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METAL PHOSPHINE COMPLEXES INCORPORATING ALKYL SUBSTITUENTS WITH ETHANE AND ETHYLENE BACKBONES

A dissertation presented by

SETSHABA D. KHANYE, B.Sc. (Hons.)

In fulfilment of the requirements of the degree

of

Masters of Science

School of Chemistry

Faculty of Science

University of the Witwatersrand December 2006



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Mr. Setshaba D. Khanye, Dr. Marcus Layh

and

Dr. Judy Caddy

Molecular Sciences Institute,

School of Chemistry, University of the Witwatersrand,

Private Bag 3, Wits, 2050, Johannesburg,

South Africa

Project AuTEK,

Mintek, Private Bag X3015,

Randburg, 2125,

South Africa

Abstract

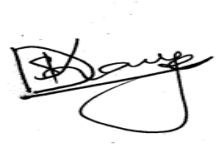
The new chelating bis-phosphine ligands 1,2-bis(butylphenylphosphino)ethane (**bppe**) and *cis*-1,2-bis(butylphenylphosphino)ethylene (**bppey**) have been synthesised by (i) a one-pot synthesis from Ph_2PBu and Li/dihalo alkyl, (ii) the reaction of 1,2-bis(diphenylphosphino)ethane (**dppe**) or *cis*-1,2-bis(diphenylphosphino)ethylene (**dppey**) and Li/*n*-BuCl and, (iii) in the case of **bppe** by sequential synthesis (all intermediates were isolated) from Ph_2PBu *via* PhBuPLi and Ph_2PH. **bppe** and **bppey** as well as the new lithium phosphide $[(TMEDA)\bullet LiPPh(Bu)]_2$ (**17**) were fully characterised by multinuclear NMR spectroscopy, mass spectrometry and, in the case of $[(TMEDA)\bullet LiPPh(Bu)]_2$ (**17**), by X-ray crystallography.

Reaction of the bis-phosphines **bppe** and **bppey** with suitable metal precursors yielded the corresponding metal complexes: $[PdCl_2(bppe)]$ (**18**), $[Pd(bppe)_2](ClO_4)_2$ (**20**), $[(AuCl)_2(bppe)]$ (**21a**), $[(AuCl)_2(bppey)]$ (**21b**), $[Au(bppe)_2]Cl$ (**22a**), $[Au(bppey)_2]Cl$ (**22b**), $[(AgNO_3)_2(bppe)]$ (**23**) and $[Au(bppe)_2]ClO_4$ (**24**) in moderate to good yields. All were characterised by multinuclear NMR spectroscopy and mass spectrometry, while **18** and **20** were further characterised by X-ray crystallography.

Preliminary stability tests showed, that of all new metal complexes only **18**, **20** and **22a** were adequately stable to justify further tests for anti-tumour activity. The cationic complexes **20** and **22a** showed activity against HeLa cells while the neutral complex **18** was not active. A comparison with the previously investigated analogous **dppe** and **dppey** complexes revealed that **20** and **22a** were found to be less active as a result of the replacement of a Ph groups with butyl groups in the phosphine ligand.

Declaration

I declare that the work presented in this dissertation was carried out exclusively by me under the supervision of Dr. Marcus Layh and Dr. Judy Caddy. It is being submitted for the degree of Masters of Science at University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination in any other University.



_____

Setshaba David Khanye

_____day of _____, 2006

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- Our Almighty God for protection throughout my MSc studies and for granting His grace to me to be where I am today.

Dedication

To my grandmother, Mrs. Sanna Khanye

and

my late grandfather, Mr. Hlakano S. Khanye

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Abbreviations

Bu	butyl
bppe	1,2-bis(butylphenylphosphino)ethane
bppey	*cis*-1,2-bis(butylphenylphosphino)ethylene
$^{13}C\{^{1}H\}$ NMR	Carbon Nuclear Magnetic Resonance
d2pype	1,2-bis(di-2-pyridylphosphino)ethane
d4pype	1,2-bis(di-4-pyridylphosphino)ethane
dpdmp	[(diphenylphosphino)phenyl]diphenylphosphine
dpmaa	2,3-bis(diphenylphosphino)maleic anhydride
dppf	1,1'-bis(diphenylphosphino)ferrocene
dppb	1,4-bis(diphenylphosphino)butane
dppe	1,2-bis(diphenylphosphino)ethane
dppey	*cis*-1,2-bis(diphenylphosphino)ethylene
dppp	1,3-bis(diphenylphosphino)propane
DCM	dichloromethane
DMF	dimethylformamide
DMSO	dimethylsulfoxide
eppe	1-(diethylphopshino)-2-(diphenylphosphino)ethane
Et_2O	diethyl ether
EI	electron ionisation
FAB	fast atomic bombardment
^{1}H-NMR	Proton Nuclear Magnetic Resonance
HeLa	human cervical adenocarcinoma
Hex	hexane
h	hours
Hz	Hertz
Me	methyl
n-BuCl	*n*-butylchloride
n-BuLi	*n*-butyllithium
NMR	Nuclear Magnetic Resonance
Ph	phenyl
PMDETA	pentamethyldiethylenetriamine

$^{31}P\{^{1}H\}$-NMR	Phosphorus Nuclear Magnetic Resonance (^{1}H decoupled)
r.t.	room temperature
t	triplet
t-BuCl	tertiary butylchloride
TMDEA	*N*,*N*,*N'*,*N'*-tetramethylethylenediamine
THF	tetrahydrofuran
d-THF	deuterated tetrahydrofuran

Chapter One

Introduction and Literature Review

1.1 Background

Cancer is described as dangerous and uncontrollable cell growth.[1,2] It is characterised by an accumulation of mutated genes that regulate cell growth. The survey conducted by the Medical Research Council (MRC) in the year 2000, showed that a large percentage of people in South Africa die from cancer.[3] It is estimated that one in six South African men and one in seven South African women are likely to develop cancer during their life time.[4]

In the same year (2000), World Cancer Report (WCR) estimated that 12 % of the 56 million deaths worldwide were the result of malignant tumours.[5] Furthermore, an estimated 5.3 million men and 4.7 million women were reported to have developed a malignant tumour and a total of 6.2 million have died from the disease. Two years later, 10.9 million new cases and 6.7 million deaths were reported. In the year 2002, an estimated 24.6 million were reported to be living with cancer worldwide.[6] According to the WCR cancer rates could further increase by 50 % to 15 million new cases per year by the year 2020.[5]

These alarming figures show that there still remains a challenge to conquer the existing problems of common types of cancer (*Table 1.1*).[2] In developing countries up to 23 % of malignancies are caused by infectious agents, including hepatitis B and C viruses (liver cancer), human palliomaviruses (cervical and ano-genital cancer), and Helicobacter pylori (stomach cancer). In developed countries cancer caused by chronic infections only amounts to 8 % of all malignancies.[5] In South Africa lung cancer is by far the leading cause of death and accounts for up to 17 % of all cancer deaths. It is closely followed by oesophogus cancer, which accounts

[1] www.wisegeek.com/what_is.
[2] www.cancerquest.org/index.cfm.
[3] www.mrc.ac.za/bod/farqcancer.html.
[4] www.health24.com/man/medica/748 - 766.
[5] www.who.int/mediacentre/news/release/2003/pr27/en/.
[6] Parkin, D.M.; Bray, F.; Ferlay, J.; Pisani, P.; *CA Cancer J. Clin*., 2005, **55**, 74 – 108.

for 14 %, cervical cancer accounting for 8 %, breast cancer accounting for 7 % and liver cancer accounting for 6.5 % of all cancer deaths.[3]

Table 1.1: The most common types of cancer affecting children, men and women.[2]

Children	Men	Women
Leukemia (24 %)	Oesophageal cancer	Breast cancer
Brain cancer (21 %)	Prostate cancer	Cervical cancer
Lymphomas (16 %)	Lung cancer	Colon-rectal cancer
Wilm's tumour (10 %)	Liver cancer	Lung cancer
Neuroblastoma	Cancer of the Larynx	Oesophageal cancer

This statistical data on cancer from MRC,[3] WCR,[5] and other organisations[4] is alarming and clearly show that cancer is a major public health problem in developing and developed countries worldwide. It is evident that there exists a need for further research to address both the prevention and treatment of cancer related diseases.

1.2 Drug resistance in cancer treatment

Drug resistance is the ability of cancer cells to adapt and resist the therapeutic effect of anti-tumour drugs.[7] Failure of chemotherapy to eradicate cancer often points towards cancer cells that have mutated to resist any given chemotherapeutic agent. Drug resistance is a major problem in cancer chemotherapy and is responsible for a large percentage of failure of therapies in cancer patients. There are several possible biochemical mechanisms that can lead to drug resistance and failure of chemotherapeutic agents. Some of these biochemical mechanisms of drug resistance are listed below:[8]

[7] Chu, E.; Sartorelli, A.C.; *Basic and Clinical Pharmacology* , 9th Ed, Katzung, B.G., ed, McGraw-Hill,Lange, San Francisco, 2004, p 899 – 930.
[8] www.chemocare.com/whatis/what_isdrug_resistance_an_analysis.asp.

- A cancer cell may produce hundreds of new gene copies (gene amplification), which may trigger an overproduction of a protein that will render the anti-cancer drugs ineffective.
- The cancer cells may pump the drug out of the cells as fast as it gets in by means of a molecule called *p*-glycoprotein.
- Cancer cells may stop taking up drugs as a result of the non-functioning of a protein that transports them across the cell membrane.
- The cancer cells may develop a mechanism for repairing DNA breaks caused by some of the administered anti-cancer drugs.
- Cancer cells may develop a mechanism that deactivates the administered anti-cancer drugs.
- Undestroyed cancer cells may mutate after treatment and become resistant to the anti-cancer drugs.

Drug resistance can be highly specific to a single drug. It is often based on a change in the genetic nature of a given tumour cell with amplification or increased expression of one or more specific genes. To minimise the common occurrence of drug resistance two or more chemotherapeutic agents are often used in combination.[7] Combination therapies have been shown to be effective in attaining the three main goals of cancer treatment: removing the entire tumour, preventing its reoccurrence, and minimising negative side effects.

1.3 Treatment of cancer and drug development

One of the reasons that the cure for cancer has been so elusive is that cancer is not a single disease but rather a complex set of diseases.[5] Thus, in order to treat or combat over 200 different variations of cancer, one has to appreciate and understand that each form of cancer requires a different method of treatment.

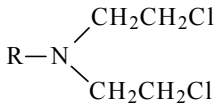
Developments in cancer treatment and drug development have improved the lives of many cancer patients. Yet, there is still a need to do more in order to control and manage the current situation worldwide. The conventional methods traditionally used for cancer treatment include surgery, radiation therapy and chemotherapy.[9,10]

[9] Sikora, K.; *Interferon and Cancer*, ed. Sikora, K.; Plenum Press, New York, 1983, p 1 – 3.

In the early 20th century, immediately after the discovery of chemotherapy, immunotherapy was introduced and became a part of cancer treatment. Surgery and radiation therapy were found to be effective in treating tumours and cancers which remain localised. However, in many cancer patients the cancer will not be localised and as a consequence[7] new drugs, antibodies, monoclonal antibodies, vaccines (to stimulate the immune system) and methods of cancer treatment remain topics at the forefront of current research.[11] As a consequence, chemotherapy has grown into a systematic method of cancer treatment and has become more dominant among the three conventional methods and today is the most preferred cancer treatment option.[12]

The era of modern chemotherapy of cancer began in the 1940s with the discovery and use of nitrogen mustard alkylating agents for the treatment of cancers such as leukemia and lymphoma.[13] Mustard gas has always been viewed as a toxic substance, resulting in a painful and often slow death. Ironically, whilst it is known to be a major cause of cancer, it has also been used as tool to treat it.[14,15] In 1919, it was noted that victims that were exposed to mustard gas had a low blood cell count (because the mustard gas had attacked white blood cells) and bone marrow aplasia (breakdown). In 1946 it was found, that nitrogen mustard and its derivatives (**Figure 1.1**) have the capability of reducing tumour growth in mice by linking two strands of DNA. It was further shown that the sensitivity of the bone marrow of mice to mustard gas is similar to that of humans and therefore research lead to clinical trials of mustard gas. Thus, nitrogen mustards became part of modern chemotherapy and were introduced as a cure for cancer of the lymph glands (Hodgkin's disease).[15,16]

[10] www.meds.com/immunotherapy/intro.html.
[11] En.wikipedia.org/wiki/Immunotherapy.
[12] Timerbaev, A.R.; Hartinger, C.G.; Aleksenko, S.S.; Keppler, B.K.; *Chem. Rev*., 2006, **106**, 2224 – 2248.
[13] en.wikipedia.org/wiki/Chemotherapy.
[14] Wilman, D.E.V.; Connors, T.A.; *Molecular Aspects of Anti-Cancer Drug Action*, ed.; Neidle, S.;Waring, M.J., MacMillan Press Limited, 1983, p 233 – 287.
[15] www.bris.ac.uk/Depts/Chemistry/MOTM/mustard/mustard.htm.
[16] www.encyclopedia.com/htm/n/nitromus.asp.



Nitrogen mustard

R = H, Me, Ph, $-CH_2CH_2Cl$, etc.

Figure 1.1: Nitrogen mustard derivatives.

The ideal anti-cancer drugs or chemotherapeutic agents would selectively eradicate all cancer cells without harming normal tissues. However, in existing chemotherapy there are currently no agents available that meet this criterium. Normally, the spread of disease in cancer patients may result in 10^{12} tumour cells throughout the body at the time of diagnosis.[7] If an effective drug was capable of killing 99.99% of tumour cells, treatment would have induced a clinical remission of the cell division associated with symptomatic improvement rather than a cure. Repeated treatments are therefore needed to destroy the 10^8 tumour cells remaining in the body due to an inherently resistant to the administered drug or chemotherapeutic agent.[7]

1.4 Obstacles towards cancer treatment

As is evident from the discussion above, the major obstacle in cancer treatment is the lack of selective toxicity by chemotherapeutic agents.[17] Selective toxicity is defined as the injury of one kind of living matter without harming another kind with which it is in intimate contact. In most cases, cancer cells are part of the normal cells or healthy cells. This means, that selective targeting of cancer cells by anti-cancer drugs is essential for effective treatment. The lack of selectivity, together with drug resistance, imposes a major obstacle in the development of drugs for cancer treatment.

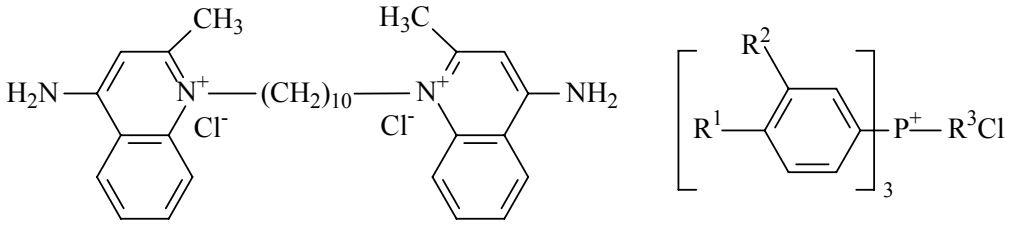
1.5 Lipophilic cations

The common occurrence of drug resistance by cancer cells and the lack of selectivity of cancer drugs in differentiating between tumour and normal cells have

[17] Albert, A.; *Selective Toxicity*, 5th Ed., Chapman and Hall Ltd, New Fetter Lane, London, 1973, p 3 – 5.

brought about the need to look for new approaches in drug development.[18] Lipophilic cationic compounds have been regarded as a new class of anti-tumour drugs which may satisfy the need for new approaches in drug developments. These types of compounds were found to concentrate in mitochondria due to their lipophilic-cationic nature.[18,19,20]

It was found that their accumulation in mitochondria can be rationalised as the result of abnormal hyperpolarisation of mitochondrial membranes of tumour cells as compared to normal cells.[21] Several classes of lipophilic cations such as dequalinium chloride and triarylalkylphosphonium salts (**Figure 1.2**) have demonstrated that the anti-tumour selectivity increases as a result of a change in the lipophilic-hydrophilic balance.[22]



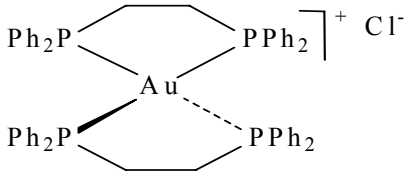
Deliqualinium chloride **Triarylalkylphosphonium salts**

Figure 1.2: Examples of lipophilic cations.

In recent years, Berners-Price and co-workers adopted the approach to modify the bis-phosphine ligand of lipophilic-cationic metal complexes such as $[Au(dppe)_2]^+$ (where dppe is 1,2-bis(diphenylphosphino)ethane) (**Figure 1.3**).[19,23] The aim was to vary the hydrophilic character of the complexes in order to increase the selectivity for tumour cells as compared to healthy cells. It was found that replacing some or

[18] Berners-Price, S.J.; Bowen, R.J.; Galettis, P.; Healy, P.C.; MeKeage, M.J.; *Coord. Chem. Rev*. 1999, **185 – 186**, 823 – 836.
[19] Berners-Price, S.J.; Girard, G.R.; Hill, D.T.; Sutton, B.M.; Jarrett, P.S.; Faucette, L.F.; Johnson, R.K.; Mirabelli, C.K.; Sadler, P.S.; *J. Med. Chem*., 1990, **33**, 1386 – 1387.
[20] Davis, S.; Weiss, M.J.; Wong, J.R.; Lampidis, T.J.; Chen, L.B.; *J. Biol. Chem*., 1985, **260**, 13844 – 13845.
[21] Hoke, G.D.; Rush, G.F.; Bossard, G.E.; McArdle, J.V.; Jensen, B.D.; Mirabelli, C.K.; *J. Biol. Chem*., 1988, **263**, 11210 – 11210.
[22] Weissig, V.; Boddappati, S.V.; D'Souza, G.G.M.; Cheng, S.M.; *Drug Design Reviews-Online*, 2004, **1**, 15 – 28.
[23] Mirabelli, C.K.; Hill, D.T.; Faucette, L.F.; McCabe, F.L.; Girard, G.R.; Bryan, D.B.; Sutton, B.M.; O'Leary Bartus, J.; Crooke, S.T.; Johnson, R.K.; *J. Med. Chem*., 1987, **30**, 2181 – 2190.

all of the phenyl moieties by hydrophilic pyridyl groups allowed one to retain the aromaticity of aryl substituents on phosphorus atoms.

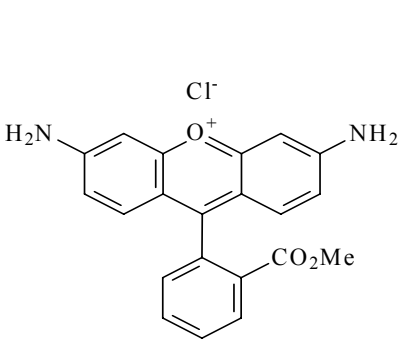


[Au(dppe)$_2$]Cl

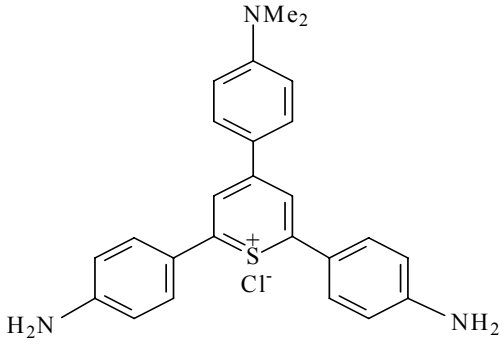
Figure 1.3: Lipophilic-cationic gold complex, $[Au(dppe)_2]^+$.

This was stimulated by the observation that the bis-chelated lipophilic-cationic Au(I) complex $[Au(d2pype)_2]Cl$ (where d2pype is 1,2-bis(di-2-pyridylphosphino)ethane) was found to exhibit activity in mice bearing P388 leukemia, whereas the related 4-pyridyl complex $[Au(d4pype)_2]Cl$ (where d4pype is 1,2-bis(di-4-pyridylphosphine)ethane) was inactive. The different solubility profiles of the complexes were found to influence their cellular uptake and thus their differences in selectivity and anti-tumour activity.

Over the past 20 years several other structurally diverse lipophilic cations such as Rhodamine-123 and Thiopyrylium AA-1 (**Figure 1.4**) have demonstrated strong activity in tumour models.[19,23] These compounds commonly known as delocalised lipophilic-cations (DLCs)[24] were found to exhibit significant selective toxicity or photocytoxicity against carcinoma both *in vitro* and *in vivo* (in animals).



Rhodamine-123

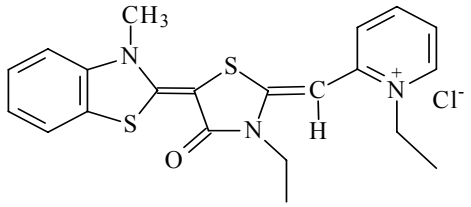


Thiopyrylium AA-1

Figure 1.4: Delocalised lipophilic-cations.

[24] Don, A.S.; Hogg, P.J.; *Trends in Molecular Medicine*, 2004, **10**, 373 – 377.

The first example of this class of compounds with this property to enter Phase I Clinical Trials was Rhodacyanine, MKT-077 (**Figure 1.5**).[23,25] It is reported that the accumulation of MKT-077 in tumour cells of the mitochondria induces ultrastructural changes and loss of mitochondrial DNA, which generally characterises mitochondrial disturbances and non-specific damage to membrane enzymes resulting in reversible impairment of mitochondrial function.[19]



MKT-077

Figure 1.5: Rhodacyanine MKT-077 as DLC compound.

1.6 Phosphine compounds as anti-tumour agents

There are twenty five elements which are known to be essential for mammalian life including phosphorus.[26] As much as it is an important element biologically, only phosphorous(V) compounds are found to be important in biological systems of mammals, while phosphorous(III) compounds are strong reducing agents..[27] Phosphorous(V) is a very stable oxidation state and forms soluble phosphates (i.e. polyphosphates such as ATP, phosphoamino acids and phosphosugars) which are readily available to all forms of life. PH_3 is an effective fumigant used against pests of stored stable food, and it is possible that the potent O-acceptor properties of tertiary phosphines may be the key to their cytotoxicity. Oxygen atoms are potentially available during many stages of metabolism, for example oxidative phosphorylation in the mitochondria.[26] The relative cytotoxic (biological) potential of phosphines often depends on several factors such as lipophilicity, redox potential and pK_a. However, there is a paucity of relevant chemical data. Phosphines are rarely studied under relevant biological conditions (i.e. where H_2O and O_2 are

[25] McKeage, M.J.; Berners-Price, S.J.; Galettis, P.; Bowen, R.J.; Brouwer, W.; Li Ding, Li Zhuang, Baguley, B.C.; *Cancer Chemother Pharmacol*., 2000, **46**, 343 – 350.
[26] Berners-Price, S.J.; Sadler, P.J.; *Chem. Brit*., 1987, 541 and reference cited therein.
[27] Berners-Price, S.J.; Sadler, P.J.;*Bioinorganic Chemistry*, Ed., Aisen, P., Springer_Verlag, Berlin Heidelberg, 1988, p 29 – 97.

present).[26] Some phosphines readily oxidise under these conditions, thus limiting their ability to reach intracellular target sites. The oxidation products (phosphine oxides) are usually not cytotoxic. Both facts account for the inactivity of alkyl bis-phosphines.

1.6.1 Metal phosphine complexes

Gold compounds have been used clinically for the treatment of rheumatoid arithritis (RA) for many decades.[28] Most of the products used medically were and are still thiolate gold complexes such as Aurothioglucose (**Figure 1.6**).[29]

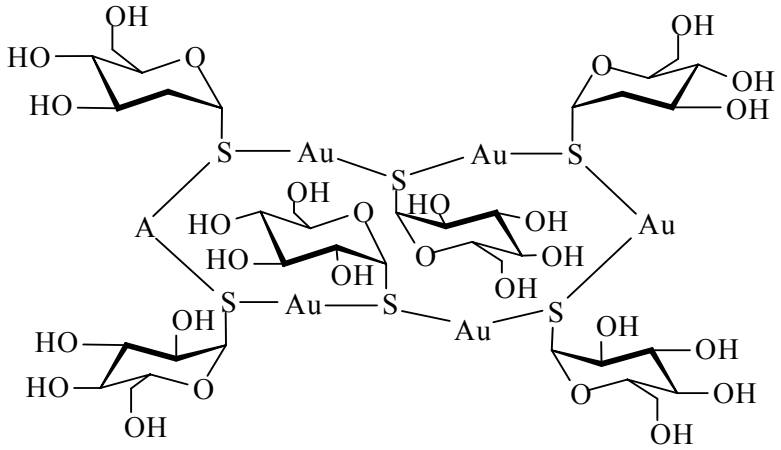


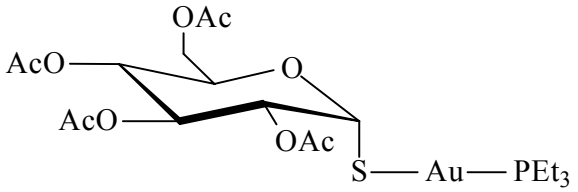
Figure 1.6: Thiolate gold complex.

In most cases thiolate gold compounds are used in form of injectable drugs for the treatment of RA. For example, sodium aurothiomalate (Myocrysin®) has been introduced clinically as an injectable drug for the treatment of RA. It was found that there were problems when these injectable drugs were given orally. The problems were linked to the low lipophilicity and the high molecular weight of the gold compounds as a result of their polymeric nature.[30] The lack of an orally active gold compound (as they are poorly absorbed in the gut) imposed a major limitation on

[28] Brown, D.H.; Smith, W.E.; *Chem. Soc. Rev.*, 1980, **9**, 217 – 241.
[29] Sneader, W.; *Drug Discovery: A History*, John Wiley and Sons Ltd, West Sussex, England, 2005, p 59 – 61.
[30] Ni Dhubhghaill, O.M.; Sadler, P.J.; *Metal Complexes in Cancer Chemotherapy*, Ed., Keppler, B.K.; VCH Verlagsgesellschaft, Weinheim, Germany, 1993, p 221 – 248.

gold treatment for arithritis. Research efforts therefore moved into the search and development of orally active and non-polymeric gold complexes.

In the mid 1960s, Blaine Sutton found a highly lipophilic gold(I) complex, triethylphosphine gold(I) chloride (TEPAuCl), with comparable potency to that of Myocrysin®. This compound was later discontinued as an orally active anti-inflammatory agent due to its high toxicity in humans.[30] Subsequently an orally active linear two coordinate gold(I) phosphine complex, Auranofin (Ridaura®), 1-thio-β-D-glucopyronose-2,3,4,6-tetraacetato-*S*)(triethylphosphine)-gold(I) complex (**Figure 1.7**), was synthesised and evaluated in animal tumour models as a supplement to injectable gold(I) drugs. It was introduced for the treatment of RA and tested for activity against B16 melanoma cells, P388 leukemia cells and cultured human cells.[31] In the year 1985, Auranofin was approved for clinical use against RA following extensive clinical trials but research for a possible cancer treatment continued.[26]

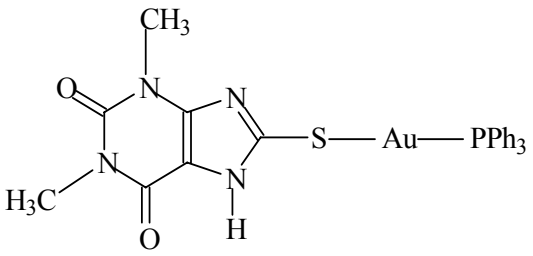


Auranofin

Figure 1.7: Linear two-coordinate gold complex.

Subsequent studies and evaluations on a number of tumour models showed that Auranofin and (8-thiotheophyllinate)(triphenylphosphine)gold(I) (tTAuP) (**Figure 1.8**) were only active on P388 leukemia cells. It was later concluded that the restricted range of activity of Auranofin and its analogues might be related to facile ligand exchange reactions in the presence of thiol groups. Taking Auranofin as an example, it was found that the thioglucose ligand in Auranofin is readily displaced by other thiolate ligands in plasma and cells. The related phosphine ligand(s) can be released and oxidised to form the oxides.[32]

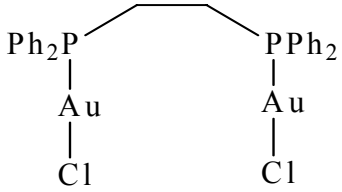
[31] McKeage, M.J.; Maharaj, L.; Berners-Price, S.J.; *Coord. Chem. Rev*., 2002, **232**, 127 – 135.
[32] Burners-Price, S.J.; Jarrett, P.S.; Sadler, P.J.; *Inorg. Chem*., 1987, **26**, 3074 – 3077.



tTAuP

Figure 1.8: Auranofin analogue.

Further work was done to overcome the drawbacks experienced with linear two-coordinate gold(I) complexes and lipophilic cationic tetrahedral four-coordinate gold(I) phosphine complexes such as $[Au(dppe)_2]Cl$ (**Figure 1.3**). Tetrahedral four-coordinate gold(I) phosphine complexes were reported to be more stable with respect to ligand-exchange reactions than their linear analogues and, more importantly, less reactive towards thiols.[20,32,33] It was reported, that in blood plasma the related bridged di-gold(I) phosphine complex $[(AuCl)_2(dppe)]$ (**Figure 1.9**) reacted to form the monomeric bis-chelated complex, $[Au(dppe)_2]Cl$ (**Figure 1.3**).[32,34]



[(AuCl)$_2$(dppe)]

Figure 1.9: Bridged gold(I) phosphine complex.

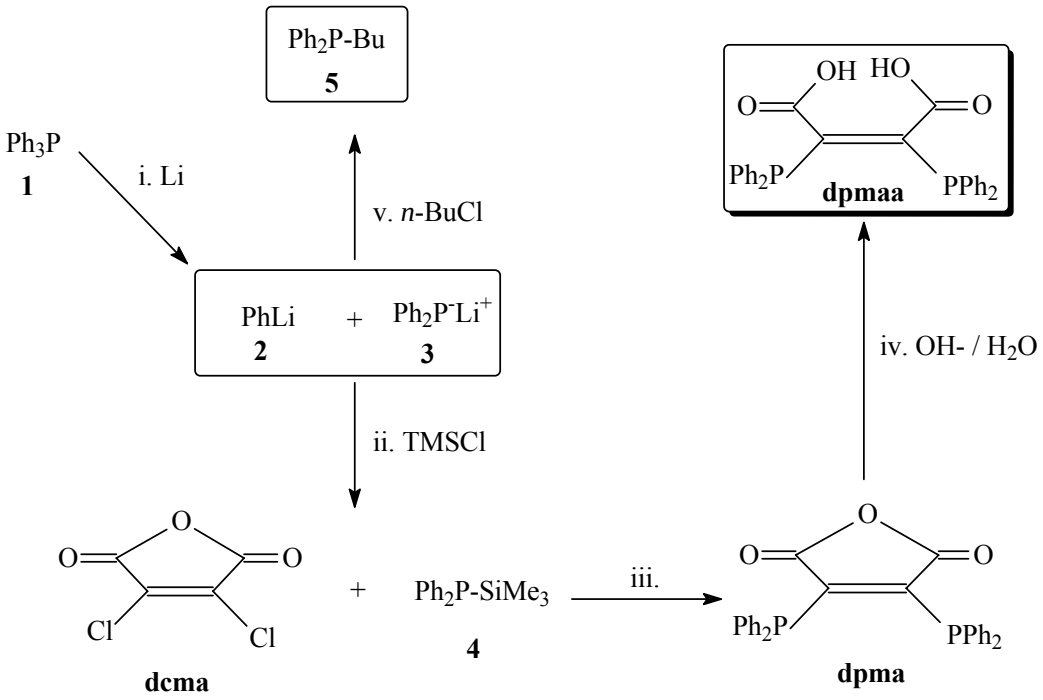
A drawback of $[Au(dppe)_2]Cl$, however, was its lack of selectivity to distinguish between tumour and healthy cells. This has resulted in the modification of this complex by replacing the phenyl groups with other aryl substituents (e.g. pyridyl groups). $[Au(d2pype)_2)]Cl$ exhibited activity against tumour cells with an increased selectivity. However, replacement of phenyl groups on the phosphorous atoms by alkyl substituents (e.g. ethyl on phosphorous atoms) resulted in the activity of Au(I) complexes being reduced.[19]

[33] Berners-Price, S.J.; Johnson, R.K.; Mirabelli, C.K.; Faucette, L.F.; McCabe, F.L.; Sadler, P.J.; *Inorg. Chem.*, 1987, **26**, 3383 – 3387.
[34] McArdle, J.V.; Bossard, G.E.; *J. Chem. Soc., Dalton Trans*., 1990, 2219 – 2224.

It was further found that the activity is restored to the ethyl analogue when Au(I) is replaced by Ag(I) (e.g. $[Ag(eppe)_2]NO_3$).[35] The highest activity of gold(I) phosphine complexes of the type $[Au(R_2P(CH_2)_nPR'_2)_2]^+$ was found where R = R' = Ph and *n* = 2, 3 or *cis*-CH=CH. Furthermore, the activity was retained when Au(I) was substituted by Ag(I) or Cu(I).[18]

1.7 The aims of the project

The project was initiated as a result of our interest in another bis-phosphine ligand, 2,3-bis(diphenylphosphino)maleic anhydride (**dpmaa**) (**Scheme 1.1**).[36]



Scheme 1.1: Schematic representation of the synthesis of phosphine ligands.

In the synthesis of **dpmaa**, Ph_3P (**1**) was reacted with two equivalents of lithium metal (step i in **Scheme 1.1**) to give PhLi (**2**) and lithium diphenylphosphide (**3**) as reactive nucleophiles (**Scheme 1.1**). The reaction mixture was treated with *t*-BuCl to destroy **2** and avoid side reactions. *In situ* treatment of **3** with Me_3SiCl (step ii in **Scheme 1.1**), resulted in the formation of diphenylphosphinotrimethylsilane (**4**).

[35] Berners-Price, S.J.; Bowen, R.J.; Hambley, T.W.; Healy, P.C.; *J. Chem. Soc., Dalton Trans*., 1999, 1337 – 1346.
[36] Mamo, M.A.; **M.Sc. Thesis**, "*Gold(I) Phosphine complexes and their Potential Applications as Anti-Cancer Agents*," **University of the Witwatersrand**, February 2005.

The reaction of **4** with 2,3-dichloromaleic anhydride (**dcma**) (step iii in **Scheme 1.1**) resulted in the formation of the **dpmaa** ligand *via* **dpma**. The accidental treatment of **3** with *n*-BuCl (step v in **Scheme 1.1**) in hexane, however, resulted in the formation of butyldiphenylphosphine (**5**), which seemed an interesting precursor for chelating phosphine ligands analogous to **dppe** and **dppey**, by replacement of one of the phenyl groups on phosphorous with an alkyl substituent. Hence, the aims of this project were: (i) to synthesise bis-phosphine (**bppe** and **bppey**) ligands with an alkyl (i.e. butyl) substituent on phosphorous atoms from butyldiphenylphosphine (**5**), (ii) to synthesise gold complexes as the primary objective, while silver and palladium were included as secondary objectives and (iii) to evaluate the anti-tumour activity of the novel complexes obtained.

Chapter Two

Bis-Phosphine Ligands

2.1 Introduction

As early as the 1960s there have been literature reports on bis-phosphine ligands, in particular bidentate phosphines.[37] Since then there has been a constantly growing interest in these type of ligands, especially those containing two $-PPh_2$ groups.[38] Bis-phosphine ligands are now among the most common ligands in coordination chemistry.[39,40] Typical examples include those of the general formula RR'P-$(CH_2)_n$-PR'R (**6**) (n = 1 – 5 and R' = Me, *t*-Bu and R = Ph) and *cis*-$R_2PCH{=}CHPR_2$ (R = Ph) (**7**) (**Figure 2.1**).[41] These ligands have found numerous applications in organometallic chemistry and have been used as chelating ligands for a wide range of transition metals.[42,43]

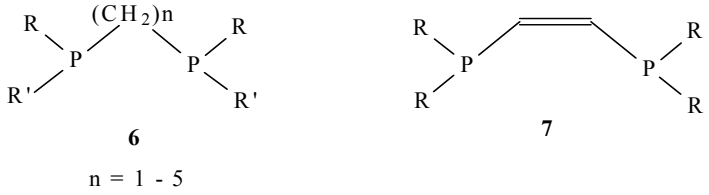


Figure 2.1: Common bis-phosphine ligands.

The metal complexes, in particular those of transition metals, have shown potential applications in the field of medicine[44] and catalysis.[45] Since the early use of 1,2-bis(diphenylphosphino)ethane (**dppe**) as chelating ligand, research efforts have been

[37] Bertrand, J.A.; Caine, D.; *J. Am. Chem. Soc.,* 1964, **86**, 2299 – 2300.
[38] Downing, J.H.; Smith, M.B.; *Comprehensive Coordination Chemistry II*, **1**, Ed. McCleverty, J.A.; Meyer, T.J.; Pergamon, Elsevier Ltd., London, 2004, p 253 – 296.
[39] Bowen, R.J.; Caddy, J.; Fernandes, M.A.; Layh, M.; Mamo, M.A.; Meijboom, R.; *J. Organom.Chem.,* 2006, **691**, 717 – 725.
[40] Fries, G.; Wolf, J.; Pfeiffer, M.; Stalke, D.; Werner, H.; *Angew. Chem. Int. Ed*., 2000, **39**, 564 – 567.
[41] Brooks, P.; Gallagher, M.J.; Sarroff, A.; *Aust. J. Chem*., 1987, **40**, 1341 – 1351.
[42] Reddy, V.S.; Katti, K.V.; Barnes, C.L.; *Inorg. Chem*., 1995, **34**, 5483 – 5488.
[43] Garrou, P.E.; *Chem. Rev*., 1981, **81**, 229 – 266.
[44] Berners-Price, S.J.; Mirabelli, C.K.; Johnson, R.K.; Mattern, M.R.; McCape, F.L.; Faucette, L.F.; Sung, C.M.; Mong, S.M.; Sadler, P.J.; Crooke, S.T.; *Cancer Research*, 1986, **46**, 5486 – 5493.
[45] Bollman, A.; Blann, K.; Dixon, J.T.; Hess, F.M.; Killian, E.; Maumela, H.; MacGuinness, D.S.; Morgan, D.H.; Nevling, A.; Otto, S.; Overett, M.; Slawin, A.M.Z.; Wasserscheid, P.; Kuhlmann, S.; *J. Am. Chem. Soc*., 2004, **126,** 14712 – 14713.

made to find ways to vary the substituents on the phosphorous atom. The properties of their corresponding metal complexes may also be modified as a result of varying the organic substituents on the phosphorous atoms.[46] Suitable tailoring of the ligands may result in desirable anti-tumour or catalytic activity in the respective metal complexes. The observation, that **dppe** analogues obtained by replacing the phenyl groups with pyridyl groups, *e.g.* 1,2-bis(di-2-pyridylphosphino)ethane (**d2pype**), exhibited a reduced lipophilicity and an enhanced activity as an anti-tumour agent, further drove these efforts (**Figure 2.2**).[47]

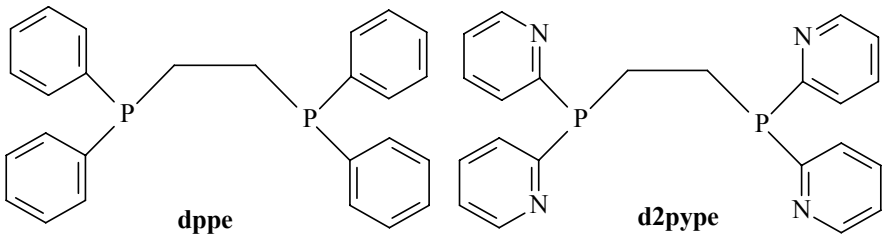


Figure 2.2: Phenyl and pyridyl substituents on phosphorous atoms.

Following reports which describe the significant change in properties of metal complexes as a result of varying organic substituents on the phosphorous atom, specifically in the case of bis-phosphine ligands, the majority of this thesis is focused on the synthesis of 1,2-bis(butylphenylphosphino)ethane (**bppe**) and *cis*-1,2-bis(butylphenylphosphino)ethylene (**bppey**) (**Figure 2.3**) as modified analogues of **dppe** and **dppey** and their respective metal complexes. Although many bis-phosphines are used in catalysis, in this work the focus is on the possible anti-tumour properties exhibited by these ligands and their corresponding metal complexes.

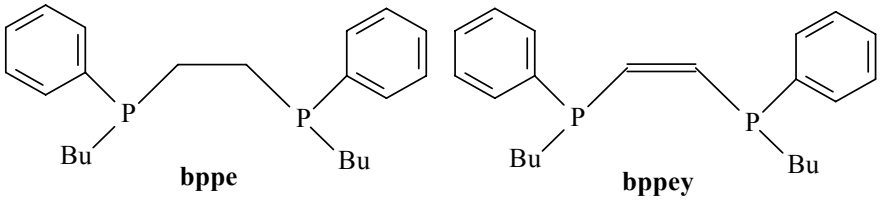
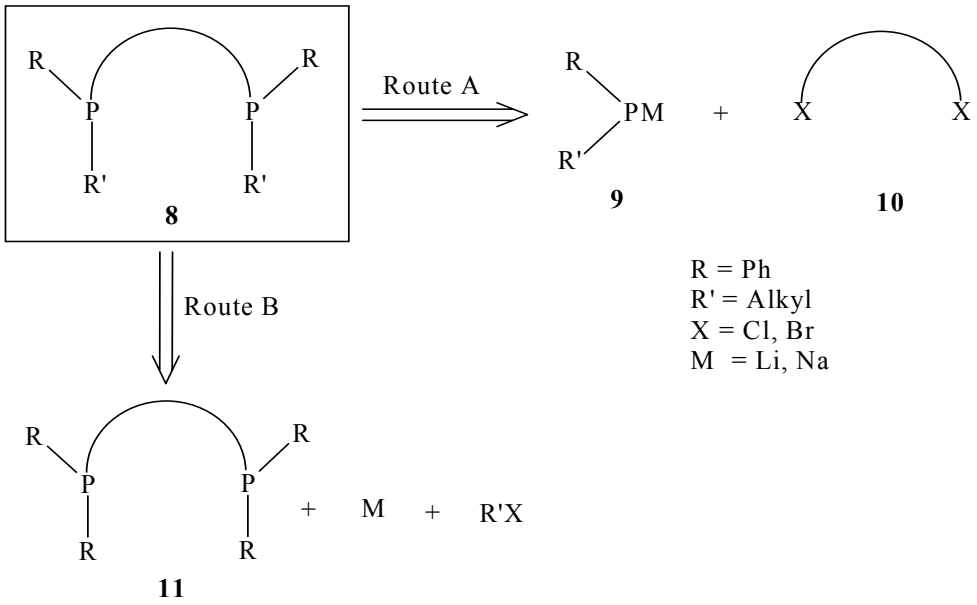


Figure 2.3: Modified dppe and dppey analogues.

[46] Bowmaker, G.A.; Williams, J.P.; *Aust. J. Chem*., 1994, **47**, 451 – 460.
[47] Bowen, R.J.; **Ph.D. Thesis**, " *Hydrophilic Bidentate Phosphines and their Group 11 Complexes: Potential Anti-tumour Agents"*, **Griffith University, Australia**, 1999.

2.2 Synthesis of bis-phosphines

Bis-phosphine ligands can be prepared by various methods. Of these methods, two will be considered in more detail. Firstly, modified bis-phosphine ligands such as **8** can be synthesised from alkali metal-phosphides (**9**) and the corresponding dihaloalkyl derivative of the backbone (**10**) as shown retrosynthetically in **Scheme 2.1** (Route A). Apart from phosphines with ethane and ethylene bridges there are other bis-phosphine ligands with more than two carbon atoms in the backbone. Examples are 1,3-bis(diphenylphosphino)propane (**dppp**) and 1,4-bis(diphenylphosphino)butane (**dppb**). Alternatively, **8** may also be obtained by modification of the phosphorous substituent in existing bis-phosphines **11** (Route B), resulting from the reaction of **11** and alkali-metal (M) and subsequent alkylation (R'X) to form **8**.



Scheme 2.1: Retrosynthetic paths for bis-phosphine ligands.

2.2.1 Route A: Alkali metal-phosphides in bis-phosphine synthesis

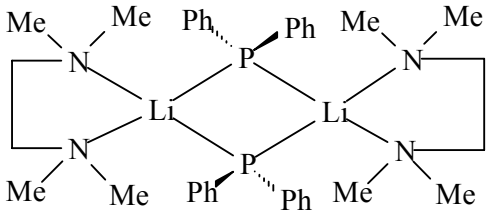
Route A involves the preparation of **8** from the correspondent dihaloalkyl derivatives and an appropriate alkali metal mono-phosphide. This method is of greatest applicability in the preparation of bis-phophine ligands.[48,49] For example, it

[48] McAulife, C.A.*; Comprehensive Coordination Chemistry: The Synthesis, Reaction, Properties and Application of Coordination Chemistry*, **2**, Ed. Gillard, R.D.; McCleverty, J.A.; Pergamon Press,

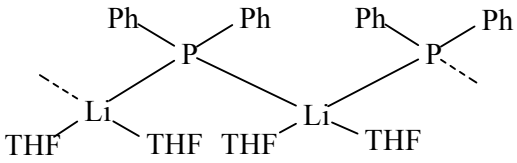
is reported that the reaction of Li-diphenylphosphide (Ph_2PLi, **3**) with diphenyl-vinylphosphine ($Ph_2PCH{=}CH_2$) and subsequent hydrolysis of the reaction intermediate resulted in the formation of **dppe**.[50] Alkali metal-phosphides are often regarded as the reactive nucleophile in P-C bond formation. Their preparation involves metallation of primary and secondary phosphines with strong bases such as *n*-BuLi (equation 1), reductive metallation of halophosphines (equation 2), cleavage of P-C bond in phosphine by an alkali metal (equation 3) and metal-halogen exchange (equation 4).[48]

Me_2PH	+	*n*-BuLi →	**Me_2PLi**	+	BuH	(1)
Ph_2PCl	+	2Li →	**Ph_2PLi**	+	LiCl(s)	(2)
Ph_3P	+	2Li →	**Ph_2PLi**	+	PhLi	(3)
Ph_2PCl	+	*n*-BuLi →	**Ph_2PLi**	+	BuCl	(4)

These metal-phosphide precursors (equation 1 – 4) are often prepared *in situ*, but can be isolated in the presence of coordinating solvents and used in the synthesis of bis-phosphine ligands as solvates. Examples are **12** (in TMEDA) and **13** (in THF) (**Figure 2.4**).[51,52] The lithium complex (**13**) further illustrates the purpose of using polar solvents to stabilise metal-phosphides.



12



13

Figure 2.4: Lithium-metal phosphide solvates.

Oxford, 1987, p 989 – 994.

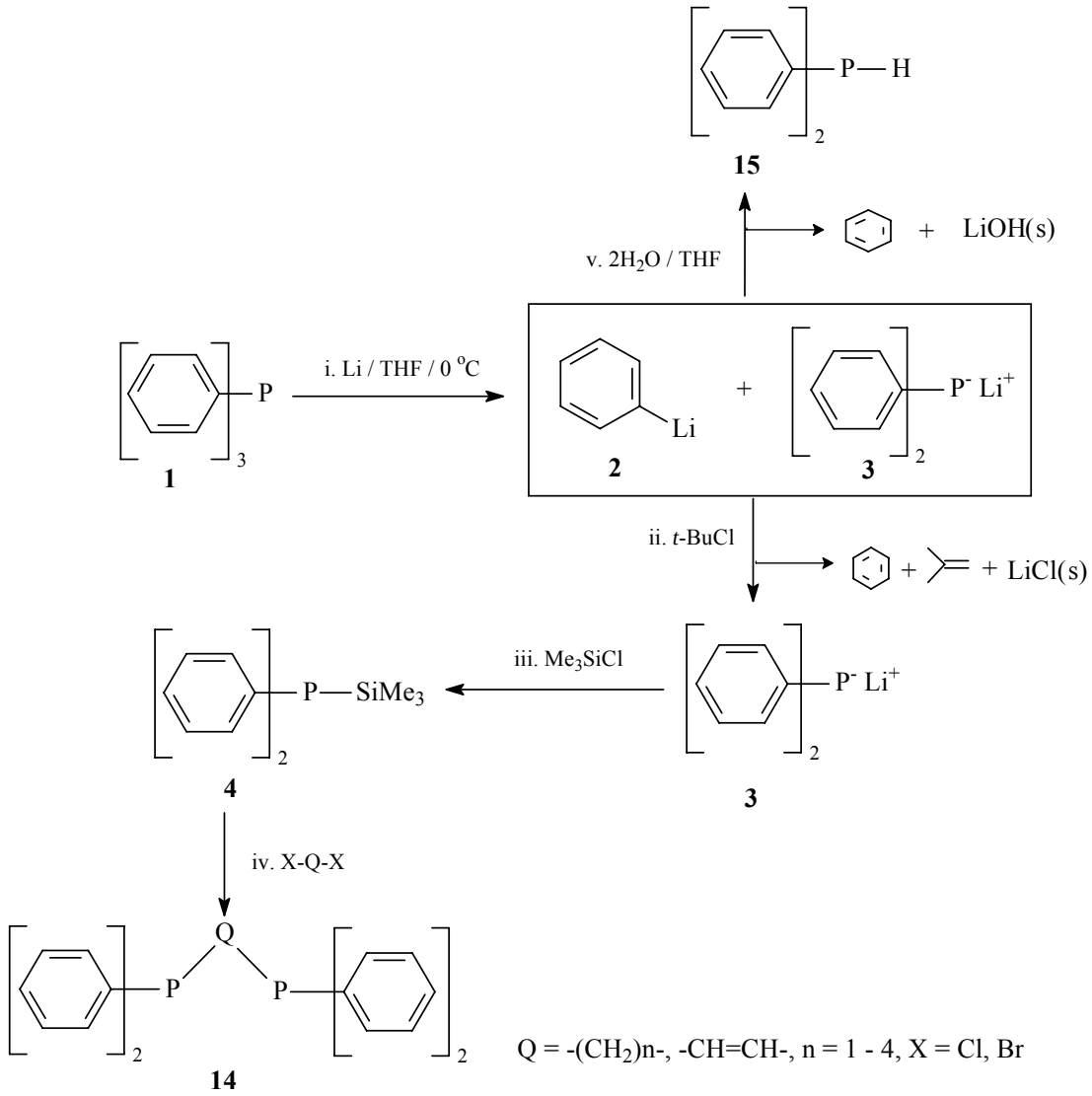
[49] Maier, L.; *Organic Phosphorus Compounds*, Vol. **1**, Ed. Kosolapoff, G.M.; Maier, L.; Wiley-Interscience, New York, 1972, p 298.

[50] Grim, S.O.; Del Gaudio, J.; Molenda, R.P.; Tolman, C.A.; Jesson, J.P.; *J. Am. Chem. Soc*., 1974, **96**, 3416 – 3422.

[51] Mulvey, R.E.; Wade, K.; Amstrong, D.R.; Walker, G.T.; Snaith, R.; Clegg, W.; Reed, D.; *Polyhedron*, 1987, **6**, 987 – 993.

[52] Barglett, R.A.; Olmstead, M.M.; Power, P.P.; *Inorg. Chem*., 1986, **25**, 1243 – 1247.

Metallation of secondary phosphines (equation 1) and the P-C bond cleavage in PPh_3 (equation 3) are the most commonly used synthetic approaches for the preparation of bis-phosphines.[38,49] The cleavage of the phenyl moiety in **1** by lithium metal in tetrahydrofuran to form Li-diphenylphosphide (**3**) is accompanied by the generation of PhLi (**2**) as side product (step i in **Scheme 2.2**).



Scheme 2.2: Metal-diphosphides in the preparation of bis-phosphines.

The addition of tertiary butylchloride (*t*-BuCl) (step ii in **Scheme 2.2**) to the reaction mixture has been regarded as being an ideal approach to selectively eliminate the side product **2**.[46,53,54] Subsequent treatment of the reaction mixture containing **3**

[53] Aguir, A.M.; Beisler, J.; Mills, A.; *J. Org. Chem.*, 1962, **27**, 1001 – 1005.

with trimethylchlorosilane (TMSCl) results in the formation of **4** (step iii in **Scheme 2.2**). Thus, the metal-diphosphide is isolated as compound **4** without repetitive and time consuming filtering required in removing lithium chloride.[36] The reaction of **4** with an appropriate dihaloalkyl derivative results in the formation of the desired bis-phosphine (**14**). However, treatment of alkali metal-phosphides (**3**) with either water or protic solvents (step v in **Scheme 2.2**) produces secondary phosphines such as diphenylphosphine (**15**).[50,55,56] Metallation of the generated **15** with *n*-BuLi in the presence of polar solvents regenerates the metal-phosphide as solvated organolithium compounds such as **12** or **13**. Coupling with an appropriate dihaloalkane results in the formation of the desired bis-phosphine ligand (Schematic detail provided in **Scheme 2.3**).

In general, tertiary alkyl and cycloaliphatic phosphines are not cleaved by alkaline metals. Only the PPh_3 and mixed alkyl/aryl phosphines can be cleaved.[38] The presence of at least one resonance-stabilised aromatic group is reported as being essential to facilitate P-C bond cleavage and the formation of alkali metal-phosphide precursors for the preparation of bis-phosphines.[50] The more electronegative group is often cleaved preferentially to the less electronegative group.[41] It is therefore believed that the mixed alkyl/aryl phosphine Ph_2PBu (**5**) with more than one resonance-stabilised aromatic group is a suitable precursor for the synthesis of novel bis-phosphines.

2.2.2 Route B: Synthesis of bis-phosphines involving bis-phosphine starting materials

Although numerous bis-phosphines have been synthesised from **1**, an attractive alternative approach, with fewer synthetic steps, is the cleavage of P-C bonds of an existing bis-phosphine by an alkali metal (e.g. Li), Route B (**Scheme 2.1**).[50,55,57,58] The resulting diphosphide can be directly alkylated resulting in the formation of new

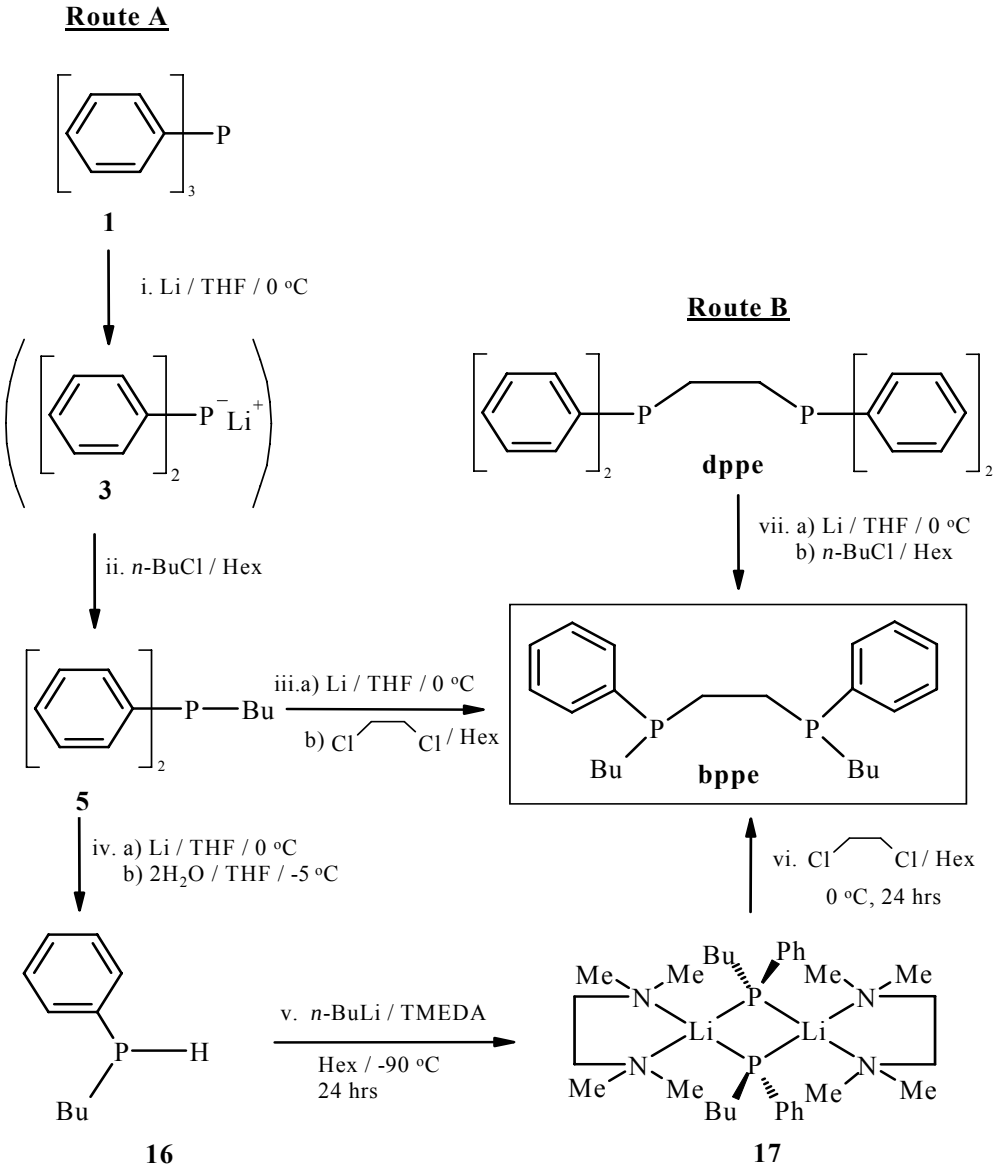
[54] Bowen, R.J.; Garner, A.C.; Berners-Price, S.J.; Jenkins, I.D.; Sue, R.E.; *J. Organom. Chem*., 1998, **554**, 181 – 184.
[55] Kimpton, B.R.; McFarlane, W.; Muir, A.S.; Patel, P.G.; Bookham, J.L.; *Polyhedron*, 1993, **12**, 2525 – 2534.
[56] Dogan, J.; Schulte, J.B.; Swiegers, G.F.; Willis, A.C.; Wild, S.B.; *J. Org. Chem*., 2000, **65**, 951 – 957.
[57] Dickson, R.S.; Elmes, P.S.; Jackson, W.R.; *Organometallics*, 1999, **18**, 2912 – 2914.
[58] Aiery, A.L.; Swiegers, G.F.; Willis, A.C.; Wild, S.B.; *Inorg. Chem*., 1997, **36**, 1588 – 1597.

asymmetrical or symmetrical substituted bis-phosphines. [59] This synthetic approach was adopted as alternative approach for the synthesis of the bis-phosphines **bppe** from **dppe** and **bppey** from **dppey** in this work.

[59] Chou , T.-S.;;Tsao, C.-H.; Hung, S. C.; *J. Org. Chem.,* 1985, **50**, 4329 – 4332.

2.3 Results and Discussion

Bppe has been synthesised *via* the two approaches discussed above and the reactions summarised in **Scheme 2.3**. The first approach (**Route A**) involved the synthesis of butyldiphenylphosphine (**5**) from the commercially available **1** with the aim of replacing the phenyl entity with a butyl group. The second approach (**Route B**) involved the synthesis of **bppe** directly from the commercially available bis-phosphine **dppe**.



Scheme 2.3: Synthetic routes towards 1,2-bis(butylphenylphosphino)ethane, bppe.

2.3.1 Route A: Synthesis of 1,2-bis(butylphenylphosphino)ethane from triphenylphosphine

2.3.1.1 Synthesis of butyldiphenylphosphine, Ph_2PBu

Ph_2PBu (**5**) was synthesised as shown in step i and ii (**Scheme 2.3**) from **1**. The reaction was accompanied by a deep red-brown colour (step i in **Scheme 2.3**) indicating the formation of the corresponding metal-phosphide Ph_2PLi (**3**). Pure isolated metal phosphides are generally lighter in colour leading to yellow solutions when redissolved in organic solvents.[41] Treatment of the dark red-brown reaction mixture with 2 equivalents of *n*-butylchloride (step ii in **Scheme 2.3**) readily resulted in the elimination of LiCl and the formation of **5** as the major product. The crude product was distilled to give a colourless, oily liquid. $^{31}P\{^1H\}$ NMR spectroscopy showed a singlet, at δ -15.3 ppm confirming the presence of the desired product. A comparable $^{31}P\{^1H\}$ NMR chemical shift has been reported before where **5** was synthesised from chlorodiphenylphosphine and *n*-butyllithium (equation 4).[60] ^1H and ^{13}C NMR spectra further confirm the composition of the product.

Treatment of **5** under the same reaction conditions with Li metal (step iii(a) in **Scheme 2.3**) led to the corresponding metal-phosphide intermediate (PhBuPLi). Attempts to prepare **bppe** *in situ* (step iii(b) in **Scheme 2.3**) by adding 1,2-dichloroethane to the filtered red-brown solution (containing PhBuPLi) gave **bppe** in poor yield, presumably a result of competing reactions.[61] The reaction was repeated to better understand the cause of the side reactions. A $^{31}P\{^1H\}$ NMR spectrum of the filtrate before the addition of 1,2-dichloroethane confirmed the formation of **3** as evident from a characteristic doublet at -49.3 ppm ($J_{P\text{-}Li}$ = 13.6 Hz). It was therefore concluded that competing reactions may be a result of the side product **2** (PhLi, see **Scheme 2.2**). The reaction mixture was therefore treated with *t*-butylchloride to eliminate **2** prior to the addition of 1,2-dichloroethane. The $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture showed, however, the presence of a mixture of products, indicating no improvement to the previous procedure.

[60] Bowen, R.J.; Camp, D.; Effendy; Healy, P.C.; Skelton, B.W.; White, A.H.; *Aust. J. Chem.*, 1994, **47**, 693 – 701.
[61] Roberts, N.K.; Wild, S.B.; *J. Am. Chem. Soc.*, 1979, **101**, 6254 – 6260.

In order to improve the yield of **bppe** and to eliminate possible side reactions the synthesis was then broken down into individual steps (iv, v, vi) to improve the reaction control. The following subsections explain each of these synthetic steps in more detail.

2.3.1.1(a) Synthesis of butylphenylphosphine, PhBuPH

As before, **5** was treated with lithium metal in THF to prepare the corresponding Li-phosphide (PhBuPLi). Adding approximately two equivalents of degassed water in THF (step iv(b) in **Scheme 2.3**) to the dark red-brown reaction mixture (Li-phosphide) at -5 – 0 ºC resulted in decolourisation of the solution. A mixture of diethyl ether and degassed water was added and the product was extracted with diethyl ether. Separation and drying of the organic layer gave, after removal of all volatiles, a colourless residue. This residue was purified by means of distillation to give a colourless, viscous oil.

The presence of a resonance peak at δ -51.4 ppm in the $^{31}P\{^{1}H\}$ NMR confirmed the formation of **16**. The doublet of triplets at δ 4.09 ppm, $^{1}J_{P\text{-}H}$ = 204.7 Hz, $^{3}J_{H\text{-}H}$ = 7.0 Hz, in the ^{1}H NMR spectrum provided good evidence for the formation of a phosphorous hydrogen bond (P-H). Similar coupling constants (*J*) have previously been reported for P-H phosphine compounds.[46] The substitution of the phenyl moiety by a hydrogen atom in **16** resulted in an upfield shift in the ^{1}H NMR signals as compared to **5**.

Phosphine compounds such as **15** (**Scheme 2.2**) and **16** (**Scheme 2.3**) are important starting materials for the synthesis of bis-phosphine ligands.[62] Metallation of either **15** or **16** with *n*-BuLi regenerates PhLi-free Li-phosphides, which may react with appropriate dihaloalkanes to form the desired bis-phosphines.

[62] Tsvetkov, E.N.; Bondareko, N.A.; Malakhova, I.G.; Kabachnik, M.I.; *Synthesis*, 1986, 198 – 207.

2.3.1.1(b) Synthesis of tetramethylethylenediamine adducts of lithium butylphenyl-phosphide [(TMEDA)•LiPPh(Bu)]$_2$ (17)

Treatment of butylphenylphosphine (**16**) with a solution of *n*-BuLi in hexane in the presence of *N,N,N',N'*-tetramethylethylendiamine (TMEDA)[51,63] (step v in **Scheme 2.3**) as a coordinating and stabilising reagent for the Li-phosphide, resulted in the formation of a dimeric organolithium phosphine complex **17** (as shown crystallographically, see **2.3.4**). TMEDA was added to the reaction mixture with the aim of increasing the reactivity of the Li-butylphenylphosphide (PhBuPLi) and to enable the isolation of the Li-phosphide. This was hoped to improve the yield as compared to the initial one pot (*in situ* step iii(b) in **Scheme 2.3**) reaction. The dimeric Li-butylphenylphosphide (**17**) was isolated as a yellow, highly air- and moisture-sensitive solid, that was soluble in organic solvents.

The disappearance of the doublet of triplets at δ 4.09 ppm found in the ^{1}H-NMR spectrum of **16** indicated the successful synthesis of **17**. The peak at δ -51.4 ppm found in **16** was replaced by a broad singlet at δ -56.5 ppm in **17** (*Table 2.1*). A similar line broadening for mono- and dimeric organolithium complexes has been reported previously.[51] A comparison of the ^{31}P{^{1}H} NMR data (*Table 2.1*) showed the well known dependence of the ^{31}P{^{1}H} NMR shift on the nature of the substituents on the phosphorous atom with an increased electron density on phosphorous resulting in a higher-field shift.

Table 2.1: Observed trends in ^{31}P{^{1}H} NMR.

Compound Number	Molecular Formula	^{31}P NMR / ppm
1	Ph_3P	-4.99
5	Ph_2PBu	-15.3
16	PhBuP-H	-51.4
17	[(TMEDA)•LiPPh(Bu)]$_2$	-56.5

[63] Liddle, S.T.; Izod, K.; *Organometallics*, 2004, **23**, 5550 – 5559.

2.3.1.1(c) Synthesis of 1,2-bis(butylphenylphosphino)ethane (bppe)

The reaction of **17** with one equivalent of 1,2-dichloroethane in hexane led to the desired ligand, **bppe** (step vi in **Scheme 2.3**) in high yield (83 %). The $^{31}P\{^{1}H\}$ NMR spectrum of the distilled reaction product exhibited two singlets at δ -19.6 (52 %) and -19.9 (48 %) ppm. The two resonance peaks were identified to be the desired ligand and consistent with a mixture of diastereomers.[46,58,59] The chemical resonances of the ethylenic protons of **bppe** (δ 1.62 ppm) were shifted upfield when compared to that of **dppe** (δ 2.12 ppm). The $^{31}P\{^{1}H\}$ NMR chemical shift of **bppe** compared well to other bis-phosphine ligands shown in *Table 2.2*.

Table 2.2: $^{31}P\{^{1}H\}$ NMR data comparison of some bis-phosphine $R(Ph)P(CH_2)_2P(Ph)R$.

$^{31}P\{^{1}H\}$ NMR / ppm ($CDCl_3$)		
R	**δ**	**J / Hz**
H	-48.8	$^{1}J_{P\text{-}H} = 204.6$
Me	-32.4	-
Bu	-19.6, 19.9*	-
Ph	-11.9	-

The data analysis showed that the substitution of phenyl groups resulted, as expected, in an increase in the shielding of the phosphorous nucleus. This is in accordance with literature reports that alkyl-substituted phosphorous nuclei exhibit resonances at a lower field than the corresponding aryl-substituted phosphorous nuclei.[46]

2.3.2 Route B: Synthesis of 1,2-bis(butylphenylphosphino)ethane from dppe

After the tedious, yet successful synthesis of **bppe** it was decided to investigate the possibility of preparing **bppe** directly from the commercially available **dppe**. Treatment of **dppe** ($Ph_2P(CH_2)_2PPh_2$) with 4.5 equivalents of lithium (step vii(a) in **Scheme 2.3**) resulted in a red-brown solution, which indicated the formation of $Li(Ph)P(CH_2)_2P(Ph)Li$.[58,59] Treating the filtered red-brown solution (containing

Li(Ph)P(CH_2)$_2$P(Ph)Li) with *n*-BuCl in hexane at 0 ºC (step vii(b) in **Scheme 2.3**) readily afforded **bppe** as a mixture of isomers in moderate yield (54 %), yet improved as compared to the *in situ* preparation from PPh_3, 17 – 30 % (Route A: step i, ii, iii in **Scheme 2.3**). The desired ligand was obtained as a colourless viscous oil *via* distillation under reduced pressure. The $^{31}P\{^1H\}$ NMR spectrum was identical to a sample obtained by Route A.

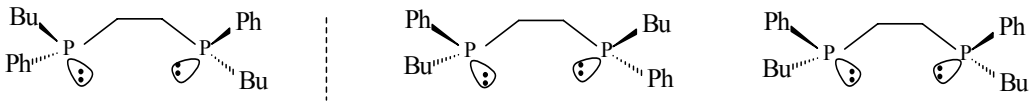
A literature survey suggested, that the still moderate yield could be the result of the cleavage of the ethane bridge in **dppe** resulting in the formation of **3** (Ph_2PLi).[41,58,59] Thus, adding a *n*-BuCl solution to the reaction mixture resulted in the formation of Ph_2PBu. The presence of Ph_2PBu in the reaction product (**bppe**) after distillation was confirmed by the $^{31}P\{^1H\}$ NMR spectrum, which showed a singlet at δ -15.9 ppm (see **2.3.1.1(a)**).

2.3.3 Mixture of diastereomers-bppe

Brooks et al.[41] reported that they had obtained an equimolar mixture of possible diastereomers of $Bu^tPhPCH_2CH_2PPhBu^t$ when a mixture of $Ph_2PCH_2CH_2PPh_2$ and Li was quenched with *t*-BuCl. *Danjo et al*.[64] in contrast reported the stereospecific synthesis of chiral (*S,S*)-$Bu^tMePCH_2CH_2PMeBu^t$, and (*R,R*)/(*S,S*)-$Bu^tPhPCH_2CH_2PPhBu^t$, starting from an enantiomerically pure starting material.

The synthesis of **bppe** was carried out with non-racemic starting materials. It was envisaged that the reaction would result in a mixture of diastereomers, *(R,R)/(S,S)*-**bppe** and *(R,S)*-**bppe** (**Figure 2.5**).[46] A mixture of diastereomers was confirmed by $^{31}P\{^1H\}$ NMR which showed two signals (see **2.3.1.1(c)**).[57,58,59,61] The mixture of diastereomers was not separated, but was used directly for complexation with Au(I), Ag(I) and Pd(II) salts (see **Chapter Three**).

[64] Danjo, H.; Sasaki, W.; Miyazaki, T.; Imamoto, T.; *Tetrahedron Lett*., 2003, **44**, 3467 – 3469.



(*R, R*) - **bppe** (*S,S*) - **bppe** (*R,S*) - **bppe**

Figure 2.5: Proposed bis-phosphine **bppe** isomers.

2.3.4 Molecular structure of [(TMEDA)•LiPPh(Bu)]$_2$ (17)

Organolithium complexes have been shown by crystallography to be monomeric (in the presence of PMDETA, *e.g.* PMDETA•$LiPPh_2$),[51] dimeric (in the presence of TMEDA, *e.g.* **12,**[51] [{2-Ph(H)C(C_5H_4N)}{Li(TMEDA)}]$_2$[65] and [TMEDA•LiN(Me)Ph])[66] or polymeric with infinite alternating chains (in the presence of either Et_2O or THF, *e.g.* **13**)[52]. The molecular structure of compound **17** and the numbering scheme used is illustrated in **Figure 2.6**. Mean values of bond distances and angles (there are six molecules in the asymmetric unit) are presented in *Table 2.3*. Comprehensive crystallographic data can be found in Appendix A1 and A2.

[65] Leung, W.-P.; Weng, L.-H.; Wang, R.-J;, Mak, T.C.W.; *Organometallics*, 1995, **14**, 4832 – 4836.
[66] Barr, D.; Clegg; W.; Mulvey, R.E.; Snaith, R.; Wright, D.S.; *J. Chem. Soc., Chem. Commun*., 1987, 716 – 718.

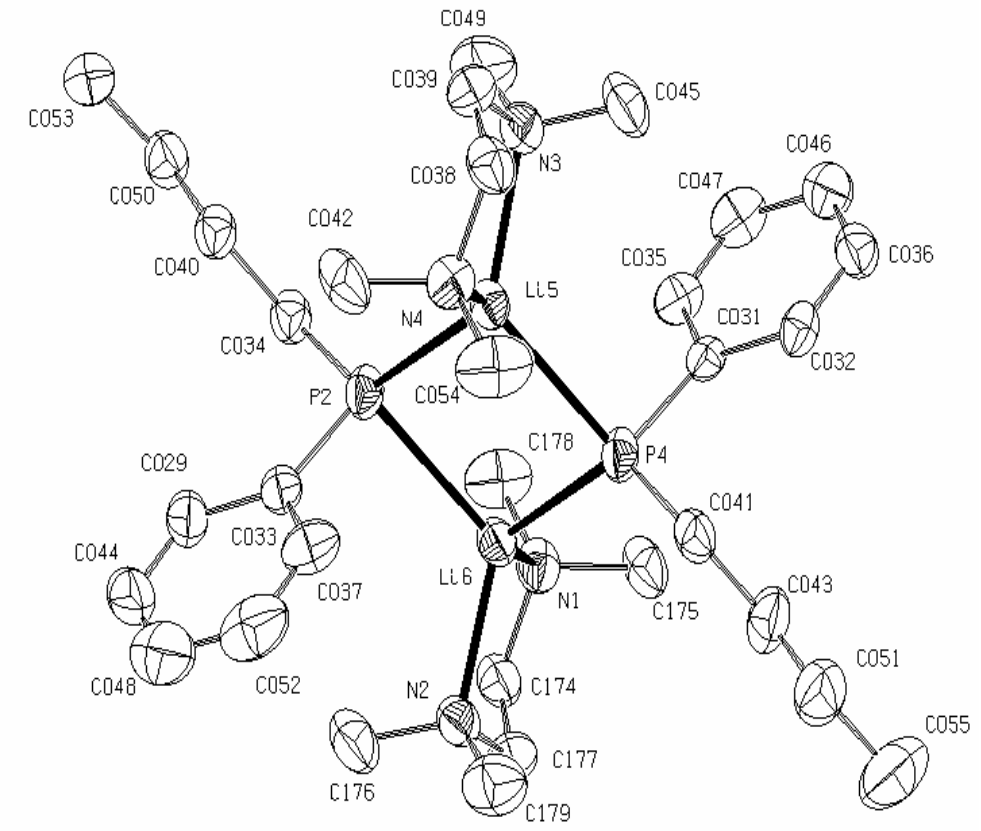


Figure 2.6: Molecular structure of **17**. Thermal ellipsoids shown at 50 % probability level. Hydrogen atoms have been omitted for clarity.

Table 2.3: Average bond lengths [Å] and angles [º] for compound **17**.

N─Li	2.140(1)	P─Li	2.588(8)
P─C	1.826(6)		

N─Li─N'	88.0(5)	P─Li─P'	91.8(4)
N─Li─P	120.1(4)	Li─P─Li'	88.2(3)
C─P─C'	103.4(3)	C─P─Li	115.1(3)

X-ray quality single crystals of compound **17** were obtained from hexane at -20 ºC. **17** crystallises in the monoclinic space group *P21/n* with six independent molecules in the asymmetric unit (**Figure 2.7**).

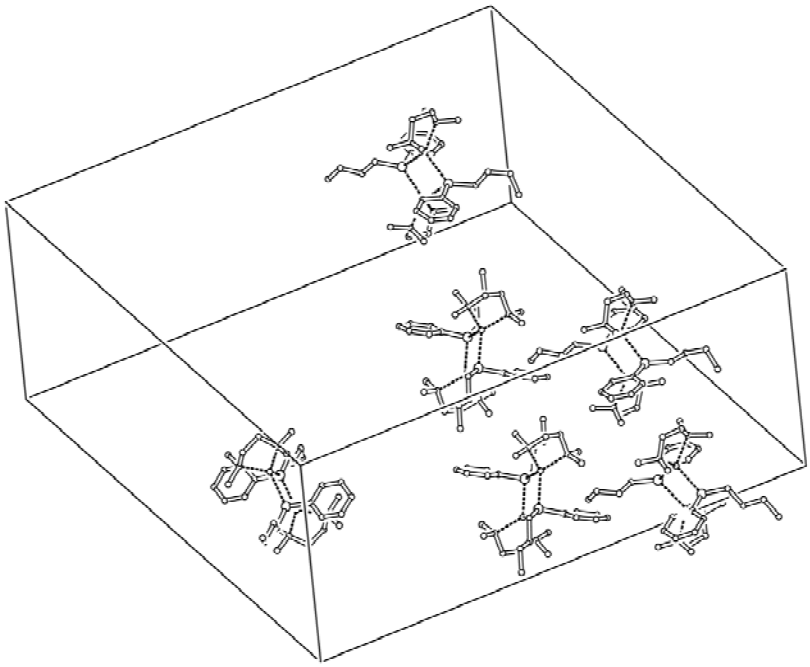


Figure 2.7: Structures of all six crystallographically independent molecules of **17**. Hydrogen atoms have been omitted for clarity.

The structural features of these six dimers are similar, with their respective bond lengths and angles differing slightly. **17** forms an approximately planar four-membered $(Li\text{-}P)_2$ ring shown in **Figure 2.8**, with phosphido groups bridging the two Li centres. Similar organolithium compounds with four-membered $(Li\text{-}N)_2$ and $(Li\text{-}P)_2$ rings have been reported for $[TMEDA{\bullet}Li\text{-}indole]_2$,[67] $[\{2\text{-}Ph(H)C(C_5H_4N)\}\{Li(TMEDA)\}]_2$,[65] $[(TMEDA){\bullet}LiN(Me)Ph]_2$[66] and ($[(TMEDA){\bullet}LiPPh_2]_2$, **12** in **Figure 2.4**).[51] The orientation of butyl and phenyl substituents are *anti* with respect to the planar $(Li\text{-}P)_2$ ring (**Figure 2.8**). The dimeric lithium complex *trans*-$[(TMEDA){\bullet}LiPPh(SiMe_3)]_2$ shows a similar geometry with a planar $(Li\text{-}P)_2$ ring and an *anti* orientation of the $SiMe_3$ and Ph groups.[68] The $(Li\text{-}P)_2$ four-membered ring in **17** is almost a perfect square with the mean angles, P─Li─P' and Li─P─Li' being 91.8(4)º and 88.2(3)º, respectively.

[67] Gregory, K.; Bremer, M.; Bauer, W.; Von Rague Schleyer, P.; Lorenzen, N.P.; Kopf, J.; Weiss, E.; *Organometallics*, 1990, **9**, 1485 – 1492.
[68] Hey, E.; Raston, C.L.; Skelton, B.W.; White, A.H.; *J. Organom. Chem*., 1989, **362**, 1 – 10.

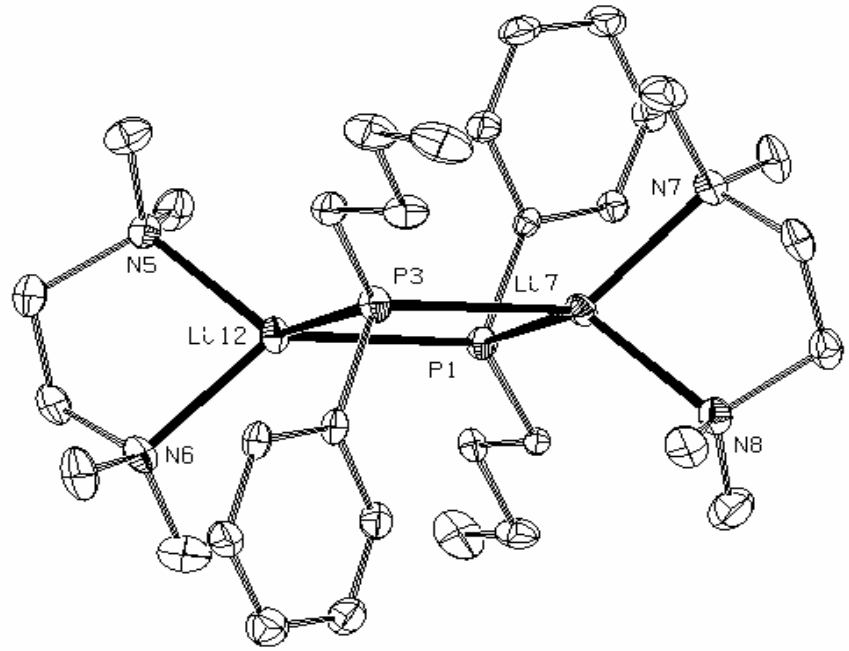


Figure 2.8: Four-membered (Li-P)$_2$ ring of 17 showing orientation of phosphorous substituents.

The Li and P atoms appear in strongly distorted tetrahedral environments with the mean angles of, Li─P─Li', C─P─C' and C─P─Li being 88.2(3)º, 103.4(3)º and 115.1(3)º, respectively, while N─Li─N', P─Li─P' and N─Li─P were 88.0(5)º, 91.8(4)º and 120.1(4)º, respectively. The previously reported lithium complexes, *trans*-[(TMEDA)•LiPPh(SiMe$_3$)]$_2$[68] and [(TMEDA)•LiPPh$_2$]$_2$[51] show similar bond angles (*Table 2.4*).

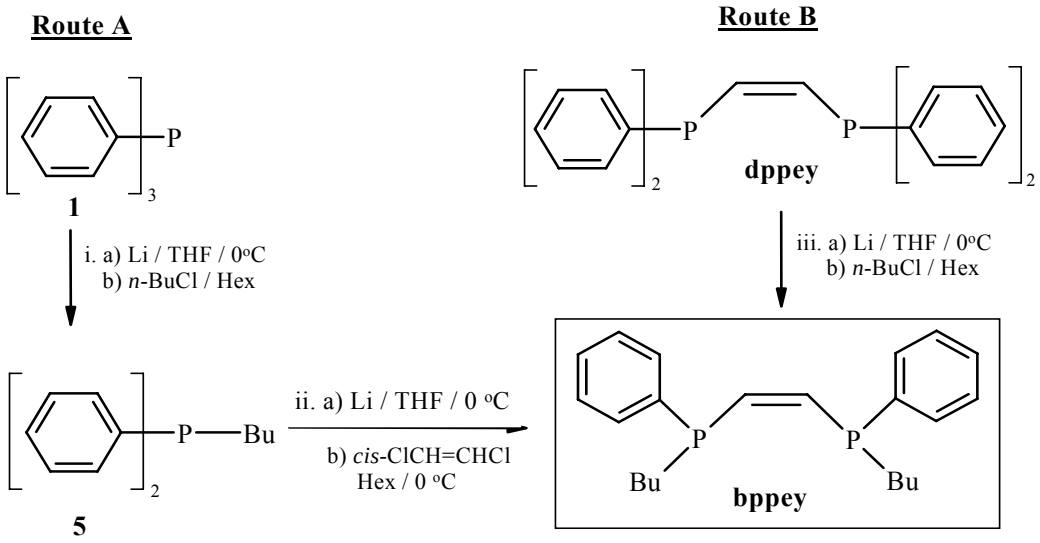
Table 2.4: Average bond angles of lithium complexes.

Bond angle	***trans*-[(TMEDA)•LiPPh(SiMe$_3$)]$_2$**	**[(TMEDA)•LiPPh$_2$]$_2$**
N─Li─N'	86.7(8)º	87.5(1)º
Li─P─Li'	89.0(7)º	88.8(5)º
P─Li─P'	93.3(6)º	91.2(5)º
C─P─Si	106.5(2)º	-
C─P─C'	-	105.0(4)º
P─Li─N	119.9(6)º	120.3(1)º

The mean P─Li and N─Li distances of **17** are within the range of 2.556(1) to 2.603(9) Å and 2.140(1) to 2.124(1) Å, while P─C is in the range of 1.781(6) to 1.872 (5) Å. Comparable P─Li, N─Li and P─C mean distances with the values of 2.610(1), 2.137(1) Å and 1.848(1) have been reported for *trans*-$[(TMEDA)\bullet LiPPh(SiMe_3)]_2$[68] and $[(TMEDA)\bullet LiPPh_2]_2$[51].

2.3.5 Synthesis of *cis*-1,2-bis(butylphenylphosphino)ethylene (bppey)

The synthesis of *cis*-1,2-bis(diphenylphosphino)ethylene (**bppey**) is summarised in **Scheme 2.4**.



Scheme 2.4: Synthetic route of *cis*-1,2-bis(butylphenylphosphino)ethylene, **bppey**.

2.3.5.1 Route A: Synthesis of *cis*-1,2-bis(butylphenylphosphino)ethylene from triphenyl-phosphine

Treating **5** with lithium metal (step i(a) in **Scheme 2.4**) resulted in a colour change to red-brown indicating the formation of the Li-phosphide (PhBuPLi). The reaction of the filtered Li-phosphide (PhBuPLi) (removal of excess Li) with *cis*-1,2-dichloroethylene at room temperature (step ii(b) in **Scheme 2.4**) resulted in a mixture of products including **bppey** (resonance at δ -16.7 ppm). The reaction was repeated and *t*-BuCl was added prior to the addition of *cis*-1,2-dichloroethylene in order to eliminate the unwanted PhLi (**2**). The $^{31}P\{^1H\}$ NMR spectrum of the

filtered and dried residue became even more complex and instead of the signal for **bppey**, a singlet at δ -31.1 ppm became the dominant signal. The latter may be assigned to the diphosphine PhBuP-PPhBu,[69] which could be the result of coupling of PhBuPCl and PhBuPLi (formed by Cl abstraction from *cis*-1,2 dichloroethene and elimination of LiCl and ethane).[70]

2.3.5.2 Route B: Synthesis of cis-1,2-bis(butylphenylphosphino)ethylene (bppey) from dppey

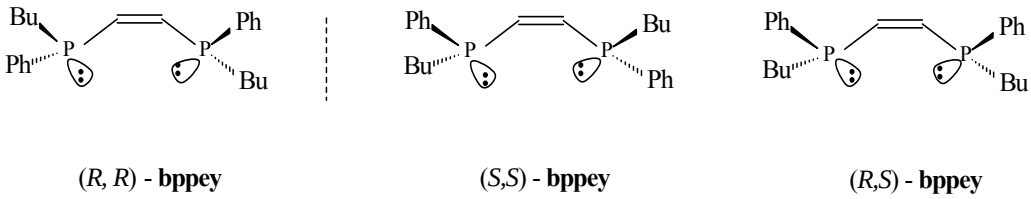
In an alternative approach **dppey** was reacted with approximately 4 equivalents of lithium metal in THF. This resulted in a colour change from colourless to red-brown indicating the formation of Li(Ph)PCH=CHP(Ph)Li (step iii(a) in **Scheme 2.4**).[41] The unreacted lithium was removed by filtration and the filtrate (a red-brown solution containing Li(Ph)PCH=CHP(Ph)Li) was reacted with approximately 4 equivalents of *n*-BuCl (step iii(b) in **Scheme 2.4**) in THF to give a clear brown solution. Dried hexane was added in order to completely precipitate the LiCl still suspended in solution. After filtration the solvent was removed and the obtained brown residue was distilled under reduced pressure to give a light yellow, viscous oil in 78 % yield.

The $^{31}P\{^{1}H\}$ NMR spectrum of the distilled product showed a singlet at δ -16.7 ppm, which was assigned to **bppey**. The disappearance of the **dppey** signal at δ-23.3 ppm provided good evidence for successful P-C bond cleavage and alkylation of the resultant phosphide Li(Ph)PCH=CHP(Ph)Li by *n*-BuCl. The ^{1}H NMR spectrum showed the appearance of three resonances: a triplet at δ 0.86 ppm integrating for 3H (CH_3), a multiplet at δ 1.28 – 1.40 ppm integrating for 4H (CH_2) and a triplet at δ 2.06 ppm integrating for 2H (CH_2), which indicated the presence of butyl groups in the correct ratio to the phenyl groups at 7.30 – 7.40 ppm. These results were complemented by ^{13}C NMR spectroscopy, which showed the appearance of four resonances at δ 13.5, 23.4, 26.4 and 27.6 ppm corresponding to the CH_3 and CH_2 groups of the butyl substituents.

[69] McFarlane, C.E.; McFarlane, W.; Nash, J.A.; *J. Chem. Soc., Dalton Trans*., 1980, 240 – 244.
[70] Gillespsie, D.G.; Walker, B.J.; *J. Chem. Soc., Perkin Trans. I*, 1983, 1689 – 1695.

2.3.6 Mixture of diastereomers-bppey

The reductive cleavage of the phenyl group in **dppey** resulted in the formation of the corresponding lithium diphosphide which on alkylation yielded the **bppey** ligand. The possible diasteomers, *(R,R)*-**bppey** and *(R,S)*-**bppey**, of **bppey** are shown below **Figure 2.9**.



(*R, R*) - **bppey** (*S,S*) - **bppey** (*R,S*) - **bppey**

Figure 2.9: Proposed bis-phosphine **bppey** isomers.

The ^{31}P-NMR spectrum of **dppey** however, showed only one singlet and gave therefore no indication for the existence of isomers.

2.4 Conclusions

In conclusion, the bis-phosphine ligand **bppe** was successfully synthesised from butylphenylphosphine (**5**). Although the synthesis was successful, yields were poor. This is believed to be due to the generation of PhLi (**2**) as a side product. *In situ* preparation of **bppe** was also not satisfactory. A sequential synthesis was therefore attempted (**Scheme 2.3**). In this approach the bis-phosphine ligand was synthesised from **5** by cleavage of the phenyl groups with stoichiometric amounts of Li, followed by controlled hydrolysis yielding the phosphine PhBuPH (**16**). Lithiation of **16** with BuLi/TMEDA and reaction with $ClCH_2CH_2Cl$ gave **bppe** in good yield (83 %).

In an alternative reaction **bppe** was successfully synthesised from 1,2-bis(diphenylphosphino)ethylene (**dppe**), Li and *n*-BuCl in an efficient and less time consuming manner under similar reaction conditions. Similarly, **bppey** was successfully synthesised from *cis*-1,2-bis(diphenylphosphino)ethylene (**dppey**) in good yield. Attempts to synthesise **bppey** from butylphenylphosphine (**5**) resulted in a mixture of products. Further attempts to resolve possible stereoisomers were

not carried out to avoid the possible oxidation of **bppe** and **bppey**. To the best of our knowledge there have been no reports of the synthesis of these two ligands (**bppe** and **bppey**) in the literature.

Chapter Three

Metal Complexes

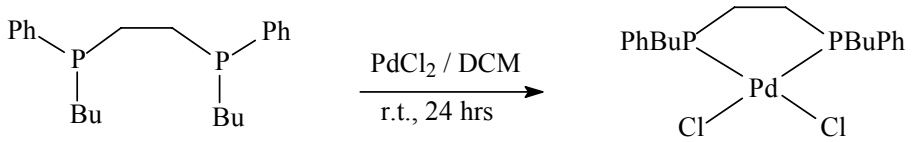
3.1 Introduction

Bis-phosphines are versatile ligands in stabilising metal ions (especially transition metals) in their low valent states.[71,72] The π-acceptor ability of phosphines enables the stabilisation of unusual oxidation states of transition metals.[73] These ligands have fundamentally contributed to the understanding of the coordination chemistry of transition metal ions.[74] In this study the synthesised ligand **bppe** was complexed to Pd(II) and Ag(I), whereas both **bppe** and **bppey** were complexed to Au(I).

3.2 Palladium complexes

3.2.1 A mono-chelated palladium complex

The synthesis of 1,2-bis(butylphenylphosphino)ethane-*cis*-dichloro-palladium(II) (**18**) is illustrated in **Scheme 3.1**. Treatment of **bppe** with equivalent amounts of palladium dichloride[75] readily afforded the monomeric complex **18** as a yellow solid in good yield (92 %).



bppe **18**

Scheme 3.1: Synthetic route for the mono-chelated Pd(II)-bppe complex.

[71] Chaudret, B.; Delavaux, B.; Poilblanc, R.; *Coord. Chem. Rev*., 1988, **86**, 191 – 243.
[72] Balakrishna, M.S.; Abhayankar, R.M.; Mague, J.T.; *J. Chem. Soc., Dalton Trans*., 1999, 1407 – 1412.
[73] Booth, G.; *Organic Phosphorus Compounds*, Vol. **1**, Ed. Kosolapoff, G.M.; Maier, L.; Wiley-Interscience, New York, 1950, p 433.
[74] Lewis, J.S.; Heath, S.L.; Powell, A.K.; Zweit, J.; Blower, P.J.; *J. Chem. Soc., Dalton Trans*., 1997, 855 – 861.
[75] Sanger, A.R.; *J. Chem. Soc., Dalton Trans*., 1977, 1971 – 1976.

The $^{31}P\{^{1}H\}$ NMR spectrum of the yellow solid exhibited two peaks at δ 72.2 (52 %) and 72.4 (48 %) ppm which were assigned to complex **18**, whilst the $^{31}P\{^{1}H\}$ NMR spectrum of the free ligand exhibited two singlets at δ -19.6 (52 %) and -19.9 (48 %) ppm. The two resonances are consistent with a possible mixture of diastereomers (see **Figure 3.3**). The $^{31}P\{^{1}H\}$ NMR spectrum of a related mono-chelated complex $[PdCl_2(dppe)]$ (*d*-THF) showed a chemical shift at δ 68.3 ppm. In DMSO, $[PdCl_2(dppe)]$ and $[PdCl_2(dppey)]$ showed $^{31}P\{^{1}H\}$ NMR resonances at δ 67.2 ppm and δ 74.1 ppm, respectively.

A large downfield shift in the $^{31}P\{^{1}H\}$ NMR spectrum of bis-phosphine ligands on coordination has been reported previously.[76] The remarkable downfield shift in $^{31}P\{^{1}H\}$ NMR signals has been attributed to an increased strain in the angles around phosphorous and carbon atoms in the five-membered chelate ring of these complexes. This deshielding effect was first observed by Merriwether in 1960s on nickel carbonylphosphine complexes, where he measured the difference (Δ) between chemical shift (δ_P) of a free ligand and a coordinated ligand to be in the order of 28.0 ppm.[43] These results showed, that bis-phosphines in five-membered chelate rings, exhibit downfield resonances compared to the free ligand and non-chelated analogues. This was attributed to a possible relationship between C-P-C and Ni-P-C bond angles in chelated complexes. As the substituents on phosphorous increase in size, C-P-C angle widens and the ^{31}P chemical shift moves to lower field in the chelate complexes.

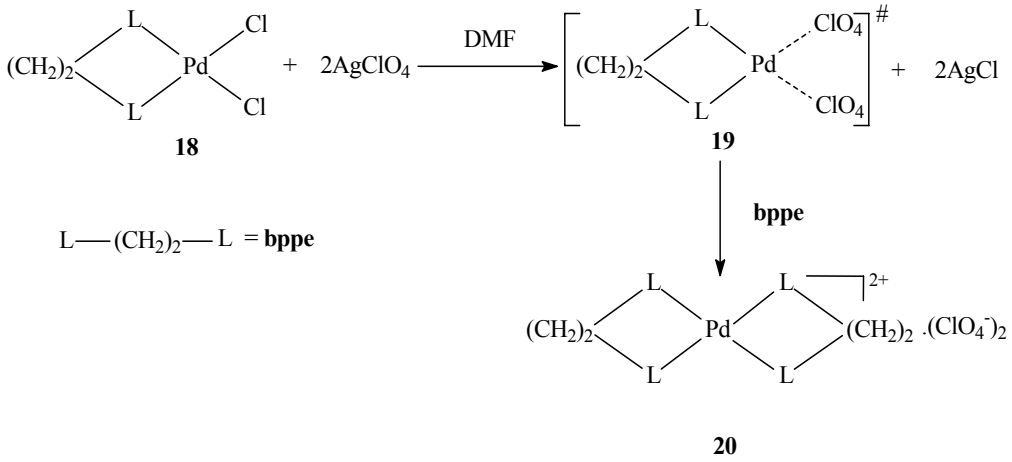
It should be noted, however, that the mono-chelate complex $[PdCl_2(dppp)]$, (where dppp = 1,3-bis(diphenylphosphino)propane), and $[PdCl_2(dppf)]$, (where dppf = 1,1'-bis(diphenylphosphino)ferrocene), showed only a small downfield shift from -17.3 and -16.9 ppm in the free ligands to δ 32.8 and 34.8 ppm in the complexes (*d*-THF), respectively.[77] Complex **18**, $[PdCl_2(dppey)]$, and $[PdCl_2(dppe)]$ form five-membered chelate rings while $[PdCl_2(dppp)]$ and $[PdCl_2(dppf)]$ form six- and seven-membered rings, respectively, and this may contribute to the difference in the $^{31}P\{^{1}H\}$ NMR resonance shifts.

[76] Grim, S.O.; Briggs, W.L.; Barth, R.C.; Tolman, C.A.; Jesson, J.P.; *Inorg. Chem*., 1974, **13**, 1095 – 1100.
[77] Broad-Strong, G.T.L.; Chaloner, P.A.; *Polyhedron*, 1993, **12**, 721 – 729.

The ^{1}H NMR spectrum of complex **18** showed doubling of all signals which further supported the existence of more than one isomer in solution. The ^{1}H and ^{13}C spectra of **18** showed the ethylenic protons and the CH_2 carbon atom of the ethane bridge in the metal complexes shifted downfield if compared to the free ligand.[78,79] The observed ion fragments in the mass spectrum (FAB) were also in agreement with the composition of complex **18**.

3.2.2 A bis-chelated palladium complex

The bis-chelated complex (**20**) was prepared by metathesis of complex **18** with silver perchlorate ($AgClO_4$) in DMF (**Scheme 3.2**). Filtration, removal of DMF *in vacuo* and washing of the crude product with DCM resulted in a light yellow solid.



Scheme 3.2: Metathesis of **18** to form **20**.

Initial attempts to prepare complex **20** from the reaction of $PdCl_2$ and two equivalents of **bppe** resulted in the formation of complex **18** irrespective of the stoichiometry. *Mason et al.*[80,81] reported the metathetical synthesis of $[Pd(dppp)_2](BF_4)_2$ in the presence of BF_4^- as non-coordinating anion (equation 5).

$$Pd(BF_4)_2.4CH_3CN + 2dppp \xrightarrow{CH_3CN} [Pd(dppp)_2](BF_4)_2 \qquad (5)$$

[78] Appleton, T.G.; Bernett, M.A.; Tomkins, I.B.; *J. Chem. Soc., Dalton Trans*., 1976, 439 – 446.
[79] Lindsay, C.H.; Benner, L.S.; Balch, A.L.; *Inorg. Chem*., 1980, **19**, 3503 – 3508.
[80] Mason, M.R.; Verkade, J.G.; *Organometallics*, 1992, **11**, 2212 – 2220.
[81] Mason, M.R.; Verkade, J.G.; *Organometallics*, 1990, **9**, 864 – 865.

Synthesis of complex **20** was only successful when $AgClO_4$ was added to abstract the coordinated anion Cl^- from Pd(II). The perchlorate anion (ClO_4^-) is believed to act as weakly coordinating anion to give the intermediate $[(P\text{-}P)Pd(ClO_4)_2]$ **19** (**Scheme 3.2**), which may easily be displaced by **bppe** to give **20**. Palladium and platinum complexes of the general formula $[(P\text{-}P)M(X_2)]$, (where P-P = bis-phosphine, M = Pd, Pt and X = OAc^-, ClO_4^-, PF_6^-, OTs^- and OTf^-) have been widely used as building blocks of supramolecules, upon displacement of weakly coordinating anions.[82,83,84]

The $^{31}P\{^1H\}$ NMR spectrum of the light yellow solid showed two resonances at δ 51.9 and 54.4 ppm, which were assigned to complex **20**, that is believed to exist as a mixture of isomers in solution (see **3.2.4.2**). The $^{31}P\{^1H\}$ NMR spectrum of the pure isolated crystals showed only one resonance at δ 51.9 and therefore gave indication for the existence of only one isomer. The $^{31}P\{^1H\}$ NMR spectrum of the bis-chelated palladium complex **20** ($CDCl_3$) showed an upfield shift compared to the mono-chelated complex **18** (*Table 3.1*). A similar observation has been made for the mono- and bis-chelated complexes, ($[PdCl_2(dppe)]$ and $[Pd(dppe)_2]Cl_2$), ($[PdCl_2(dppp)]$ and $[Pd(dppp)_2]Cl_2$), and ($[PdCl_2(dppf)]$ and $[Pd(dppf)_2]$) in *d*-THF (*Table 3.1*).[77] Mass spectrometry (FAB) and X-ray crystallographic studies confirmed the formation of complex **20**.

Table 3.1: Comparison of $^{31}P\{^1H\}$ NMR spectroscopic data of Pd(II) complexes.

Ligand Type	δ[P-P]	$\delta[PdCl_2(P\text{-}P)]$	$\delta[Pd(P\text{-}P)_2]$	Solvent
bppe*	**-19.7**	**72.2, 72.4**	**51.9**[a]	$CDCl_3$
dppe	-12.6	68.3	34.0	*d*-THF
dppp	-17.3	13.0	4.0	*d*-THF
dppf	-16.9	34.8	7.4	*d*-THF
dppb	-17.1	32.8	5.0	*d*-THF

[82] Devic, T.; Batail, P.; Fourmigue, M.; Avarvari, N.; *Inorg. Chem.,* 2004, **43**, 3136 – 3141.
[83] Bianchini, C.; Meli, A.; Oberhauser, W.; *Organometallics*, 2003, **22**, 4281 – 4285.
[84] Goel, A.B.; Goel, S.; *Inorg. Chim. Acta*, 1982, **59**, 237 – 240.

3.2.3 X-Ray structure determination of mono- and bis-chelated palladiumcomplexes of bppe

3.2.3.1 Molecular structrure of [$PdCl_2$(bppe)] (18)

The molecular structure of complex **18** and the atom numbering scheme used in corresponding tables is shown in **Figure 3.1(a)**. Selected bond lengths and angles are presented in *Table 3.2(a)*. Additional crystallographic data can be found in Appendix, A1 and A3.

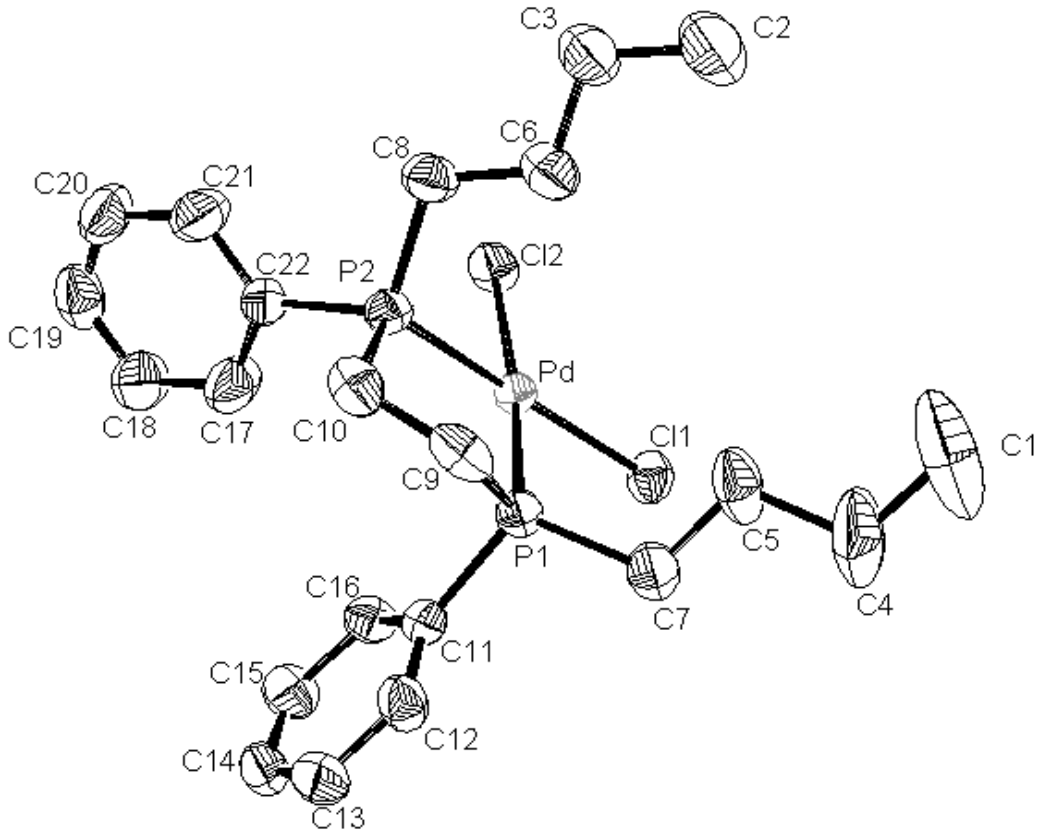


Figure 3.1(a): Molecular structure of **18**. Thermal ellipsoids are shown at 50% probability level. Hydrogen atoms have been omitted for clarity.

Table 3.2(a): Selected bond lengths [Å] and angles [º] for complex **18**.

P1─Pd	2.234(1)	P2─Pd	2.240(1)
Cl1─Pd	2.367(1)	Cl2─Pd	2.369(1)
C9─C10	1.531(7)		

P1─Pd─P2	85.4(4)	Cl1─Pd─Cl2	96.1(4)
P1─Pd─Cl2	172.8(4)	P2─Pd─Cl1	175.8(4)
P1─Pd─Cl1	91.1(4)	P2─Pd─Cl2	87.0(4)
C9─P1─Pd	108.0(1)	C10─P2─Pd	110.0(1)
C10─C9─P1	108.9(3)	C9─C10─P2	109.7(3)

X-ray quality crystals of complex **18** were obtained from a solvent mixture of hexane and dichloromethane at room temperature. Complex **18** crystallises in the orthorhombic space group *Pna21* with one molecule in the asymmetric unit. The unit cell of complex **18** shows four molecules. This was also observed for the complexes $[PdCl_2(dppe)]$[85] and $[PtCl_2(dppe)]$.[86] Complex **18** is four coordinate with two chlorine atoms exhibiting *cis* arrangement in accordance with the reported crystallographically characterised square planar Pd(II) and Pt(II) complexes {($[PdCl_2(dppe)]$, $[PdCl_2(dppm)]$, $[PdCl_2(dppp)]$)[85] and $[PtCl_2(dppe)]$[86]}. The phenyl and butyl substituents are above and below the plane defined by the atoms Pd, P1, P2, Cl1 and Cl2 (**Figure 3.1(b)**) and the crystal therefore represent the (*R,S*) isomer (see **Figure 3.3**).

[85] Steffen, W.L.; Palenik, G.J.; *Inorg. Chem.*, 1976, **15**, 2432 – 2439.
[86] Engelhardt, L.M.; Patrick, J.M.; Raston, C.L.; Twiss, P.; White, A.H.; *Aust. J. Chem.*, 1984, **37**, 2193 – 2200.

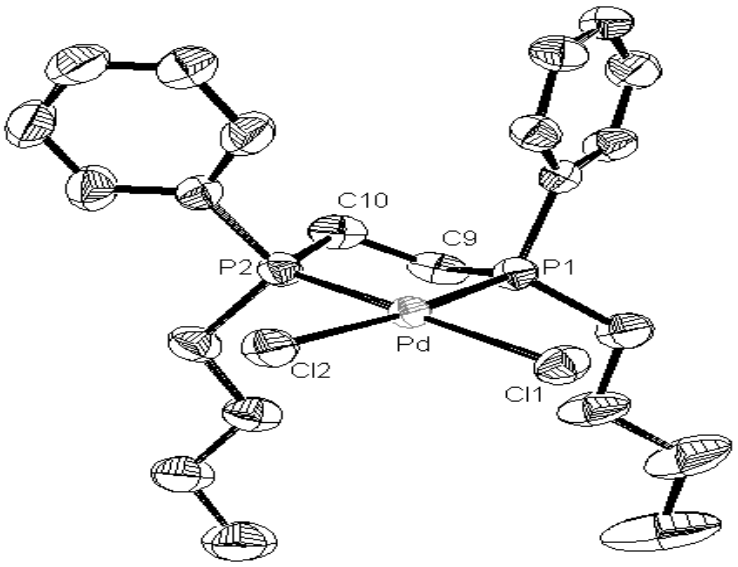


Figure 3.1(b): Relative position of the substituents on the phosphorous atoms.

A least-squares plane through Pd, P1, P2, Cl1 and Cl2 shows that these atoms deviate slightly from planarity (largest deviation from plane P2 0.232 Å) with bridging carbon atoms (C10 and C9) positioned above and below the plane defined by P1, Pd, P2, Cl1 and Cl2 (**Figure 3.1(b)**). The deviations of C9 and C10 from the plane P_2PdCl_2 are -0.378 and 0.179 Å. All atoms defining the plane P_2PdCl_2 (i.e. Pd, P1, P2, Cl1, and Cl2) show deviations from the plane (*Table 3.2(b)*).

Table 3.2(b): Atomic distances (Å) from least-squares planes (x,y,z in crystal coordinates).

15.8881 (0.0057) x - 0.7135 (0.0071) y + 5.8874 (0.0040) z = 8.5551 (0.0076)	
* -0.0328 (0.0011)Cl1	* 0.2324 (0.0014)P1
* -0.0844 (0.0010)Cl2	* 0.0299 (0.0016)P2
* 0.0532 (0.0005)Pd	

Rms deviation of fitted atoms = 0.1854

In complex **18** palladium displays a distorted square-planar (as seen in a least-square planes) geometry with a bite angle [P2─Pd─P1] of 85.9(4)º (less than 90°). Comparable P─Pd─P' bite angles of 85.8(7)º, 86.8(9)º and 86.7(11)º have been

reported for $[PdCl_2(dppe)]$,[85] $[PtCl_2(dppe)]$[86] and $[PtCl_2(dppey)]$.[87] Complex $[PdCl_2(dppf)]$[88] and $[PdCl_2(dppp)]$,[85] however, showed a widening of the P─Pd─P' bite angle. This opening is the result of the presence of bulky groups (cyclopentadienyl rings) adopting a staggered conformation to minimise steric interactions in the case of **dppf** and an increase in the ring size in the case of **dppp**. It has been reported in the literature that increasing the bite size of the bis-phosphine results in an increase of P─M─P' (M = Ni, Pd, Rh, etc.) bite angle with a larger deviation from a square-planar geometry.[89] This increase in the P─Pd─P' bite angle results in a decrease of the Cl─Pd─Cl' angle (*Table 3.3*).

Table 3.3: Angles P─Pd─P' and Cl─Pd─Cl' in complexes $[PdCl_2(P\text{-}P)]$.

$[PdCl_2(P\text{-}P)]$	P—Pd—P'	Cl—Pd—Cl'
$[PdCl_2(bppe)]$*	**85.9***	**96.1***
$[PdCl_2(dppe)]$	85.6	94.2
$[PdCl_2(dppp)]$	90.6	90.8
$[PdCl_2(dppf)]$	99.1	87.8

*This work

For complex $[(Me_2PhP)_2PdCl_2]$ with a non-chelating phosphine ligand a P─Pd─P' angle of 97.3(7)º has been reported,[90] presumably as a consequence of the bulk of the phenyl group of the $PhPMe_2$ ligand. The replacement of a Ph group with a butyl group has almost no effect on the bite angle of chelating phosphines (*c.f.* complex **18** and $[PdCl_2(dppe)]$). The P1─Pd─Cl1 and P2─Pd─Cl2 angles with values of 91.1º and 87.0º, respectively, are also comparable to those of $[PdCl_2(dppe)]$ (90.3º and 89.7º).[85]

The Pd─P1 and Pd─P2 bond lengths of 2.234(1) and 2.240(1) Å in complex **18** compare well to those found in the related mono-chelated complex $[PdCl_2(dppe)]$,[85] that shows values of 2.233(2) and 2.226(2) Å, respectively. The Pd─Cl1 and Pd─Cl2 bond lengths of 2.367(1) and 2.369(1) Å are similar to those of the mono-

[87] Obernhauser, W.; Bachmann, C.; Bruggeller, P.; *Inorg. Chim. Acta*, 1995, **238**, 35 – 43.
[88] Hayashi, T.; Konishi, M.; Kobori, Y.; Kumada, M.; Hguchi, T.; Hirotsu, K.; *J. Am. Chem. Soc*., 1984, **106**, 158 – 163.
[89] Miedaner, A.; Haltiwanger, R.C.; DuBois, D.L.; *Inorg. Chem*.,1991, **30**, 417 – 427.
[90] Martin, L.L.; Jacobson, R.A.; *Inorg. Chem*., 1971, **10**, 1795 – 1798.

chelated complex [$PdCl_2$(dppe)]. In a comparison of **18**, [$PdCl_2$(dppe)] and [$PtCl_2$(dppe)] with [$PdCl_2$(dppf)] and [$PdCl_2$(dppp)], the later ones showed a lengthening of the Pd─P and a shortening of the Pd─Cl bond with average bond distances of 2.299(1) and 2.348(1) Å, and 2.247(1) and 2.355, respectively. This is due to the increase of P─Pd─P' bite angle.

3.2.3.2 Molecular structure of $[Pd(bppe)_2](ClO_4)_2$ (20)

The molecular structure of complex **20** and the atom numbering scheme is illustrated below (**Figure 3.2**). Selected bond distances and angles are presented in *Table 3.4*. Other crystallographic data can be found in Appendix, A1 and A4.

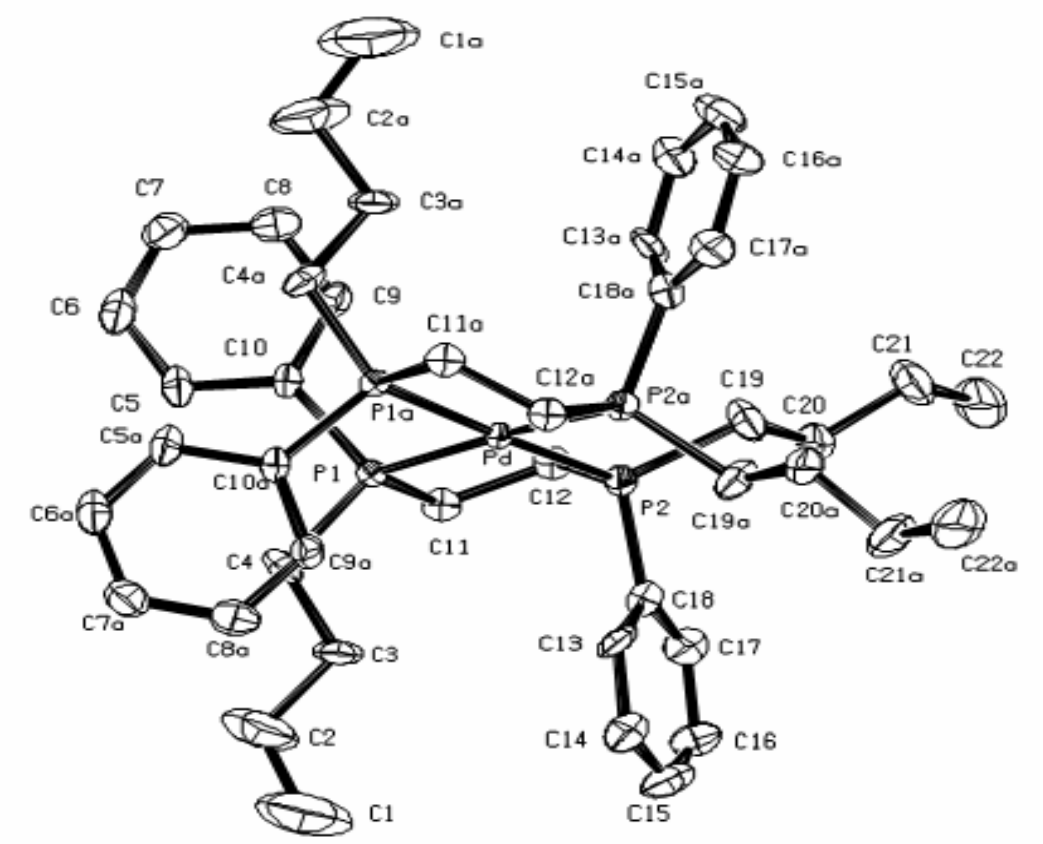


Figure 3.2: Molecular structure of **20**. Thermal ellipsoids are shown at 40% probability level. Hydrogen atoms have been omitted for clarity.

Table 3.4: Selected bond lengths [Å] and angles [º] for complex **20**.

P1─Pd	2.330(3)	Pd2─P2	2.321(3)
C11─P1	1.825(1)	C12─P2	1.829(1)
C11─C12	1.520(1)		

P1─Pd─P2	83.7(9)	P2─Pd─2a	97.8(1)
P1a─Pd─P1	95.1(1)	P2─Pd─P1a	176.6(1)
P2a─Pd─P1	176.6(1)	C12─P2─Pd	105.4(4)
C11─P1─Pd	108.6(4)	C11─C12─P2	108.7(8)
C12─C11─P1	111.7(8)		

X-ray quality crystals of complex **20** were obtained from dichloromethane at room temperature. The molecular structure of **20** shows the presence of four $[Pd(bppe)_2]^{2+}$ cations and eight ClO_4^- anions per unit cell. Complex **20** crystallises in the orthorhombic space group *Pbcn* with one molecule in the asymmetric unit. The Pd atom lies on a crystallographic inversion center. The ClO_4^- anion in complex **20** adopts a tetrahedral geometry similar to that of complex $[Rh(dppe)_2]ClO_4$[91] or other ClO_4^- containing complexes. The ion pairs are well separated and held together by electrostatic interaction in the crystal with no unusual close contacts. The Pd(II) metal centre is planar but deviates from the ideal square. The two aliphatic carbon atoms, C11 and C12, bridging the two phosphorous atoms lie above and below the plane defined by PdP_4, with a P1─C11─C12─P2 torsion angle of 47.5(9)º.

Compared to the mono-chelated complex **18**, the P1─Pd─P2 bite angle of **20** departs from an ideal square geometry (*Table 3.4*). This was also observed for Pt mono- and bis-chelated complexes, $[PtCl_2(dppe)]$ and $[Pt(dppe)_2]Cl_2$,[86] $[PtCl_2(dppey)]$ and $[Pt(dppey)_2](BPh_4)_2$.[87] The P1─Pd─P2 bite angle of **20** is comparable to other related bis-chelated metal complexes (i.e Ni(II), Pd(II), Pt(II) and Rh(I)) in *Table 3.5*.

[91] Hall, M.C.; Kilbourn, B.T.; Taylor, K.A.; *J. Chem. Soc. (A)*, 1970, 2539 – 2540.

Table 3.5: Comparison of P─Pd─P' bite angle for bis-chelated complexes.

$[M(P\text{-}P)_2]X_2$				
M	**P-P**	**X**	**P-Pd-P(Angles) [°]**	**Reference**
Pd	**bppe***	ClO_4^-	83.7(9)	-
Pd	**dppe**	Cl^-	81.7(8)	86
Pt	**dppe**	$I^-.CDCl_3$	82.1(5)	92
Pt	**dppe**	Cl^-	82.0(8)	86
Pt	**dppey**	BPh_4^-	84.6(1)	87
Rh	**dppe**	ClO_4^-	82.7(1)	91
Ni	**dppe**	ClO_4^-	84.2(2)	93

*This work

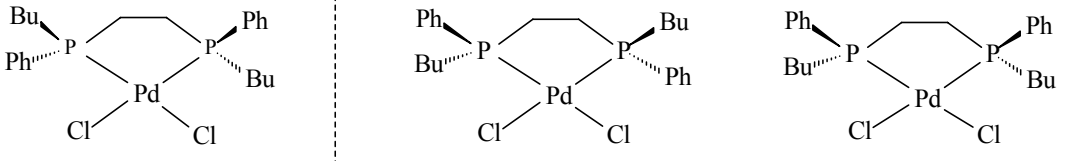
The Pd─P1 and Pd─P2 bond lengths of 2.330(3) and 2.321(3) Å for complex **20** are comparable to those reported bis-chelated Pd(II) and Pt(II) complexes,[86] however, they are significantly elongated if compared to the mono-chelated complex **18** (2.234(1) and 2.240(1) Å). A similar trend was observed for the pair $[PtCl_2(dppe)]$ and $[Pt(dppe)_2]^{2+}$, with Pt-P bond lengthening in $[Pt(dppe)_2]^{2+}$ being attributed to steric crowding.[87] In contrast to complex **18**, the butyl and phenyl substituents on the phosphorous atoms in complex **20** are "*trans"* to each other as expected for the (*R,R / R,R*) isomer (see **Figure 3.4**).

3.2.4 Diastereomeric mixture of Pd(II) complexes

3.2.4.1 Diastereomers of mono-chelated palladium complex

Reaction of **bppe**, that exists as a mixture of diastereomers (**Scheme 3.1**), with $PdCl_2$ resulted in the formation of the mono-chelated Pd(II) complex as a mixture of diastereomers. The $^{31}P\{^1H\}$ NMR spectrum of complex **18** showed two resonances in close proximity (see **3.2.1**). This provided an indication for the existence of at least more than one Pd(II) isomer in solution. The X-ray crystallography study, however, showed (*R,S*)-Pd(II)-**bppe** (**18c**) as the only isomer, that afforded suitable crystals during the crystallisation process (**Figure 3.3**).

[92] Ferguson, G.; Lough, A.J.; McAlees, A.J.; McCrindle, R.; *Acta Cryst*., 1993, **C49**, 573 - 576
[93] Williams, A.F.; *Acta Cryst*., 1989, **C45**, 1002 – 1005.



18a
(*R*,*R*) - Pd(II)-**bppe**

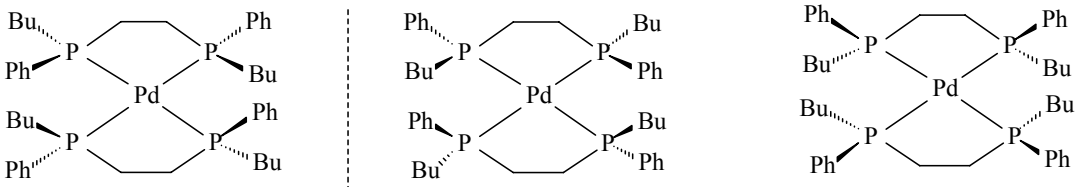
18b
(*S*,*S*) - Pd(II)-**bppe**

18c
(*R*,*S*) - Pd(II)-**bppe**
obtained crystallographically

Figure 3.3: Proposed isomers for the mono-chelated palladium(II) complex.

3.2.4.2 Diastereomers of bis-chelated palladium complex

The proposed mixture of diastereomers for the bis-chelated Pd(II) complex (**20**) from the reaction of **18** (*(R,R),(S,S)*-Pd(II)-**bppe** and (*R,S*)-Pd(II)-**bppe**) with **bppe** (*(R,R),(S,S)*-**bppe** and *(R,S)*-**bppe**) is illustrated below (**Figure 3.4**). The ^{1}H and $^{31}P\{^{1}H\}$ NMR spectra showed a doubling of each signal indicative of the existence of more than one isomer in solution. The X-ray crystallographic studies, however, showed only *(R,R),(R,R)*-Pd(II)-**bppe** (**20a**) as the only isomer of complex **20**, that was obtained as single crystal in the solid state (**Figure 3.4**).



20a
(*R*,*R*), (*R*,*R*) - Pd(II)-**bppe**
obtained crystallographically

20b
(*S*,*S*), (*S*,*S*) - Pd(II)-**bppe**

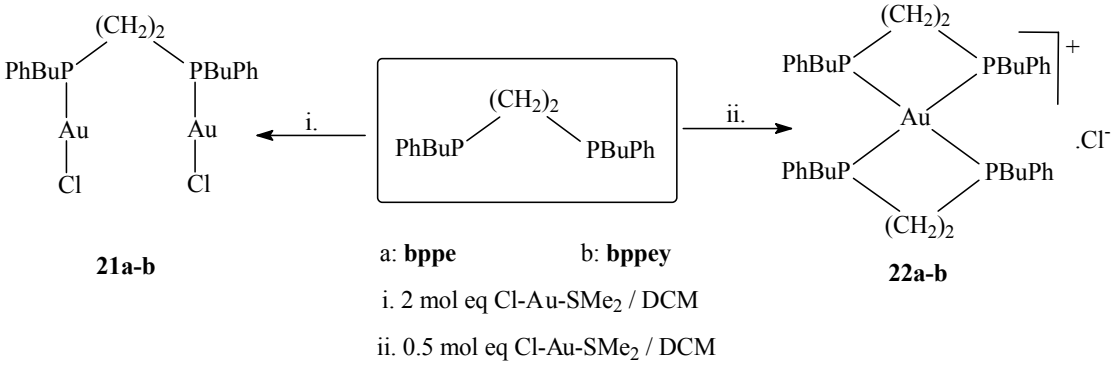
20c
(*S*,*R*), (*R*,*S*) - Pd(II)-**bppe**

Figure 3.4: Proposed isomers of complex **20**.

3.3 Gold complexes

Gold(I) has been known to form numerous complexes with phosphine ligands, the majority of them being two-coordinate. In was not until 1984, that $^{31}P\{^{1}H\}$ NMR studies of the bis-phosphine bridged di-gold complex $[(AuCl)_2dppe]$ in the presence of free **dppe** demonstrated the formation of a four-coordinate complex

$[Au(dppe)_2]Cl$.[94,95,96] The synthesis of the two-coordinate bridged di-gold(I) complexes **21a-b** and four-coordinate bis-chelated gold(I) complexes **22a-b** is summarised in **Scheme 3.3**.



21a-b a: **bppe** b: **bppey** **22a-b**

i. 2 mol eq Cl-Au-SMe_2 / DCM

ii. 0.5 mol eq Cl-Au-SMe_2 / DCM

Scheme 3.3: Synthesis of gold(I) complexes.

3.3.1 Bridged di-gold(I) complexes

The bridged di-gold(I) complexes, $[(AuCl)_2(bppe)]$ (**21a**) and $[(AuCl)_2(bppey)]$ (**21b**), were synthesised by the same procedure described for $[(AuCl)_2dppe]$.[97] The addition of 0.5 mol equivalents of the appropriate ligand (step i in **Scheme 3.3**) to a solution of $[ClAuSMe_2]$ in DCM resulted in the formation of **21a** (57 %) and **21b** (78 %) as a white and light-brown solid, respectively.

The $^{31}P\{^1H\}$ NMR spectrum of the white solid showed two singlets at δ 32.3 and 33.2 ppm, that were assigned to the bridged di-gold complex (**21a**), presenting a mixture of diastereomers in solution. For comparison the $^{31}P\{^1H\}$ NMR spectrum of $[(AuCl)_2dppe]$ in $CDCl_3$ showed a peak at δ 31.5 ppm.[98] The ^1H NMR spectrum of **21a** showed a downfield shift of the ethylenic protons (δ_{CH2} = 2.09 ppm) of the ethane bridge compared to the free ligand (δ_{CH2} = 1.61 ppm). The deshielding of the ethylenic protons has been reported for various complexes such as $[(AuCl)_2dnpype]$,

[94] Mays, M.J.; Vergnano, P.A.; *J. Chem. Soc., Dalton Trans*., 1979, 1112 – 1115.
[95] Parish, R.V.; Parry, O.; McAuliffe, C.A.; *J. Chem. Soc., Dalton Trans*., 1981, 2098 – 2104.
[96] Colburn, C.B.; McAuliffe, C.A.; Parish, R.V.; *J. Chem. Soc., Chem. Commun*., 1979, 218 – 219.
[97] Berners-Price, S.J.; Sadler, P.J.; *Inorg. Chem*., 1986, **25**, 3822 – 3827.
[98] Berners-Price, S.J.; Mazid, M.A.; Sadler, P.J.; *J. Chem. Soc., Dalton Trans*., 1984, 969 – 974.

where n = 2 – 4, in the literature.[99] Mass spectrometry further confirmed the formation of **21a**.

The $^{31}P\{^{1}H\}$ NMR spectrum of the light brown solid in DMSO showed a singlet at δ 31.5 ppm and was identified as the desired bridged di-gold(I) complex (**21b**). The reported $^{31}P\{^{1}H\}$ resonance signal for the analogous bridged di-gold(I) complex $[AuCl_2(dppey)]$ is found at δ 12.8 ppm.[95] Mass spectrometry further confirmed the formation of **21b**.

Attempts to grow crystal suitable of X-ray crystallography study proved unsuccessful. The freely rotating butyl substituents on the phosphorous atoms may have impeded the crystallisation process. Molecular structures of bridged di-gold(I) complexes have only been reported for complexes with phenyl groups on the phosphorous atom.[100,101]

3.3.2 Bis-chelated gold(I) complexes

The bis-chelated gold(I) complexes were conveniently synthesised by the reaction of 2 mol equivalents of the appropriate ligand (**bppe** and **bppey**) with a solution of $(ClAuSMe_2)$ in DCM (step ii in **Scheme 3.3**) as white ($[Au(bppe)_2]Cl$, **22a**) and brown solids ($[Au(bppey)_2]Cl$, **22b**), respectively. The $^{31}P\{^{1}H\}$ NMR spectra showed resonances at δ 15.1, 15.5 and 15.8 (isomeric mixture) and 22.3 ppm (broad singlet), which were assigned to complex **22a** and **22b**. Complex **22a** and **22b** were synthesised with the well established 2:1 ratio of (P-P):Au(I) reported in various literature reports.[96,97] Both complexes **22a** and **22b** exhibited downfield shifts in their $^{31}P\{^{1}H\}$ NMR signals compared to the bridged di-gold(I) complexes **21a** and **21b** (*Table 3.6*). The observed trend in the $^{31}P\{^{1}H\}$ NMR spectra of bis-chelated gold(I) complexes compared to the shift in the bridged di-gold(I) complexes is consistent with that found in $[(AuCl)_2(dppe)]$ and $[Au(dppe)_2]Cl$. The complexes $[(AuCl)_2(dppey)]$ and $[(AuCl)_2(dpmaa)]$ showed in contrast an upfield shift in the

[99] Berners-Price, S.J.; Bowen, R.J.; Hambley, T.W.; Healy, P.C.; *J. Chem. Soc., Dalton Trans.*, 1999, 1337 – 1346.
[100] Bates, P.A.; Waters, J.M.; *Inorg. Chim. Acta*, 1985, **98**, 125 – 129.
[101] Schimidbaur, H.; Reber, G.; Schier, A.; Magner, F.E.; Müller, G.; *Inorg. Chim. Acta*, 1988, **147**, 143 – 150.

$^{31}P\{^{1}H\}$ NMR spectrum if compared to [Au(dppey)]Cl and [Au(dpmaa)]Cl (*Table 3.6*).

Table 3.6: $^{31}P\{^{1}H\}$ chemical shift resonances of bridged and bis-chelated gold(I).

$^{31}P\{^{1}H\}$ NMR / ppm				
Ligand	**δ[P-P]**	**δ[$(AuCl)_2$(P-P)]**	**δ[Au(P-P)$_2$]Cl**	**Solvent**
bppe*	**-19.6**	**32.3, 33.2**	**15.1, 15.5**	**$CDCl_3$**
dppe	-11.9	31.5	20.8	$CDCl_3$
bppey*	**-16.7**	**31.5**	**22.3**	**DMSO**
dppey	-23.5	12.8	22.4	$CDCl_3$
dpmaa	-10.9	21.9	28.1	*d*-Acetone

The formation of **22a** and **22b** was further confirmed by mass spectrometry. Various attempts to obtain crystals suitable for X-ray crystallography were unsuccessful. The exchange of counter ions to promote crystallisation also yielded no results.

3.3.3 Diastereomers and enantiomers of gold(I) complexes

The possible enantiomers and diastereomers of gold(I) complexes that may arise from the reaction of **bppe** and **bppey** (mixture of isomers) are illustrated below (**Figure 3.5** and **3.6**). $^{31}P\{^{1}H\}$ NMR data have previously shown, that gold(I) phosphine complexes can exist in more than one form.[47]

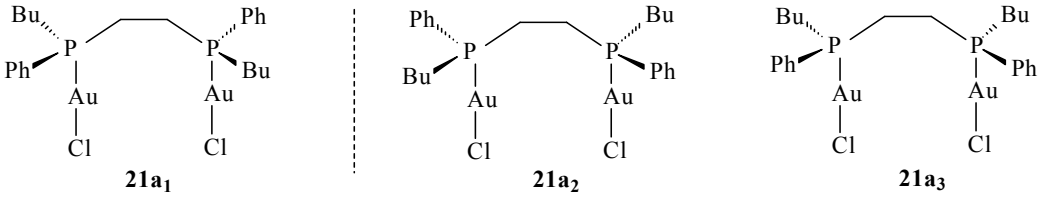


Figure 3.5: Proposed bridged di-gold(I) isomers.

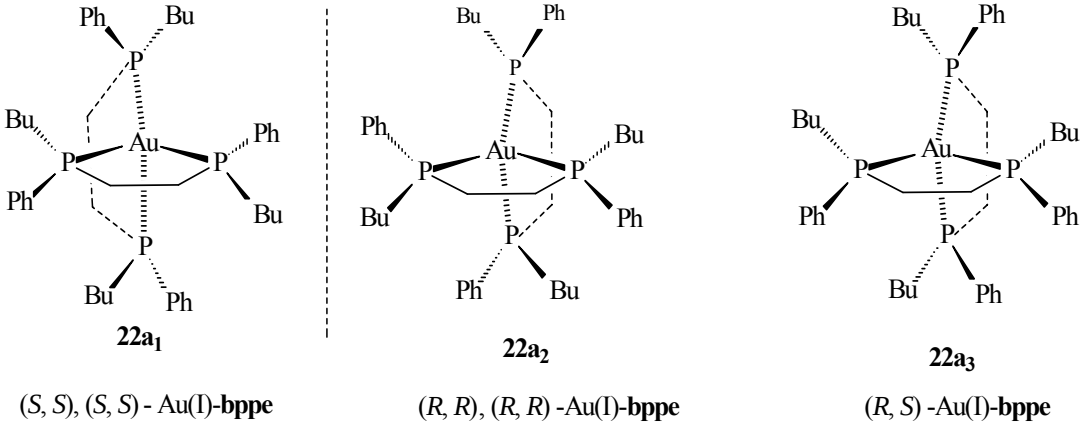
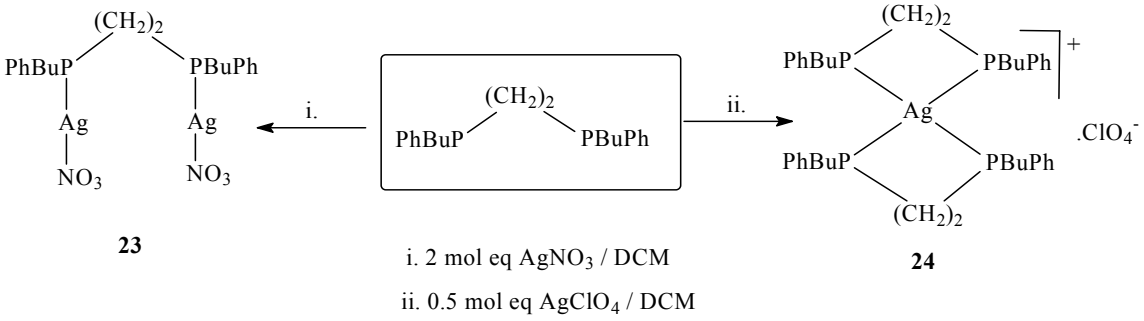


Figure 3.6: Proposed bis-chelated gold(I) isomers.

3.4 Silver complexes

Silver is another important group 11 transition metal that can coordinate to phosphine ligands to form phosphine complexes. Numerous silver phosphine complexes including bridged,[102] bis-chelated[103] to polynuclear[104] have been reported previously. The bis-phosphine **bppe** ligand was used to synthesise the bridged di-silver (**23**) and bis-chelated silver (**24**) complexes as illustrated below (**Scheme 3.4**).[103,105,106]



Scheme 3.4: Synthesis of silver(I) bppe complexes.

[102] Van der Ploeg, A.F.M.J.; Van Koten, G.; *Inorg. Chim., Acta*, 1981, **51**, 225 – 239.
[103] Berners-Price, S.J.; Brevard, C.; Pagelot, A.; Sadler, P.J.; *Inorg. Chem*., 1985, **24**, 4278 – 4281.
[104] Van der Ploeg, A.F.M.J.; Van Koten, G.; Spek, A.L.; *Inorg. Chem*., 1979, **18**, 1052 – 1060.
[105] Levason, W.; McAuliffe, C.A.; *Inorg. Chim. Acta*, 1974, **8**, 25 – 26.
[106] Berners-Price, S.J.; Bowen, R.J.; Harvey, P.J.; Healy, P.C.; Koutsantonis, G.A.; *J. Chem. Soc.*, *Dalton Trans*., 1998, 1743 – 1750.

3.4.1 Bridged di-silver(I) complex

The reaction of **bppe** with 2 mol equivalents of $AgNO_3$ in DCM at room temperature (step i in **Scheme 3.4**) resulted in the formation of $[(AgNO_3)_2(bppe)]$ (**23**) as brown solid in moderate yield (51 %). The $^{31}P\{^1H\}$ NMR spectrum of the crude brown solid showed a doublet at δ 9.5 ppm with coupling constant J = 223 Hz consistent with the bridged silver(I) complex **23**. A bridged silver complex $[(Ag_2O_4C_{12}H_6(dppe)]$ with a carboxylate group bridging two silver atoms showed a doublet peak at δ 4.56 ppm with coupling constant J_{Ag-P} = 230 Hz.[104] The mass spectrometry further confirmed the formation of **23** with *m/z* 574.0 and 465.4 corresponding to the fragments $[Ag_2(bppe)]^+$ and $[Ag(bppe)]^+$. The ^1H NMR spectrum of **23** appeared downfield compared to the free ligand, which further supported the silver coordination of bppe to form complex **23**. Any attempts to obtain suitable single X-ray crystals of complex **23** were unsuccessful.

3.4.2 Bis-chelated silver(I) complex

The bis-chelated silver(I) complex, $[Ag(bppe)_2]ClO_4$ (**24**) was conveniently synthesised by reacting 0.5 mol of $AgClO_4$ with 1 mol of **bppe** in DCM at room temperature (step ii in **Scheme 3.4**). Removal of volatiles resulted in a white solid. The $^{31}P\{^1H\}$ NMR spectrum of the crude material showed a doublet at δ -2.09 ppm and J_{Ag-P} = 240 Hz consistent with the formation of the bis-chelated silver complex (**24**). The observed coupling constant J_{Ag-P} for complex **24** is in agreement with other reported bis-chelated silver(I) complexes. Reported silver complexes such as $[Ag(dppe)_2]NO_3$ and $[Ag(eppe)_2]NO_3$ showed chemical shifts in the $^{31}P\{^1H\}$ NMR spectrum at δ 4.40 and -2.30 ppm with coupling constants of J_{Ag-P} = 231 / 266 Hz and J_{Ag-P} = 290 / 232 Hz, respectively.[102] The formation of **24** was further confirmed by mass spectrometry which showed a mass spectrum with the formula units with the values of *m/z* of 465.3 and 823.5 in agreement with the predicted molecular ions $[Ag(bppe)]^+$ and $[Ag(bppe)_2]^+$. Due to unsuccessful attempts in obtaining single crystals of complex **24** crystallographic studies could not be undertaken.

3.5 Biological studies on metal complexes

Traditionally pharmaceutical agents have been dominated by purely organic compounds.[107,108] The potential of metal-based drugs has previously been undervalued, although certain transition metals play a key role in many biological systems.[109] The potential of inorganic drugs can not be better illustrated than in the discovery of Cisplatin as anti-cancer drug in 1969. The anti-tumour activity shown by some platinum(II) complexes has led to the investigation of metal-based compounds as potential cytotoxic and anti-tumour agents.[110,111] In recent years metal-based compounds have found application in the treatment of various diseases: gold complexes against arithritis, cancer, malaria[112,113,114] and bismuth complexes against peptic ulcer,[107] to mention only a few.

3.5.1 Anti-tumour activity of lipophilic, cationic bis-phosphine complexes

Tetrahedral bis-phosphine metal complexes of gold(I), silver(I) and copper(I) have been shown to display anti-tumour activity.[115] The anti-tumour activity displayed by some of these complexes is comparable to those of *cis*-diamine dichloroplatimun(II), Cisplatin. Unlike neutral two-coordinate linear gold complexes (***e.g.*** Auranofin and its analogues) cationic $[Au(dppe)_2]Cl$ has shown stability towards ligand exchange reactions, in particular towards thiols in serum in biological systems. It has emerged that the activity of these complexes against tumour cells is related to their lipophilic character.[116] The higher the lipophilic character of the complex, the higher the activity.

[107] Abrams, M.J.; Murrer, B.A.; *Science*, 1993, **261**, 725 – 730.
[108] Timerbaev, A.R.; Hartinger, C.G.; Aleksenko, S.S.; Keppler, B.K.; *Chem. Rev*., 2006, **106**, 2224 – 2248.
[109] Best, S.L.; Sadler, P.J.; *Gold Bulletin*, 1996, **29**, 87 – 93.
[110] Marcon, G.; Messori, L.; Orioli, P.; Cinellu, M.A.; Minghetti, G.; *Eur. J. Biochem*., 2003, **270**, 4655 – 4661.
[111] Mirabelli, C.K.; Hill, D.T.; Faucette, L.F.; McCabe, F.L.; Girard, G.R.; Bryan, D.B.; Sutton, B.M.; O'Leary Bartus, J.; Crooke, S.T.; Johnson, R.K.; *J. Med. Chem*., 1987, **30**, 2181 – 2190.
[112] Shaw, C.F.; *Chem. Rev*., 1999, **99**, 2589 – 2600.
[113] Mirabelli, C.K.; Johnson, R.K.; Hill, D.T.; Faucette, L.F.; Girard, G.R.; Kuo, G.Y.; Crooke, S.T.; *J. Med. Chem*., 1986, **29**, 218 – 223.
[114] Guo, Z.; Sadler, P.J.; *Angew. Chem. Int. Ed*., 1999, **38**, 1512 – 1531.
[115] Berners-Price, S.J.; Girard, G.R.; Hill, D.T.; Sutton, B.M.; Jarrett, P.S.; Faucette, L.F.; Johnson, R.K.; Mirabelli, C.K.; Sadler, P.J.; *J. Med. Chem*., 1990, **33**, 1386 – 1392.
[116] Berners-Price, S.J.; Jarrette, P.S.; Sadler, P.J.; *Inorg. Chem*., 1987, **26**, 3074 – 3077.

The activity of the synthesised neutral mono-chelated Pd(II) and cationic bis-chelated gold(I) and Pd(II) bis-phosphine complexes against HeLa cells is discussed below. Biological tests on the complexes were conducted in the Department of Pharmacology at the University of Pretoria.

3.5.2 Selection of the metal-complexes for primary screening

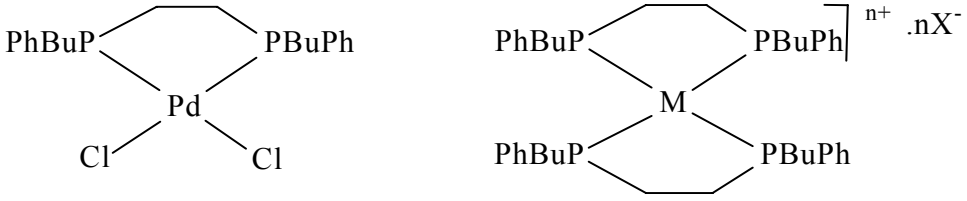
For any compound to be eligible for biological testing (primary screening) it must be stable under specified pharmacological conditions. It was decided that the bridged bimetal complexes should not undergo primary screening as they were found to be unstable in solution as evident from the deposition of metallic gold from solutions of the di-gold(I) complexes $[(AuCl)_2(bppe)]$ (**21a**) and $[(AuCl)_2(bppey)]$ (**21b**) in DCM, that were left overnight at room temperature. Hence, further stability studies on these complexes were not deemed necessary. Stability studies were therefore only carried out for the bis-chelated complexes: $[Pd(bppe)_2](ClO_4)_2$ (**20**), $[Au(bppe)_2]Cl$ (**22a**), $[Au(bppey)_2]Cl$ (**22b**), and $[Ag(bppe)_2]ClO_4$ (**24**) according to the following regimen: Instant ($^{31}P\{^1H\}$ NMR experiments carried out immediately after dissolving the four complexes in DMSO), 24 h / 37 ºC ($^{31}P\{^1H\}$ NMR experiments carried out after keeping the samples for 24 hours at 37 ºC in DMSO) and 7 days / 37 ºC ($^{31}P\{^1H\}$ NMR experiments carried out after keeping the samples for seven days at 37 ºC in DMSO). The results obtained are shown in *Table 3.7*.

Table 3.7: Stability studies on selected bis-chelated phosphine complexes.

	$^{31}P\{^1H\}$ NMR / ppm (DMSO)			
	20	**22a**	**22b**	**24**
Instant	57.9	16.8	22.3	-0.50
24 hrs / (37 ºC)	59.1	16.2	5.26	-0.49
7 days / (37 ºC)	58.0	16.3	-0.08	-0.51

A stability study for the mono-chelated palladium complex $[PdCl_2(bppe)_2]$ (**18**) was deemed unnecessary as it was adequately stable when exposed to moist air and in solution for several days. As can be seen from the $^{31}P\{^1H\}$ NMR data, complex **20**, **22a** and **24** showed no significant change in the $^{31}P\{^1H\}$ NMR spectrum, while **22b**

showed a significant change in the $^{31}P\{^{1}H\}$ NMR spectrum due to instability in solution. Although complex **24** showed no change in the $^{31}P\{^{1}H\}$ NMR spectrum it was excluded from further tests as it was easily oxidised on exposure to air. Thus, the following complexes showed adequate stability to justify testing for anti-tumour activity against HeLa cells (**Figure 3.7**). The results of the preliminary screening of the selected complexes are shown in *Table 3.8*.



18

20: M = Pd, n =2, $X^- = ClO_4^-$

22a: M = Au, n = 1, $X^- = Cl^-$

Figure 3.7: Complexes used for primary screening against HeLa cells.

Table 3.8: IC_{50} (μM) values of tested complexes on HeLa cell line.

Complex	IC_{50} / μM	IC_{50}CisP / μM	No. experiment
18	30.908	0.349	3
20	11.485	0.349	3
22	2.196	0.349	3

IC_{50} = Concentration at which 50% of cell growth is inhibited

3.5.3 Analysis of the results

The bis-chelated complexes **20** and **22a** are cationic complexes, while the mono-chelated complex **18** is a neutral complex. For better identification of the potency of these complexes the results were compared with those of Cisplatin as a standard. The bis-chelated cationic complex showed a higher activity than its neutral mono-chelated counterpart **18**. Complex **22a** showed in comparison with $[Au(dppe)_2]$ (IC_{50} = 0.747 μM) a lower activity against HeLa cells. The introduction of a butyl group in **bppe** resulted in a reduced activity of the gold(I) complexes. No conclusion can be drawn on whether the replacement of Au(I) for Ag(I) would have

shown an improved activity since the primary screening was not carried out for complex **24** due to its instability.

3.6 Conclusions

The new bis-phosphine ligand **bppe** was coordinated to various metal ions [i.e. Au(I), Ag(I) and Pd(II)] to yield new metal bis-phosphine complexes. The mono-chelated Pd(II) complex, $[PdCl_2(bppe)]$ (**18**) was obtained from the reaction of **bppe** and $PdCl_2$ irrespective of the stochiometric ratio of the reagents (**bppe** : $PdCl_2$: 1 : 1 or 0.5 : 1). The bis-chelated complex $[Pd(bppe)_2](ClO_4)_2$ (**20**) was obtained by replacing the Cl of the mono-chelated Pd(II) complex with a non-coordinating counter ion and adding an excess of **bppe**. The successful formation of both mono- and bis-chelated palladium complexes was confirmed by NMR spectroscopy, mass spectrometry, elemental analysis and X-ray crystallography.

X-ray analysis showed, that in both complexes Pd(II) assumes a square-planar geometry, that is comparable with those of the related **dppe** and **dppey** complexes, $[PdCl_2(dppe)]$, $[Pd(dppe)_2](ClO_4)_2$, $[PtCl_2(dppey)]$ and $[Pt(dppey)_2]Cl_2$. The substitution of the phenyl moieties on the phosphorous atoms with butyl groups does not substantially alter the geometry or the bond lengths of the Pd(II) complexes obtained.

The reaction of **bppe** and **bppey** with stoichiometric (1 : 2 or 2 : 1) amounts of $[AuCl(SMe_2)]$ resulted in the formation of bridged ($[(AuCl)_2(bppe)]$ (**21a**) and $[(AuCl)_2(bppey)]$ (**21b**)) and bis-chelated ($[Au(bppe)_2]Cl$ (**22a**) and $[Au(bppey)_2]Cl$ (**22b**)) gold(I) complexes. Their successful formation was confirmed by NMR spectroscopy and mass spectrometry. The ^{1}H and $^{31}P\{^{1}H\}$ NMR spectra of bridged and bis-chelated complexes, particularly those of **bppe**, showed double peaks in the NMR spectra due to the possible existence of isomers in solution. No attempts were made in separating these isomers

Further reaction of **bppe** with stoichiometric (1 : 2 or 2 : 1) amounts of silver salts resulted in the formation of bridged and bis-chelated silver(I) complexes. It was noted from the mass spectrum of the bridged di-silver(I) complex, that the reaction

of $AgNO_3$ and **bppe** also resulted in the formation of a bis-chelated silver(I) complex.

The synthesised bis-chelated complexes showed activity against HeLa cells. The cationic bis-chelated palladium(II) complex **20** showed higher activity than its neutral mono-chelated analogue **18**. The introduction of butyl groups on the phosphorous atoms resulted in a reduced activity as compared to phenyl substituents as evident by the comparison with $[Au(dppe)_2]Cl$. Although the bis-chelated gold(I) complex **22b** (**bppey** as chelating ligand) was synthesised, no comparison was possible with **22a** (**bppe** as chelating ligand) since the former complex was inadequately stable to withstand preliminary screening experiments. It was also not possible to determine whether the replacement of Au(I) with Ag(I) resulted in a change of activity since the primary screening on HeLa cells could not be carried out due to inadequate stability of complexes, $[(AgNO_3)_2(bppe)]$ (**23**) and $[Ag(bppe)_2]ClO_4$ (**24**).

Chapter Four

Experimental Procedures

4.1 Reagents and general procedures

All manipulations (unless stated otherwise) were carried out under an argon atmosphere using standard Schlenk techniques. Solvents were distilled from sodium/benzophenone ketyl or calcium hydride and degassed. Deuterated solvents were degassed by freeze-drying and kept under argon and molecular sieves. NMR spectra were recorded in $CDCl_3$ (in most cases), d_6-DMSO or C_6D_6 at 298 K using the following Bruker instruments, *AVANCE* 300 (^{1}H 300.13; ^{31}P 121.5; ^{13}C 75.5 MHz) *AVANCE* DRX 400 (^{1}H 400.13; ^{31}P 161.9; ^{13}C 100.6 MHz) and referenced internally to residual solvent resonances (data in δ) in the case of ^{1}H and ^{13}C spectra, while the ^{31}P spectra were referenced externally to 85% H_3PO_4. All NMR spectra other than ^{1}H NMR were proton-decoupled. FAB-MS spectra were collected using a VG70-SEQ instrument in positive ion mode. Elemental analyses were determined on a Thermo Flash EA1112 CHNS-O elemental analyzer by the University of Cape Town. The following abbreviations are used throughout the experimental section: br s = broad singlet, d = doublet, dt = doublet of triplet, m = multiplet, s = singlet. Coupling constants, *J*, were measured in Hertz (Hz). Melting points were recorded in unsealed capillaries and are uncorrected.

4.2 Crystal structure determinations

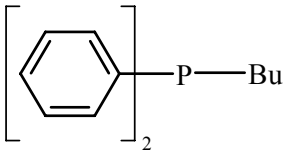
Intensity data were collected on a Bruker SMART 1k CCD area detector diffractometer with graphite monochromated Mo K_α radiation (50 kV, 30 mV). The collection method involved ω-scans of width 0.3º. Data reduction was carried out using the program *SAINT*+.[117] The crystal structures were solved by direct methods using *SHELXTL*.[118] Non-hydrogen atoms were first refined isotropically followed by anisotropic refinement by full matrix least-squares calculation based on F^2 using

[117] Bruker, SAINT+. Version 6.02 (includes XPREP and SADABS). Bruker AXS INC., Madison, Wisconsin, USA, 1999; G.M. Sheldrick, SADABS, University of Göttingen, 1997.
[118] Bruker, 1999. SHELXTL, Version 5.1 (includes XS, XL, XP, XSHELL), Bruker AXS INC., Madison, Wisconsin, USA, 1999.

SHELXTL.[118] Hydrogen atoms were located from the difference map and then positioned geometrically and allowed to ride on their respective parent atoms. Diagrams and publication materials were generated using *SHEXTL*,[118] *PLATON*[119] and *ORTEP*.[120]

4.3 Synthesis of the precursors

4.3.1 Synthesis of butyldiphenylphosphine, Ph_2PBu



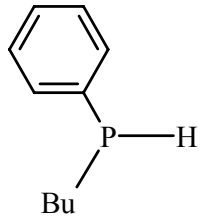
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26.4 g (104.8 mmol) of Ph_3P were dissolved in 100 cm^3 of tetrahydrofuran (THF). The solution was added dropwise at 0 ºC to a suspension of 1.60 g (230.5 mmol) granular lithium metal in 100 cm^3 of THF. The reaction was stirred at 0 ºC for 1 h. The colourless solution became red-brown. The mixture was allowed to warm to room temperature and then stirred for 72 h. The un-reacted lithium metal was removed by filtration and 22.7 cm^3 (217.4 mmol) of *n*-butylchloride in 20 cm^3 hexane were added dropwise to the red-brown filtrate at 0 ºC while rapidly stirring. The reaction mixture was then stirred at room temperature overnight. After removing the volatiles *in vacuo* 100 cm^3 of dried hexane were added to the red-brown viscous oil to precipitate LiCl from the solution. The colourless solution was filtered by means of a cannula to remove LiCl. Hexane was removed from the filtrate *in vacuo* to give a yellow viscous oil, which yielded a colourless liquid after distillation *in vacuo*.

Yield: 13.97 g, 64 %. Boiling point: 105 – 110 ºC / 85.5 x 10^{-4} mmHg (lit.[60] 100 – 102 ºC / 2.63 x 10^{-4} mmHg). NMR data are in agreement with reported literature values.[60]

[119] Spek, A.L.; *J. Appl. Crystallogr*., 2003, **36**, 7 – 13.
[120] Farrugia, L.J.; *J. Appl. Crystallogr*., 1997, **30**, 565

4.3.2 Synthesis of butylphenylphosphine, PhBuPH

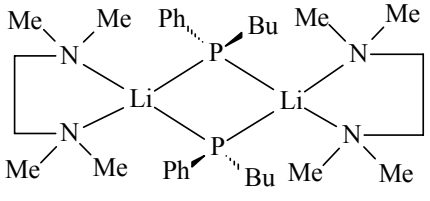


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A solution of 10.0 g (41.3 mmol) of Ph_2BuP in 25 cm^3 of THF was added dropwise to a suspension of 0.67 g (90.8 mmol) granular lithium metal in 60 cm^3 of THF at 0 ºC. The reaction mixture was stirred at 0 ºC for 1 h, which resulted in a colour-change from colourless to red-brown. The mixture was allowed to warm to room temperature and then stirred for 72 h. The un-reacted lithium metal was removed by filtration. 10 cm^3 of distilled and degassed water in 10 cm^3 of THF were added to the red-brown filtrate at -5 ºC while stirring rapidly. The resulting colourless reaction mixture was stirred for 5 minutes at -5 ºC. After removing the volatiles *in vacuo* 30 cm^3 of diethyl ether were added to the residue, and the reaction product was extracted with diethyl ether (5 x 30 cm^3). The organic layer was dried over $MgSO_4$, filtered and the volatiles were removed *in vacuo* to give a yellow viscous oil. A colourless liquid was obtained after distillation *in vacuo*.

Yield: 3.83 g, 56 %. Boiling point: 110 – 120 ºC / 78.9 mmHg, Lit.[46] 110 – 130 ºC / 20 mmHg. ^{1}H-NMR (C_6D_6): δ 1.18 [t, CH_3, 3H, $^3J_{H\text{-}H}$ = 7.2 Hz], 1.16 – 1.36 [m, CH_2, 4H], 1.55 – 1.68 [m, CH_2, 2H], 4.09 [dt, P-H, 1H, $^1J_{H\text{-}P}$ = 204.7 Hz, $^3J_{H\text{-}H}$ = 7.0 Hz], 7.06 – 7.08 [m, *m/p*-Ph, 3H], 7.35 – 7.40 [m, *o*-Ph, 2H]. ^{31}P-NMR (C_6D_6): δ -51.4. ^{13}C-NMR (C_6D_6): δ 13.8 [m, CH_3], 23.4 [d, CH_2, $J_{C\text{-}P}$ = 11.5 Hz], 24.2 [d, CH_2 $J_{C\text{-}P}$ = 8.8], 30.8 [d, CH_2, $J_{C\text{-}P}$ = 8.2 Hz], 128.2 [s, *p*-Ph], 133.7 [d, *o/m*-P, $J_{C\text{-}P}$ = 9.9 Hz], 134.0 [d, *o/m*-Ph, $J_{C\text{-}P}$ = 15.5 Hz], 136.5 [d, *ipso*-Ph, $^1J_{C\text{-}P}$ = 12.2 Hz].

4.3.3 Synthesis of [(TMEDA)•LiPPh(Bu)]$_2$



17

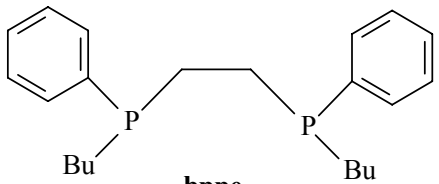
A solution of 7.71 cm^3 (11.7 mmol; 1.52 molar solution in hexane) of *n*-BuLi in 10 cm^3 of hexane and 1.36 g (11.7 mmol) of TMEDA were added dropwise to 1.94 g (11.7 mmol) of PhBuP(H) in 25 cm^3 of hexane at -90 ºC. The reaction mixture was allowed to warm to room temperature. After stirring overnight a yellow precipitate had formed and the reaction mixture was filtered. The obtained

yellow solid was dried *in vacuo* to give a yellow powder. The filtrate was concentrated until crystallisation started and then stored at -20 ºC for further crystallisation.

Yield: 2.80 g, 83 %. ^{1}H-NMR (C_6D_6): δ = 1.11 [t, CH_3, 3H, $^{3}J_{H\text{-}H}$ = 7.3 Hz], 1.67 – 1.73 [m, CH_2, 2H], 1.80 [s, NCH_2, 4H], 1.88 – 1.96 [m, CH_2, 2H], 1.99 [s, NCH_3], 2.28 – 2.33 [m, CH_2, 2H], 6.77 [t, *p*-Ph, 1H, *J* = 7.2 Hz] 7.12 – 7.18 [m, *m*-Ph, 2H], 7.40 [d, *o*-Ph, 2H, *J* = 7.2 Hz]. ^{31}P-NMR (C_6D_6): δ -56.5 [bs]. ^{13}C-NMR (C_6D_6): δ 14.6 [s, CH_3], 21.5 [s, CH_2], 26.0 [s, CH_2], 35.5 [s, CH_2], 46.1 [s, NCH_3], 57.2 [s, NCH_2], 117.7 [s, *p*-Ph], 127.3 [s, o/*m*-Ph], 127.5 [s, *o/m*-Ph], 133.9 [d, *ipso*-Ph, $^{1}J_{C\text{-}P}$ = 15.6 Hz].

4.4 Synthesis of ligands

4.4.1 Synthesis of $Ph(Bu)PCH_2CH_2P(Bu)Ph$



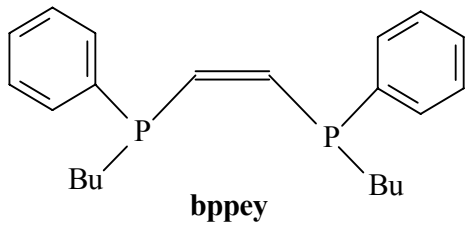
bppe

Method A: A solution of 5 g (20.6 mmol) of Ph_2BuP in 25 cm^3 THF was added dropwise to a suspension of 0.29 g (41.2 mmol) of granular lithium metal in 60 cm^3 of THF at 0 ºC and the reaction mixture was stirred for 1 h at 0 ºC, whereupon the colourless solution had turned red-brown. The mixture was allowed to warm to room temperature and then stirred for 72 h. The un-reacted lithium metal was removed by filtration. 1.02 g (3.71 mmol) of 1,2-dichloroethane in 25 cm^3 hexane were added dropwise to the red-brown filtrate at 0 ºC while rapidly stirring. The reaction mixture was stirred at room temperature overnight. After removal of THF the white-yellow reaction mixture was extracted with hexane. The hexane was removed *in vacuo* to give a yellow oil (0.5 g, 17 %). **Method B**: 0.083 cm^3 (1.04 mmol) of 1,2-dichloroethane in 10 cm^3 of hexane were added dropwise over a period of five minutes to a magnetically stirred solution of 0.60 g (1.04 mmol) of $[(TMEDA)\bullet LiPPh(Bu)]_2$ in 25 cm^3 of hexane at 0 ºC. The reaction mixture was stirred for 30 minutes at 0 ºC. It was allowed to warm to room temperature and stirred overnight. The colourless solution was filtered by means of a cannula to remove LiCl. The hexane was removed from the filtrate *in vacuo* to give colourless viscous oil (0.31 g, 83 %). **Method C**: 10.0 g (25.1 mmol) of 1,2-

bis(diphenylphosphino)ethane (**dppe**) were dissolved in 100 cm^3 of THF. The solution was added dropwise to a suspension of 0.784 g (112.9 mmol) granular lithium metal in 120 cm^3 of THF at 0 ºC. The reaction mixture was stirred at 0 ºC for 1 h and became red-brown. The mixture was allowed to warm to room temperature and then stirred for 24 h. The un-reacted lithium metal was removed by filtration. 12.0 cm^3 (112.9 mmol) of *n*-butylchloride in 20 cm^3 of THF were added dropwise to the red-brown filtrate at -30 ºC while rapidly stirring. The reaction mixture was allowed to warm to room temperature and then stirred overnight. After removing the solvent *in vacuo* 100 cm^3 of hexane were added to the light brown, viscous oil to precipitate LiCl from the solution. The hexane was removed *in vacuo* to give yellow, viscous oil, which, after distillation, yielded colourless oil.

Yield: 4.85 g, 54 % (Mixture of diastereoisomers). Boiling point: 170 – 175 ^oC/140 mmHg. ^{1}H-NMR ($CDCl_3$): δ 0.79 [t, CH_3, 6H, $^3J_{H\text{-}H}$ = 6.9 Hz], 1.27 [unresolved t, CH_2, 8H], 1.56 – 1.61 [m, CH_2, 8H], 7.34 – 7.37 [m, 2Ph, 10H]. ^{31}P-NMR ($CDCl_3$): δ -19.6, -19.9. ^{13}C-NMR ($CDCl_3$): δ 13.7 [s, CH_3], 24.1 – 24.3 [pseudo triplet, CH_2], 27.2 – 28.0 [mm, CH_2], 128.2 [m, *p*-Ph], 128.6 [d, *o/m*-Ph, *J* = 3.3 Hz], 132.1 – 132.4 [mm, *o/m*-Ph], 137.9 - 138.0 [m, *ipso*-Ph]. Mass spectrum (EI): *m/z* = 358.2 (10 %) [M^+], 301.3 (18 %) [M^+-Bu].

4.4.2 Synthesis of *cis*-Ph(Bu)PCH=CHP(Bu)Ph



bppey

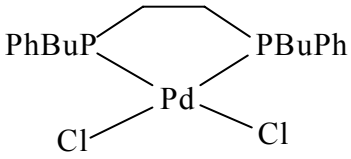
3.0 g (7.57 mmol) of $Ph_2PCH=CHPPh_2$ were dissolved in 100 cm^3 of THF. The solution was then added dropwise to a suspension of 0.29 g (41.8 mmol) granular lithium metal in 100 cm^3 of THF at 0 ºC and the reaction mixture was stirred at 0 ºC for 1 h, whereupon the colourless solution turned red-brown. The mixture was allowed to warm to room temperature and was then stirred for 24 h. The un-reacted lithium metal was removed by filtration. 4 cm^3 (34.1 mmol) of *n*-butylchloride in 30 cm^3 hexane were added dropwise to the red-brown filtrate at 0 ºC while rapidly stirring. The reaction mixture was stirred at room temperature overnight. The solvent was removed *in vacuo* to give a red-brown oil. Dry hexane (2 x 100 cm^3) was added and a yellow-

white precipitate formed, which was separated by filtration. The solvent was removed *in vacuo* and the remaining viscous oil was distilled to give a yellow oil.

Yield: 2.09 g, 78 %. Boiling Point: 110 – 115 ºC / 131.6 mmHg. ^{1}H NMR (DMSO): δ 0.86 [t, CH_3, 3H, $^{3}J_{H-H}$ = 6.8 Hz], 1.28 – 1.40 [m, CH_2, 4H], 2.06 [pseudo t, CH_2, 2H, *J* = 7.2 Hz], 7.30 – 7.40 [m, Ph, CH=CH, 6H]. ^{31}P NMR (DMSO): δ -16.7 ppm. ^{13}C NMR (DMSO): δ 13.5 [s, CH_3], 23.4 [d, CH_2, J_{C-P} = 13.1 Hz], 26.4 [d, CH_2, J_{C-P} = 11.1 Hz], 27.6 [d, CH_2, J_{C-P} = 15.8 Hz], 128.3 [s, *p*-Ph], 128.4 [s, *m/o*-Ph], 132.1 [s, *o/m*-Ph] 132.3 [s, CH=CH], 138.5 [d, *ipso*-Ph, $^{1}J_{C-P}$ = 14.1 Hz]. Mass spectrum (EI): *m/z* = 356.2 (10 %) [M^+], 243.2 (100 %) [M^+-2Bu].

4.5 Synthesis of metal complexes

4.5.1 Synthesis of [$PdCl_2$(Ph(Bu)PCH_2CH_2P(Bu)Ph)]

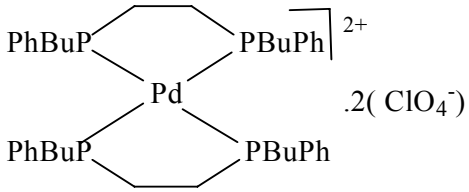


18

0.74 g (4.19 mmol) of $PdCl_2$ were suspended in 10 cm^3 of CH_2Cl_2 and 1.64 g of Ph(Bu)PCH_2CH_2P(Bu)Ph in 10 cm^3 of CH_2Cl_2 were then added dropwise to the mixture at room temperature. After stirring the mixture overnight it was filtered by means of a cannula and the solvent was removed *in vacuo* to give a yellow solid.

Yield: 2.26 g, 92 %. Melting point: 163 – 165 ºC. Calc. for $C_{22}H_{32}P_2PdCl_2$: C, 49.3; H, 6.02 %. Found: C, 49.9; H, 6.28 %. ^{1}H NMR ($CDCl_3$): δ 0.79 [t, CH_3, 3H, $^{3}J_{H-H}$ = 7.1 Hz], 0.91 [t, CH_3, 3H, $^{3}J_{H-H}$ = 7.1 Hz], 1.0 – 1.8 [m, 4xCH_2, 8H], 1.81 – 2.0 [m, 2xCH_2, 4H], 2.1 – 3.0 [m, 4xCH_2, 8H], 7.1 – 7.4 [m, *m/p*-Ph, 6H], 7.80, 8.02 [2xt, *o*-Ph, 4H, J = 7.8, 8.1 Hz]. ^{31}P-NMR ($CDCl_3$): δ 72.2, 72.4. ^{13}C-NMR ($CDCl_3$): δ 13.1 [s, CH_3], 23.5 [m, CH_2], 24.5 [m, CH_2,], 26.2 [d, CH_2, $^{1}J_{C-P}$ = 21.0 Hz], 27.9 [m, CH_2], 128.9 – 129.2 [m, *m*-Ph], 131.7 [s, *p*-Ph], 132.0 [s, *p*-Ph], 132.4 [t, *o*-Ph, *J* = 5.3 Hz], 133.2 [pseudo t, *o*-Ph]. Mass spectrum (FAB): *m/z* = 501.2 (20 %) [M^+-Cl], 407.1 (5 %) [Pd(bppe)$^+$-Bu].

4.5.2 Synthesis of $[Pd(Ph(Bu)PCH_2CH_2P(Bu)Ph)_2](ClO_4)_2$

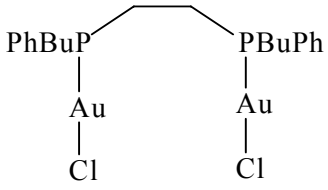


20

0.19 g (0.35 mmol) of **18** were dissolved in 10 cm^3 of DMF. 0.078 g (0.39 mmol) of $AgClO_4$ were added to the mixture at room temperature and the reaction mixture was stirred overnight. 0.067 g of $Ph(Bu)PCH_2CH_2P(Bu)Ph$ in 5.0 cm^3 of CH_2Cl_2 were added to the reaction mixture. After stirring the reaction mixture overnight the mixture was filtered and the solvent was removed to give a sticky yellow residue. 20 cm^3 of CH_2Cl_2 were added and the light yellow solution was filtered by means of a cannula. The solvent was removed *in vacuo* to give a cream-white solid.

Yield: 0.1 g, 54 %. Calc. for $C_{44}H_{64}P_4Pd(ClO_4)_2$: C, 51.7; H, 6.3 %. Found: C, 49.4; H, 6.33 %. ^{31}P-NMR ($CDCl_3$): δ 51.9 and 54.4 (Isomeric mixture). ^{1}H NMR ($CDCl_3$): δ 0.75 [t, CH_3, 12H, $^3J_{H\text{-}H}$ = 6.9Hz], 1.13 – 1.19 [br m, CH_2, 16H], 1.25 – 1.50 [m, CH_2, 16H], 7.39 - 7.65 [m, Ph, 20H]. ^{31}P-NMR ($CDCl_3$): δ 51.9, (Both ^{1}H and ^{31}P NMR spectroscopic data were from the grown crystals of **20**). Mass spectrum (FAB): *m/z* = 822.5 (34 %) [M^+ - $2ClO_4^-$], 765.5 (62 %) [M^+-Bu].

4.5.3 Synthesis of $ClAu(Ph(Bu)PCH_2CH_2P(Bu)Ph)AuCl$



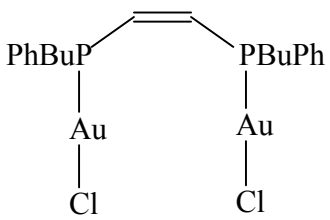
21a

0.17 g (0.56 mmol) of $[AuCl(SMe_2)]$ were dissolved in 10 cm^3 of CH_2Cl_2. A solution of 0.10 g (0.28 mmol) of $Ph(Bu)PCH_2CH_2P(Bu)Ph$ in 5 cm^3 of CH_2Cl_2 was then added slowly to the reaction mixture at room temperature. After the mixture was stirred for 2 h at room temperature the reaction mixture was filtered by means of a cannula and the solvent removed *in vacuo* to give a white solid.

Yield: 0.17 g, 74 %. ^{1}H NMR ($CDCl_3$): δ 0.81 – 0.92 [m, $2CH_3$, 6H], 1.35 – 1.42 [m, CH_2, 8H], 2.07 – 2.10 [m, CH_2, 4H], 2.40 – 2.44 [m, CH_2, 2H], 7.46 – 7.63 [m,

Ph, 10H]. ^{31}P-NMR ($CDCl_3$): δ 33.2, 32.4. Mass spectrum (FAB): *m/z* = 786.7 (100 %) [M^+-Cl], 555.4 (18 %) $[Au(bppe)]^+$.

4.5.4 Synthesis of ClAu(Ph(Bu)PCH=CHP(Bu)Ph)AuCl

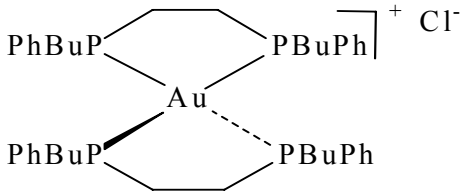


21b

0.17 g (0.56 mmol) of [$AuCl(SMe_2)$] were dissolved in 10 cm^3 of CH_2Cl_2. A solution of 0.10 g (0.28 mmol) of Ph(Bu)PCHCHP(Bu)Ph in 5.0 cm^3 of CH_2Cl_2 was then added slowly to the reaction mixture at room temperature. After the mixture was stirred for 3 h at room temperature the brown mixture was filtered by means of a cannula and the solvent was removed *in vacuo* to give a brown solid.

Yield: 0.18 g, 78 %. ^{1}H NMR (DMSO): δ 0.69 [t, CH_3, 3H, $^3J_{H\text{-}H}$ = 6.7 Hz], 1.24 [s, CH_2, 4H], 2.44 [m, CH_2, 2H], 7.40 – 7.60 [m, Ph / HC=CH, 6H]. ^{31}P-NMR (DMSO): δ 31.5. Mass spectrum (FAB): *m/z* = 785.2 (0.5 %) [M^+-Cl], 439.2 (25 %) $[Au(PhPCH=CHPPh)]^+$.

4.5.5 Synthesis of [Au{Ph(Bu)PCH$_2$CH$_2$P(Bu)Ph}$_2$]Cl



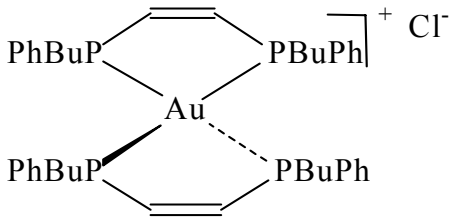
22a

0.49 g (1.68 mmol) of [$AuCl(SMe_2)$] were dissolved in 10 cm^3 of CH_2Cl_2. A solution of 1.20 g (3.35 mmol) of Ph(Bu)PCH$_2$CH$_2$P(Bu)Ph in 10 cm^3 of CH_2Cl_2 was then added dropwise to the reaction mixture at room temperature. The reaction mixture was stirred overnight at room temperature. The colourless mixture was filtered by means of a cannula and the solvent removed *in vacuo* to give a white solid.

Yield: 1.35 g, 85 %. Calc. for $C_{44}H_{64}AuP_4Cl$: C, 55.7; H, 6.79 %. Found: C, 53.7; H, 6.77 %. ^{1}H NMR ($CDCl_3$): δ 0.70 – 0.86 [m, CH_3, 12H], 0.91 – 1.45 [m, CH_2, 16H], 1.91 – 2.15 [m, CH_2, 16H], 7.27 – 7.65 [m, Ph, 20H]. ^{31}P-NMR ($CDCl_3$): δ 15.1 and 15.5 (Isomeric mixture). ^{13}C-NMR ($CDCl_3$): δ 13.3 [s, CH_3], 23.6 [s,

CH_2], 24.0 [s, CH_2], 27.4 [m, CH_2], 29.0 [m, CH_2], 128.8 [d, Ph, $J_{C\text{-}P}$ = 9.8 Hz], 129.1 [br s, Ph], 130.4 [s, Ph], 133.0 [d, *ipso*-Ph, $^1J_{C\text{-}P}$ = 13.9 Hz]. Mass spectrum (FAB): *m/z* = 913.2 (100 %) [M^+-Cl], 555.2 (22 %) [Au(bppe)$^+$].

4.5.6 Synthesis of [Au(Ph(Bu)PHC=CHP(Bu)Ph)$_2$]Cl

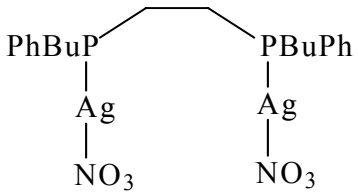


22b

0.44 g (1.49 mmol) of [AuCl(SMe$_2$)] were dissolved in 15 cm^3 of CH_2Cl_2. A solution of 1.09 g (2.97 mmol) of Ph(Bu)PHC=CHP(Bu)Ph in 20 cm^3 of CH_2Cl_2 was then added dropwise to the reaction mixture at room temperature and the mixture was stirred overnight. The brown mixture was filtered by means of a cannula and the solvent was removed *in vacuo* to give a brown solid. The solid was washed with a mixture of CH_2Cl_2/hexane and then dried *in vacuo*.

Yield: 1.31 g, 93 %. Calc. for $C_{44}H_{60}AuP_4Cl$: C, 55.9; H, 6.4 %. Found: C, 53.2; H, 5.97 %. ^{1}H NMR (DMSO): δ 0.73 [m, CH_3, 12H], 1.28 [m, CH_2, 18H], 2.36 [m, CH_2, 6H], 7.40 – 7.51 [m, Ph, CH=CH, 24H]. ^{31}P-NMR (DMSO): δ 22.3. ^{13}C-NMR (DMSO): δ 13.7 [s, CH_3], 20.4, [s, CH_2], 24.5 [m, CH_2], 28.0 [m, CH_2], 129.3 [s, *p*-Ph], 131.9 [m, *o/m*-Ph], 132.3 [m, *o/m*-Ph], 133.9 [s, -CH=CH-], 135.5 [m, *ipso*-Ph]. Mass spectrum (FAB): *m/z* = 909.3 (1.5 %) [M^+-Cl], 795.2 (6.0 %) [M^+-2Bu], 681.3 (100 %) [M^+-4Bu].

4.5.7 Synthesis of [(NO$_3$)Ag(Ph(Bu)PCH$_2$CH$_2$P(Bu)Ph)Ag(NO$_3$)]

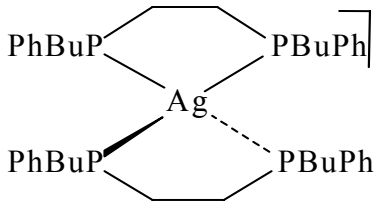


23

0.096 g (0.57 mmol) of $AgNO_3$ were suspended in 15 cm^3 of CH_2Cl_2. A solution of 0.10 g (0.28 mmol) of Ph(Bu)PCH$_2$CH$_2$P(Bu)Ph in 10 cm^3 CH_2Cl_2 was slowly added to the reaction mixture at room temperature. After the mixture was stirred for 90 minutes at room temperature the mixture was filtered by means of a cannula and the solvent removed to give a brown solid.

Yield: 0.1 g, 51 %. ^{1}H NMR ($CDCl_3$): δ 0.71 – 0.87 [m, 2xCH_3, 6H], 1.22 – 1.29 [m, 4xCH_2, 8H], 1.87 – 2.24 [m, 4xCH_2, 8H], 7.31 – 7.60 [m, 2xPh, 10H]. ^{31}P-NMR ($CDCl_3$): δ 9.5 ppm [d, J = 223 Hz]. ^{13}C-NMR ($CDCl_3$): δ 13.50 [s, CH_3], 13.52 [s, CH_3], 23.8 [s, CH_2], 24.0 [s, CH_2], 27.7 [s, CH_2], 125.5 – 133.5 (m, Ph). Mass spectrum (FAB): *m/z* = 636.2 (6.8 %) [Ag_2(bppe)NO_3^+], 466.3 (61 %) [Ag(bppe)]$^+$.

4.5.8 Synthesis of [Ag(Ph(Bu)P(CH_2CH_2P(Bu)Ph)$_2$]ClO_4



24

0.36 g (1.68 mmol) $AgClO_4$ were suspended in 10 cm^3 of CH_2Cl_2. A solution of 1.20 g (3.35 mmol) of Ph(Bu)PCH_2CH_2P(Bu)Ph in 10 cm^3 of CH_2Cl_2 was then added dropwise to the reaction mixture at room temperature and stirred overnight. The colourless solution was filtered by means of a cannula and the solvent was removed *in vacuo* to give a white solid.

Yield: 1.40 g, 91 %. Calc. for $C_{44}H_{64}AgClO_4$: C, 57.2; H, 7.0 %. Found: C, 55.8; H, 6.82 %. ^{1}H NMR ($CDCl_3$): δ 0.72 – 0.88 [m, CH_3, 3H], 1.29 -1.4 [m, CH_2, 4H], 1.9 – 2.3 [m, CH_2, 4H], 7.34 – 7.50 [m, Ph, 5H]. ^{31}P-NMR ($CDCl_3$): δ -2.07 [d, $J_{Ag\text{-}P}$ = 240 Hz]. ^{13}C-NMR ($CDCl_3$): δ 13.6 [s, CH_3], 24.1 [s, br, CH_2], 27.8 [s, br, CH_2], 128.9 – 132.7 (Ph). Mass spectrum (FAB): *m/z* = 823.5 (31 %) [M^+-ClO_4^-], 465.2(100 %) [Ag(bppe)]$^+$.

Appendix 1

Crystallographic data for compound **17**, **18** and **20**.

Table A1: Summary data for collection and refinement for compound **17**, **18**, **20**.

Compound	**17**	**18**	**20**
Empirical formula	$C_{32}H_{60}Li_2N_4P_2$	$C_{22}H_{32}Cl_2P_2Pd$	$C_{44}H_{64}Cl_2O_8P_4Pd$
Formula weight	576.66	535.72	1022.13
Temperature (K)	173(2)	173(2)	173(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic	Orthorhombic
Space group	*P2(1)/n*	*Pna21*	*Pbcn*
a (Å)	37.6222(18)	19.7168(10)	15.213(5)
b (Å)	15.5696(7)	12.6146(6)	17.937(5)
c (Å)	38.5633(18)	9.9877(4)	17.937(5)
α (º)	90	90	90
β (º)	91.659(4)	90	90
γ (º)	90	90	90
Volume ($Å^3$)	22579.5(18)	2484.1(2)	4895(3)

Table A1: *continued…*

Z, cal. dens. Mg m-3)	24, 1.018	4, 1.432	4, 1.387
Abs. oeff.(mm-1)	0.139	1.096	0.667
F(000)	7584	1096	2128
Crystal size (mm)	0.36 x 0.32 x 0.18	0.42 x 0.34 x 0.16	0.36 x 0.28 x 0.16
2θ Range (º)	0.77 to 26.00	1.92 to 27.50	1.76 to 26.00
Index ranges	-46<=h<=46	-19<=h<=25	-18<=h<=18
	-16<=k<=19	-12<=k<=16	-20<=k<=22
	-47<=l<=34	-12<=l<=12	-21<=l<=21
Reflection collected	69123	13077	40863
Indep. Refs.	43740 [R(int) = 0.0991]	5500 [R(int) = 0.0474]	4799 [R(int) = 0.1560]
Completeness to 2θ (%)	26.00, 98.6 %	27.50, 100.0 %	26.00, 99.8 %
Max. and min. trns.	0.9754 0.9516	0.8441 0.6560	0.9008 and 0.7952
Refinement method	Full-matrix least-squares on F2	Full-matrix least-squares on F2	Full-matrix least-squares on F2
Data/rest./parameters	43740 / 1926 / 2161	5500 / 1 / 244	4799 / 0 / 257
Good.-of-fit on F2	1.025	0.997	1.163
Final R indices [I>2sigma(I)]	R1 = 0.0964	R1 = 0.0355	R1 = 0.1212

Table A1: *continued…*

R indices (all data)	wR2 = 0.2015 R1 = 0.2857 wR2 = 0.2836	wR2 = 0.0831 R1 = 0.0442, wR2 = 0.0868	wR2 = 0.2514 R1 = 0.1665 wR2 = 0.2788
Largest difference peak and hole	0.586 and -0.339 e.A^{-3}	0.895 and -0.374 e.Å^{-3}	5.318 and -1.750 e.Å^{-3}

Appendix 2

Comprehensive crystallographic data for **17**.

Table A2.1: Bond lengths [Å] for **17**.

N(16)-C(304)	1.444(8)	N(8)-C(020)	1.483(7)
N(16)-C(411)	1.497(8)	N(8)-C(005)	1.495(7)
N(16)-C(106)	1.494(7)	N(8)-Li(7)	2.138(11)
N(16)-Li(10)	2.137(11)	C(005)-C(011)	1.489(8)
N(17)-C(303)	1.452(8)	C(006)-C(017)	1.318(7)
N(17)-C(410)	1.481(8)	C(007)-C(022)	1.367(8)
N(17)-C(302)	1.485(7)	C(008)-C(018)	1.544(8)
N(17)-Li(10)	2.137(12)	C(009)-C(014)	1.514(7)
C(200)-C(025)	1.519(9)	C(010)-C(012)	1.386(8)
Li(11)-N(18)	2.118(11)	C(012)-C(023)	1.365(8)
Li(11)-N(19)	2.149(12)	C(013)-C(022)	1.404(8)
Li(11)-P(10)	2.541(10)	C(013)-C(017)	1.409(8)
Li(11)-P(9)	2.589(10)	C(014)-C(021)	1.554(7)
Li(11)-Li(14)	3.544(15)	C(015)-C(019)	1.351(8)
Li(10)-P(7)	2.597(10)	C(018)-C(025)	1.503(8)
Li(10)-P(8)	2.597(10)	C(019)-C(023)	1.394(8)
Li(10)-C(410)	2.804(13)	C(021)-C(024)	1.520(8)
C(311)-N(15)	1.418(10)	P(2)-C(033)	1.795(6)
C(12)-N(15)	1.480(9)	P(2)-C(034)	1.826(5)
C(310)-C(156)	1.290(15)	P(2)-Li(5)	2.578(9)
C(310)-N(14)	1.518(12)	P(2)-Li(6)	2.603(9)
C(310)-Li(3)	2.773(15)	P(4)-C(031)	1.803(6)
Li(12)-N(6)	2.134(10)	P(4)-C(041)	1.837(5)
Li(12)-N(5)	2.117(11)	P(4)-Li(6)	2.553(9)
Li(12)-P(1)	2.577(9)	P(4)-Li(5)	2.595(9)
Li(12)-P(3)	2.606(9)	N(4)-C(054)	1.474(7)
Li(12)-C(184)	2.795(11)	N(4)-C(042)	1.466(7)
P(1)-C(001)	1.786(5)	N(4)-C(038)	1.503(7)
P(1)-C(009)	1.850(5)	N(4)-Li(5)	2.108(11)
P(1)-Li(7)	2.599(9)	C(029)-C(044)	1.335(9)
P(3)-C(003)	1.801(6)	C(029)-C(033)	1.409(7)
P(3)-C(008)	1.840(5)	N(3)-C(039)	1.480(7)
P(3)-Li(7)	2.569(9)	N(3)-C(049)	1.463(7)
C(001)-C(007)	1.421(7)	N(3)-C(045)	1.462(6)
C(001)-C(006)	1.430(7)	N(3)-Li(5)	2.123(10)
N(7)-C(027)	1.458(7)	C(031)-C(035)	1.410(7)
N(7)-C(011)	1.496(8)	C(031)-C(032)	1.419(7)
N(7)-C(016)	1.462(6)	C(032)-C(036)	1.335(7)
N(7)-Li(7)	2.136(10)	C(033)-C(037)	1.410(8)
C(003)-C(015)	1.416(8)	C(034)-C(040)	1.529(7)
C(003)-C(010)	1.425(7)	C(035)-C(047)	1.395(8)
N(8)-C(026)	1.473(7)	C(036)-C(046)	1.408(8)

Table A2.1: *continued...*

C(037)-C(052)	1.381(9)	P(6)-C(082)	1.770(6)
C(038)-C(039)	1.470(8)	P(6)-C(085)	1.861(5)
C(039)-Li(5)	2.774(11)	C(082)-C(083)	1.423(7)
C(040)-C(050)	1.538(7)	C(082)-C(084)	1.439(8)
C(041)-C(043)	1.545(8)	C(083)-C(088)	1.366(8)
C(043)-C(051)	1.474(8)	C(084)-C(087)	1.346(8)
C(044)-C(048)	1.387(10)	C(085)-C(086)	1.524(7)
C(046)-C(047)	1.375(8)	C(086)-C(090)	1.536(7)
C(048)-C(052)	1.397(10)	C(087)-C(089)	1.414(9)
C(050)-C(053)	1.517(8)	C(088)-C(089)	1.376(10)
C(051)-C(055)	1.555(9)	C(090)-C(091)	1.528(8)
Li(6)-N(1)	2.099(11)	P(7)-C(096)	1.789(6)
Li(6)-N(2)	2.170(10)	P(7)-C(100)	1.861(5)
Li(6)-C(177)	2.792(11)	P(7)-Li(3)	2.651(11)
P(5)-C(056)	1.787(6)	P(8)-C(098)	1.781(6)
P(5)-C(068)	1.855(5)	P(8)-C(094)	1.875(5)
P(5)-Li(8)	2.564(9)	P(8)-Li(3)	2.631(11)
P(5)-Li(9)	2.607(9)	P(9)-C(135)	1.818(7)
C(056)-C(060)	1.411(7)	P(9)-C(141)	1.852(6)
C(056)-C(058)	1.417(7)	P(9)-Li(14)	2.585(11)
N(23)-C(075)	1.456(7)	P(101)-C(306)	1.804(6)
N(23)-C(081)	1.461(6)	P(101)-C(095)	1.872(5)
N(23)-C(070)	1.491(7)	P(101)-Li(2)	2.613(10)
N(23)-Li(9)	2.162(10)	P(101)-Li(1)	2.640(10)
C(058)-C(059)	1.351(7)	P(100)-C(093)	1.798(6)
C(059)-C(065)	1.412(8)	P(100)-C(103)	1.847(6)
C(060)-C(067)	1.382(8)	P(100)-Li(2)	2.527(10)
N(25)-C(076)	1.448(7)	P(100)-Li(1)	2.562(11)
N(25)-C(072)	1.468(7)	N(18)-C(145)	1.433(8)
N(25)-C(066)	1.498(7)	N(18)-C(154)	1.452(7)
N(25)-Li(8)	2.112(11)	N(18)-C(155)	1.498(8)
N(24)-C(077)	1.470(7)	C(093)-C(105)	1.407(7)
N(24)-C(074)	1.471(6)	C(093)-C(115)	1.420(7)
N(24)-C(069)	1.489(7)	C(094)-C(107)	1.521(7)
N(24)-Li(8)	2.195(10)	C(095)-C(128)	1.499(7)
N(22)-C(071)	1.459(7)	C(096)-C(116)	1.434(8)
N(22)-C(078)	1.463(7)	C(096)-C(110)	1.425(8)
N(22)-C(064)	1.482(7)	N(10)-C(147)	1.449(8)
N(22)-Li(9)	2.116(11)	N(10)-C(134)	1.487(8)
C(064)-C(070)	1.498(8)	N(10)-C(140)	1.483(7)
C(065)-C(067)	1.396(7)	N(10)-Li(1)	2.136(11)
C(066)-C(069)	1.467(8)	C(098)-C(113)	1.437(8)
C(068)-C(073)	1.559(8)	C(098)-C(099)	1.401(7)
C(073)-C(079)	1.433(8)	C(099)-C(120)	1.440(8)
Li(8)-P(6)	2.573(10)	C(100)-C(119)	1.506(7)
Li(9)-P(6)	2.576(9)	C(101)-C(102)	1.508(8)
C(079)-C(080)	1.567(11)	C(101)-C(159)	1.519(8)

Table A2.1: *continued...*

C(102)-C(103)	1.536(8)	C(148)-C(161)	1.517(8)
N(14)-C(158)	1.383(10)	Li(3)-C(156)	2.782(15)
N(14)-C(152)	1.502(8)	C(149)-C(151)	1.332(10)
N(14)-Li(3)	2.109(13)	Li(2)-N(12)	2.151(11)
C(105)-C(108)	1.384(8)	Li(2)-N(13)	2.160(11)
C(306)-C(109)	1.411(7)	P(10)-C(163)	1.842(6)
C(306)-C(111)	1.412(7)	P(10)-C(165)	1.848(6)
C(107)-C(125)	1.513(8)	P(10)-Li(14)	2.577(11)
C(108)-C(124)	1.390(8)	C(162)-C(169)	1.510(8)
C(109)-C(122)	1.390(8)	C(163)-C(167)	1.371(8)
C(110)-C(146)	1.386(8)	C(163)-C(170)	1.395(7)
C(111)-C(123)	1.429(8)	C(164)-C(165)	1.500(8)
N(11)-C(157)	1.465(8)	C(166)-C(167)	1.407(8)
N(11)-C(143)	1.487(8)	C(168)-C(170)	1.351(8)
N(11)-C(150)	1.497(7)	C(168)-C(171)	1.375(9)
N(11)-Li(1)	2.175(12)	N(1)-C(178)	1.471(7)
C(113)-C(142)	1.391(8)	N(1)-C(174)	1.482(7)
N(19)-C(144)	1.438(8)	N(1)-C(175)	1.475(6)
N(19)-C(153)	1.445(8)	N(2)-C(179)	1.463(7)
N(19)-C(139)	1.459(8)	N(2)-C(176)	1.461(7)
C(115)-C(117)	1.391(8)	N(2)-C(177)	1.488(7)
C(116)-C(137)	1.362(8)	C(174)-C(177)	1.457(8)
C(117)-C(124)	1.348(8)	N(5)-C(186)	1.442(7)
C(118)-C(119)	1.512(8)	N(5)-C(183)	1.451(7)
C(118)-C(136)	1.536(8)	N(6)-C(184)	1.486(8)
C(120)-C(126)	1.339(8)	N(6)-C(185)	1.468(6)
C(121)-C(123)	1.329(8)	N(6)-C(187)	1.467(7)
C(121)-C(122)	1.422(8)	C(182)-C(184)	1.452(8)
C(125)-C(127)	1.477(9)	N(13)-C(193)	1.431(8)
C(126)-C(142)	1.378(8)	N(13)-C(191)	1.453(9)
C(128)-C(132)	1.531(8)	N(13)-C(195)	1.468(7)
C(129)-C(161)	1.508(8)	N(12)-C(190)	1.454(8)
C(130)-C(146)	1.386(9)	N(12)-C(192)	1.456(8)
C(130)-C(137)	1.390(9)	N(12)-C(194)	1.459(7)
C(131)-C(151)	1.367(9)	C(191)-C(192)	1.445(10)
C(131)-C(135)	1.405(8)	N(21)-C(401)	1.474(8)
C(132)-C(415)	1.448(9)	N(21)-C(421)	1.457(9)
C(133)-C(135)	1.392(8)	N(21)-C(402)	1.500(7)
C(133)-C(160)	1.390(9)	N(21)-Li(14)	2.112(12)
C(134)-C(143)	1.468(9)	C(411)-C(410)	1.446(10)
N(15)-C(156)	1.465(12)	N(20)-C(430)	1.386(9)
N(15)-Li(3)	2.182(13)	N(20)-C(403)	1.505(8)
C(139)-C(145)	1.530(10)	N(20)-Li(14)	2.168(13)
C(141)-C(148)	1.516(8)	Li(14)-C(421)	2.775(13)

Table A2.2: Bond angles [°] for **17**.

C(304)-N(16)-C(411)	112.0(6)	C(001)-P(1)-C(009)	103.4(2)
C(304)-N(16)-C(106)	108.9(5)	C(001)-P(1)-Li(12)	113.9(3)
C(411)-N(16)-C(106)	108.7(5)	C(009)-P(1)-Li(12)	128.4(3)
C(304)-N(16)-Li(10)	117.9(5)	C(001)-P(1)-Li(7)	96.3(3)
C(411)-N(16)-Li(10)	100.3(5)	C(009)-P(1)-Li(7)	123.6(3)
C(106)-N(16)-Li(10)	108.5(5)	Li(12)-P(1)-Li(7)	87.3(3)
C(303)-N(17)-C(410)	111.2(6)	C(003)-P(3)-C(008)	103.0(3)
C(303)-N(17)-C(302)	108.6(5)	C(003)-P(3)-Li(7)	113.0(3)
C(410)-N(17)-C(302)	109.7(5)	C(008)-P(3)-Li(7)	125.8(3)
C(303)-N(17)-Li(10)	118.4(5)	C(003)-P(3)-Li(12)	97.8(3)
C(410)-N(17)-Li(10)	100.1(5)	C(008)-P(3)-Li(12)	127.1(3)
C(302)-N(17)-Li(10)	108.5(5)	Li(7)-P(3)-Li(12)	87.3(3)
N(18)-Li(11)-N(19)	87.9(4)	C(007)-C(001)-C(006)	111.9(5)
N(18)-Li(11)-P(10)	119.4(4)	C(007)-C(001)-P(1)	120.1(4)
N(19)-Li(11)-P(10)	115.6(5)	C(006)-C(001)-P(1)	127.9(4)
N(18)-Li(11)-P(9)	121.0(5)	C(027)-N(7)-C(011)	109.4(5)
N(19)-Li(11)-P(9)	122.4(5)	C(027)-N(7)-C(016)	109.7(5)
P(10)-Li(11)-P(9)	93.2(3)	C(011)-N(7)-C(016)	110.0(5)
N(18)-Li(11)-Li(14)	139.5(5)	C(027)-N(7)-Li(7)	114.0(5)
N(19)-Li(11)-Li(14)	132.4(5)	C(011)-N(7)-Li(7)	99.1(4)
P(10)-Li(11)-Li(14)	46.6(2)	C(016)-N(7)-Li(7)	114.1(4)
P(9)-Li(11)-Li(14)	46.7(2)	C(015)-C(003)-C(010)	114.5(6)
N(17)-Li(10)-N(16)	88.8(4)	C(015)-C(003)-P(3)	119.5(4)
N(17)-Li(10)-P(7)	120.7(4)	C(010)-C(003)-P(3)	125.9(5)
N(16)-Li(10)-P(7)	118.8(4)	C(026)-N(8)-C(020)	110.8(5)
N(17)-Li(10)-P(8)	120.8(5)	C(026)-N(8)-C(005)	111.3(5)
N(16)-Li(10)-P(8)	119.2(4)	C(020)-N(8)-C(005)	109.7(5)
P(7)-Li(10)-P(8)	91.5(3)	C(026)-N(8)-Li(7)	113.3(5)
N(17)-Li(10)-C(410)	31.3(2)	C(020)-N(8)-Li(7)	110.4(4)
N(16)-Li(10)-C(410)	58.3(3)	C(005)-N(8)-Li(7)	101.0(4)
P(7)-Li(10)-C(410)	139.4(4)	C(011)-C(005)-N(8)	111.5(5)
P(8)-Li(10)-C(410)	126.6(4)	C(017)-C(006)-C(001)	125.2(6)
C(156)-C(310)-N(14)	121.0(11)	C(022)-C(007)-C(001)	124.2(6)
C(156)-C(310)-Li(3)	77.0(8)	C(018)-C(008)-P(3)	114.4(4)
N(14)-C(310)-Li(3)	48.8(5)	C(014)-C(009)-P(1)	116.2(4)
N(6)-Li(12)-N(5)	87.8(4)	C(012)-C(010)-C(003)	121.3(6)
N(6)-Li(12)-P(1)	123.9(4)	N(7)-C(011)-C(005)	112.2(5)
N(5)-Li(12)-P(1)	116.4(4)	C(023)-C(012)-C(010)	121.9(6)
N(6)-Li(12)-P(3)	117.1(4)	C(022)-C(013)-C(017)	116.6(6)
N(5)-Li(12)-P(3)	122.4(4)	C(009)-C(014)-C(021)	114.3(5)
P(1)-Li(12)-P(3)	92.5(3)	C(019)-C(015)-C(003)	123.2(6)
N(6)-Li(12)-C(184)	31.6(2)	C(006)-C(017)-C(013)	121.5(6)
N(5)-Li(12)-C(184)	57.7(3)	C(025)-C(018)-C(008)	114.3(6)
P(1)-Li(12)-C(184)	125.3(4)	C(015)-C(019)-C(023)	121.1(7)
P(3)-Li(12)-C(184)	139.3(4)	C(024)-C(021)-C(014)	115.2(5)

Table A2.2: *continued...*

C(007)-C(022)-C(013)	120.5(6)	N(3)-C(039)-Li(5)	49.1(3)
C(012)-C(023)-C(019)	118.0(7)	C(038)-C(039)-Li(5)	76.5(4)
N(7)-Li(7)-N(8)	88.4(4)	C(034)-C(040)-C(050)	114.3(5)
N(7)-Li(7)-P(3)	121.3(4)	C(043)-C(041)-P(4)	115.7(4)
N(8)-Li(7)-P(3)	117.6(4)	C(051)-C(043)-C(041)	114.5(6)
N(7)-Li(7)-P(1)	119.8(4)	C(029)-C(044)-C(048)	121.0(8)
N(8)-Li(7)-P(1)	119.8(4)	C(047)-C(046)-C(036)	117.4(6)
P(3)-Li(7)-P(1)	92.9(3)	C(035)-C(047)-C(046)	120.8(6)
C(018)-C(025)-C(200)	112.8(6)	C(044)-C(048)-C(052)	119.2(8)
C(033)-P(2)-C(034)	104.1(3)	C(053)-C(050)-C(040)	113.1(5)
C(033)-P(2)-Li(5)	114.0(3)	C(043)-C(051)-C(055)	111.3(7)
C(034)-P(2)-Li(5)	127.2(3)	C(037)-C(052)-C(048)	118.3(8)
C(033)-P(2)-Li(6)	96.8(3)	N(1)-Li(6)-N(2)	87.9(4)
C(034)-P(2)-Li(6)	123.4(3)	N(1)-Li(6)-P(4)	118.4(4)
Li(5)-P(2)-Li(6)	87.6(3)	N(2)-Li(6)-P(4)	122.2(4)
C(031)-P(4)-C(041)	103.7(2)	N(1)-Li(6)-P(2)	120.5(4)
C(031)-P(4)-Li(6)	114.4(3)	N(2)-Li(6)-P(2)	118.6(4)
C(041)-P(4)-Li(6)	124.9(3)	P(4)-Li(6)-P(2)	92.2(3)
C(031)-P(4)-Li(5)	97.6(3)	N(1)-Li(6)-C(177)	57.5(3)
C(041)-P(4)-Li(5)	125.2(3)	N(2)-Li(6)-C(177)	31.9(2)
Li(6)-P(4)-Li(5)	88.4(3)	P(4)-Li(6)-C(177)	125.2(4)
C(054)-N(4)-C(042)	109.8(5)	P(2)-Li(6)-C(177)	139.9(4)
C(054)-N(4)-C(038)	110.9(5)	N(4)-Li(5)-N(3)	88.3(4)
C(042)-N(4)-C(038)	109.4(5)	N(4)-Li(5)-P(4)	119.8(4)
C(054)-N(4)-Li(5)	114.3(5)	N(3)-Li(5)-P(4)	120.7(4)
C(042)-N(4)-Li(5)	110.8(4)	N(4)-Li(5)-P(2)	119.1(4)
C(038)-N(4)-Li(5)	101.3(4)	N(3)-Li(5)-P(2)	120.1(4)
C(044)-C(029)-C(033)	123.5(7)	P(4)-Li(5)-P(2)	91.8(3)
C(039)-N(3)-C(049)	110.6(5)	N(4)-Li(5)-C(039)	57.9(3)
C(039)-N(3)-C(045)	110.0(5)	N(3)-Li(5)-C(039)	31.8(2)
C(049)-N(3)-C(045)	108.5(5)	P(4)-Li(5)-C(039)	141.3(4)
C(039)-N(3)-Li(5)	99.1(4)	P(2)-Li(5)-C(039)	124.2(4)
C(049)-N(3)-Li(5)	115.9(5)	C(056)-P(5)-C(068)	103.0(2)
C(045)-N(3)-Li(5)	112.3(4)	C(056)-P(5)-Li(8)	109.8(3)
C(035)-C(031)-C(032)	113.9(5)	C(068)-P(5)-Li(8)	127.4(3)
C(035)-C(031)-P(4)	119.5(4)	C(056)-P(5)-Li(9)	93.2(3)
C(032)-C(031)-P(4)	126.4(4)	C(068)-P(5)-Li(9)	129.6(3)
C(036)-C(032)-C(031)	123.7(6)	Li(8)-P(5)-Li(9)	88.7(3)
C(029)-C(033)-C(037)	114.1(6)	C(060)-C(056)-C(058)	113.6(5)
C(029)-C(033)-P(2)	127.1(5)	C(060)-C(056)-P(5)	119.3(4)
C(037)-C(033)-P(2)	118.8(5)	C(058)-C(056)-P(5)	127.1(4)
C(040)-C(034)-P(2)	117.2(4)	C(075)-N(23)-C(081)	109.0(5)
C(047)-C(035)-C(031)	122.6(5)	C(075)-N(23)-C(070)	110.8(5)
C(032)-C(036)-C(046)	121.5(6)	C(081)-N(23)-C(070)	110.2(5)
C(052)-C(037)-C(033)	123.8(7)	C(075)-N(23)-Li(9)	114.7(5)
C(039)-C(038)-N(4)	109.8(5)	C(081)-N(23)-Li(9)	112.4(4)
N(3)-C(039)-C(038)	113.1(5)	C(070)-N(23)-Li(9)	99.4(4)

Table A2.2: *continued...*

C(059)-C(058)-C(056)	123.6(5)	Li(8)-P(6)-Li(9)	89.2(3)
C(058)-C(059)-C(065)	121.9(5)	C(083)-C(082)-C(084)	113.7(6)
C(067)-C(060)-C(056)	123.6(5)	C(083)-C(082)-P(6)	126.2(5)
C(076)-N(25)-C(072)	111.0(5)	C(084)-C(082)-P(6)	119.9(4)
C(076)-N(25)-C(066)	110.5(5)	C(088)-C(083)-C(082)	122.6(7)
C(072)-N(25)-C(066)	109.7(5)	C(087)-C(084)-C(082)	123.6(6)
C(076)-N(25)-Li(8)	113.0(5)	C(086)-C(085)-P(6)	116.5(4)
C(072)-N(25)-Li(8)	109.9(5)	C(085)-C(086)-C(090)	113.0(5)
C(066)-N(25)-Li(8)	102.5(4)	C(084)-C(087)-C(089)	120.2(7)
C(077)-N(24)-C(074)	108.3(5)	C(083)-C(088)-C(089)	121.6(7)
C(077)-N(24)-C(069)	110.0(5)	C(088)-C(089)-C(087)	118.2(7)
C(074)-N(24)-C(069)	109.4(5)	C(091)-C(090)-C(086)	113.5(6)
C(077)-N(24)-Li(8)	116.4(5)	C(096)-P(7)-C(100)	100.9(3)
C(074)-N(24)-Li(8)	113.4(4)	C(096)-P(7)-Li(10)	96.1(3)
C(069)-N(24)-Li(8)	98.9(4)	C(100)-P(7)-Li(10)	123.2(3)
C(071)-N(22)-C(078)	110.2(5)	C(096)-P(7)-Li(3)	102.7(3)
C(071)-N(22)-C(064)	109.7(5)	C(100)-P(7)-Li(3)	137.1(3)
C(078)-N(22)-C(064)	109.7(5)	Li(10)-P(7)-Li(3)	89.2(3)
C(071)-N(22)-Li(9)	110.9(4)	C(098)-P(8)-C(094)	101.8(3)
C(078)-N(22)-Li(9)	114.2(5)	C(098)-P(8)-Li(10)	101.7(3)
C(064)-N(22)-Li(9)	101.8(4)	C(094)-P(8)-Li(10)	129.1(3)
N(22)-C(064)-C(070)	111.2(5)	C(098)-P(8)-Li(3)	97.3(3)
C(067)-C(065)-C(059)	116.2(6)	C(094)-P(8)-Li(3)	130.7(3)
C(069)-C(066)-N(25)	112.2(5)	Li(10)-P(8)-Li(3)	89.6(3)
C(060)-C(067)-C(065)	121.1(6)	C(135)-P(9)-C(141)	105.5(3)
C(073)-C(068)-P(5)	114.7(4)	C(135)-P(9)-Li(14)	101.9(3)
C(066)-C(069)-N(24)	112.5(5)	C(141)-P(9)-Li(14)	123.2(3)
N(23)-C(070)-C(064)	112.2(5)	C(135)-P(9)-Li(11)	104.6(3)
C(079)-C(073)-C(068)	115.8(6)	C(141)-P(9)-Li(11)	131.0(3)
N(25)-Li(8)-N(24)	87.1(4)	Li(14)-P(9)-Li(11)	86.5(3)
N(25)-Li(8)-P(5)	120.1(4)	C(306)-P(101)-C(095)	102.4(2)
N(24)-Li(8)-P(5)	119.1(4)	C(306)-P(101)-Li(2)	103.9(3)
N(25)-Li(8)-P(6)	120.3(4)	C(095)-P(101)-Li(2)	132.9(3)
N(24)-Li(8)-P(6)	122.0(4)	C(306)-P(101)-Li(1)	94.8(3)
P(5)-Li(8)-P(6)	91.6(3)	C(095)-P(101)-Li(1)	129.1(3)
N(22)-Li(9)-N(23)	87.9(4)	Li(2)-P(101)-Li(1)	86.6(3)
N(22)-Li(9)-P(6)	116.6(4)	C(093)-P(100)-C(103)	104.7(3)
N(23)-Li(9)-P(6)	119.9(4)	C(093)-P(100)-Li(2)	101.2(3)
N(22)-Li(9)-P(5)	123.8(4)	C(103)-P(100)-Li(2)	120.6(3)
N(23)-Li(9)-P(5)	121.4(4)	C(093)-P(100)-Li(1)	102.7(3)
P(6)-Li(9)-P(5)	90.5(3)	C(103)-P(100)-Li(1)	132.9(3)
C(073)-C(079)-C(080)	111.1(7)	Li(2)-P(100)-Li(1)	90.1(3)
C(082)-P(6)-C(085)	104.0(3)	C(145)-N(18)-C(154)	109.7(6)
C(082)-P(6)-Li(8)	93.8(3)	C(145)-N(18)-C(155)	110.0(6)
C(085)-P(6)-Li(8)	124.6(3)	C(154)-N(18)-C(155)	107.8(6)
C(082)-P(6)-Li(9)	110.9(3)	C(145)-N(18)-Li(11)	103.2(5)
C(085)-P(6)-Li(9)	129.1(3)	C(154)-N(18)-Li(11)	109.6(5)

Table A2.2: *continued...*

C(155)-N(18)-Li(11)	116.4(5)	C(153)-N(19)-C(139)	111.0(6)
C(105)-C(093)-C(115)	114.7(5)	C(144)-N(19)-Li(11)	115.5(5)
C(105)-C(093)-P(100)	119.2(4)	C(153)-N(19)-Li(11)	110.7(5)
C(115)-C(093)-P(100)	126.1(4)	C(139)-N(19)-Li(11)	100.8(5)
C(107)-C(094)-P(8)	113.5(4)	C(117)-C(115)-C(093)	120.9(6)
C(128)-C(095)-P(101)	112.4(4)	C(137)-C(116)-C(096)	125.6(7)
C(116)-C(096)-C(110)	113.1(6)	C(124)-C(117)-C(115)	122.2(6)
C(116)-C(096)-P(7)	119.6(5)	C(119)-C(118)-C(136)	114.6(5)
C(110)-C(096)-P(7)	127.3(5)	C(118)-C(119)-C(100)	114.8(5)
C(147)-N(10)-C(134)	110.7(5)	C(126)-C(120)-C(099)	122.7(6)
C(147)-N(10)-C(140)	109.3(5)	C(123)-C(121)-C(122)	119.6(6)
C(134)-N(10)-C(140)	110.9(5)	C(109)-C(122)-C(121)	118.9(6)
C(147)-N(10)-Li(1)	113.3(5)	C(121)-C(123)-C(111)	122.7(6)
C(134)-N(10)-Li(1)	100.3(5)	C(108)-C(124)-C(117)	119.4(6)
C(140)-N(10)-Li(1)	112.1(5)	C(127)-C(125)-C(107)	114.8(7)
C(113)-C(098)-C(099)	114.1(6)	C(120)-C(126)-C(142)	119.2(7)
C(113)-C(098)-P(8)	118.8(5)	C(095)-C(128)-C(132)	113.9(5)
C(099)-C(098)-P(8)	127.1(5)	C(146)-C(130)-C(137)	120.5(7)
C(098)-C(099)-C(120)	120.4(6)	C(151)-C(131)-C(135)	122.6(7)
C(119)-C(100)-P(7)	112.9(4)	C(415)-C(132)-C(128)	116.6(7)
C(102)-C(101)-C(159)	112.2(6)	C(135)-C(133)-C(160)	123.0(7)
C(101)-C(102)-C(103)	112.5(5)	C(143)-C(134)-N(10)	113.1(6)
C(102)-C(103)-P(100)	118.2(4)	C(133)-C(135)-C(131)	114.8(7)
C(158)-N(14)-C(152)	109.7(8)	C(133)-C(135)-P(9)	118.5(5)
C(158)-N(14)-C(310)	113.6(8)	C(131)-C(135)-P(9)	126.8(6)
C(152)-N(14)-C(310)	108.5(7)	C(116)-C(137)-C(130)	118.0(7)
C(158)-N(14)-Li(3)	113.4(6)	C(311)-N(15)-C(156)	111.7(8)
C(152)-N(14)-Li(3)	112.8(6)	C(311)-N(15)-C(12)	106.8(7)
C(310)-N(14)-Li(3)	98.4(7)	C(156)-N(15)-C(12)	110.3(8)
C(108)-C(105)-C(093)	123.7(6)	C(311)-N(15)-Li(3)	113.9(6)
C(109)-C(306)-C(111)	116.9(5)	C(156)-N(15)-Li(3)	97.5(7)
C(109)-C(306)-P(101)	118.2(4)	C(12)-N(15)-Li(3)	116.5(6)
C(111)-C(306)-P(101)	124.9(4)	N(19)-C(139)-C(145)	114.1(6)
C(125)-C(107)-C(094)	114.1(5)	C(148)-C(141)-P(9)	116.3(5)
C(124)-C(108)-C(105)	119.1(6)	C(126)-C(142)-C(113)	119.7(6)
C(306)-C(109)-C(122)	122.7(5)	C(134)-C(143)-N(11)	112.1(6)
C(146)-C(110)-C(096)	122.3(6)	N(18)-C(145)-C(139)	113.5(6)
C(306)-C(111)-C(123)	119.3(5)	C(130)-C(146)-C(110)	120.4(7)
C(157)-N(11)-C(143)	111.9(6)	C(141)-C(148)-C(161)	113.9(6)
C(157)-N(11)-C(150)	108.6(6)	N(14)-Li(3)-N(15)	89.2(5)
C(143)-N(11)-C(150)	109.3(5)	N(14)-Li(3)-P(8)	120.6(5)
C(157)-N(11)-Li(1)	117.1(5)	N(15)-Li(3)-P(8)	116.7(5)
C(143)-N(11)-Li(1)	101.2(5)	N(14)-Li(3)-P(7)	123.5(5)
C(150)-N(11)-Li(1)	108.3(5)	N(15)-Li(3)-P(7)	120.3(5)
C(142)-C(113)-C(098)	123.9(6)	P(8)-Li(3)-P(7)	89.6(4)
C(144)-N(19)-C(153)	109.3(6)	N(14)-Li(3)-C(156)	58.1(4)
C(144)-N(19)-C(139)	109.3(6)	N(15)-Li(3)-C(156)	31.5(3)

Table A2.2: *continued...*

P(8)-Li(3)-C(156)	126.0(5)	C(174)-N(1)-Li(6)	102.0(4)
P(7)-Li(3)-C(156)	139.7(5)	C(175)-N(1)-Li(6)	110.8(4)
N(14)-Li(3)-C(310)	32.8(3)	C(179)-N(2)-C(176)	110.3(5)
N(15)-Li(3)-C(310)	56.8(4)	C(179)-N(2)-C(177)	109.5(5)
P(8)-Li(3)-C(310)	136.1(5)	C(176)-N(2)-C(177)	109.8(5)
P(7)-Li(3)-C(310)	132.9(5)	C(179)-N(2)-Li(6)	115.7(5)
C(156)-Li(3)-C(310)	26.9(3)	C(176)-N(2)-Li(6)	113.0(4)
N(10)-Li(1)-N(11)	86.9(5)	C(177)-N(2)-Li(6)	97.8(4)
N(10)-Li(1)-P(100)	121.3(5)	C(177)-C(174)-N(1)	111.6(5)
N(11)-Li(1)-P(100)	118.5(4)	C(174)-C(177)-N(2)	113.3(5)
N(10)-Li(1)-P(101)	120.5(4)	C(174)-C(177)-Li(6)	75.6(4)
N(11)-Li(1)-P(101)	122.1(5)	N(2)-C(177)-Li(6)	50.4(3)
P(100)-Li(1)-P(101)	90.9(3)	C(186)-N(5)-C(183)	110.7(5)
C(151)-C(149)-C(160)	118.6(8)	C(186)-N(5)-C(182)	109.6(5)
C(149)-C(151)-C(131)	122.2(8)	C(183)-N(5)-C(182)	110.0(5)
C(310)-C(156)-N(15)	122.1(11)	C(186)-N(5)-Li(12)	114.8(5)
C(310)-C(156)-Li(3)	76.2(8)	C(183)-N(5)-Li(12)	109.9(4)
N(15)-C(156)-Li(3)	51.0(5)	C(182)-N(5)-Li(12)	101.5(4)
N(12)-Li(2)-N(13)	86.4(4)	C(184)-N(6)-C(185)	109.9(5)
N(12)-Li(2)-P(100)	114.9(4)	C(184)-N(6)-C(187)	110.7(5)
N(13)-Li(2)-P(100)	121.6(4)	C(185)-N(6)-C(187)	109.2(5)
N(12)-Li(2)-P(101)	124.8(4)	C(184)-N(6)-Li(12)	99.5(4)
N(13)-Li(2)-P(101)	120.1(4)	C(185)-N(6)-Li(12)	112.5(4)
P(100)-Li(2)-P(101)	92.3(3)	C(187)-N(6)-Li(12)	114.7(5)
C(133)-C(160)-C(149)	118.9(8)	C(184)-C(182)-N(5)	111.0(5)
C(129)-C(161)-C(148)	115.0(6)	N(6)-C(184)-C(182)	112.8(5)
C(163)-P(10)-C(165)	104.5(3)	N(6)-C(184)-Li(12)	48.8(3)
C(163)-P(10)-Li(11)	99.4(3)	C(182)-C(184)-Li(12)	76.6(4)
C(165)-P(10)-Li(11)	123.0(3)	C(193)-N(13)-C(191)	109.8(7)
C(163)-P(10)-Li(14)	101.5(3)	C(193)-N(13)-C(195)	109.1(6)
C(165)-P(10)-Li(14)	134.9(3)	C(191)-N(13)-C(195)	110.4(6)
Li(11)-P(10)-Li(14)	87.6(3)	C(193)-N(13)-Li(2)	115.9(5)
C(169)-C(162)-C(164)	113.5(6)	C(191)-N(13)-Li(2)	102.4(5)
C(167)-C(163)-C(170)	116.7(6)	C(195)-N(13)-Li(2)	109.1(5)
C(167)-C(163)-P(10)	117.3(5)	C(190)-N(12)-C(192)	108.8(6)
C(170)-C(163)-P(10)	125.9(5)	C(190)-N(12)-C(194)	109.8(6)
C(165)-C(164)-C(162)	114.8(6)	C(192)-N(12)-C(194)	110.1(6)
C(164)-C(165)-P(10)	118.9(5)	C(190)-N(12)-Li(2)	112.5(5)
C(171)-C(166)-C(167)	117.7(7)	C(192)-N(12)-Li(2)	102.9(5)
C(163)-C(167)-C(166)	123.4(6)	C(194)-N(12)-Li(2)	112.5(5)
C(170)-C(168)-C(171)	122.8(6)	C(192)-C(191)-N(13)	117.5(7)
C(168)-C(170)-C(163)	120.8(6)	C(191)-C(192)-N(12)	116.3(7)
C(168)-C(171)-C(166)	118.6(6)	C(401)-N(21)-C(421)	108.4(6)
C(178)-N(1)-C(174)	111.9(5)	C(401)-N(21)-C(402)	110.6(6)
C(178)-N(1)-C(175)	109.1(5)	C(421)-N(21)-C(402)	111.2(6)
C(174)-N(1)-C(175)	109.4(5)	C(401)-N(21)-Li(14)	114.3(6)
C(178)-N(1)-Li(6)	113.5(5)	C(421)-N(21)-Li(14)	100.4(5)

Table A2.2: *continued...*

C(402)-N(21)-Li(14)	111.6(5)
C(410)-C(411)-N(16)	114.7(7)
C(411)-C(410)-N(17)	115.5(7)
C(411)-C(410)-Li(10)	75.7(5)
N(17)-C(410)-Li(10)	48.6(4)
C(430)-N(20)-C(420)	111.4(7)
C(430)-N(20)-C(403)	108.8(7)
C(420)-N(20)-C(403)	109.3(6)
C(430)-N(20)-Li(14)	117.0(6)
C(420)-N(20)-Li(14)	100.0(5)
C(403)-N(20)-Li(14)	110.1(5)
N(21)-Li(14)-N(20)	89.0(5)
N(21)-Li(14)-P(9)	119.3(5)
N(20)-Li(14)-P(9)	122.1(5)
N(21)-Li(14)-P(10)	119.5(5)
N(20)-Li(14)-P(10)	117.3(5)
P(9)-Li(14)-P(10)	92.5(4)
N(21)-Li(14)-C(421)	31.1(3)
N(20)-Li(14)-C(421)	59.9(4)
P(9)-Li(14)-C(421)	142.6(5)
P(10)-Li(14)-C(421)	120.7(4)
N(21)-Li(14)-Li(11)	132.9(5)
N(20)-Li(14)-Li(11)	138.1(5)
P(9)-Li(14)-Li(11)	46.8(2)
P(10)-Li(14)-Li(11)	45.8(2)
C(421)-Li(14)-Li(11)	158.5(5)
N(20)-C(420)-C(421)	112.0(6)
N(21)-C(421)-C(420)	112.1(6)
N(21)-C(421)-Li(14)	48.5(4)
C(420)-C(421)-Li(14)	76.6(5)

Table A2.3: Torsion angles [º] for **17**.

C(303)-N(17)-Li(10)-N(16)	133.9(5)
C(410)-N(17)-Li(10)-N(16)	13.0(5)
C(302)-N(17)-Li(10)-N(16)	-101.8(5)
C(303)-N(17)-Li(10)-P(7)	-102.9(6)
C(410)-N(17)-Li(10)-P(7)	136.2(5)
C(302)-N(17)-Li(10)-P(7)	21.4(7)
C(303)-N(17)-Li(10)-P(8)	10.1(8)
C(410)-N(17)-Li(10)-P(8)	-110.8(6)
C(302)-N(17)-Li(10)-P(8)	134.4(5)
C(303)-N(17)-Li(10)-C(410)	120.9(7)
C(302)-N(17)-Li(10)-C(410)	-114.8(6)
C(304)-N(16)-Li(10)-N(17)	133.0(5)
C(411)-N(16)-Li(10)-N(17)	11.2(5)
C(106)-N(16)-Li(10)-N(17)	-102.8(5)
C(304)-N(16)-Li(10)-P(7)	8.1(8)
C(411)-N(16)-Li(10)-P(7)	-113.7(6)
C(106)-N(16)-Li(10)-P(7)	132.4(5)
C(304)-N(16)-Li(10)-P(8)	-101.9(6)
C(411)-N(16)-Li(10)-P(8)	136.3(5)
C(106)-N(16)-Li(10)-P(8)	22.3(7)
C(304)-N(16)-Li(10)-C(410)	140.8(6)
C(411)-N(16)-Li(10)-C(410)	19.0(4)
C(106)-N(16)-Li(10)-C(410)	-94.9(5)
N(6)-Li(12)-P(1)-C(001)	138.3(5)
N(5)-Li(12)-P(1)-C(001)	32.0(5)
P(3)-Li(12)-P(1)-C(001)	-96.4(3)
C(184)-Li(12)-P(1)-C(001)	99.7(5)
N(6)-Li(12)-P(1)-C(009)	6.0(7)
N(5)-Li(12)-P(1)-C(009)	-100.3(5)
P(3)-Li(12)-P(1)-C(009)	131.4(3)
C(184)-Li(12)-P(1)-C(009)	-32.6(6)
N(6)-Li(12)-P(1)-Li(7)	-126.1(5)
N(5)-Li(12)-P(1)-Li(7)	127.6(5)
P(3)-Li(12)-P(1)-Li(7)	-0.7(3)
C(184)-Li(12)-P(1)-Li(7)	-164.7(5)
N(6)-Li(12)-P(3)-C(003)	18.4(5)
N(5)-Li(12)-P(3)-C(003)	124.2(5)
P(1)-Li(12)-P(3)-C(003)	-112.1(3)
C(184)-Li(12)-P(3)-C(003)	47.7(7)
N(6)-Li(12)-P(3)-C(008)	-94.5(5)
N(5)-Li(12)-P(3)-C(008)	11.4(6)
P(1)-Li(12)-P(3)-C(008)	135.1(3)
C(184)-Li(12)-P(3)-C(008)	-65.2(7)
N(6)-Li(12)-P(3)-Li(7)	131.2(5)
N(5)-Li(12)-P(3)-Li(7)	-123.0(5)
P(1)-Li(12)-P(3)-Li(7)	0.7(3)
C(184)-Li(12)-P(3)-Li(7)	160.5(7)
C(009)-P(1)-C(001)-C(007)	170.1(5)

Table A2.3: *continued...*

Li(12)-P(1)-C(001)-C(007)	26.7(6)	P(3)-C(003)-C(010)-C(012)	175.9(5)
Li(7)-P(1)-C(001)-C(007)	-63.1(5)	C(027)-N(7)-C(011)-C(005)	165.2(5)
C(009)-P(1)-C(001)-C(006)	-15.1(6)	C(016)-N(7)-C(011)-C(005)	-74.2(6)
Li(12)-P(1)-C(001)-C(006)	-158.5(5)	Li(7)-N(7)-C(011)-C(005)	45.6(6)
Li(7)-P(1)-C(001)-C(006)	111.7(5)	N(8)-C(005)-C(011)-N(7)	-62.9(7)
C(008)-P(3)-C(003)-C(015)	-168.7(5)	C(003)-C(010)-C(012)-C(023)	0.0(10)
Li(7)-P(3)-C(003)-C(015)	-30.2(6)	P(1)-C(009)-C(014)-C(021)	-176.6(4)
Li(12)-P(3)-C(003)-C(015)	60.2(5)	C(010)-C(003)-C(015)-C(019)	-1.4(9)
C(008)-P(3)-C(003)-C(010)	15.1(6)	P(3)-C(003)-C(015)-C(019)	-177.9(5)
Li(7)-P(3)-C(003)-C(010)	153.7(5)	C(001)-C(006)-C(017)-C(013)	0.8(10)
Li(12)-P(3)-C(003)-C(010)	-115.9(5)	C(022)-C(013)-C(017)-C(006)	-1.5(9)
C(026)-N(8)-C(005)-C(011)	159.6(5)	P(3)-C(008)-C(018)-C(025)	178.5(4)
C(020)-N(8)-C(005)-C(011)	-77.5(6)	C(003)-C(015)-C(019)-C(023)	3.5(11)
Li(7)-N(8)-C(005)-C(011)	39.1(6)	C(009)-C(014)-C(021)-C(024)	-176.9(5)
C(007)-C(001)-C(006)-C(017)	0.0(9)	C(001)-C(007)-C(022)-C(013)	-0.8(10)
P(1)-C(001)-C(006)-C(017)	-175.2(5)	C(017)-C(013)-C(022)-C(007)	1.5(10)
C(006)-C(001)-C(007)-C(022)	0.0(9)	C(010)-C(012)-C(023)-C(019)	2.0(10)
P(1)-C(001)-C(007)-C(022)	175.6(5)	C(015)-C(019)-C(023)-C(012)	-3.7(11)
C(003)-P(3)-C(008)-C(018)	68.0(5)	C(027)-N(7)-Li(7)-N(8)	-133.9(5)
Li(7)-P(3)-C(008)-C(018)	-63.3(6)	C(011)-N(7)-Li(7)-N(8)	-17.8(4)
Li(12)-P(3)-C(008)-C(018)	178.4(4)	C(016)-N(7)-Li(7)-N(8)	99.0(5)
C(001)-P(1)-C(009)-C(014)	-69.2(4)	C(027)-N(7)-Li(7)-P(3)	-12.2(7)
Li(12)-P(1)-C(009)-C(014)	66.7(5)	C(011)-N(7)-Li(7)-P(3)	103.9(5)
Li(7)-P(1)-C(009)-C(014)	-176.2(4)	C(016)-N(7)-Li(7)-P(3)	-139.4(5)
C(015)-C(003)-C(010)-C(012)	-0.4(9)	C(027)-N(7)-Li(7)-P(1)	102.3(6)

Table A2.3: *continued...*

C(011)-N(7)-Li(7)-P(1)	-141.6(5)	Li(12)-P(1)-Li(7)-N(8)	124.9(5)
C(016)-N(7)-Li(7)-P(1)	-24.8(7)	C(001)-P(1)-Li(7)-P(3)	114.4(3)
C(026)-N(8)-Li(7)-N(7)	-129.7(5)	C(009)-P(1)-Li(7)-P(3)	-135.0(3)
C(020)-N(8)-Li(7)-N(7)	105.4(5)	Li(12)-P(1)-Li(7)-P(3)	0.7(3)
C(005)-N(8)-Li(7)-N(7)	-10.6(4)	C(008)-C(018)-C(025)-C(200)	175.7(5)
C(026)-N(8)-Li(7)-P(3)	105.4(5)	C(041)-P(4)-C(031)-C(035)	167.2(5)
C(020)-N(8)-Li(7)-P(3)	-19.5(6)	Li(6)-P(4)-C(031)-C(035)	28.0(6)
C(005)-N(8)-Li(7)-P(3)	-135.5(5)	Li(5)-P(4)-C(031)-C(035)	-63.7(5)
C(026)-N(8)-Li(7)-P(1)	-5.9(7)	C(041)-P(4)-C(031)-C(032)	-17.5(6)
C(020)-N(8)-Li(7)-P(1)	-130.8(5)	Li(6)-P(4)-C(031)-C(032)	-156.7(5)
C(005)-N(8)-Li(7)-P(1)	113.2(5)	Li(5)-P(4)-C(031)-C(032)	111.7(5)
C(003)-P(3)-Li(7)-N(7)	-135.6(4)	C(035)-C(031)-C(032)-C(036)	1.0(9)
C(008)-P(3)-Li(7)-N(7)	-8.2(6)	P(4)-C(031)-C(032)-C(036)	-174.5(5)
Li(12)-P(3)-Li(7)-N(7)	127.1(5)	C(044)-C(029)-C(033)-C(037)	-2.0(10)
C(003)-P(3)-Li(7)-N(8)	-29.3(5)	C(044)-C(029)-C(033)-P(2)	176.8(6)
C(008)-P(3)-Li(7)-N(8)	98.0(5)	C(034)-P(2)-C(033)-C(029)	12.5(6)
Li(12)-P(3)-Li(7)-N(8)	-126.6(5)	Li(5)-P(2)-C(033)-C(029)	155.1(5)
C(003)-P(3)-Li(7)-P(1)	96.6(3)	Li(6)-P(2)-C(033)-C(029)	-114.5(6)
C(008)-P(3)-Li(7)-P(1)	-136.0(3)	C(034)-P(2)-C(033)-C(037)	-168.7(5)
Li(12)-P(3)-Li(7)-P(1)	-0.7(3)	Li(5)-P(2)-C(033)-C(037)	-26.2(6)
C(001)-P(1)-Li(7)-N(7)	-14.4(5)	Li(6)-P(2)-C(033)-C(037)	64.3(5)
C(009)-P(1)-Li(7)-N(7)	96.2(5)	C(033)-P(2)-C(034)-C(040)	71.4(5)
Li(12)-P(1)-Li(7)-N(7)	-128.2(5)	Li(5)-P(2)-C(034)-C(040)	-64.4(6)
C(001)-P(1)-Li(7)-N(8)	-121.3(4)	Li(6)-P(2)-C(034)-C(040)	179.6(4)
C(009)-P(1)-Li(7)-N(8)	-10.7(6)	C(032)-C(031)-C(035)-C(047)	-0.4(9)

Table A2.3: *continued...*

P(4)-C(031)-C(035)-C(047)	175.5(5)	C(041)-C(043)-C(051)-C(055)	-179.1(6)
C(031)-C(032)-C(036)-C(046)	-0.5(10)	C(033)-C(037)-C(052)-C(048)	-0.4(11)
C(029)-C(033)-C(037)-C(052)	2.0(10)	C(044)-C(048)-C(052)-C(037)	-1.3(12)
P(2)-C(033)-C(037)-C(052)	-176.9(6)	C(031)-P(4)-Li(6)-N(1)	29.2(6)
C(054)-N(4)-C(038)-C(039)	162.5(5)	C(041)-P(4)-Li(6)-N(1)	-100.1(5)
C(042)-N(4)-C(038)-C(039)	-76.2(6)	Li(5)-P(4)-Li(6)-N(1)	126.8(5)
Li(5)-N(4)-C(038)-C(039)	40.8(6)	C(031)-P(4)-Li(6)-N(2)	136.2(4)
C(049)-N(3)-C(039)-C(038)	167.3(5)	C(041)-P(4)-Li(6)-N(2)	6.9(6)
C(045)-N(3)-C(039)-C(038)	-72.8(7)	Li(5)-P(4)-Li(6)-N(2)	-126.2(5)
Li(5)-N(3)-C(039)-C(038)	45.1(6)	C(031)-P(4)-Li(6)-P(2)	-97.6(3)
C(049)-N(3)-C(039)-Li(5)	122.2(5)	C(041)-P(4)-Li(6)-P(2)	133.1(3)
C(045)-N(3)-C(039)-Li(5)	-117.9(5)	Li(5)-P(4)-Li(6)-P(2)	0.1(3)
N(4)-C(038)-C(039)-N(3)	-63.5(7)	C(031)-P(4)-Li(6)-C(177)	97.8(5)
N(4)-C(038)-C(039)-Li(5)	-30.1(4)	C(041)-P(4)-Li(6)-C(177)	-31.5(6)
P(2)-C(034)-C(040)-C(050)	171.7(4)	Li(5)-P(4)-Li(6)-C(177)	-164.6(5)
C(031)-P(4)-C(041)-C(043)	-69.7(5)	C(033)-P(2)-Li(6)-N(1)	121.0(5)
Li(6)-P(4)-C(041)-C(043)	63.8(5)	C(034)-P(2)-Li(6)-N(1)	9.1(6)
Li(5)-P(4)-C(041)-C(043)	-179.6(4)	Li(5)-P(2)-Li(6)-N(1)	-125.2(5)
P(4)-C(041)-C(043)-C(051)	-173.8(5)	C(033)-P(2)-Li(6)-N(2)	15.1(5)
C(033)-C(029)-C(044)-C(048)	0.4(12)	C(034)-P(2)-Li(6)-N(2)	-96.8(5)
C(032)-C(036)-C(046)-C(047)	-0.8(10)	Li(5)-P(2)-Li(6)-N(2)	128.9(5)
C(031)-C(035)-C(047)-C(046)	-0.7(10)	C(033)-P(2)-Li(6)-P(4)	-113.9(3)
C(036)-C(046)-C(047)-C(035)	1.3(10)	C(034)-P(2)-Li(6)-P(4)	134.2(3)
C(029)-C(044)-C(048)-C(052)	1.3(12)	Li(5)-P(2)-Li(6)-P(4)	-0.1(3)
C(034)-C(040)-C(050)-C(053)	177.7(5)	C(033)-P(2)-Li(6)-C(177)	46.4(7)

Table A2.3: *continued...*

C(034)-P(2)-Li(6)-C(177)	-65.5(7)	C(031)-P(4)-Li(5)-N(4)	-120.3(5)
Li(5)-P(2)-Li(6)-C(177)	160.3(7)	C(041)-P(4)-Li(5)-N(4)	-7.5(6)
C(054)-N(4)-Li(5)-N(3)	-132.2(5)	Li(6)-P(4)-Li(5)-N(4)	125.3(5)
C(042)-N(4)-Li(5)-N(3)	103.1(5)	C(031)-P(4)-Li(5)-N(3)	-12.8(5)
C(038)-N(4)-Li(5)-N(3)	-12.9(4)	C(041)-P(4)-Li(5)-N(3)	100.0(5)
C(054)-N(4)-Li(5)-P(4)	-7.3(7)	Li(6)-P(4)-Li(5)-N(3)	-127.1(5)
C(042)-N(4)-Li(5)-P(4)	-132.0(5)	C(031)-P(4)-Li(5)-P(2)	114.3(3)
C(038)-N(4)-Li(5)-P(4)	112.0(5)	C(041)-P(4)-Li(5)-P(2)	-132.9(3)
C(054)-N(4)-Li(5)-P(2)	103.9(5)	Li(6)-P(4)-Li(5)-P(2)	-0.1(3)
C(042)-N(4)-Li(5)-P(2)	-20.8(6)	C(031)-P(4)-Li(5)-C(039)	-45.6(7)
C(038)-N(4)-Li(5)-P(2)	-136.8(5)	C(041)-P(4)-Li(5)-C(039)	67.2(7)
C(054)-N(4)-Li(5)-C(039)	-141.9(5)	Li(6)-P(4)-Li(5)-C(039)	-160.0(7)
C(042)-N(4)-Li(5)-C(039)	93.4(4)	C(033)-P(2)-Li(5)-N(4)	-29.5(5)
C(038)-N(4)-Li(5)-C(039)	-22.6(3)	C(034)-P(2)-Li(5)-N(4)	102.7(5)
C(039)-N(3)-Li(5)-N(4)	-15.7(4)	Li(6)-P(2)-Li(5)-N(4)	-125.9(5)
C(049)-N(3)-Li(5)-N(4)	-134.0(5)	C(033)-P(2)-Li(5)-N(3)	-136.0(4)
C(045)-N(3)-Li(5)-N(4)	100.4(5)	C(034)-P(2)-Li(5)-N(3)	-3.8(6)
C(039)-N(3)-Li(5)-P(4)	-139.9(5)	Li(6)-P(2)-Li(5)-N(3)	127.6(5)
C(049)-N(3)-Li(5)-P(4)	101.8(6)	C(033)-P(2)-Li(5)-P(4)	96.4(3)
C(045)-N(3)-Li(5)-P(4)	-23.8(7)	C(034)-P(2)-Li(5)-P(4)	-131.3(3)
C(039)-N(3)-Li(5)-P(2)	107.3(5)	Li(6)-P(2)-Li(5)-P(4)	0.1(3)
C(049)-N(3)-Li(5)-P(2)	-11.0(7)	C(033)-P(2)-Li(5)-C(039)	-98.6(5)
C(045)-N(3)-Li(5)-P(2)	-136.5(5)	C(034)-P(2)-Li(5)-C(039)	33.7(6)
C(049)-N(3)-Li(5)-C(039)	-118.3(6)	Li(6)-P(2)-Li(5)-C(039)	165.0(5)
C(045)-N(3)-Li(5)-C(039)	116.1(6)	N(3)-C(039)-Li(5)-N(4)	161.3(5)

Table A2.3: *continued...*

C(038)-C(039)-Li(5)-N(4)	23.4(3)	C(059)-C(065)-C(067)-C(060)	2.1(10)
C(038)-C(039)-Li(5)-N(3)	-137.9(6)	C(056)-P(5)-C(068)-C(073)	-69.2(5)
N(3)-C(039)-Li(5)-P(4)	62.4(7)	Li(8)-P(5)-C(068)-C(073)	58.8(6)
C(038)-C(039)-Li(5)-P(4)	-75.6(7)	Li(9)-P(5)-C(068)-C(073)	-174.6(4)
N(3)-C(039)-Li(5)-P(2)	-93.2(5)	N(25)-C(066)-C(069)-N(24)	62.1(7)
C(038)-C(039)-Li(5)-P(2)	128.9(5)	C(077)-N(24)-C(069)-C(066)	-167.0(5)
C(068)-P(5)-C(056)-C(060)	165.8(5)	C(074)-N(24)-C(069)-C(066)	74.2(6)
Li(8)-P(5)-C(056)-C(060)	27.6(6)	Li(8)-N(24)-C(069)-C(066)	-44.5(6)
Li(9)-P(5)-C(056)-C(060)	-62.2(5)	C(075)-N(23)-C(070)-C(064)	164.2(5)
C(068)-P(5)-C(056)-C(058)	-17.5(6)	C(081)-N(23)-C(070)-C(064)	-75.1(6)
Li(8)-P(5)-C(056)-C(058)	-155.7(5)	Li(9)-N(23)-C(070)-C(064)	43.1(6)
Li(9)-P(5)-C(056)-C(058)	114.5(5)	N(22)-C(064)-C(070)-N(23)	-62.7(6)
C(060)-C(056)-C(058)-C(059)	0.4(9)	P(5)-C(068)-C(073)-C(079)	-175.1(5)
P(5)-C(056)-C(058)-C(059)	-176.5(5)	C(076)-N(25)-Li(8)-N(24)	129.6(5)
C(056)-C(058)-C(059)-C(065)	1.5(10)	C(072)-N(25)-Li(8)-N(24)	-105.8(4)
C(058)-C(056)-C(060)-C(067)	-0.9(9)	C(066)-N(25)-Li(8)-N(24)	10.7(4)
P(5)-C(056)-C(060)-C(067)	176.2(5)	C(076)-N(25)-Li(8)-P(5)	-108.2(6)
C(071)-N(22)-C(064)-C(070)	-76.0(6)	C(072)-N(25)-Li(8)-P(5)	16.3(7)
C(078)-N(22)-C(064)-C(070)	162.9(5)	C(066)-N(25)-Li(8)-P(5)	132.9(5)
Li(9)-N(22)-C(064)-C(070)	41.5(6)	C(076)-N(25)-Li(8)-P(6)	3.8(7)
C(058)-C(059)-C(065)-C(067)	-2.7(9)	C(072)-N(25)-Li(8)-P(6)	128.4(5)
C(076)-N(25)-C(066)-C(069)	-159.9(5)	C(066)-N(25)-Li(8)-P(6)	-115.1(5)
C(072)-N(25)-C(066)-C(069)	77.4(6)	C(077)-N(24)-Li(8)-N(25)	134.7(5)
Li(8)-N(25)-C(066)-C(069)	-39.3(6)	C(074)-N(24)-Li(8)-N(25)	-98.7(5)
C(056)-C(060)-C(067)-C(065)	-0.3(10)	C(069)-N(24)-Li(8)-N(25)	17.0(4)

Table A2.3: *continued...*

C(077)-N(24)-Li(8)-P(5)	11.6(7)	C(081)-N(23)-Li(9)-N(22)	101.3(5)
C(074)-N(24)-Li(8)-P(5)	138.2(5)	C(070)-N(23)-Li(9)-N(22)	-15.2(4)
C(069)-N(24)-Li(8)-P(5)	-106.1(5)	C(075)-N(23)-Li(9)-P(6)	-13.7(7)
C(077)-N(24)-Li(8)-P(6)	-101.0(6)	C(081)-N(23)-Li(9)-P(6)	-139.0(5)
C(074)-N(24)-Li(8)-P(6)	25.6(7)	C(070)-N(23)-Li(9)-P(6)	104.5(5)
C(069)-N(24)-Li(8)-P(6)	141.3(5)	C(075)-N(23)-Li(9)-P(5)	97.6(6)
C(056)-P(5)-Li(8)-N(25)	34.2(6)	C(081)-N(23)-Li(9)-P(5)	-27.7(7)
C(068)-P(5)-Li(8)-N(25)	-91.0(5)	C(070)-N(23)-Li(9)-P(5)	-144.2(5)
Li(9)-P(5)-Li(8)-N(25)	127.2(5)	C(056)-P(5)-Li(9)-N(22)	-127.6(5)
C(056)-P(5)-Li(8)-N(24)	139.0(4)	C(068)-P(5)-Li(9)-N(22)	-17.8(6)
C(068)-P(5)-Li(8)-N(24)	13.8(6)	Li(8)-P(5)-Li(9)-N(22)	122.6(5)
Li(9)-P(5)-Li(8)-N(24)	-128.1(5)	C(056)-P(5)-Li(9)-N(23)	-16.7(5)
C(056)-P(5)-Li(8)-P(6)	-92.6(3)	C(068)-P(5)-Li(9)-N(23)	93.1(6)
C(068)-P(5)-Li(8)-P(6)	142.2(3)	Li(8)-P(5)-Li(9)-N(23)	-126.5(5)
Li(9)-P(5)-Li(8)-P(6)	0.4(3)	C(056)-P(5)-Li(9)-P(6)	109.4(3)
C(071)-N(22)-Li(9)-N(23)	103.1(5)	C(068)-P(5)-Li(9)-P(6)	-140.8(3)
C(078)-N(22)-Li(9)-N(23)	-131.7(5)	Li(8)-P(5)-Li(9)-P(6)	-0.4(3)
C(064)-N(22)-Li(9)-N(23)	-13.5(4)	C(068)-C(073)-C(079)-C(080)	-179.2(6)
C(071)-N(22)-Li(9)-P(6)	-19.6(6)	N(25)-Li(8)-P(6)-C(082)	122.0(5)
C(078)-N(22)-Li(9)-P(6)	105.6(5)	N(24)-Li(8)-P(6)-C(082)	14.9(5)
C(064)-N(22)-Li(9)-P(6)	-136.2(4)	P(5)-Li(8)-P(6)-C(082)	-111.3(3)
C(071)-N(22)-Li(9)-P(5)	-129.9(5)	N(25)-Li(8)-P(6)-C(085)	12.2(6)
C(078)-N(22)-Li(9)-P(5)	-4.7(7)	N(24)-Li(8)-P(6)-C(085)	-95.0(5)
C(064)-N(22)-Li(9)-P(5)	113.5(5)	P(5)-Li(8)-P(6)-C(085)	138.9(3)
C(075)-N(23)-Li(9)-N(22)	-133.4(5)	N(25)-Li(8)-P(6)-Li(9)	-127.1(5)

Table A2.3: *continued...*

N(24)-Li(8)-P(6)-Li(9)	125.8(5)	C(082)-C(084)-C(087)-C(089)	2.6(11)
P(5)-Li(8)-P(6)-Li(9)	-0.4(3)	C(082)-C(083)-C(088)-C(089)	-0.3(11)
N(22)-Li(9)-P(6)-C(082)	-34.7(5)	C(083)-C(088)-C(089)-C(087)	1.1(11)
N(23)-Li(9)-P(6)-C(082)	-138.6(4)	C(084)-C(087)-C(089)-C(088)	-2.3(11)
P(5)-Li(9)-P(6)-C(082)	94.1(3)	C(085)-C(086)-C(090)-C(091)	176.3(5)
N(22)-Li(9)-P(6)-C(085)	95.5(5)	N(17)-Li(10)-P(7)-C(096)	26.2(5)
N(23)-Li(9)-P(6)-C(085)	-8.5(7)	N(16)-Li(10)-P(7)-C(096)	133.5(5)
P(5)-Li(9)-P(6)-C(085)	-135.8(3)	P(8)-Li(10)-P(7)-C(096)	-101.6(3)
N(22)-Li(9)-P(6)-Li(8)	-128.4(5)	C(410)-Li(10)-P(7)-C(096)	59.8(7)
N(23)-Li(9)-P(6)-Li(8)	127.7(5)	N(17)-Li(10)-P(7)-C(100)	-81.1(6)
P(5)-Li(9)-P(6)-Li(8)	0.4(3)	N(16)-Li(10)-P(7)-C(100)	26.3(6)
C(085)-P(6)-C(082)-C(083)	14.4(6)	P(8)-Li(10)-P(7)-C(100)	151.2(3)
Li(8)-P(6)-C(082)-C(083)	-112.7(6)	C(410)-Li(10)-P(7)-C(100)	-47.5(8)
Li(9)-P(6)-C(082)-C(083)	156.8(5)	N(17)-Li(10)-P(7)-Li(3)	128.9(6)
C(085)-P(6)-C(082)-C(084)	-170.2(5)	N(16)-Li(10)-P(7)-Li(3)	-123.7(5)
Li(8)-P(6)-C(082)-C(084)	62.7(5)	P(8)-Li(10)-P(7)-Li(3)	1.2(3)
Li(9)-P(6)-C(082)-C(084)	-27.9(6)	C(410)-Li(10)-P(7)-Li(3)	162.5(7)
C(084)-C(082)-C(083)-C(088)	0.4(9)	N(17)-Li(10)-P(8)-C(098)	133.8(5)
P(6)-C(082)-C(083)-C(088)	176.1(5)	N(16)-Li(10)-P(8)-C(098)	26.1(6)
C(083)-C(082)-C(084)-C(087)	-1.7(9)	P(7)-Li(10)-P(8)-C(098)	-98.5(3)
P(6)-C(082)-C(084)-C(087)	-177.6(5)	C(410)-Li(10)-P(8)-C(098)	96.6(5)
C(082)-P(6)-C(085)-C(086)	67.9(5)	N(17)-Li(10)-P(8)-C(094)	17.9(7)
Li(8)-P(6)-C(085)-C(086)	172.7(4)	N(16)-Li(10)-P(8)-C(094)	-89.9(6)
Li(9)-P(6)-C(085)-C(086)	-64.7(6)	P(7)-Li(10)-P(8)-C(094)	145.6(3)
P(6)-C(085)-C(086)-C(090)	176.1(4)	C(410)-Li(10)-P(8)-C(094)	-19.4(7)

Table A2.3: *continued...*

N(17)-Li(10)-P(8)-Li(3)	-128.8(6)	P(9)-Li(11)-N(18)-C(155)	5.0(8)
N(16)-Li(10)-P(8)-Li(3)	123.4(6)	Li(14)-Li(11)-N(18)-C(155)	-53.1(9)
P(7)-Li(10)-P(8)-Li(3)	-1.2(3)	C(103)-P(100)-C(093)-C(105)	177.7(5)
C(410)-Li(10)-P(8)-Li(3)	-166.1(5)	Li(2)-P(100)-C(093)-C(105)	51.6(6)
N(18)-Li(11)-P(9)-C(135)	127.9(5)	Li(1)-P(100)-C(093)-C(105)	-41.0(6)
N(19)-Li(11)-P(9)-C(135)	18.6(6)	C(103)-P(100)-C(093)-C(115)	-1.9(6)
P(10)-Li(11)-P(9)-C(135)	-104.7(3)	Li(2)-P(100)-C(093)-C(115)	-128.0(6)
Li(14)-Li(11)-P(9)-C(135)	-101.4(3)	Li(1)-P(100)-C(093)-C(115)	139.3(6)
N(18)-Li(11)-P(9)-C(141)	1.5(7)	C(098)-P(8)-C(094)-C(107)	-176.6(5)
N(19)-Li(11)-P(9)-C(141)	-107.8(6)	Li(10)-P(8)-C(094)-C(107)	-60.6(6)
P(10)-Li(11)-P(9)-C(141)	128.9(4)	Li(3)-P(8)-C(094)-C(107)	73.0(7)
Li(14)-Li(11)-P(9)-C(141)	132.3(4)	C(306)-P(101)-C(095)-C(128)	-177.9(5)
N(18)-Li(11)-P(9)-Li(14)	-130.7(6)	Li(2)-P(101)-C(095)-C(128)	-55.1(6)
N(19)-Li(11)-P(9)-Li(14)	120.0(6)	Li(1)-P(101)-C(095)-C(128)	75.3(6)
P(10)-Li(11)-P(9)-Li(14)	-3.3(3)	C(100)-P(7)-C(096)-C(116)	180.0(5)
N(19)-Li(11)-N(18)-C(145)	11.6(6)	Li(10)-P(7)-C(096)-C(116)	54.4(6)
P(10)-Li(11)-N(18)-C(145)	130.1(6)	Li(3)-P(7)-C(096)-C(116)	-36.1(6)
P(9)-Li(11)-N(18)-C(145)	-115.5(6)	C(100)-P(7)-C(096)-C(110)	2.7(7)
Li(14)-Li(11)-N(18)-C(145)	-173.6(7)	Li(10)-P(7)-C(096)-C(110)	-122.9(6)
N(19)-Li(11)-N(18)-C(154)	-105.2(5)	Li(3)-P(7)-C(096)-C(110)	146.6(6)
P(10)-Li(11)-N(18)-C(154)	13.2(7)	C(094)-P(8)-C(098)-C(113)	178.8(5)
P(9)-Li(11)-N(18)-C(154)	127.7(6)	Li(10)-P(8)-C(098)-C(113)	44.2(6)
Li(14)-Li(11)-N(18)-C(154)	69.5(9)	Li(3)-P(8)-C(098)-C(113)	-46.9(6)
N(19)-Li(11)-N(18)-C(155)	132.2(6)	C(094)-P(8)-C(098)-C(099)	-1.4(7)
P(10)-Li(11)-N(18)-C(155)	-109.4(7)	Li(10)-P(8)-C(098)-C(099)	-135.9(6)

Table A2.3: *continued...*

Li(3)-P(8)-C(098)-C(099)	132.9(6)	C(093)-C(105)-C(108)-C(124)	1.1(11)
C(113)-C(098)-C(099)-C(120)	1.3(9)	C(111)-C(306)-C(109)-C(122)	-1.6(10)
P(8)-C(098)-C(099)-C(120)	-178.6(5)	P(101)-C(306)-C(109)-C(122)	176.8(5)
C(096)-P(7)-C(100)-C(119)	172.8(5)	C(116)-C(096)-C(110)-C(146)	1.9(10)
Li(10)-P(7)-C(100)-C(119)	-82.5(6)	P(7)-C(096)-C(110)-C(146)	179.4(5)
Li(3)-P(7)-C(100)-C(119)	50.3(7)	C(109)-C(306)-C(111)-C(123)	1.2(9)
C(159)-C(101)-C(102)-C(103)	177.1(5)	P(101)-C(306)-C(111)-C(123)	-177.0(5)
C(101)-C(102)-C(103)-P(100)	-178.0(4)	C(099)-C(098)-C(113)-C(142)	-0.9(10)
C(093)-P(100)-C(103)-C(102)	75.3(5)	P(8)-C(098)-C(113)-C(142)	179.0(5)
Li(2)-P(100)-C(103)-C(102)	-171.8(4)	N(18)-Li(11)-N(19)-C(144)	131.7(6)
Li(1)-P(100)-C(103)-C(102)	-48.3(6)	P(10)-Li(11)-N(19)-C(144)	9.9(8)
C(156)-C(310)-N(14)-C(158)	148.9(13)	P(9)-Li(11)-N(19)-C(144)	-102.3(7)
Li(3)-C(310)-N(14)-C(158)	120.2(8)	Li(14)-Li(11)-N(19)-C(144)	-43.6(9)
C(156)-C(310)-N(14)-C(152)	-88.8(14)	N(18)-Li(11)-N(19)-C(153)	-103.4(5)
Li(3)-C(310)-N(14)-C(152)	-117.6(7)	P(10)-Li(11)-N(19)-C(153)	134.8(5)
C(156)-C(310)-N(14)-Li(3)	28.7(15)	P(9)-Li(11)-N(19)-C(153)	22.6(8)
C(115)-C(093)-C(105)-C(108)	-2.7(10)	Li(14)-Li(11)-N(19)-C(153)	81.3(7)
P(100)-C(093)-C(105)-C(108)	177.6(5)	N(18)-Li(11)-N(19)-C(139)	14.1(5)
C(095)-P(101)-C(306)-C(109)	175.8(5)	P(10)-Li(11)-N(19)-C(139)	-107.7(6)
Li(2)-P(101)-C(306)-C(109)	35.2(6)	P(9)-Li(11)-N(19)-C(139)	140.1(6)
Li(1)-P(101)-C(306)-C(109)	-52.5(6)	Li(14)-Li(11)-N(19)-C(139)	-161.2(6)
C(095)-P(101)-C(306)-C(111)	-6.0(6)	C(105)-C(093)-C(115)-C(117)	2.0(9)
Li(2)-P(101)-C(306)-C(111)	-146.6(5)	P(100)-C(093)-C(115)-C(117)	-178.4(5)
Li(1)-P(101)-C(306)-C(111)	125.7(6)	C(110)-C(096)-C(116)-C(137)	-2.2(10)
P(8)-C(094)-C(107)-C(125)	171.1(5)	P(7)-C(096)-C(116)-C(137)	-179.9(6)

Table A2.3: *continued...*

C(093)-C(115)-C(117)-C(124)	0.4(11)	Li(14)-P(9)-C(135)-C(131)	130.5(6)
C(136)-C(118)-C(119)-C(100)	67.1(8)	Li(11)-P(9)-C(135)-C(131)	-140.1(6)
P(7)-C(100)-C(119)-C(118)	173.7(5)	C(096)-C(116)-C(137)-C(130)	1.6(12)
C(098)-C(099)-C(120)-C(126)	-1.2(11)	C(146)-C(130)-C(137)-C(116)	-0.5(12)
C(306)-C(109)-C(122)-C(121)	1.5(11)	C(144)-N(19)-C(139)-C(145)	-159.9(7)
C(123)-C(121)-C(122)-C(109)	-0.9(11)	C(153)-N(19)-C(139)-C(145)	79.5(8)
C(122)-C(121)-C(123)-C(111)	0.6(11)	Li(11)-N(19)-C(139)-C(145)	-37.9(8)
C(306)-C(111)-C(123)-C(121)	-0.8(10)	C(135)-P(9)-C(141)-C(148)	-75.2(6)
C(105)-C(108)-C(124)-C(117)	1.4(11)	Li(14)-P(9)-C(141)-C(148)	168.8(5)
C(115)-C(117)-C(124)-C(108)	-2.1(12)	Li(11)-P(9)-C(141)-C(148)	50.8(7)
C(094)-C(107)-C(125)-C(127)	67.6(9)	C(120)-C(126)-C(142)-C(113)	-0.1(11)
C(099)-C(120)-C(126)-C(142)	0.6(12)	C(098)-C(113)-C(142)-C(126)	0.3(11)
P(101)-C(095)-C(128)-C(132)	167.1(6)	N(10)-C(134)-C(143)-N(11)	-61.6(7)
C(095)-C(128)-C(132)-C(415)	61.0(10)	C(157)-N(11)-C(143)-C(134)	163.7(6)
C(147)-N(10)-C(134)-C(143)	164.9(6)	C(150)-N(11)-C(143)-C(134)	-76.0(7)
C(140)-N(10)-C(134)-C(143)	-73.6(7)	Li(1)-N(11)-C(143)-C(134)	38.2(7)
Li(1)-N(10)-C(134)-C(143)	45.0(7)	C(154)-N(18)-C(145)-C(139)	81.0(8)
C(160)-C(133)-C(135)-C(131)	-0.7(11)	C(155)-N(18)-C(145)-C(139)	-160.6(6)
C(160)-C(133)-C(135)-P(9)	178.2(6)	Li(11)-N(18)-C(145)-C(139)	-35.8(8)
C(151)-C(131)-C(135)-C(133)	-0.1(11)	N(19)-C(139)-C(145)-N(18)	55.0(9)
C(151)-C(131)-C(135)-P(9)	-178.9(6)	C(137)-C(130)-C(146)-C(110)	0.3(12)
C(141)-P(9)-C(135)-C(133)	-178.0(6)	C(096)-C(110)-C(146)-C(130)	-1.1(11)
Li(14)-P(9)-C(135)-C(133)	-48.2(7)	P(9)-C(141)-C(148)-C(161)	-179.9(5)
Li(11)-P(9)-C(135)-C(133)	41.2(7)	C(158)-N(14)-Li(3)-N(15)	-128.2(8)
C(141)-P(9)-C(135)-C(131)	0.8(7)	C(152)-N(14)-Li(3)-N(15)	106.3(7)

Table A2.3: *continued...*

C(310)-N(14)-Li(3)-N(15)	-7.9(7)	C(12)-N(15)-Li(3)-C(310)	103.7(7)
C(158)-N(14)-Li(3)-P(8)	110.8(8)	C(098)-P(8)-Li(3)-N(14)	-26.7(6)
C(152)-N(14)-Li(3)-P(8)	-14.7(9)	C(094)-P(8)-Li(3)-N(14)	85.7(7)
C(310)-N(14)-Li(3)-P(8)	-128.9(7)	Li(10)-P(8)-Li(3)-N(14)	-128.5(6)
C(158)-N(14)-Li(3)-P(7)	-1.6(10)	C(098)-P(8)-Li(3)-N(15)	-132.9(5)
C(152)-N(14)-Li(3)-P(7)	-127.1(7)	C(094)-P(8)-Li(3)-N(15)	-20.5(8)
C(310)-N(14)-Li(3)-P(7)	118.7(8)	Li(10)-P(8)-Li(3)-N(15)	125.3(6)
C(158)-N(14)-Li(3)-C(156)	-133.3(8)	C(098)-P(8)-Li(3)-P(7)	102.9(3)
C(152)-N(14)-Li(3)-C(156)	101.2(7)	C(094)-P(8)-Li(3)-P(7)	-144.7(3)
C(310)-N(14)-Li(3)-C(156)	-13.0(7)	Li(10)-P(8)-Li(3)-P(7)	1.1(3)
C(158)-N(14)-Li(3)-C(310)	-120.3(10)	C(098)-P(8)-Li(3)-C(156)	-97.4(6)
C(152)-N(14)-Li(3)-C(310)	114.2(9)	C(094)-P(8)-Li(3)-C(156)	14.9(8)
C(311)-N(15)-Li(3)-N(14)	-126.1(7)	Li(10)-P(8)-Li(3)-C(156)	160.8(6)
C(156)-N(15)-Li(3)-N(14)	-8.3(7)	C(098)-P(8)-Li(3)-C(310)	-64.1(8)
C(12)-N(15)-Li(3)-N(14)	108.8(7)	C(094)-P(8)-Li(3)-C(310)	48.3(9)
C(311)-N(15)-Li(3)-P(8)	-1.9(9)	Li(10)-P(8)-Li(3)-C(310)	-165.9(8)
C(156)-N(15)-Li(3)-P(8)	116.0(8)	C(096)-P(7)-Li(3)-N(14)	-137.8(6)
C(12)-N(15)-Li(3)-P(8)	-126.9(7)	C(100)-P(7)-Li(3)-N(14)	-16.0(9)
C(311)-N(15)-Li(3)-P(7)	104.7(7)	Li(10)-P(7)-Li(3)-N(14)	126.1(7)
C(156)-N(15)-Li(3)-P(7)	-137.4(7)	C(096)-P(7)-Li(3)-N(15)	-26.2(6)
C(12)-N(15)-Li(3)-P(7)	-20.3(9)	C(100)-P(7)-Li(3)-N(15)	95.6(7)
C(311)-N(15)-Li(3)-C(156)	-117.8(9)	Li(10)-P(7)-Li(3)-N(15)	-122.3(6)
C(12)-N(15)-Li(3)-C(156)	117.1(10)	C(096)-P(7)-Li(3)-P(8)	94.9(3)
C(311)-N(15)-Li(3)-C(310)	-131.2(8)	C(100)-P(7)-Li(3)-P(8)	-143.3(3)
C(156)-N(15)-Li(3)-C(310)	-13.4(8)	Li(10)-P(7)-Li(3)-P(8)	-1.1(3)

Table A2.3: *continued...*

C(096)-P(7)-Li(3)-C(156)	-59.3(9)	C(150)-N(11)-Li(1)-N(10)	104.5(5)
C(100)-P(7)-Li(3)-C(156)	62.5(10)	C(157)-N(11)-Li(1)-P(100)	103.5(6)
Li(10)-P(7)-Li(3)-C(156)	-155.3(8)	C(143)-N(11)-Li(1)-P(100)	-134.6(5)
C(096)-P(7)-Li(3)-C(310)	-97.4(7)	C(150)-N(11)-Li(1)-P(100)	-19.7(7)
C(100)-P(7)-Li(3)-C(310)	24.5(10)	C(157)-N(11)-Li(1)-P(101)	-7.8(8)
Li(10)-P(7)-Li(3)-C(310)	166.6(7)	C(143)-N(11)-Li(1)-P(101)	114.2(6)
C(156)-C(310)-Li(3)-N(14)	-155.0(14)	C(150)-N(11)-Li(1)-P(101)	-131.0(6)
C(156)-C(310)-Li(3)-N(15)	15.5(8)	C(093)-P(100)-Li(1)-N(10)	-133.4(5)
N(14)-C(310)-Li(3)-N(15)	170.5(8)	C(103)-P(100)-Li(1)-N(10)	-9.0(7)
C(156)-C(310)-Li(3)-P(8)	-80.0(11)	Li(2)-P(100)-Li(1)-N(10)	125.1(5)
N(14)-C(310)-Li(3)-P(8)	75.0(10)	C(093)-P(100)-Li(1)-N(11)	-28.4(5)
C(156)-C(310)-Li(3)-P(7)	117.9(11)	C(103)-P(100)-Li(1)-N(11)	95.9(6)
N(14)-C(310)-Li(3)-P(7)	-87.1(8)	Li(2)-P(100)-Li(1)-N(11)	-129.9(5)
N(14)-C(310)-Li(3)-C(156)	155.0(14)	C(093)-P(100)-Li(1)-P(101)	99.5(3)
C(147)-N(10)-Li(1)-N(11)	-135.2(5)	C(103)-P(100)-Li(1)-P(101)	-136.2(3)
C(134)-N(10)-Li(1)-N(11)	-17.2(5)	Li(2)-P(100)-Li(1)-P(101)	-2.0(3)
C(140)-N(10)-Li(1)-N(11)	100.5(5)	C(306)-P(101)-Li(1)-N(10)	-22.1(6)
C(147)-N(10)-Li(1)-P(100)	-13.4(7)	C(095)-P(101)-Li(1)-N(10)	88.2(6)
C(134)-N(10)-Li(1)-P(100)	104.6(6)	Li(2)-P(101)-Li(1)-N(10)	-125.8(6)
C(140)-N(10)-Li(1)-P(100)	-137.7(5)	C(306)-P(101)-Li(1)-N(11)	-129.3(5)
C(147)-N(10)-Li(1)-P(101)	98.9(6)	C(095)-P(101)-Li(1)-N(11)	-19.1(7)
C(134)-N(10)-Li(1)-P(101)	-143.1(5)	Li(2)-P(101)-Li(1)-N(11)	127.0(5)
C(140)-N(10)-Li(1)-P(101)	-25.4(8)	C(306)-P(101)-Li(1)-P(100)	105.7(3)
C(157)-N(11)-Li(1)-N(10)	-132.3(6)	C(095)-P(101)-Li(1)-P(100)	-144.1(3)
C(143)-N(11)-Li(1)-N(10)	-10.3(5)	Li(2)-P(101)-Li(1)-P(100)	2.0(3)

Table A2.3: *continued...*

C(160)-C(149)-C(151)-C(131)	-0.7(14)	C(103)-P(100)-Li(2)-P(101)	144.4(3)
C(135)-C(131)-C(151)-C(149)	0.9(13)	Li(1)-P(100)-Li(2)-P(101)	2.0(3)
N(14)-C(310)-C(156)-N(15)	-45(2)	C(306)-P(101)-Li(2)-N(12)	26.7(6)
Li(3)-C(310)-C(156)-N(15)	-23.2(12)	C(095)-P(101)-Li(2)-N(12)	-95.6(6)
N(14)-C(310)-C(156)-Li(3)	-21.8(11)	Li(1)-P(101)-Li(2)-N(12)	120.7(6)
C(311)-N(15)-C(156)-C(310)	149.0(13)	C(306)-P(101)-Li(2)-N(13)	134.9(5)
C(12)-N(15)-C(156)-C(310)	-92.4(15)	C(095)-P(101)-Li(2)-N(13)	12.7(7)
Li(3)-N(15)-C(156)-C(310)	29.5(15)	Li(1)-P(101)-Li(2)-N(13)	-131.0(5)
C(311)-N(15)-C(156)-Li(3)	119.5(7)	C(306)-P(101)-Li(2)-P(100)	-96.1(3)
C(12)-N(15)-C(156)-Li(3)	-121.9(7)	C(095)-P(101)-Li(2)-P(100)	141.7(3)
N(14)-Li(3)-C(156)-C(310)	15.6(8)	Li(1)-P(101)-Li(2)-P(100)	-2.0(3)
N(15)-Li(3)-C(156)-C(310)	-154.6(14)	C(135)-C(133)-C(160)-C(149)	0.9(13)
P(8)-Li(3)-C(156)-C(310)	122.4(10)	C(151)-C(149)-C(160)-C(133)	-0.1(13)
P(7)-Li(3)-C(156)-C(310)	-90.2(12)	C(141)-C(148)-C(161)-C(129)	-67.1(9)
N(14)-Li(3)-C(156)-N(15)	170.2(8)	N(18)-Li(11)-P(10)-C(163)	30.7(6)
P(8)-Li(3)-C(156)-N(15)	-83.0(8)	N(19)-Li(11)-P(10)-C(163)	133.6(5)
P(7)-Li(3)-C(156)-N(15)	64.4(10)	P(9)-Li(11)-P(10)-C(163)	-97.9(3)
C(310)-Li(3)-C(156)-N(15)	154.6(14)	Li(14)-Li(11)-P(10)-C(163)	-101.2(3)
C(093)-P(100)-Li(2)-N(12)	128.7(4)	N(18)-Li(11)-P(10)-C(165)	-83.5(6)
C(103)-P(100)-Li(2)-N(12)	14.0(6)	N(19)-Li(11)-P(10)-C(165)	19.4(6)
Li(1)-P(100)-Li(2)-N(12)	-128.4(5)	P(9)-Li(11)-P(10)-C(165)	147.9(3)
C(093)-P(100)-Li(2)-N(13)	27.0(6)	Li(14)-Li(11)-P(10)-C(165)	144.6(4)
C(103)-P(100)-Li(2)-N(13)	-87.7(5)	N(18)-Li(11)-P(10)-Li(14)	131.9(6)
Li(1)-P(100)-Li(2)-N(13)	129.9(5)	N(19)-Li(11)-P(10)-Li(14)	-125.2(5)
C(093)-P(100)-Li(2)-P(101)	-100.9(3)	P(9)-Li(11)-P(10)-Li(14)	3.3(3)

Table A2.3: *continued...*

C(165)-P(10)-C(163)-C(167)	178.3(5)	P(2)-Li(6)-N(1)-C(174)	-111.1(5)
Li(11)-P(10)-C(163)-C(167)	50.6(6)	C(177)-Li(6)-N(1)-C(174)	21.5(3)
Li(14)-P(10)-C(163)-C(167)	-38.9(6)	N(2)-Li(6)-N(1)-C(175)	-105.1(4)
C(165)-P(10)-C(163)-C(170)	-0.5(7)	P(4)-Li(6)-N(1)-C(175)	20.9(6)
Li(11)-P(10)-C(163)-C(170)	-128.2(6)	P(2)-Li(6)-N(1)-C(175)	132.6(5)
Li(14)-P(10)-C(163)-C(170)	142.3(6)	C(177)-Li(6)-N(1)-C(175)	-94.8(4)
C(169)-C(162)-C(164)-C(165)	175.2(5)	N(1)-Li(6)-N(2)-C(179)	132.7(5)
C(162)-C(164)-C(165)-P(10)	179.2(4)	P(4)-Li(6)-N(2)-C(179)	10.0(7)
C(163)-P(10)-C(165)-C(164)	76.4(5)	P(2)-Li(6)-N(2)-C(179)	-103.3(6)
Li(11)-P(10)-C(165)-C(164)	-172.0(4)	C(177)-Li(6)-N(2)-C(179)	116.1(6)
Li(14)-P(10)-C(165)-C(164)	-46.8(7)	N(1)-Li(6)-N(2)-C(176)	-98.8(5)
C(170)-C(163)-C(167)-C(166)	-1.8(10)	P(4)-Li(6)-N(2)-C(176)	138.5(5)
P(10)-C(163)-C(167)-C(166)	179.3(5)	P(2)-Li(6)-N(2)-C(176)	25.2(7)
C(171)-C(166)-C(167)-C(163)	0.7(11)	C(177)-Li(6)-N(2)-C(176)	-115.4(6)
C(171)-C(168)-C(170)-C(163)	-0.2(11)	N(1)-Li(6)-N(2)-C(177)	16.6(4)
C(167)-C(163)-C(170)-C(168)	1.5(10)	P(4)-Li(6)-N(2)-C(177)	-106.1(5)
P(10)-C(163)-C(170)-C(168)	-179.7(5)	P(2)-Li(6)-N(2)-C(177)	140.6(5)
C(170)-C(168)-C(171)-C(166)	-0.9(12)	C(178)-N(1)-C(174)-C(177)	-161.4(5)
C(167)-C(166)-C(171)-C(168)	0.6(11)	C(175)-N(1)-C(174)-C(177)	77.6(6)
N(2)-Li(6)-N(1)-C(178)	131.8(4)	Li(6)-N(1)-C(174)-C(177)	-39.7(6)
P(4)-Li(6)-N(1)-C(178)	-102.3(5)	N(1)-C(174)-C(177)-N(2)	63.1(7)
P(2)-Li(6)-N(1)-C(178)	9.4(7)	N(1)-C(174)-C(177)-Li(6)	29.0(4)
C(177)-Li(6)-N(1)-C(178)	142.1(5)	C(179)-N(2)-C(177)-C(174)	-165.7(5)
N(2)-Li(6)-N(1)-C(174)	11.2(4)	C(176)-N(2)-C(177)-C(174)	73.1(6)
P(4)-Li(6)-N(1)-C(174)	137.2(4)	Li(6)-N(2)-C(177)-C(174)	-44.8(6)

Table A2.3: *continued...*

C(179)-N(2)-C(177)-Li(6)	-120.9(5)	P(1)-Li(12)-N(6)-C(185)	139.9(5)
C(176)-N(2)-C(177)-Li(6)	117.9(5)	P(3)-Li(12)-N(6)-C(185)	26.2(7)
N(1)-Li(6)-C(177)-C(174)	-22.2(3)	C(184)-Li(12)-N(6)-C(185)	-116.3(6)
N(2)-Li(6)-C(177)-C(174)	138.1(6)	N(5)-Li(12)-N(6)-C(187)	135.0(5)
P(4)-Li(6)-C(177)-C(174)	-126.1(5)	P(1)-Li(12)-N(6)-C(187)	14.4(7)
P(2)-Li(6)-C(177)-C(174)	78.2(7)	P(3)-Li(12)-N(6)-C(187)	-99.4(5)
N(1)-Li(6)-C(177)-N(2)	-160.2(5)	C(184)-Li(12)-N(6)-C(187)	118.1(6)
P(4)-Li(6)-C(177)-N(2)	95.8(6)	C(186)-N(5)-C(182)-C(184)	-161.1(5)
P(2)-Li(6)-C(177)-N(2)	-59.9(7)	C(183)-N(5)-C(182)-C(184)	77.0(6)
N(6)-Li(12)-N(5)-C(186)	129.1(5)	Li(12)-N(5)-C(182)-C(184)	-39.3(6)
P(1)-Li(12)-N(5)-C(186)	-103.8(5)	C(185)-N(6)-C(184)-C(182)	72.8(6)
P(3)-Li(12)-N(5)-C(186)	8.0(7)	C(187)-N(6)-C(184)-C(182)	-166.5(5)
C(184)-Li(12)-N(5)-C(186)	139.4(5)	Li(12)-N(6)-C(184)-C(182)	-45.5(6)
N(6)-Li(12)-N(5)-C(183)	-105.4(5)	C(185)-N(6)-C(184)-Li(12)	118.3(6)
P(1)-Li(12)-N(5)-C(183)	21.7(6)	C(187)-N(6)-C(184)-Li(12)	-121.0(5)
P(3)-Li(12)-N(5)-C(183)	133.6(5)	N(5)-C(182)-C(184)-N(6)	62.4(6)
C(184)-Li(12)-N(5)-C(183)	-95.0(4)	N(5)-C(182)-C(184)-Li(12)	28.9(4)
N(6)-Li(12)-N(5)-C(182)	10.9(4)	N(5)-Li(12)-C(184)-N(6)	-159.9(5)
P(1)-Li(12)-N(5)-C(182)	138.1(4)	P(1)-Li(12)-C(184)-N(6)	98.8(6)
P(3)-Li(12)-N(5)-C(182)	-110.1(5)	P(3)-Li(12)-C(184)-N(6)	-56.2(7)
C(184)-Li(12)-N(5)-C(182)	21.3(3)	N(6)-Li(12)-C(184)-C(182)	137.5(6)
N(5)-Li(12)-N(6)-C(184)	16.9(4)	N(5)-Li(12)-C(184)-C(182)	-22.4(3)
P(1)-Li(12)-N(6)-C(184)	-103.7(5)	P(1)-Li(12)-C(184)-C(182)	-123.7(5)
P(3)-Li(12)-N(6)-C(184)	142.5(5)	P(3)-Li(12)-C(184)-C(182)	81.3(7)
N(5)-Li(12)-N(6)-C(185)	-99.4(5)	N(12)-Li(2)-N(13)-C(193)	128.9(6)

Table A2.3: *continued...*

P(100)-Li(2)-N(13)-C(193)	-114.0(7)	C(106)-N(16)-C(411)-C(410)	77.4(7)
P(101)-Li(2)-N(13)-C(193)	0.3(8)	Li(10)-N(16)-C(411)-C(410)	-36.3(7)
N(12)-Li(2)-N(13)-C(191)	9.5(6)	N(16)-C(411)-C(410)-N(17)	56.0(8)
P(100)-Li(2)-N(13)-C(191)	126.6(6)	N(16)-C(411)-C(410)-Li(10)	27.3(5)
P(101)-Li(2)-N(13)-C(191)	-119.2(6)	C(303)-N(17)-C(410)-C(411)	-164.3(6)
N(12)-Li(2)-N(13)-C(195)	-107.5(5)	C(302)-N(17)-C(410)-C(411)	75.5(8)
P(100)-Li(2)-N(13)-C(195)	9.6(7)	Li(10)-N(17)-C(410)-C(411)	-38.4(7)
P(101)-Li(2)-N(13)-C(195)	123.9(6)	C(303)-N(17)-C(410)-Li(10)	-125.9(6)
N(13)-Li(2)-N(12)-C(190)	128.2(5)	C(302)-N(17)-C(410)-Li(10)	113.9(6)
P(100)-Li(2)-N(12)-C(190)	4.9(7)	N(17)-Li(10)-C(410)-C(411)	144.7(7)
P(101)-Li(2)-N(12)-C(190)	-107.2(6)	N(16)-Li(10)-C(410)-C(411)	-20.0(4)
N(13)-Li(2)-N(12)-C(192)	11.3(5)	P(7)-Li(10)-C(410)-C(411)	78.6(7)
P(100)-Li(2)-N(12)-C(192)	-112.0(6)	P(8)-Li(10)-C(410)-C(411)	-124.9(6)
P(101)-Li(2)-N(12)-C(192)	135.9(6)	N(16)-Li(10)-C(410)-N(17)	-164.7(6)
N(13)-Li(2)-N(12)-C(194)	-107.2(5)	P(7)-Li(10)-C(410)-N(17)	-66.1(7)
P(100)-Li(2)-N(12)-C(194)	129.5(5)	P(8)-Li(10)-C(410)-N(17)	90.4(6)
P(101)-Li(2)-N(12)-C(194)	17.4(8)	C(401)-N(21)-Li(14)-N(20)	-135.5(5)
C(193)-N(13)-C(191)-C(192)	-154.9(7)	C(421)-N(21)-Li(14)-N(20)	-19.7(6)
C(195)-N(13)-C(191)-C(192)	84.8(8)	C(402)-N(21)-Li(14)-N(20)	98.2(6)
Li(2)-N(13)-C(191)-C(192)	-31.3(9)	C(401)-N(21)-Li(14)-P(9)	97.7(6)
N(13)-C(191)-C(192)-N(12)	47.4(11)	C(421)-N(21)-Li(14)-P(9)	-146.5(6)
C(190)-N(12)-C(192)-C(191)	-151.9(7)	C(402)-N(21)-Li(14)-P(9)	-28.6(8)
C(194)-N(12)-C(192)-C(191)	87.8(8)	C(401)-N(21)-Li(14)-P(10)	-14.4(8)
Li(2)-N(12)-C(192)-C(191)	-32.4(9)	C(421)-N(21)-Li(14)-P(10)	101.4(6)
C(304)-N(16)-C(411)-C(410)	-162.2(6)	C(402)-N(21)-Li(14)-P(10)	-140.7(6)

Table A2.3: *continued...*

C(401)-N(21)-Li(14)-C(421)	-115.8(7)	Li(11)-P(9)-Li(14)-N(20)	128.0(6)
C(402)-N(21)-Li(14)-C(421)	117.9(8)	C(135)-P(9)-Li(14)-P(10)	107.4(3)
C(401)-N(21)-Li(14)-Li(11)	41.0(9)	C(141)-P(9)-Li(14)-P(10)	-134.8(3)
C(421)-N(21)-Li(14)-Li(11)	156.8(6)	Li(11)-P(9)-Li(14)-P(10)	3.3(3)
C(402)-N(21)-Li(14)-Li(11)	-85.3(8)	C(135)-P(9)-Li(14)-C(421)	-46.7(9)
C(430)-N(20)-Li(14)-N(21)	-129.2(7)	C(141)-P(9)-Li(14)-C(421)	71.0(9)
C(420)-N(20)-Li(14)-N(21)	-8.9(5)	Li(11)-P(9)-Li(14)-C(421)	-150.9(8)
C(403)-N(20)-Li(14)-N(21)	106.0(6)	C(135)-P(9)-Li(14)-Li(11)	104.2(3)
C(430)-N(20)-Li(14)-P(9)	-4.7(9)	C(141)-P(9)-Li(14)-Li(11)	-138.1(4)
C(420)-N(20)-Li(14)-P(9)	115.6(6)	C(163)-P(10)-Li(14)-N(21)	-138.2(5)
C(403)-N(20)-Li(14)-P(9)	-129.5(6)	C(165)-P(10)-Li(14)-N(21)	-14.0(8)
C(430)-N(20)-Li(14)-P(10)	107.7(7)	Li(11)-P(10)-Li(14)-N(21)	122.7(6)
C(420)-N(20)-Li(14)-P(10)	-132.0(5)	C(163)-P(10)-Li(14)-N(20)	-32.6(6)
C(403)-N(20)-Li(14)-P(10)	-17.0(8)	C(165)-P(10)-Li(14)-N(20)	91.6(6)
C(430)-N(20)-Li(14)-C(421)	-140.9(7)	Li(11)-P(10)-Li(14)-N(20)	-131.7(5)
C(420)-N(20)-Li(14)-C(421)	-20.5(4)	C(163)-P(10)-Li(14)-P(9)	95.8(3)
C(403)-N(20)-Li(14)-C(421)	94.4(5)	C(165)-P(10)-Li(14)-P(9)	-140.0(3)
C(430)-N(20)-Li(14)-Li(11)	54.6(10)	Li(11)-P(10)-Li(14)-P(9)	-3.3(3)
C(420)-N(20)-Li(14)-Li(11)	174.9(7)	C(163)-P(10)-Li(14)-C(421)	-102.1(5)
C(403)-N(20)-Li(14)-Li(11)	-70.2(9)	C(165)-P(10)-Li(14)-C(421)	22.1(7)
C(135)-P(9)-Li(14)-N(21)	-18.7(6)	Li(11)-P(10)-Li(14)-C(421)	158.8(5)
C(141)-P(9)-Li(14)-N(21)	99.0(6)	C(163)-P(10)-Li(14)-Li(11)	99.1(3)
Li(11)-P(9)-Li(14)-N(21)	-122.9(6)	C(165)-P(10)-Li(14)-Li(11)	-136.7(4)
C(135)-P(9)-Li(14)-N(20)	-127.8(5)	N(18)-Li(11)-Li(14)-N(21)	-178.2(6)
C(141)-P(9)-Li(14)-N(20)	-10.1(7)	N(19)-Li(11)-Li(14)-N(21)	-5.3(10)

Table A2.3: *continued...*

P(10)-Li(11)-Li(14)-N(21)	-92.0(7)
P(9)-Li(11)-Li(14)-N(21)	92.6(6)
N(18)-Li(11)-Li(14)-N(20)	-3.4(12)
N(19)-Li(11)-Li(14)-N(20)	169.5(6)
P(10)-Li(11)-Li(14)-N(20)	82.8(7)
P(9)-Li(11)-Li(14)-N(20)	-92.6(7)
N(18)-Li(11)-Li(14)-P(9)	89.3(7)
N(19)-Li(11)-Li(14)-P(9)	-97.9(6)
P(10)-Li(11)-Li(14)-P(9)	175.4(5)
N(18)-Li(11)-Li(14)-P(10)	-86.2(7)
N(19)-Li(11)-Li(14)-P(10)	86.7(6)
P(9)-Li(11)-Li(14)-P(10)	-175.4(5)
N(18)-Li(11)-Li(14)-C(421)	-144.4(11)
N(19)-Li(11)-Li(14)-C(421)	28.4(16)
P(10)-Li(11)-Li(14)-C(421)	-58.2(12)
P(9)-Li(11)-Li(14)-C(421)	126.3(13)
C(430)-N(20)-C(420)-C(421)	160.4(7)
C(403)-N(20)-C(420)-C(421)	-79.4(8)
Li(14)-N(20)-C(420)-C(421)	36.2(7)
C(401)-N(21)-C(421)-C(420)	166.2(6)
C(402)-N(21)-C(421)-C(420)	-72.1(8)
Li(14)-N(21)-C(421)-C(420)	46.0(7)
C(401)-N(21)-C(421)-Li(14)	120.1(6)
C(402)-N(21)-C(421)-Li(14)	-118.2(7)
N(20)-C(420)-C(421)-N(21)	-61.5(8)
N(20)-C(420)-C(421)-Li(14)	-27.8(6)
N(20)-Li(14)-C(421)-N(21)	157.1(6)
P(9)-Li(14)-C(421)-N(21)	52.4(8)
P(10)-Li(14)-C(421)-N(21)	-97.1(7)
Li(11)-Li(14)-C(421)-N(21)	-52.0(13)
N(21)-Li(14)-C(421)-C(420)	-136.7(7)
N(20)-Li(14)-C(421)-C(420)	20.3(4)
P(9)-Li(14)-C(421)-C(420)	-84.3(9)

Appendix 3

Comprehensive crystallographic data for **18**.

Table A3.1: Bond lengths [Å] for **18**.

C(1)-C(4)	1.491(10)
C(2)-C(3)	1.495(7)
C(3)-C(6)	1.520(6)
C(4)-C(5)	1.543(8)
C(5)-C(7)	1.518(7)
C(6)-C(8)	1.530(6)
C(7)-P(1)	1.805(4)
C(8)-P(2)	1.810(4)
C(9)-C(10)	1.531(7)
C(9)-P(1)	1.822(5)
C(10)-P(2)	1.846(5)
C(11)-C(12)	1.369(6)
C(11)-C(16)	1.393(5)
C(11)-P(1)	1.829(4)
C(12)-C(13)	1.388(6)
C(13)-C(14)	1.376(7)
C(14)-C(15)	1.372(7)
C(15)-C(16)	1.400(6)
C(17)-C(22)	1.379(6)
C(17)-C(18)	1.404(6)
C(18)-C(19)	1.364(8)
C(19)-C(20)	1.353(8)
C(20)-C(21)	1.398(7)
C(21)-C(22)	1.378(6)
C(22)-P(2)	1.818(4)
P(1)-Pd	2.2326(10)
P(2)-Pd	2.2297(11)
Cl(1)-Pd	2.3661(10)
Cl(2)-Pd	2.3675(10)

Symmetry transformations used to generate equivalent atoms:

Table A3.2: Bond angles [°] for **18**.

C(2)-C(3)-C(6)	112.4(5)
C(1)-C(4)-C(5)	112.9(7)
C(7)-C(5)-C(4)	111.1(5)
C(3)-C(6)-C(8)	113.4(4)
C(5)-C(7)-P(1)	112.4(3)
C(6)-C(8)-P(2)	113.0(3)
C(10)-C(9)-P(1)	108.9(3)
C(9)-C(10)-P(2)	109.7(3)
C(12)-C(11)-C(16)	119.6(4)
C(12)-C(11)-P(1)	120.8(3)
C(16)-C(11)-P(1)	119.5(3)
C(11)-C(12)-C(13)	120.1(4)
C(14)-C(13)-C(12)	120.9(5)
C(15)-C(14)-C(13)	119.4(4)
C(14)-C(15)-C(16)	120.2(4)
C(11)-C(16)-C(15)	119.7(4)
C(22)-C(17)-C(18)	120.9(5)
C(19)-C(18)-C(17)	119.1(5)
C(20)-C(19)-C(18)	121.2(5)
C(19)-C(20)-C(21)	119.6(5)
C(22)-C(21)-C(20)	121.0(5)
C(21)-C(22)-C(17)	118.1(4)
C(21)-C(22)-P(2)	123.2(4)
C(17)-C(22)-P(2)	118.6(3)
C(7)-P(1)-C(9)	107.9(2)
C(7)-P(1)-C(11)	108.02(19)
C(9)-P(1)-C(11)	102.79(19)
C(7)-P(1)-Pd	116.84(17)
C(9)-P(1)-Pd	107.65(15)
C(11)-P(1)-Pd	112.60(13)
C(8)-P(2)-C(22)	107.8(2)
C(8)-P(2)-C(10)	107.1(2)
C(22)-P(2)-C(10)	105.9(2)
C(8)-P(2)-Pd	111.85(16)
C(22)-P(2)-Pd	114.19(15)
C(10)-P(2)-Pd	109.60(15)
P(2)-Pd-P(1)	85.91(4)
P(2)-Pd-Cl(1)	175.79(4)
P(1)-Pd-Cl(1)	91.06(4)
P(2)-Pd-Cl(2)	87.01(4)
P(1)-Pd-Cl(2)	172.79(4)
Cl(1)-Pd-Cl(2)	96.08(4)

Symmetry transformations used to generate equivalent atoms:

Table A3.3: Torsion angles [°] for **18**.

C(1)-C(4)-C(5)-C(7)	-179.8(5)
C(2)-C(3)-C(6)-C(8)	-177.1(4)
C(4)-C(5)-C(7)-P(1)	-176.0(4)
C(3)-C(6)-C(8)-P(2)	179.8(4)
P(1)-C(9)-C(10)-P(2)	-44.4(4)
C(16)-C(11)-C(12)-C(13)	-2.9(7)
P(1)-C(11)-C(12)-C(13)	172.4(4)
C(11)-C(12)-C(13)-C(14)	-0.5(7)
C(12)-C(13)-C(14)-C(15)	3.0(7)
C(13)-C(14)-C(15)-C(16)	-2.0(7)
C(12)-C(11)-C(16)-C(15)	3.9(6)
P(1)-C(11)-C(16)-C(15)	-171.5(3)
C(14)-C(15)-C(16)-C(11)	-1.4(7)
C(22)-C(17)-C(18)-C(19)	1.3(10)
C(17)-C(18)-C(19)-C(20)	-1.1(10)
C(18)-C(19)-C(20)-C(21)	1.6(9)
C(19)-C(20)-C(21)-C(22)	-2.5(9)
C(20)-C(21)-C(22)-C(17)	2.7(8)
C(20)-C(21)-C(22)-P(2)	-176.5(4)
C(18)-C(17)-C(22)-C(21)	-2.1(9)
C(18)-C(17)-C(22)-P(2)	177.1(5)
C(5)-C(7)-P(1)-C(9)	-62.5(4)
C(5)-C(7)-P(1)-C(11)	-173.0(4)
C(5)-C(7)-P(1)-Pd	58.9(4)
C(10)-C(9)-P(1)-C(7)	170.6(3)
C(10)-C(9)-P(1)-C(11)	-75.4(3)
C(10)-C(9)-P(1)-Pd	43.7(3)
C(12)-C(11)-P(1)-C(7)	57.8(4)
C(16)-C(11)-P(1)-C(7)	-126.9(4)
C(12)-C(11)-P(1)-C(9)	-56.1(4)
C(16)-C(11)-P(1)-C(9)	119.2(3)
C(12)-C(11)-P(1)-Pd	-171.6(3)
C(16)-C(11)-P(1)-Pd	3.6(4)
C(6)-C(8)-P(2)-C(22)	-169.6(4)
C(6)-C(8)-P(2)-C(10)	76.8(4)
C(6)-C(8)-P(2)-Pd	-43.3(4)
C(21)-C(22)-P(2)-C(8)	-16.2(5)
C(17)-C(22)-P(2)-C(8)	164.5(4)
C(21)-C(22)-P(2)-C(10)	98.2(5)
C(17)-C(22)-P(2)-C(10)	-81.1(5)
C(21)-C(22)-P(2)-Pd	-141.2(4)
C(17)-C(22)-P(2)-Pd	39.6(5)
C(9)-C(10)-P(2)-C(8)	-94.6(3)
C(9)-C(10)-P(2)-C(22)	150.5(3)
C(9)-C(10)-P(2)-Pd	26.9(3)
C(8)-P(2)-Pd-P(1)	118.13(18)
C(22)-P(2)-Pd-P(1)	-119.07(16)

Table A3.3: *continued...*

C(10)-P(2)-Pd-P(1)	-0.49(15)
C(8)-P(2)-Pd-Cl(2)	-63.23(18)
C(22)-P(2)-Pd-Cl(2)	59.57(16)
C(10)-P(2)-Pd-Cl(2)	178.16(15)
C(7)-P(1)-Pd-P(2)	-142.8(2)
C(9)-P(1)-Pd-P(2)	-21.28(14)
C(11)-P(1)-Pd-P(2)	91.31(14)
C(7)-P(1)-Pd-Cl(1)	34.3(2)
C(9)-P(1)-Pd-Cl(1)	155.78(13)
C(11)-P(1)-Pd-Cl(1)	-91.63(14)

Symmetry transformations used to generate equivalent atoms:

Appendix 4

Comprehensive crystallographic data for **20**.

Table A4.1: Bond lengths [Å] for **20**.

C(1)-C(2)	1.39(3)
C(2)-C(3)	1.514(19)
C(3)-C(4)	1.503(16)
C(4)-P(1)	1.813(11)
C(5)-C(6)	1.381(17)
C(5)-C(10)	1.382(14)
C(6)-C(7)	1.373(18)
C(7)-C(8)	1.379(17)
C(8)-C(9)	1.380(16)
C(9)-C(10)	1.388(15)
C(10)-P(1)	1.798(10)
C(11)-C(12)	1.520(15)
C(11)-P(1)	1.824(11)
C(12)-P(2)	1.828(11)
C(13)-C(18)	1.367(17)
C(13)-C(14)	1.367(17)
C(14)-C(15)	1.38(2)
C(15)-C(16)	1.34(2)
C(16)-C(17)	1.397(17)
C(17)-C(18)	1.374(16)
C(18)-P(2)	1.808(12)
C(19)-C(20)	1.506(17)
C(19)-P(2)	1.820(11)
C(20)-C(21)	1.518(17)
C(21)-C(22)	1.50(2)
Pd-P(2)	2.321(3)
Pd-P(2a)	2.321(3)
Pd-P(1a)	2.330(3)
Pd-P(1)	2.330(3)
Cl(1)-O(2)	1.310(13)
Cl(1)-O(1)	1.376(13)
Cl(1)-O(4)	1.390(10)
Cl(1)-O(3)	1.408(17)

Table A4.2: Bond angles [º] for **20**.

C(1)-C(2)-C(3)	116(2)
C(4)-C(3)-C(2)	112.2(13)
C(3)-C(4)-P(1)	115.1(8)
C(6)-C(5)-C(10)	119.6(12)
C(7)-C(6)-C(5)	121.5(11)
C(6)-C(7)-C(8)	119.5(12)
C(7)-C(8)-C(9)	119.0(12)
C(8)-C(9)-C(10)	122.0(10)
C(5)-C(10)-C(9)	118.4(10)
C(5)-C(10)-P(1)	123.1(9)
C(9)-C(10)-P(1)	118.5(7)
C(12)-C(11)-P(1)	111.7(8)
C(11)-C(12)-P(2)	108.7(8)
C(18)-C(13)-C(14)	120.0(12)
C(13)-C(14)-C(15)	119.7(14)
C(16)-C(15)-C(14)	120.6(13)
C(15)-C(16)-C(17)	120.1(13)
C(18)-C(17)-C(16)	119.0(13)
C(13)-C(18)-C(17)	120.5(11)
C(13)-C(18)-P(2)	117.9(9)
C(17)-C(18)-P(2)	121.5(9)
C(20)-C(19)-P(2)	117.4(9)
C(19)-C(20)-C(21)	112.6(11)
C(22)-C(21)-C(20)	112.9(13)
P(2)-Pd-P(2a)	97.71(14)
P(2)-Pd-P(1a)	176.48(10)
P(2a)-Pd-P(1a)	83.72(9)
P(2)-Pd-P(1)	83.72(9)
P(2a)-Pd-P(1)	176.48(10)
P(1a)-Pd-P(1)	95.03(14)
C(10)-P(1)-C(4)	106.2(5)
C(10)-P(1)-C(11)	105.9(5)
C(4)-P(1)-C(11)	104.5(5)
C(10)-P(1)-Pd	112.4(4)
C(4)-P(1)-Pd	118.4(4)
C(11)-P(1)-Pd	108.6(4)
C(18)-P(2)-C(19)	110.5(6)
C(18)-P(2)-C(12)	105.9(5)
C(19)-P(2)-C(12)	104.2(6)
C(18)-P(2)-Pd	110.5(4)
C(19)-P(2)-Pd	119.2(4)
C(12)-P(2)-Pd	105.4(4)
O(2)-Cl(1)-O(1)	112.1(13)
O(2)-Cl(1)-O(4)	111.2(9)
O(1)-Cl(1)-O(4)	110.3(8)
O(2)-Cl(1)-O(3)	108.8(15)
O(1)-Cl(1)-O(3)	101.8(11)
O(4)-Cl(1)-O(3)	112.4(9)

Symmetry transformations used to generate equivalent atoms.

Table A4.3: Torsion angles [°] for **20**.

C(1)-C(2)-C(3)-C(4)	173(2)
C(2)-C(3)-C(4)-P(1)	-172.8(11)
C(10)-C(5)-C(6)-C(7)	-1.0(19)
C(5)-C(6)-C(7)-C(8)	2(2)
C(6)-C(7)-C(8)-C(9)	-1.4(19)
C(7)-C(8)-C(9)-C(10)	0.4(19)
C(6)-C(5)-C(10)-C(9)	0.0(17)
C(6)-C(5)-C(10)-P(1)	179.5(9)
C(8)-C(9)-C(10)-C(5)	0.3(17)
C(8)-C(9)-C(10)-P(1)	-179.2(9)
P(1)-C(11)-C(12)-P(2)	47.5(9)
C(18)-C(13)-C(14)-C(15)	3(2)
C(13)-C(14)-C(15)-C(16)	-2(2)
C(14)-C(15)-C(16)-C(17)	2(2)
C(15)-C(16)-C(17)-C(18)	-2(2)
C(14)-C(13)-C(18)-C(17)	-2.7(18)
C(14)-C(13)-C(18)-P(2)	175.0(9)
C(16)-C(17)-C(18)-C(13)	2.4(18)
C(16)-C(17)-C(18)-P(2)	-175.2(10)
P(2)-C(19)-C(20)-C(21)	175.3(11)
C(19)-C(20)-C(21)-C(22)	-178.8(14)
C(5)-C(10)-P(1)-C(4)	-0.9(11)
C(9)-C(10)-P(1)-C(4)	178.6(9)
C(5)-C(10)-P(1)-C(11)	109.8(10)
C(9)-C(10)-P(1)-C(11)	-70.8(10)
C(5)-C(10)-P(1)-Pd	-131.8(9)
C(9)-C(10)-P(1)-Pd	47.7(9)
C(3)-C(4)-P(1)-C(10)	178.6(9)
C(3)-C(4)-P(1)-C(11)	67.0(10)
C(3)-C(4)-P(1)-Pd	-53.9(10)
C(12)-C(11)-P(1)-C(10)	96.6(8)
C(12)-C(11)-P(1)-C(4)	-151.5(8)
C(12)-C(11)-P(1)-Pd	-24.2(8)
P(2)-Pd-P(1)-C(10)	-121.3(4)
P(1a)-Pd-P(1)-C(10)	55.4(4)
P(2)-Pd-P(1)-C(4)	114.3(5)
P(1a)-Pd-P(1)-C(4)	-69.0(5)
P(2)-Pd-P(1)-C(11)	-4.5(4)
P(1a)-Pd-P(1)-C(11)	172.2(4)
C(13)-C(18)-P(2)-C(19)	116.5(10)
C(17)-C(18)-P(2)-C(19)	-65.9(11)
C(13)-C(18)-P(2)-C(12)	-131.2(9)
C(17)-C(18)-P(2)-C(12)	46.4(11)
C(13)-C(18)-P(2)-Pd	-17.6(10)
C(17)-C(18)-P(2)-Pd	160.1(9)
C(20)-C(19)-P(2)-C(18)	59.6(12)
C(20)-C(19)-P(2)-C(12)	-53.7(12)

Table A4.3: *continued...*

C(20)-C(19)-P(2)-Pd	-170.9(9)
C(11)-C(12)-P(2)-C(18)	67.9(8)
C(11)-C(12)-P(2)-C(19)	-175.5(8)
C(11)-C(12)-P(2)-Pd	-49.2(8)
P(2a)-Pd-P(2)-C(18)	89.5(4)
P(1)-Pd-P(2)-C(18)	-87.3(4)
P(2a)-Pd-P(2)-C(19)	-40.1(5)
P(1)-Pd-P(2)-C(19)	143.2(5)
P(2a)-Pd-P(2)-C(12)	-156.6(4)
P(1)-Pd-P(2)-C(12)	26.6(4)

Symmetry transformations used to generate equivalent atoms.