was washed thoroughly with distilled water. The organic layer was dried by $MgSO_4$ and the mixture was filtered. The filtrate was pumped to dryness under reduced pressure to give an oil which was proved by spectroscopic data to be starting material.

Tetra(2,6-dimethylphenyl)biphosphine (4.18 g, 8.68 mmol) was dissolved in dry THF (50 cm^3) under nitrogen to give a clear solution. Potassium (3.39 g, 0.09 mol) was chopped into pieces before adding to the THF solution. This was left to stir at room temperature under nitrogen for 20 hours. The solution was turned a dark red colour. The mixture was filtered and dry dichloromethane (0.6 cm^3, 8.68 mmol) was added dropwise to the dark red solution at –78°C. After the addition was complete, the reaction was warmed to room temperature and was stirred under nitrogen for another 20 hours. The solution was pumped to dryness under reduced pressure to give an oil. This was redissolved in dichloromethane and was washed thoroughly with distilled water. The organic layer was dried by $MgSO_4$. The mixture was filtered and the filtrate was pumped to dryness under reduced pressure to give an oil which was proved by spectroscopic data that it was starting material.

Liquid ammonia (50 cm^3) was condensed into a three-necked round bottom flask equipped with a condenser and a bubbler under a flow of nitrogen at –78°C. Sodium metal (0.17 g, 7.0 mmol) was placed into the ammonia and a dark blue solution was formed. Tetra(2,6-dimethylphenyl)biphosphine (1.69 g, 3.5 mmol) was added and the solution gradually turned yellow. After 1.5 hour, dry dichloromethane (0.25 cm3, 3.5 mmol) was added dropwise. After 1 hour, the colour of the solution lightened. The solution was allowed to warm to room temperature leaving **33** as a white solid (0.58 g, 61%). ^{1}H NMR ($CDCl_3$): δ 7.32 (dt, 2H, $J_{H\text{-}H}$ = 1.2 Hz, $J_{H\text{-}H}$ = 7.8 Hz, Ar), 7.07 (dd, 4H, $J_{H\text{-}H}$ = 2.9 Hz, $J_{H\text{-}H}$ = 4.7 Hz, Ar), 6.58 (d, 2H, $J_{H\text{-}H}$ = 3.1 Hz, NH_2), 2.72 (d, 3H, $J_{P\text{-}H}$ = 13.2 Hz, Me), 4.45 (s, 12H, Me); ^{31}P-{^{1}H} NMR ($CDCl_3$): δ 18.95 (s); mass spectrum (EI): *m/z* 256 ($Ar_2PCH_3^+$); elemental analysis calc. for $PNClC_{17}H_{23}$: C, 66.34; H, 7.48; N, 4.55; Cl, 11.54; P, 10.08. Found C, 66.20; H, 7.71; N, 4.02; Cl, 11.60; P, 9.78.

Bis(2,6-dimethylphenyl)chlorophosphine (6.46 g, 0.023 mol) was dissolved in dry THF (100 cm^3) under nitrogen. Lithium metal (0.91 g, 0.117 mol) was hammered and was cut into strips before adding to the THF solution. The reaction mixture was stirred at room temperature under nitrogen for 20 hours. It gradually turned into a dark-red solution. After that, dry dichloromethane (0.7 cm^3, 0.012 mol) was added to the dark red solution at 0°C. After the addition was complete, the solution was stirred for another hour. It was then pumped to dryness to yield an oil. This was redissolved in dichloromethane and was washed thoroughly with distilled water. The organic layer was dried by $MgSO_4$. The mixture was filtered and the filtrate was pumped to dryness to give an oil which was a mixture of compounds but no product was detected.

Attempted synthesis of (o-tolyl)$_2$PCMe$_2$P(o-tolyl)$_2$

(o-tolyl)$_2$PCl **29** (4.76 g, 0.019 mol) was dissolved in dry THF (100 cm^3) under nirogen. Lithium metal (0.34 g, 0.048 mol) was hammered and was cut into strips before adding to the THF solution. The reaction was left to stir under nitrogen at room temperature for 20 hours. After that, the reaction mixture was filtered and 2,2-dichloropropane (1 cm^3, 9.57 mmol) was added dropwise to the dark red solution at 0°C. The resulting solution was refluxed under nitrogen for 20 hours. The solution was pumped to dryness under reduced pressure to give an oil which was redissolved in dichloromethane and washed thoroughly with distilled water. The organic layer was dried by $MgSO_4$. The mixture was filtered and the filtrate was pumped to dryness under reduced pressure to give an oil which was proved by spectroscopic data that there was a mixture of compounds but no product was detected.

Preparation of *cis*-[W(CO)$_4${η^2-(o-tolyl)$_2$PCH$_2$P(o-tolyl)$_2$}] (35)

Cis-[W(CO)$_4$(pip)$_2$] (0.23 g, 0.49 mmol) and bis(di-o-tolylphosphino)methane **30** (0.22 g, 0.49 mmol) were dissolved in 15 cm^3 of dichloromethane under nitrogen. The solution was refluxed for 2.5 hours. The yellow solution was pumped to dryness to yield a yellow solid which was recrystallised from dichloromethane and methanol. Yellow block-shaped crystals of **35** (0.24 g, 66%) were formed. IR (CH_2Cl_2): 2015s (CO), 1900s (CO), 1866s (CO) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.62 (dd, 4H, $J_{H\text{-}H}$ = 7.3 Hz, $J_{P\text{-}H}$ = 13.9 Hz, Ar), 7.30 (t, 4H, $J_{H\text{-}H}$ = 7.4 Hz, Ar), 7.17 (t, 4H, $J_{H\text{-}H}$ = 7.5 Hz, Ar), 7.12 (d, 4H, $J_{H\text{-}H}$ = 7.2 Hz, Ar), 4.91 (t, 2H, $J_{P\text{-}H}$ = 8.4 Hz, CH_2), 2.03 (s, 12H, Me); ^{31}P-{^{1}H} NMR ($CDCl_3$): δ -37.79 (s + ^{183}W satellites, $J_{W\text{-}P}$ = 196 Hz); mass spectrum (FAB): *m/z* 736 (M$^+$), 707 (M$^+$-

CO), 680 (M^+-2CO), 622 (M^+-4CO); elemental analysis calc. for $WP_2O_4C_{33}H_{30}.0.5CH_2Cl_2$: C, 51.64; H, 3.98; P, 7.96. Found C, 52.45; H, 3.98; P, 7.69.

Preparation of *cis*-[Mo(CO)$_4${η^2-(o-tolyl)$_2$PCH$_2$P(o-tolyl)$_2$}] (36)

Cis-[Mo(CO)$_4$(pip)$_2$] (0.10 g, 0.26 mmol) and bis(di-o-tolylphosphino)methane **30** (0.11 g, 0.26 mmol) were dissolved in 15 cm^3 of dichloromethane under nitrogen. The orange solution was refluxed for 4 hours. Then 15 cm^3 of methanol was added and the solution was reduced until precipitate was formed. The mixture was filtered and the residue was washed with methanol and air-dried. The tan solid was recrystallised from dichloromethane and methanol to yield some colourless block-shaped crystals of **36** (0.10 g, 62%). IR (CH_2Cl_2): 2019s (CO), 1909s (CO), 1872s (CO) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.63 (dd, 4H, $J_{H\text{-}H}$ = 7.2 Hz, $J_{P\text{-}H}$ = 13.2 Hz, Ar), 7.29 (t, 4H, $J_{H\text{-}H}$ = 7.5 Hz, Ar), 7.14 (t, 4H, $J_{H\text{-}H}$ = 7.6 Hz, Ar), 7.11 (d, 4H, $J_{H\text{-}H}$ = 7.6 Hz, Ar) 4.43 (t, 2H, $J_{P\text{-}H}$ = 7.9 Hz, CH_2), 2.04 (s, 12H, Me); ^{31}P-{^{1}H} NMR ($CDCl_3$): δ -14.22 (s); mass spectrum (FAB): *m/z* 650 (M^+), 623 (M^+-CO), 594 (M^+-2CO), 538 (M^+-4CO); elemental analysis calc. for $MoP_2O_4C_{33}H_{30}$: C, 61.11; H, 4.63; P, 9.57. Found C, 60.41; H, 4.77; P, 9.15.

Preparation of *cis*-[Cr(CO)$_4${η^2-(o-tolyl)$_2$PCH$_2$P(o-tolyl)$_2$}] (37)

[Cr(CO)$_5$Cl][NEt$_4$] (0.59 g, 1.66 mmol) and bis(di-o-tolylphosphino)methane **30** (0.37 g, 0.83 mmol) were dissolved in dry dichloromethane (25 cm^3). The green solution was refluxed under nitrogen for 5 hours. It was then cooled to room temperature and was filtered. The filtrate was washed thoroughly with distilled water and the dichloromethane extract was dried by $MgSO_4$. This was filtered and the filtrate was pumped to dryness under reduced pressure to yield **37** as a yellow solid (0.37 g, 73%). IR (CH_2Cl_2): 2006s (CO), 1896s (CO), 1867s (CO) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.69 (dd, 4H, $J_{H\text{-}H}$ = 8.0 Hz, $J_{P\text{-}H}$ = 12.4 Hz, Ar), 7.30 (t, 4H, $J_{H\text{-}H}$ = 7.4 Hz, Ar), 7.18-7.14 (t, 4H, $J_{H\text{-}H}$ = 7.5 Hz, Ar), 7.12-7.10 (dd, 4H, $J_{H\text{-}H}$ = 7.5 Hz, $J_{P\text{-}H}$ = small, Ar), 4.38 (t, 2H, $J_{P\text{-}H}$ = 8.5 Hz, CH_2), 2.00 (s, 12H, Me); ^{31}P-{^{1}H} NMR ($CDCl_3$): δ 9.76 (s); mass spectrum (FAB): *m/z* 604 (M^+), 520 (M^+-3CO), 492 (M^+-4CO); elemental analysis calc. for $CrP_2O_4C_{33}H_{30}$: C, 65.56; H, 4.97; P, 10.26. Found C, 65.03; H, 5.06; P, 9.79.

Preparation of *cis*-[$PdCl_2\{\eta^2$-(o-tolyl)$_2PCH_2P$(o-tolyl)$_2$}] (38)

cis-[Pd(PhCN)$_2Cl_2$] (0.16 g, 0.42 mmol) and bis(di-o-tolylphosphino)methane **30** (0.19 g, 0.42 mmol) were dissolved in dry dichloromethane (15 cm^3) under nitrogen. This was refluxed for 20 hours. The brown solution was pumped to dryness under reduced pressure to give **38** as a brown powder (0.19 g, 75%) which was washed with methanol and was air-dried. IR (KBr): 3055w (CH), 2963w (CH), 2920w (CH) cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.97 (dd, 4H, J_{H-H} = 7.7 Hz, J_{P-H} = 8.2 Hz, Ar), 7.45 (t, 4H, J_{H-H} = 7.6 Hz, Ar), 7.25-7.19 (m, 8H, Ar), 4.33 (t, 2H, J_{P-H} = 9.9 Hz, CH_2), 2.32 (s, 12H, Me); ^{31}P-{^1H} NMR ($CDCl_3$): δ -69.00 (s); mass spectrum (FAB): *m/z* 583 (M^+-Cl), 545 (M^+-2Cl); elemental analysis calc.for $PdP_2Cl_2C_{29}H_{30}$.0.2PhCN: C, 54.83; H, 4.85; N, 0.44; Cl, 11.11; P, 9.70. Found C, 54.49; H, 4.54; N, 0.44; Cl, 12.80; P, 9.70.

Preparation of *cis*-[$PtCl_2\{\eta^2$-(o-tolyl)$_2PCH_2P$(o-tolyl)$_2$}] (39)

cis-[Pt(PhCN)$_2Cl_2$] (0.21 g, 0.44 mmol) and bis(di-o-tolylphosphino)methane **30** (0.21 g, 0.44 mmol) were dissolved in 15cm^3 of dry dichloromethane under nitrogen. The solution was refluxed for 10 hours. A white precipitate was formed. Hexane was added to precipitate more solids. The mixture was filtered and the residue was washed with hexane and air-dried. A white powder was obtained which was recrystallised from dichloromethane and methanol to yield **39** as colourless plates (0.28 g, 92%). IR (KBr): 3056w (CH), 3011w (CH), 2960w (CH), 2919w (CH), 2904w (CH), 2856w (CH) cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.96 (dd, 4H, J_{H-H} = 7.9 Hz, J_{P-H} = 8.1 Hz, Ar), 7.43 (t, 4H, J_{H-H} = 7.3 Hz, Ar), 7.25-7.20 (m, 8H, Ar), 4.59 (t, 2H, J_{P-H} = 10 Hz, CH_2), 2.26 (s, 12H, Me); ^{31}P-{^1H} NMR ($CDCl_3$): δ -77.94 (s + ^{195}Pt satellites, J_{Pt-P} = 3097 Hz); mass spectrum (FAB): *m/z* 1484 ($2M^+$+2Cl), 1409 ($2M^+$), 742 (M^++Cl), 671 (M^+-Cl), 634 (M^+-2Cl); elemental analysis calc. for $PtP_2Cl_2C_{29}H_{30}$: C, 49.29; H, 4.25; Cl, 10.06; P, 8.78. Found C, 48.70; H, 4.08; Cl, 10.75; P, 8.48.

Preparation of *cis*-[$PtBr_2\{\eta^2$-(o-tolyl)$_2PCH_2P$(o-tolyl)$_2$}] (40)

cis-[$PtCl_2${η^2-(o-tolyl)$_2$$PCH_2P$(o-tolyl)$_2$}] **39** (0.05 g, 0.08 mmol) and LiBr (0.01 g, 0.15 mmol) were dissolved in dry THF (15 cm^3) under nitrogen. The mixture was stirred at room temperature for 20 hours. The solvent was distilled off and the residue was redissolved in dichloromethane. This was washed thoroughly with distilled water and the dichloromethane extract was dried by $MgSO_4$. The mixture was filtered and the filtrate was pumped to dryness under reduced pressure to give **40** as a yellow powder (0.05 g, 78%). ^{1}H NMR ($CDCl_3$): δ 7.98 (dd, 4H, $J_{H\text{-}H}$ = 7.7 Hz, $J_{P\text{-}H}$ = 7.6 Hz, Ar), 7.44 (t, 4H, $J_{H\text{-}H}$ = 7.3 Hz, Ar), 7.25-7.21 (m, 8H, Ar); 4.65 (t, 2H, $J_{P\text{-}H}$ = 10.2 Hz, CH_2), 2.27 (s, 12H, $J_{Pt\text{-}H}$ 73.8, Me); ^{31}P-{^{1}H} NMR ($CDCl_3$): δ -80.32 (s + ^{195}Pt satellites, $J_{Pt\text{-}P}$ = 7549 Hz); mass spectrum (FAB): *m/z* 715 (M^+-Br), 634 (M^+-2Br); elemental analysis calc. for $PtBr_2P_2C_{29}H_{30}$: C, 43.77; H, 3.77; Br, 20.13; P, 7.80. Found C, 41.38; H, 4.44; Br, 16.74; P, 6.63.

Preparation of *cis*-[PtI_2{η^2-(o-tolyl)$_2$$PCH_2P$(o-tolyl)$_2$}] (41)

cis-[$PtCl_2${η^2-(o-tolyl)$_2$$PCH_2P$(o-tolyl)$_2$}] **39** (0.05 g, 0.08 mmol) and LiI (0.02 g, 0.15 mmol) were dissolved in 15 cm^3 of THF under nitrogen. The yellow solution was stirred at room temperature for 20 hours. Then it was pumped under reduced pressure to yield a yellow solid. The solid was redissolved in dichloromethane and was washed with water three times. The yellow solution was pumped to dryness under reduced pressure to give **41** as a yellow powder (0.04 g, 62%). ^{31}P-{^{1}H} NMR ($CDCl_3$): δ -87.73 (s + ^{195}Pt satellites, $J_{Pt\text{-}P}$ = 2876 Hz); mass spectrum (FAB): *m/z* 1652 (MH^+-I), 889 (M^+), 762 (M^+-I); elemental analysis calc. for $PtP_2I_2C_{29}H_{30}$: C, 39.15; H, 3.37; I, 28.57; P, 6.97. Found C, 39.08; H, 3.69; I, 28.63; P, 7.18.

Preparation of *cis*-[W(CO)$_4${η^2-(o-tolyl)$_2$PCH(Me)P(o-tolyl)$_2$}] (42)

cis-[W(CO)$_4${η^2-(o-tolyl)$_2$$PCH_2P$(o-tolyl)$_2$}] **35** (0.11 g, 0.15 mmol) was dissolved in 10 cm^3 of THF under nitrogen. ^{n}BuLi (0.08 cm^3, 0.19 mmol) was added to the yellow solution which immediately darkened. After 1 hour, MeI (0.012 cm^3, 0.19 mmol) was added and the reaction was stirred at room temperature for 20 hours. The solution was pumped to dryness under reduced pressure and the solid was redissolved in dichloromethane. The yellow solution was washed with water three times and was dried by $MgSO_4$. The solution was pumped to dryness under reduced pressure to yield **42** as a yellow powder which was recrystallised from dichloromethane and methanol. Yellow block-shaped crystals (0.07 g, 62%) were formed. IR (CH_2Cl_2): 2016s (CO), 1895s (CO), 1863s (CO) cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.17-8.11 (m, 4H, Ar), 7.38-7.20 (m, 8H, Ar), 7.07-7.02 (m, 4H, Ar), 6.01 (q, 1H, J_{H-H} = 7.3 Hz, CH), 2.11 (s, 6H, Me), 2.04 (s, 6H, Me), 1.02 (dt, 3H, J_{H-H} = 7.7 Hz, J_{P-H} = 15.5 Hz, Me); ^{31}P-{^1H} NMR ($CDCl_3$): δ -18.03 (s + ^{183}W satellites, J_{W-P} 199); mass spectrum (FAB): *m/z* 750 (M^+), 722 (M^+-CO), 694 (M^+-2CO), 666 (M^+-3CO), 636 (M^+-4CO-2H); elemental analysis calc.for $WP_2O_4C_{34}H_{32}.CH_2Cl_2$: C, 50.30; H, 4.07; P, 7.43. Found C, 50.23; H, 4.01; P, 7.46.

Preparation of *cis*-[Mo(CO)$_4${η^2-(o-tolyl)$_2$PCH(Me)P(o-tolyl)$_2$}] (43)

cis-[Mo(CO)$_4${η^2-(o-tolyl)$_2$PCH$_2$P(o-tolyl)$_2$}] **36** (0.30 g, 0.46 mmol) was dissolved in dry THF (15 cm^3) under nitrogen. ^{n}BuLi (0.37 cm^3, 0.60 mmol) was added to the yellow solution. The solution immediately turned darker yellow. It was left to stir at room temperature under nitrogen for 1 hour. MeI (0.04 cm^3, 0.60 mmol) diluted in dry THF (1cm^3) was then added to the yellow solution. The reaction was left to stir under nitrogen for 20 hours. The colour of the solution gradually lightened. After 20 hours, the solution was pumped to dryness under reduced pressure to yield a yellow solid which was redissolved in dichloromethane. This solution was washed thoroughly with distilled water and was dried by $MgSO_4$. The mixture was filtered and the filtrate was pumped to dryness under reduced pressure to yield a yellow solid. This was recrystallised from dichloromethane and methanol to give **43** as yellow blocks (0.18 g, 59%). IR (CH_2Cl_2): 2020s (CO), 1921s (CO), 1905s (CO), 1869s (CO) cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.14-8.10 (m, 4H, Ar), 7.33-7.22 (m, 8H, Ar), 7.08-7.06 (m, 4H, Ar), 5.38 (q, 1H, J_{H-H} = 7.7 Hz, CH), 2.14 (s, 6H, Me), 2.07 (s, 6H, Me), 1.08 (dt, 3H, J_{H-H} 7.7, J_{P-H} = 14.8 Hz, Me); ^{31}P-{^1H} NMR ($CDCl_3$): δ 4.96 (s); mass spectrum (FAB): *m/z* 664 (M^+), 608 (M^+-2CO), 552 (M^+-4CO); elemental analysis calc. for $MoP_2O_4C_{34}H_{32}.0.5CH_2Cl_2$: C, 58.76; H, 4.88; P, 8.80. Found C, 58.18; H, 5.69; P, 9.43.

Preparation of *cis*-[Cr(CO)$_4${η^2-(o-tolyl)$_2$PCH(Me)P(o-tolyl)$_2$}] (44)

cis-[Cr(CO)$_4${η^2-(o-tolyl)$_2$PCH$_2$P(o-tolyl)$_2$}] **37** (0.33 g, 0.55 mmol) was dissolved in dry THF (25 cm^3) under nitrogen. ^{n}BuLi (0.7 cm^3, 1.09 mmol) was added and the yellow solution immediately darkened. This was left to stir under nitrogen at room temperature for 1 hour. MeI (0.07 cm^3, 1.09 mmol) was then added to the solution and its colour lightened. The reaction mixture was left to stir under nitrogen for 20 hours, and was pumped to dryness under reduced pressure. The solid was redissolved in dichloromethane and was washed thoroughly with distilled water. The dichloromethane extract was dried by MgSO$_4$ and was filtered. The solution was pumped to dryness under reduced pressure to yield a yellow powder which was recrystallised from dichloromethane and methanol to give **44** as yellow blocks (0.33 g, 99%). IR (CH$_2$Cl$_2$): 2006s (CO), 1913s (CO), 1893s (CO), 1865s (CO) cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 8.27-8.26 (m, 4H, Ar), 7.38-7.33 (m, 8H, Ar), 7.05 (m, 4H, Ar), 5.39 (q, 1H, J_{H-H} = 7.2 Hz, CH), 2.09 (s, 6H, Me), 2.00 (s, 6H, Me), 1.06 (dt, 3H, J_{H-H} 7.3, J_{P-H} = 15.9 Hz, Me); ^{31}P-{^{1}H} NMR (CDCl$_3$) δ 27.88 (s); mass spectrum (FAB): *m/z* 618 (M$^+$), 562 (M$^+$-2CO), 534 (M$^+$-3CO), 506 (M$^+$-4CO); elemental analysis calc.for CrP$_2$O$_4$C$_{34}$H$_{32}$.0.75CH$_2$Cl$_2$: C, 61.17; H, 4.91; P, 9.09. Found C, 60.64; H, 4.96; P, 9.21.

Preparation of *cis*-[Mo(CO)$_4${η^2-(o-tolyl)$_2$PCH(Et)P(o-tolyl)$_2$}] (45)

cis-[Mo(CO)$_4${η^2-(o-tolyl)$_2$PCH$_2$P(o-tolyl)$_2$}] **36** (0.33 g, 0.50 mmol) was dissolved in dry THF (25 cm^3) under nitrogen to form a pale yellow solution. ^{n}BuLi (0.5 cm^3, 0.75 mmol) was added and the solution immediately darkened. After stirring at room temperature under nitrogen for an hour, EtI (0.06 cm^3, 0.75 mmol) was then added and the reaction mixture stirred for a further 20 hours. The solvent was removed and the solid was redissolved in dichloromethane and washed thoroughly with distilled water. The dichloromethane extract was dried by MgSO$_4$ and the mixture was filtered. The filtrate was pumped to dryness under reduced pressure to give **45** as a yellow solid (0.24 g, 72%). IR (CH$_2$Cl$_2$): 2018s (CO), 1906s (CO), 1870s (CO) cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 7.94 (dt, 4H, J_{H-H} = 5.2 Hz, Ar), 7.85 (dd, 4H, J_{H-H} = 7.5 Hz, Ar), 7.36-7.16 (m, 4H, Ar), 7.11 (d, 4H, J_{H-H} = 6.3 Hz, Ar), 4.77 (tt, 1H, J_{H-H} = 4.8 Hz, CH), 2.18 (s, 6H, Me), 2.05 (s, 6H, Me), 1.87 (dm, 2H, J_{H-H} = 2.1 Hz, J_{H-H} = 7.4 Hz, CH$_2$), 0.77 (t, 3H, J_{H-H} = 7.4 Hz, CH$_3$); ^{31}P-{^{1}H} NMR (CDCl$_3$): δ 5.90 (s); mass spectrum (FAB): *m/z* 762 (M$^+$+3CO), 734 (M^++2CO), 706 (M^++CO), 692 (M^++Me), 678 (M^+), 664 (M^+-Me), 649 (M^+-Et), 622 (M^+-2CO), 566 (M^+-4CO); elemental analysis calc.for $MoP_2O_4C_{35}H_{34}$: C, 62.13; H, 5.03; P, 9.17. Found C, 62.16; H, 5.55; P, 10.85.

Preparation of *cis*-[W(CO)$_4${η^2-(o-tolyl)$_2$PCH(Et)P(o-tolyl)$_2$}] (46)

cis-[W(CO)$_4${η^2-(o-tolyl)$_2$PCH$_2$P(o-tolyl)$_2$}] **35** (0.25 g, 0.35 mmol) was dissolved in dry THF (25cm^3) under nitrogen to form a pale yellow solution. ^{n}BuLi (0.3 cm^3, 0.52 mmol) was added and the solution immediately darkened. This was left to stir at room temperature under nitrogen for an hour. EtI (0.04 cm^3, 0.52 mmol) was then added and the solution was stirred under nitrogen for 20 hours. The solvent was removed and the solid was redissolved in dichloromethane. This was washed thoroughly with distilled water. The dichloromethane extract was dried by $MgSO_4$ and the mixture was filtered. The filtrate was pumped to dryness under reduced pressure to give a yellow powder. This was recrystallised from dichloromethane and methanol to give **46** as yellow blocks (0.19 g, 72%). IR (CH_2Cl_2): 2016s (CO), 1900s (CO), 1866s (CO) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.99 (dt, 4H, J_{H-H} = 3.3 Hz, Ar), 7.89 (dd, 4H, J_{H-H} = 7.5 Hz, Ar), 7.34 (t, 4H, J_{H-H} = 7.2 Hz), 7.26 (m, 4H, Ar), 7.09 (m, 4H, Ar), 5.29 (brs, 1H, CH), 2.13 (s, 6H, Me), 2.01 (s, 6H, Me), 1.81 (dm, 2H, J_{P-H} = 2.1 Hz, J_{H-H} = 7.4 Hz, CH_2), 0.79 (t, 3H, J_{H-H} = 7.3 Hz, Me); ^{31}P-{^{1}H} NMR ($CDCl_3$): δ -15.75 (s); mass spectrum (FAB): *m/z* 818 (M^++2CO), 790 (M^++CO), 778 (M^++Me), 764 (M^+), 750 (M^+-Me), 736 (M^+-CO), 708 (M^+-2CO), 680 (M^+-3CO), 650 (M^+-4CO); elemental analysis calc. for $WP_2O_4C_{35}H_{34}$: C, 54.97; H, 4.45; P, 8.12. Found C, 54.36; H, 4.84; P, 7.51.

Preparation of *cis*-[Mo(CO)$_4${η^2-(o-tolyl)$_2$PCH(CH$_2$Ph)P(o-tolyl)$_2$}] (47)

cis-[Mo(CO)$_4${η^2-(o-tolyl)$_2$PCH$_2$P(o-tolyl)$_2$}] **36** (0.33 g, 0.51 mmol) was dissolved in dry THF (25 cm^3) under nitrogen. ^{n}BuLi (0.5 cm^3, 0.77 mmol) was added and the solution immediately darkened. The reaction was stirred under nitrogen at room temperature for 1 hour. Benzyl bromide (0.09 cm^3, 0.77 mmol) was added and the solution was stirred for another 20 hours. The solvent was removed and the residue was redissolved in dichloromethane. This was washed thoroughly with distilled water. The organic layer was dried by $MgSO_4$ and the mixture was filtered. The filtrate was pumped to dryness under reduced pressure to give an oil. This was recrystallised from dichloromethane and methanol to give **47** as yellow plates (0.13 g, 34%). IR (CH_2Cl_2): 2020s (CO), 1898s (CO), 1869s (CO) cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.05 (brs, 2H, Ph), 7.91 (brs, 2H, Ph), 7.34-6.91 (m, 16H, Ar), 6.54 (d, 2H, J_{H-H} = 7.3 Hz, Ar), 5.53 (brs, 1H, CH), 3.04 (dt, 2H, J_{H-H} = 5.4 Hz, J_{P-H} = 14.2 Hz, CH_2), 2.16 (s, 6H, Me), 1.80 (s, 6H, Me); ^{31}P-{^1H} NMR ($CDCl_3$): δ 6.95 (s); mass spectrum (FAB): *m/z* 740 (M^+), 713 (M^+-CO), 684 (M^+-2CO), 628 (M^+-4CO); elemental analysis calc. for $MoP_2O_4C_{40}H_{36}.0.25CH_2Cl_2$: C, 63.62; H, 4.81; P, 8.17. Found C, 64.31; H, 4.84; P, 8.12.

Preparation of *cis*-[W(CO)$_4${η^2-(o-tolyl)$_2$PCH(CH$_2$Ph)P(o-tolyl)$_2$}] (48)

cis-[W(CO)$_4${η^2-(o-tolyl)$_2$PCH$_2$P(o-tolyl)$_2$}] **35** (0.11 g, 0.15 mmol) was dissolved in dry THF (25 cm^3) under nitrogen. ^{n}BuLi (0.14 cm^3, 0.23 mmol) was added and the solution immediately darkened. The reaction was stirred under nitrogen at room temperature for 1 hour. Benzyl bromide (0.03 cm^3, 0.23 mmol) was added and the solution was stirred for another 20 hours. The solvent was removed and the residue was redissolved in dichloromethane. This was washed thoroughly with distilled water. The organic layer was dried by $MgSO_4$ and the mixture was filtered. The filtrate was pumped to dryness under reduced pressure to give a yellow powder. This was recrystallised from dichloromethane and methanol to give **48** as yellow blocks (0.05 g, 40%). IR (CH_2Cl_2): 2016s (CO), 1912s (CO), 1896s (CO), 1866s (CO) cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.13 (brs, 2H, Ph), 8.02 (brs, 2H, Ph), 7.38-6.85 (m, 16H, Ar), 6.55 (d, 2H, J_{H-H} = 7.3 Hz, Ar), 6.17 (brs, 1H, CH), 2.98 (dt, 2H, J_{H-H} = 5.6 Hz, J_{P-H} = 15.0 Hz, CH_2), 2.10 (s, 6H, Me), 1.71 (s, 6H, Me); ^{31}P-{^1H} NMR ($CDCl_3$): δ -15.62 (s); mass spectrum (FAB): *m/z* 826 (M^+), 798 (M^+-CO), 770 (M^+-2CO), 742 (M^+-3CO), 712 (M^+-4CO); elemental analysis calc. for $WP_2O_4C_{40}H_{36}$: C, 58.11; H, 4.36; P, 7.51. Found C, 57.67; H, 4.20; P, 7.40.

Attempted synthesis of [W(CO)$_2${η^6-C$_6$H$_4$Me-P(o-tolyl)CHMeP(o-tolyl)$_2$}]

cis-[W(CO)$_4${η^2-(o-tolyl)$_2$PCH(Me)P(o-tolyl)$_2$}] **42** (0.26 g, 0.34 mmol) was refluxed in decalin (20 cm^3) under nitrogen for 60 hours. After 1.5 hour, the yellow solution turned green. After 3 hours, the reaction turned blue. After 60 hours, the reaction mixture was pumped to dryness to give a blue powder. Spectroscopic data proved that the blue powder was decomposition of the starting material.

Preparation of [Mo(CO)$_3${η^2-(o-tolyl)$_2$PCH(Me)P(o-tolyl)$_2$}] (49)

cis-[Mo(CO)$_4${η^2-(o-tolyl)$_2$PCH(Me)P(o-tolyl)$_2$}] **43** (0.19 g, 0.28 mmol) was refluxed in xylene (15 cm^3) under nitrogen for 60 hours. The solvent was pumped to dryness under reduced pressure to give **49** as a black solid (0.11 g, 62%). IR (CH_2Cl_2): 1901s (CO), 1840s (CO); ^{1}H NMR ($CDCl_3$): δ 7.41-6.98 (m, 16H, Ar), 3.27 (q, 1H, J_{H-H} = 7.1 Hz, CH), 2.49 (s, 6H, Me), 2.23 (s, 6H, Me), 0.97 (dt, 3H, J_{H-H} = 4.0 Hz, J_{P-H} = 11.1 Hz, Me); ^{31}P-{^{1}H} NMR ($CDCl_3$): δ -46.70 (s); mass spectrum (FAB): *m/z* 606 (M$^+$-CO), 592 (M$^+$-Me-CO), 576 (M$^+$-2CO), 561 (M$^+$-2CO-Me), 552 (M$^+$-3CO);

Attempted synthesis of *cis*-[W(CO)$_4${η^2-(o-tolyl)$_2$PCMe$_2$P(o-tolyl)$_2$}]

cis-[W(CO)$_4${η^2-(o-tolyl)$_2$PCH(Me)P(o-tolyl)$_2$}] **42** (0.33 g, 0.44 mmol) was dissolved in dry THF (25 cm^3) under nitrogen to give a pale yellow solution. MeLi (0.7 cm^3, 0.89 mmol) was added and the solution immediately turned orange. This was left to stir under nitrogen at room temperature for 1 hour. MeI (0.06 cm^3, 0.89 mmol) was then added and the solution turned from orange to yellow. This was continued to stir for another 20 hours. The solvent was removed and the residue was redissolved in dichloromethane. This was washed thoroughly with distilled water. The organic layer was dried by $MgSO_4$. The mixture was filtered and the filtrate was pumped to dryness under reduced pressure to give a yellow powder which was shown by spectroscopic data to be the starting material.

Attempted synthesis of *cis*-[Mo(CO)$_4${η^2-(o-tolyl)$_2$PCMe$_2$P(o-tolyl)$_2$}]

cis-[Mo(CO)$_4${η^2-(o-tolyl)$_2$PCH(Me)P(o-tolyl)$_2$}] **43** (0.22 g, 0.33 mmol) was dissolved in dry benzene (10 cm^3) under nitrogen to give a pale yellow solution. Dry TMEDA (0.2

cm^3, 1.33 mmol) was added followed by MeLi (0.95 cm^3, 1.33 mmol). The solution immediately turned bright yellow. This was left to stir at room temperature under nitrogen for 1 hour. MeI (0.08 cm^3, 1.33 mmol) was added and the solution immediately turned cloudy. The reaction was warmed to 45°C-55°C under nitrogen for 5 hours. After cooling to room temperature, the solvent was removed and the solid was redissolved in dichloromethane. This was washed thoroughly with distilled water and the organic layer was dried by $MgSO_4$. The mixture was filtered and the filtrate was pumped to dryness under reduced pressure to give a yellow powder which was shown by spectroscopic data to be the starting material.

Attempted synthesis of *cis*-[Cr(CO)$_4${η^2-(o-tolyl)$_2$PCMe(D)P(o-tolyl)$_2$}]

cis-[Cr(CO)$_4${η^2-(o-tolyl)$_2$PCH(Me)P(o-tolyl)$_2$}] **44** (0.30 g, 0.49 mmol) was dissolved in dry THF (25 cm^3) under nitrogen to give a pale yellow solution. MeLi (0.52 cm^3, 0.73 mmol) was added and the solution immediately turned bright yellow. This was left to stir under nitrogen at room temperature for 1 hour. D_2O (0.01 cm^3, 0.73 mmol) was added and the reaction was continued to stir for another 20 hours. The solvent was removed and the residue was redissolved in dichloromethane, and washed thoroughly with distilled water. The organic layer was dried by $MgSO_4$. The mixture was filtered and the filtrate was pumped to dryness under reduced pressure to give a yellow powder which was proved by spectroscopic data that it was starting material.

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