# I. Synthesis and Reactivity of Novel β-Diketiminato-cadmium Complexes

# II. Synthesis of Lead Selenide Nanoparticles for Use in Solar Cells

Ву

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#### Abstract

Rising levels of carbon dioxide (CO<sub>2</sub>) in the atmosphere has led to metal amide and alkoxide complexes being explored as potential CO<sub>2</sub> activators. A wide variety of M–O and M–N bonds have been shown to activate CO<sub>2</sub>, however to date there are no examples with cadmium. A range of novel cadmium amide and alkoxide complexes have been synthesised, using the  $\beta$ -diketiminato ligand (BDI) as an ancilliary ligand. Initial reactivity studies have suggested CO<sub>2</sub> activation may be possible, although no products were isolated.

Homonuclear metallic bonding (M–M) has been explored since the 1950's and complexes containing M–M bonds are known for almost all transition and main group metals. There are only two reported Cd–Cd bonds, both using sterically bulky monoanionic ligands, like the  $\beta$ -diketiminato ligand. A novel  $\beta$ -diketiminato-cadmium chloride complex was synthesised and treated with a range of different reducing agents to generate a Cd–Cd bond. Different reactivities were observed for the reducing agents, however evidence of a Cd–Cd bond was not obtained.

Group 14-16 materials, such as lead selenide, are p-type semi-conductors and have the potential to replacing silicon as a photon acceptor in solar cells. Lead selenide nanoparticles display quantum confinement effects, which allows one to tailor the band gap energies to maximise their absorbance of solar energy. The synthesis of PbSe nanoparticles is described in this study from the reaction between selenium and the lead complex [(BDI<sub>Ph</sub>)<sub>2</sub>Pb], as well as from the decomposition of [(BDI<sub>DIPP</sub>)PbSeP{Se}Cy<sub>2</sub>]. Differences in the size and shapes of the nanoparticles was observed, highlighting the need for controlled nucleation and growth conditions.

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### Glossary of Terms

δ	Chemical shift (ppm).
<sup>13</sup> C NMR	Carbon nuclear magnetic resonance.
<sup>1</sup> H NMR	Hydrogen nuclear magnetic resonance.
<sup>31</sup> P NMR	Phosphorus nuclear magnetic resonance.
BDI	β-Dikeiminate ligand
br	Broad.
C <sub>6</sub> D <sub>6</sub>	Deuterated benzene.
CDCl₃	Deuterated Chloroform
CH <sub>2</sub> Cl <sub>2</sub>	Dichloromethane
CO2	Carbon dioxide
d	Doublet.
dd	Doublet of doublets.
DIPP	2,6-diisopropylphenyl.
DMF	Dimethylformamide
DMP	Dimethylphenyl
EDS	Energy dispersive X-ray spectroscopy
IPP	<i>iso</i> -Propylphenyl
IR	Infrared spectroscopy
HMDSO	Hexamethyldisiloxide
J	Scalar coupling constant (Hz).
m	Multiplet.
M-M	Homonuclear metallic bond
Mes	Mesityl ligand.
N <sub>2</sub>	Nitrogen gas
NacNac	β-Dikeiminate ligand
NCCCN/C <sub>3</sub> N <sub>2</sub>	The plane defined by the atoms $N_1\mathchar`-C_2\mathchar`-C_2\mathchar`-N_2$ on the $\beta\mathchar`-dikeiminate ligand$
NMR	Nuclear magnetic resonance spectroscopy.
Ph	Phenyl
р <i>К</i> а	Logarithmic acid dissociation constant
Ppm	Parts per million.
S	Singlet.
sept	Septet.
t	Triplet.
ТОР	Trioctylphosphine
ТОРО	Trioctylphosphine oxide
Тр*	Trispyrazoylborate ligand
THF	Tetrahydrofuran.

# Chapter 1

# Synthesis and Reactivity of Novel β-Diketiminato-cadmium Complexes

# Introduction

#### 1.1 History

Cadmium was discovered in 1817 in Hanover by F. Stromeyer and K.S.L. Hermann, when they independently examined samples of zinc oxide formed by oxidising a naturally occurring form of zinc carbonate, *cadmia*. Instead of the expected pure white colour, sometimes the product was discoloured by a trace amount of an unknown component. It was deduced that this must be due to the presence of another element. After it was separated out as a brown oxide, the new component was heated in the presence of carbon black to give a blue-grey metal, which was named cadmium after the name of the mineral. For 100 years Germany remained the only significant producer of cadmium, however in the 1930s and 1940s, potential uses for cadmium grew and industrial scale productions began.

Almost all the cadmium manufactured is in the form of cadmium oxide, a by-product of the metallurgy of zinc. Cadmium oxide is easily isolated as it is far more volatile than zinc oxide. Originally the major application of cadmium was a coating for iron and steel to prevent corrosion. Cadmium sulfides and selenides were also commonly used as red, orange and yellow pigments dyes, where it showed an astonishing ability to tolerate high temperatures and pressures without fading. The use of cadmium in these applications declined in the 1980s and 1990s due to environmental and health regulations. A new application for cadmium has since arisen, which is an electrode in rechargeable nickel-cadmium batteries

The toxicity of cadmium is similar to that of lead and mercury, although human uptake of cadmium generally comes from food and cigarettes. Cadmium from cigarette smoke is absorbed in the respiratory tract where it acts as an intense irritant and can result in pulmonary oedema, as well as

increasing the risk of chronic lung disease. When ingested, even in small amounts, cadmium builds up in the liver and kidneys and can cause salivating, vomiting, nausea, convulsions and kidney stones.

#### 1.2 The $\beta$ -Diketiminate Ligand

The  $\beta$ -diketiminato ligand, commonly shortened to NacNac or BDI, has been widely researched in inorganic and organometallic chemistry as a sterically bulky bidentate monoanionic ligand. Each position on the N–C–C–C–N ligand backbone can be individually and alternatively substituted (Figure 1), allowing the electronic and steric properties of the ligand to be fine tuned. Upon coordination to a metal centre via the two nitrogens forming a metallocycle, the  $\pi$  electrons delocalise across the C<sub>3</sub>N<sub>2</sub> backbone.



Figure 1 The BDI ligand backbone showing potential substitution sites.

The metallocycle of three coordinate BDI complexes generally adopts a planar geometry; however, if the metal centre is too sterically crowded then a boat shape conformation is observed (Figure 2).<sup>1</sup> The bonding modes of the  $\beta$ -diketiminato ligand, modelled as planar C<sub>3</sub>N<sub>2</sub>H<sub>5</sub>, have been examined with Amsterdam Density Functional Theory calculations.<sup>2</sup> The metal bonding orbitals are in plane, out of phase nitrogen centred orbitals with lobes directed at the metal, meaning the nitrogen atoms are forming  $\sigma$ -bonds with the metal. As such, the  $\beta$ -diketiminato ligand is a 4-electron donor. If the metallocycle is in a boat conformation, an occupied out of phase  $\pi$  orbital may also bond to the metal, resulting in a 6 electron,  $2\sigma+\pi$  process, however this only occurs with highly puckered Ti(IV) and Zr(IV) systems.

Planar

Boat shaped

(С<sup>N</sup>)м

N/M

Figure 2 Planar and boat conformations of the BDI ligand.

#### 1.3 Project Aims

The aim of this project was to synthesise and investigate the reactivity of novel cadmium amide and alkoxide complexes. Reactivity with  $CO_2$  or other heterocumulenes have not been reported for any cadmium amide or alkoxide complexes. The  $\beta$ -diketiminate ligand was chosen as an ancillary ligand to stabilise the cadmium complexes. This is a monomeric ligand with sufficient steric bulk to prevent oligomerisation of the resulting cadmium complex. To date, only a handful of cadmium complexes bearing the  $\beta$ -diketiminate ligand have been synthesised, generally via toxic dialkyl complexes. A second aim of this project is to synthesise a low coordinate monomeric  $\beta$ -diketiminato-cadmium halide complex and investigate its reactivity towards reducing agents in an attempt to synthesise a homonuclear cadmium dimer.

#### 1.4 Synthesis of Group 12 Homonuclear M–M Bonds

Research into compounds containing homonuclear metallic bonds (M–M) began in the 1950's. Prior to this there were a few compounds known containing M–M bonds. However these compounds were made by accident and were considered curiosities. The development of M–M chemistry was dependant on the rise of X-ray crystal structural analysis which could demonstrate the existence of this type of bonding in the solid state. Previously, only atomic positions in very simple complexes could be determined by Fourier series, which was first demonstated in the 1920's for Hg<sub>2</sub>Cl<sub>2</sub>.<sup>3</sup> Since the 1950's the field has been thoroughly explored, with homonuclear bonds known for almost all main group and transition metals, ranging in strength from weak interactions, such as  $[Cr_2Cl_9^{3-}]$  I,<sup>26</sup> to formal quadruple bonds,  $[Cr_2(N_2CPh)_2]$  II,<sup>4</sup> (Figure 3).



*Figure 3* Homonuclear Cr–Cr bonding, ranging in strength from a partial bond  $[Cr_2Cl_9^{3-}]$  I to a formal quadruple bond  $[Cr_2(N_2CPh)_2]$  II.

A low oxidation is required for M–M bond formation for a number of reasons.<sup>5,6,7</sup> For instance, complexes with high oxidation states have many polar M–X bonds, where X = halogen, alkyl group, carbonyl etc. The nuclear charge on the valence shell orbitals of the metal is therefore high, contracting the orbitals, thus minimising their ability to overlap and form M–M bonds. Thermodynamically, in the formation of the complex M<sub>m</sub>X<sub>x</sub>, (equation 1) the vaporisation of M<sub>s</sub> and the bond dissociation of X–X are both very endothermic processes. When the *x/m* ratio is low, only a small number of M–X bonds are formed, meaning not enough energy is released via M–X bond formation to match the energy spent vaporising M<sub>s</sub> and dissociating X–X. Only the formation of other bonds, specifically M–M bonds, can stabilise this reaction. Steric factors also play a role as compounds with high oxidation states tend to be surrounded by many non-metal atoms, meaning the two metal centres cannot interact. Metal hydride complexes are formed in several studies which report complexes with an M–M bond, where they can often be thought of as intermediates, decomposing to give M–M bonds.<sup>8,9</sup> These are often stabilised with low-coordinate sterically bulky ancillary ligands.

$$M_s + \chi - \chi \longrightarrow M_m \chi_{\chi}$$
 (1)

#### 1.4.1 Homonuclear Mercury – Mercury Bonds

Of the group 12 elements, the chemistry of cadmium is more similar to that of zinc than mercury. Zinc and cadmium adopt primarily a divalent oxidation state and examples of monovalent complexes are rare. In contrast  $[Hg_2]^{2+}$  cations, in which the mercury is formally monovalent, are reasonably common in the literature, however are considered salt-like ionic species often containing complex oligomeric structures. For example, the mercury atoms in  $Hg_2Cl_2$  is actually bonded to six chloride atoms, two close and four more distant.<sup>10</sup> Despite this, it was not until 1999 that a stable molecular mercury complex was synthesised containing a  $\sigma$ -bonded Hg–Hg unit.<sup>11</sup> Until then these molecular R–Hg–Hg–R complexes, were short lived intermediates and had not been structurally characterised. The compound  $[Hg_2{Si(SiMe_2SiMe_3)_3}_2]$  V was synthesised by addition of two equivalents of HSi(SiMe\_2SiMe\_3)\_3 III with  $(Bu^1)_2$ Hg IV (equation 2). The crystal structure revealed that the Si–Hg–Hg–Si core of the molecule is linear, with a Hg–Hg bond length of 2.656 Å. This bond length is larger in comparison to most ionic  $[Hg-Hg]^{2+}$  bonds as well as the mercury halides where reported bond lengths lie between 2.49 – 2.59 Å.



#### 1.4.2 Homonuclear Zinc – Zinc Bonds

There is some spectroscopic evidence for the formation of  $[Zn_2]^{2+}$  cations in Zn/ZnCl<sub>2</sub> melts at high temperatures.<sup>12</sup> The absorption spectrum of these melts reveals a reduced species and magnetic susceptibility measurements suggesting a  $[Zn_2]^{2+}$  structure rather than the paramagnetic Zn<sup>+1</sup>. These results are unconfirmed as the corresponding low valence zinc species were never isolated. The first example of a molecular homonuclear Zn–Zn bond was discovered in 2004, when  $[Zn_2(n^5-C_5Me_5)_2]$  VII was formed unexpectedly from the reaction between  $[Zn(C_5Me_5)_2]$  VII and  $[Zn(C_2H_5)_2]$  VI at -10 °C (equation 3).<sup>13</sup> The decamethyldizincocene complex VIII was found to be extremely air and moisture sensitive, however it was indefinitely stable in an argon environment at room temperature. X-ray crystallography was used to determine the molecular structure. The complex was found to be almost linear, with a (C<sub>5</sub>Me<sub>5</sub>)-Zn-Zn average bond angle of 177.4 ° and a Zn–Zn bond distance of 2.305 Å. This is the first example of a linear metallocene based metal-metal bond unsupported by bridging ligands.



In 2005 another complex bearing a Zn–Zn bond was reported utilising the  $\beta$ -diketiminate ligand, [(2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)N(Me)C}<sub>2</sub>CH]<sup>-</sup> (BDI<sub>dipp</sub>) as an ancilliary ligand.<sup>14</sup> The  $\beta$ -diketiminato ligand was chosen as it had been recently used to stabilise homonuclear indium and manganese bonds. The Zn–Zn bond was formed by reducing the species [(BDI<sub>dipp</sub>)Zn( $\mu$ -I)<sub>2</sub>Li(OEt<sub>2</sub>)<sub>2</sub>] **IX** with potassium to form [(BDI<sub>dipp</sub>)Zn– Zn(BDI<sub>DIPP</sub>)] **X** (equation 4). The Zn–Zn bond of **X** was 2.358 Å, 0.05 Å longer than the Zn–Zn bond of decamethyldizincocene **VIII**. The ligand backbone forms a 6 puckered membered metallocycle with the zinc, which lies outside the NCCCN plane by 0.65 Å. Each zinc atom is three coordinate and adopts a trigonal planar geometry, with the Zn–N bond distances of 2.005(3) Å and 2.014(3) Å amongst the longest ever reported. DFT calculations were performed, which confirmed that the metallocycles were more energetically favourable in a puckered conformation, rather than planar, due to steric crowding around the zinc centres.



#### 1.4.3 Homonuclear Cadmium – Cadmium Bonds

The low valence cadmium cation  $[Cd_2]^{2+}$  was first discovered by manipulating the equilibrium between divalent and zerovalent cadmium and the cadmium(I) dimer.<sup>15</sup> Normally this equilibrium lies significantly in favour of the divalent and zerovalent cadmium, however it was shown that adding a Lewis acid, in this case AlCl<sub>3</sub>, would shift the equilibrium right. In this example, molten  $[Cd(AlCl_4)_2]$  **XI** was reduced with cadmium metal to give a mixture of  $[Cd(AlCl_4)_2]$  **XI** and  $[Cd(AlCl_4)]$  **XII**. Crystals of **XII** were isolated and were found to be diamagnetic, suggesting a dimeric cadmium complex. This hypothesis was further supported by Raman data. The structure of **XII** was determined by X-Ray crystallography 30 years later and revealed that the cadmium cation  $[Cd_2]^{2+}$  is bound to three almost tetrahedral  $[AlCl_4]^-$  species at an overall Cd:Al ratio of 1:1 (Figure 4).<sup>16</sup> The cadmium-cadmium bond length in this complex is 2.576 Å, which is longer than any reported zinc or mercury homonuclear bond. The tetrahedral  $[AlCl_4]^-$  anions were only slightly distorted, with Cl–Al–Cl bond angles ranging from 107-111 ° and averaging 109.45 °. This suggests that they are only weakly coordinated to the  $[Cd_2]^{2+}$  cation and can be thought of as linking the cations into polymeric sheets.



*Figure 4* Diagram of Cd(AlCl<sub>4</sub>) **XII** the geometry around one cadmium atom (left) and a fragment showing two connected  $[Cd_2]^{2+}$  units (right).

The first molecular complex containing a homonuclear Cd–Cd bond was discovered simultaneously with the first molecular complex containing a cadmium hydride bond by Reger and coworkers, using a substituted trispyrazolylborate ligand [HB(3,5–Me<sub>2</sub>Pz)<sub>3</sub><sup>-</sup>] (Tp\*) as an ancillary ligand.<sup>8</sup> The Tp\* ligand had previously been shown to complex tin, which has similar chemistry to that of cadmium.<sup>7</sup> A range of organometallic cadmium complexes, [(Tp\*)CdR] **XIV** had previously been synthesised by Reger and co-workers.<sup>8</sup> The synthesis involves generating the [RCdCl] *in situ* by treating CdCl<sub>2</sub> with the appropriate organo-anion source. This is followed by addition of the thallium trispyrazolylborate species, Tl[HB(3,5–Me<sub>2</sub>Pz)<sub>3</sub>] **XIII** to form the desired organometallic complex (equation 5).



R = methyl, ethyl, *n*-propyl, *i*-propyl, *n*-butyl sec-butyl, *i*-butyl, *t*-butyl, phenyl

When potassium borohydride (KBH<sub>4</sub>) was used instead of the organo-anion source, the product formed was [HB(3,5-Me<sub>2</sub>Pz)<sub>3</sub>CdBH<sub>4</sub>.] **XV.** The cadmium borohydride complex **XV** is  $\eta^2$ -coordinated to the cadmium through two hydrogen atoms (equation 6). Interestingly the mass spectrum of this compound showed a cluster of peaks corresponding to the dimer [CdHB(3,5-Me<sub>2</sub>Pz)<sub>3</sub>]<sub>2</sub>**XVI**. When the reaction was performed utilising lithium triethylborohydride (LiBHEt<sub>3</sub>) as the hydride source, a different complex was observed in the <sup>1</sup>H NMR which contained resonances which were consistent with a dimeric cadmium complexes (equation 7). A resonance was observed in the <sup>113</sup>Cd NMR spectrum, suggesting that the complex contained a Cd – Cd bond, with <sup>111</sup>Cd satellites (J<sub>111Cd-113Cd</sub> = 20646 Hz). This extremely large coupling constant is the first reported <sup>111</sup>Cd-<sup>113</sup>Cd coupling constant and indicates a formal bond between the two cadmium centres. No other coupling was observed to indicate any coordinated hydrogen atoms. Unfortunately crystals suitable for an X-ray diffraction study were not able to be grown.



When the larger Tp<sup>tBu</sup> ligand was used,  $[HB(3,5^{t}Bu_2Pz)_3^{-}]$ ,  $[(Tp^{tBu}CdH)$  **XVII** was isolated when either KBH<sub>4</sub> or LiBHEt<sub>3</sub> was utilised as the hydride source (equation 8). A hydride resonance at  $\delta$  6.30 ppm was observed in the <sup>1</sup>H NMR spectrum with both <sup>111</sup>Cd (J = 2411 Hz) and <sup>113</sup>Cd (J = 2522 Hz) satellites. The <sup>113</sup> Cd spectrum revealed a doublet with a Cd–H coupling constant, matching that seen in the <sup>1</sup>H spectrum. These syntheses not only give the first examples of molecular cadmium hydride and cadmium – cadmium bonds, but demonstrate how different products can be formed with minor changes to the reaction conditions and the steric bulk of the ligand.



Only one other molecular complex bearing a homonuclear cadmium – cadmium bond, ArCdCdAr (Ar =  $C_6H_3$ -2,6- $(C_6H_3$ -2,6- $Pr_2^i)_2$ ) **XVIII** has been reported.<sup>9</sup> This complex was synthesised from the reduction of aryl cadmium iodide [ArCdI] **XIX** (equation 9). In the attempted synthesis of ArCdCdAr **XVIII**, [ArCdI] **XIX** was treated with a variety of reducing agents and hydride sources, resulting in a variety of different outcomes, ranging from no reaction to over-reduction of [ArCdI] as observed by the formation of

protonated ligand and cadmium metal. However, when two equivalents of sodium hydride were added to **XIX** at room temperature, ArCdCdAr **XVIII** was formed in <10 % yields.



The Cd–Cd bond length of ArCdCdAr **XVIII**, 2.626 Å, is similar to the bond length for the  $[Cd_2]^{2+}$  ion found in the sheet like structure of CdAlCl<sub>4</sub> **XII**.<sup>8</sup> It also is significantly longer than molecular zinc complexes, **VIII** and **X**,<sup>13,14</sup> which lie in the range of 2.30 and 2.35 Å, and slightly shorter than the bond lengths of the molecular mercury complex,  $[Hg_2{Si(SiMe_2SiMe_3)_3}_2]$  **V**, at 2.656 Å.<sup>11</sup> Theoretical calculations suggest that the covalent radius of mercury should be smaller than that of cadmium.<sup>17</sup> To examine this, isostructural zinc **XX** and mercury **XXI** analogues, ArMMAr, were synthesised via reduction of the corresponding ArMI complexes. The M–M homonuclear bond lengths of the three complexes varied from 2.359 Å for Zn–Zn to 2.626 Å for Cd–Cd and 2.574 Å for Hg–Hg. DFT calculations showed that the p-character in the M–M bond decreases as the group descends. The calculated bond enthalpy corresponds to the M–M bond length, with the Zn–Zn bond the strongest (55.6 kcal/mol), followed by the Hg–Hg bond (50.1 kcal/mol) and the weakest being the Cd–Cd bond (48.2 kcal/mol).

The related group 12 metal hydrides were also generated during the course of the above studies (equation 10).<sup>18</sup> Exploring the metal hydride complexes is important as a mechanism for the reduction of the aryl metal halides to form the homonuclear M–M bond is unclear. The hydride complexes, [ArMH], are a rare example of organometallic group 12 hydride complexes as they tend to thermally decompose at room temperature. There are some examples of organometallic zinc hydride complexes where the hydride exists both in a bridging structure and as a terminal hydride.<sup>19</sup> Organometallic cadmium hydrides are rarer with just one other example in the literature, HB(3,5–Bu<sup>t</sup>Pz)<sub>3</sub>CdH **XVII**, as previously described.<sup>8</sup> There are no examples of structurally characterised organometallic mercury hydride complexes.



M = Zn XXII, Cd XXIII, Hg XXIV

The zinc XXII and cadmium XXIII hydride complexes were synthesised from the treatment of the corresponding aryl metal iodide, ArMI, with NaH. For the zinc hydride complex a dimer was formed in the solid state with similar Zn–H distances, 1.69(2) Å and 1.73(3) Å, suggesting the hydrides bond equally to each zinc atom. For the cadmium hydride complex, an asymmetric dimer was formed in the solid state with unequal Cd–H distances. Each cadmium was bonded to one hydride at distances of 1.78 Å and 2.27 Å. This suggests the cadmium has a loosely associated dimer structure. The cadmium hydride was found to be thermally unstable and decomposed after a few hours to form the Cd–Cd bonded ArCdCdAr XVIII. The <sup>1</sup>H NMR spectrum of the analogous mercury hydride, ArHgH XXIV, revealed a resonance at  $\delta$  14.59 ppm ( $J(^{113}Hg^1H) = 2900 Hz$ ), attributed to the hydride ligand, along with a doublet in the <sup>199</sup>Hg NMR spectrum at  $\delta$ –659 ppm ( $J(^{113}Hg^1H) = 2910 Hz$ ). Unfortunately crystals of XXIV suitable for X-ray analysis were not able to be grown.

#### 1.5 Group 12 Reactivity with Heterocumulenes

Carbon dioxide activation has been an important area of research in recent years due to the environmental benefits of removing carbon dioxide from the atmosphere. Potential carbon dioxide activators include metal complexes with bound amide or alkoxide ligands, allowing carbon dioxide to insert into the M–O or M–N bonds.<sup>20</sup> The mechanism for this insertion has been postulated as a 2,2 cycloaddition through a four membered transition state (Scheme 1). An open coordination site on the metal is required and the driving force of the reaction has been presumed to be the due to the nucleophilicity of the alkoxide or amide ligand. However, recent results by Fulton revealed that the Lewis acidity of the metal also plays an important role.<sup>21</sup>



Scheme 1 2+2 Cycloaddition leading to the Insertion product for heterocumulenes

#### 1.5.1 Reactivity of Zinc Alkoxides

The activation of carbon dioxide and other heterocumulenes has been studied with trispyrazolylborate zinc alkoxide complexes.<sup>20f</sup> The zinc alkoxides tested were  $[Tp^{Ph,Me}ZnOCH_3]$  **XXV** and  $[Tp^{Ph,Me}ZnOC_2H_5]$  **XXVI**, where  $Tp^{Ph,Me} = HB(3-Ph,5-MePz)_3$ . The insertion of CO<sub>2</sub> into the Zn–O bond

was a slow process, requiring prolonged bubbling of CO<sub>2</sub> through the solution, or applying CO<sub>2</sub> pressure in an autoclave (equation 11). However, the reaction went to completion to form [Tp<sup>Ph,Me</sup>ZnO(CO)OR] (R = Me, **XXVII** Et **XXVIII**) with no other products present in <sup>1</sup>H and <sup>13</sup>C NMR spectra, or the IR spectrum. The zinc centre is formally four coordinate, however a long range interaction with the carbonyl oxygen of the carbonate donor is observed, thus resulting in a distorted tetrahedral geometry, or a trigonal bipyramidal geometry if this long distance interaction is included. The Zn–O bond of the partial bond (2.77 Å) is significantly longer than the formal bond (1.89 Å) indicating the interaction is weak.



Similar results were observed with the insertion of carbon disulfide into the Zn–O bond of the zinc alkoxides [Tp<sup>Ph,Me</sup>ZnOCH<sub>3</sub>] **XXV** and [Tp<sup>Ph,Me</sup>ZnOC<sub>2</sub>H<sub>5</sub>] **XXVI**, although the reaction was significantly more facile. The structure of the product again tended towards a trigonal bypyramidal structure with a sulfur bonded directly to the zinc, and the oxygen of the alkoxide weakly coordinating to the zinc centre. Reactions with isothiocyanates, phenyl isocyanate and *p*-nitrophenylisothiocyante, were also performed, with a similar trigonal bipyramidal geometry observed. These insertion reactions were found to be slower than carbon disulfide but considerably faster than carbon dioxide, indicating that the reaction rates of these insertions is dependent on the nucleophilicity of the heterocumulene (Figure 5). This indicates that the rate determining step involves interaction between the zinc and the donor atom of the heterocumulene, supporting a 2+2 cycloaddition mechanism.



*Figure 5* Effect of heterocumulene nucleophilicity on insertion into  $[Tp^{Ph,Me}ZnOCH_3]$  **XXV** and  $[Tp^{Ph,Me}ZnOC_2H_5]$  **XXVI**.

#### 1.5.2 Synthesis of β-Diketiminato-zinc Amides and Alkoxides

The  $\beta$ -diketiminato ligand has been used to stabilise zinc amide and alkoxide species.<sup>22,23</sup> The complex [(BDI<sub>DIPP</sub>)ZnN(SiMe<sub>3</sub>)<sub>2</sub>] **XXIX** was synthesised by the treatment of zinc bis(trimethyldisilyl)amine with protonated ligand, BDI<sub>dipp</sub>-H.<sup>23</sup> The zinc centre lies in a distorted trigonal planar geometry with the bis(trimethylsilyl)amido group lying perpendicular to this plane, presumably due to the steric repulsion with substituted aryl rings from the  $\beta$ -diketiminate ligand. Treatment of [(BDI<sub>DIPP</sub>)ZnN(SiMe<sub>3</sub>)<sub>2</sub>] **XXIX** with HN<sup>′</sup>Pr<sub>2</sub> generated [(BDI<sub>DIPP</sub>)ZnN<sup>′</sup>Pr<sub>2</sub>] **XXX**.<sup>15</sup> The ZnN<sub>3</sub> centre of **XXX** was also found to be trigonal planar similar to the zinc amide **XXX**, however the NC<sub>2</sub> plane of the N<sup>′</sup>Pr<sub>2</sub> ligand is not perpendicular to ZnN<sub>2</sub> plane of the  $\beta$ -diketiminate ligand as one would expect due to steric effects, (Figure 6), instead lying 43.5 ° to each other. If the two planes were parallel to each other the N p<sub>π</sub> to Zn p<sub>π</sub> bonding would be maximised. The disorder suggests that electronic effects are competing with the steric effects and for **XXX** a compromise between these two effects is formed.



*Figure 6*  $N(Pr)_2$  ligand of [(BDI<sub>dipp</sub>)ZnN(Pr)<sub>2</sub>] **XXIX** lying perpendicular due to sterics (left) and planar due to electronics (right) to the  $\beta$  – diketiminate ligand.

The complex  $[(BDI_{DIPP})Zn(\mu-O'Pr)_2]$  **XXXI** was synthesised from  $[(BDI_{DIPP})ZnN(SiMe_3)_2]$  **XXIX** through the addition of <sup>*i*</sup>PrOH. The geometry of **XXXI** in the solid state is an *iso*-propoxide bridged dimer and the zinc centres have a distorted tetrahedral geometry.  $[(BDI_{DIPP})ZnO^tBu]$  **XXXII** was also synthesised from the zinc amide,  $[(BDI_{DIPP})ZnN'Pr_2]$ , the diisopropylamide proving a better leaving group than bistrimethylsilylamide. The zinc alkoxide, **XXXII**, was found to be monomeric, unlike  $[(BDI_{DIPP})Zn(\mu-O'Pr)_2]$  **XXXI** (Figure 7), with the zinc possessing a distorted trigonal planar geometry. The <sup>*t*</sup>Bu group lies above the plane with a Zn–O–C angle of 138°, although the O lies in the metallocycle plane created by the β-diketiminato ligand, allowing for O p<sub>π</sub> to Zn p<sub>π</sub> bonding.<sup>31</sup>



Figure 7 The different structures of  $[(BDI_{DIPP})Zn(\mu-O^{i}Pr)_{2}]$  XXXI and  $[(BDI_{DIPP})ZnO^{t}Bu]$  XXXII.

#### 1.6 Previously reported $\beta$ –Diketiminato-cadmium Complexes

There are a limited number of  $\beta$ -diketiminato-cadmium complexes in the literature. For instance, two  $\beta$ -diketiminato-cadmium alkyl complexes have been reported. [(BDI<sub>DIPP</sub>)Cd(C<sub>6</sub>F<sub>5</sub>)] **XXXIII** was synthesised in very good yields, upon the addition of BDI<sub>DIPP</sub>-H to a solution of [Cd(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>·2MeCN].<sup>24</sup> Two separate crystal structures were obtained by varying the crystallisation conditions (Figure 8). When crystals were grown from CDCl<sub>3</sub> and H<sub>2</sub>O, a three coordinate cadmium complex was found in the unit cell, [(BDI<sub>DIPP</sub>)Cd(C<sub>6</sub>F<sub>5</sub>)]. The product was also recrystallized from a dilute mixture of dimethyl formamide (DMF) and pentane. The cadmium centre was solvated by DMF, now lying in a four coordinate geometry with the C<sub>6</sub>F<sub>5</sub> <sup>-</sup> ligand bent out of the plane. Pang *et al.*, synthesised another cadmium alkyl complex, [(BDI<sub>DIPP</sub>)CdMe] **XXXIV** by reacting dimethylcadmium, CdMe<sub>2</sub> **XXXV**, with BDI<sub>dipp</sub>-H in a solution of benzene and refluxing under N<sub>2</sub> for 16 hours. <sup>25</sup> The product was isolated as a white powder and analysed by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy as well as X-ray analysis. A solution of **XXXIV** was then allowed to stand with [B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>] **XXXVI** for two hours, which resulted in the formation of the previously isolated pentafluorophenyl complex **XXXIII**.



XXXIII

Figure 8 The three and four coordinate cadmium centres for XXXIII

A cadmium halide has also been synthesised with the  $\beta$ -diketiminate ligand, [(BDI<sub>DIPP</sub>)CdI<sub>2</sub>Li(OEt)<sub>2</sub>] **XXXVIII**, when a solution of [(BDI<sub>DIPP</sub>)Li(OEt)<sub>2</sub>] **XXXVII** was added to a suspension of CdI<sub>2</sub> in ether (equation 12).<sup>26</sup> The product was isolated in reasonable yields, however BDI<sub>DIPP</sub>-H was observed as a major by-product. The crystal structure revealed a distorted tetrahedral geometry at cadmium, which lies in a 6-membered metallocycle created by the BDI<sub>DIPP</sub> ligand and a 4-membered ring with the two bridging iodide atoms. The two iodide atoms lie perpendicular to the N<sub>2</sub>Cd plane and the ring formed by Cd–I–Li–I has a dihedral angle of 14.1 °. The coordination sphere of the lithium is filled with two solvent molecules. In an attempt to form a low valent cadmium species, reduction reactions were attempted. However, these were found to be unsuccessful when sodium or potassium was used as the reductant.



# Results and discussion

#### 1.7 Attempted Synthesis of β-Diketiminato-cadmium lodide

The reaction between  $BDI_{DIPP}$ -H and n-BuLi in toluene gives the lithiated product  $BDI_{DIPP}$ -Li. This compound can be isolated or formed *in situ* and further reacted with a metal halide (equation 13). Cadmium diiodide was treated with lithiated  $BDI_{DIPP}$  at -78 ° C in diethyl ether, however [ $(BDI_{DIPP})Cd(\mu$ -I)<sub>2</sub>Li(OEt)<sub>2</sub>.] **XXVIII** was formed. This bimetallic complex was stable, as lithium iodide could not be separated from [ $(BDI_{DIPP})CdI$ ], limiting the usability of this compound. Several variations on this reaction were examined, including changing the solvent to THF or toluene, generating  $BDI_{DIPP}$ -Li *in situ* or even changing the cadmium source to  $CdCI_2$ . In many of these reaction mixtures,  $BDI_{DIPP}$ -H was formed along with other unidentifiable products, as evident in the <sup>1</sup>H NMR spectra.



#### 1.8 Synthesis of $\beta$ -Diketiminato-cadmium Hexamethyldisilazane

A new pathway to the cadmium  $\beta$ -diketiminato complex was attempted via the known cadmium hexamethyldisilazane complex, [Cd(HMDS)<sub>2</sub>]. Addition of two equivalents of [Li(HMDS)] to a suspension of CdCl<sub>2</sub> in THF gives Cd(HMDS)<sub>2</sub> after stirring overnight at room temperature in THF. This compound was isolated as a brown oil and the <sup>1</sup>H NMR spectrum in chloroform revealed a shift in the methyl peaks from  $\delta$  0.13 ppm for [Li(HMDS)] to  $\delta$  0.21 ppm for [Cd(HMDS)<sub>2</sub>]. The product proved difficult to isolate, as the solvent could not be entirely removed which caused errors when weighing. As such, [Cd(HMDS)<sub>2</sub>] was generated *in situ* prior to use. After stirring a 1:1 mixture of BDI<sub>DIPP</sub>-H and [Cd(HMDS)<sub>2</sub>] overnight at room temperature no reaction was observed. Upon heating of this reaction mixture to 55 °C, three products were formed. These were identified by three indicative signals in the <sup>1</sup>H NMR spectrum, including HMDS–H at  $\delta$  0.06 ppm and two compounds bearing the  $\beta$ -diketiminato ligand at  $\delta$  4.79 and 4.64 ppm, corresponding to the  $\gamma$ –CH proton on the BDI<sub>DIPP</sub> backbone. After filtering the solution, removing the volatiles and redissolving in a minimum amount of toluene, crystals were grown overnight at -30 °C (equation 14).

The <sup>1</sup>H NMR spectrum of the crystals revealed that the complex contains a  $\beta$ -diketiminato ligand as observed by a singlet resonance at  $\delta$  4.79 ppm. The resonances corresponding to the methyl groups off the BDI-backbone are found at  $\delta$  1.78 ppm. Two doublet resonances for the *iso*-propyl methyl groups on the *N*-aryl group are observed at  $\delta$  1.27 and  $\delta$  1.20 ppm integrating to twelve hydrogens each. The corresponding methine signal, (formally a quartet of quartets, but will be referred to as a heptet), is found at  $\delta$  3.22 ppm. A resonance at  $\delta$  -0.31 ppm, integrating to 18 hydrogens is also observed, corresponding to the methyl groups on the bound HMDS ligand. Together these signals are consistent with [(BDI<sub>DIPP</sub>)Cd(HMDS)] (**1**).

An X-ray diffraction study was performed on [(BDI<sub>DIPP</sub>)Cd(HMDS)] **1** (Figure 9). X-ray diffraction studies in this thesis were solved by Associate Professor Martyn Coles. A distorted trigonal planar geometry is observed at the cadmium centre, with the two  $\beta$ -diketiminate nitrogens, N(1) and N(2) having a fixed bite angle of 90.08(6)°. This bite angle is slightly smaller than the reported bite angle for Prust's [(BDI<sub>DIPP</sub>)Cd(µ–I)<sub>2</sub>Li(OEt)<sub>2</sub>] **XXVIII** (91.46(9)°).<sup>19</sup> The hexamethylsilyl-amido nitrogen is trigonal planar with a Cd–N(3) bond length of 2.0892(16) Å, slightly shorter than the Cd–N(1) and Cd–N(2) bond lengths, 2.1710(15) Å and 2.1919(15) Å respectively. The Cd–N(3) distance of 2.0892(16) Å is very similar to the hexamethylsilyl-amido nitrogen cadmium bond distance reported by Mountford for tris(pyrazoyl)methanide cadmium hexamethyldisilazane complex, [(HC(py)<sub>3</sub>)Cd(HMDS)], at 2.104(2).<sup>27</sup> Relevant bond lengths and angles are reported in Table 1.



*Figure 9* ORTEP diagram of [(BDI<sub>DIPP</sub>)Cd(HMDS)] **1**. Thermal elipsoids are shown at 30 %. Structure solved by Associate Professor Martyn Coles.

The plane consisting of the Si(1)–N(3)–Si(2) atoms lies perpendicular to the plane consisting of the N(1)-C(1)-C(2)-C(3)-N(2) atoms (referred to as the BDI<sub>DIPP</sub> backbone) presumably as this geometry minimises the steric interactions between the two ligands. The Cd–N(3)–Si(2) angle, 111.09(8) °, is smaller than the Cd–N(3)–Si(1) angle, 123.47(9) °, although this is be a function of the crystal packing as <sup>1</sup>H NMR spectrum clearly shows that this molecule is symmetric on the NMR time scale. A second molecule with slightly different bond lengths and bond angles was found in the unit cell, however the overall molecular geometry is similar to the first molecule in the unit cell.

*Table 1* Selected bond lengths (Å) and angles (deg) for compound **1** of both molecules contained in the unit cell.

	Selected bond lengths (Å)			
Cd(1)-N(1)	2.1710(15)	Cd(2)–N(4)	2.1821(15)	
Cd(1)-N(2)	2.1919(15)	Cd(2)–N(5)	2.1766(15)	
Cd(1)-N(3)	2.0892(16)	Cd(2)–N(6)	2.0837(16)	
N(3)–Si(1)	1.7158(17)	N(6)–Si(3)	1.7099(17)	
N(3)–Si(2)	1.7076(17)	N(6)–Si(4)	1.7149(17)	
	Selected bor	nd angles (°)		
N(1)-Cd(1)-N(2)	90.08(6)	N(4)–Cd(2)–N(5)	89.86(6)	
N(1)-Cd(1)-N(3)	132.06(6)	N(4)-Cd(2)-N(6)	137.89(6)	
N(2)-Cd(1)-N(3)	137.66(6)	N(5)–Cd(2)–N(6)	132.05(6)	
Cd(1)-N(3)-Si(1)	123.47(9)	Cd(2)–N(6)–Si(3)	112.28(9)	
Cd(1)-N(3)-Si(2)	111.09(8)	Cd(2)–N(6)–Si(4)	124.76(10)	

When the reaction was performed at higher temperatures, a second product,  $[(BDI_{DIPP})Cd(\mu-CI)_2Li(THF)_2]$  (2) was isolated in a 24% yield. The <sup>1</sup>H NMR spectrum of 2 revealed a singlet at  $\delta$  4.64 ppm, corresponding to the  $\gamma$ -CH of the BDI ligand. No signals were observed around 0 ppm, consistent with a lack of hexamethylsilyl groups in the compound. Two resonances was observed at  $\delta$  3.48 and  $\delta$  1.27 ppm, integrating to 8 protons each and corresponding to two coordinating THF molecules. White crystals were grown from THF at -30 °C and the structure was determined by an X-Ray diffraction study, the ORTEP diagram is shown in Figure 10.<sup>26</sup> Selected bond lengths of 2, as well as Prust's  $[(BDI_{DIPP})Cd(\mu-I)_2Li(OEt_2)_2]$  XXXVIII are reported in Table 2.

The geometry of cadmium in **2** is distorted tetrahedral. The cadmium lies in both a 6-membered ring with the  $\beta$ -diketiminato ligand and a 4-membered ring with the bridging chloride atoms. The bite angle created by the  $\beta$ -diketiminato ligand is 90.09(5) °, slightly smaller than the bite angle reported for [(BDI<sub>DIPP</sub>)Cd(µ–I)<sub>2</sub>Li(OEt<sub>2</sub>)<sub>2</sub>] **XXXVIII** of 91.46(9) °. The Cl(1)–Cd–Cl(2) angle for **2** is 93.756(16) °, significantly less than the I(1)–Cd–I(2) angle made by **XXXVIII** of 101.13(3) °. This is presumably due to the size of the halide atoms, with the ionic radii of iodine (2.06 Å) significantly larger than that of the

chloride (1.67 Å). The cadmium lithium distance is significantly larger in Prust's structure **XXXVIII** (3.683 Å) compared with **2** (3.204 Å), where the latter lies within the sum of its van der Waals atomic radii (3.400 Å).



*Figure 10* ORTEP diagram of  $[(BDI_{DIPP})Cd(\mu-CI)_2Li(THF)_2]$  **2**. Thermal elipsoids are shown at 30 %. Structure solved by Associate Professor Martyn Coles.

In contrast to the relatively planar cadmium in **1**, the 6-membered ring formed by the cadmium and the NCCCN of the BDI<sub>DIPP</sub> backbone possesses a boat conformation with cadmium at the prow, 0.402(3) Å out of the N(1)C(1)C(3)N(2) plane. The boat conformation reveals that the four coordinate cadmium centre is sterically crowded and consistent with other four-coordinate metal centres bearing a  $\beta$ -diketiminato ligand. However, the BDI ring is not puckered enough to suggest any  $\pi$ -bonding between cadmium and the  $\beta$ -diketiminato ligand. A similar boat conformation is observed in [(BDI<sub>DIPP</sub>)Cd( $\mu$ -I)<sub>2</sub>Li(OEt<sub>2</sub>)<sub>2</sub>] **XXXVIII** with the cadmium slightly further from of the N(1)C(1)C(3)N(2) plane at 0.441(3) Å. The  $\pi$ -electrons are delocalised as the C(1)–N(1) and C(3)–N(2) bond lengths are equal within experimental error at 1.326(2) Å and 1.327(2) Å respectively. These are also within experimental error of the C(1)–N(1) and C(3)–N(2) bond lengths for **1**, 1.323(2) Å and 1.330(2) Å. Likewise the C(1)–C(2)

and C(2)–C(3) bond lengths are equal at 1.411(2) Å and 1.408(2) Å and similar to those found in **1**, 1.402(3) and 1.411(3). These also correspond to typical C–N and C–C bonds in aromatic systems.

Table 2 Selected bond lengths (Å) and angles (deg) for compound 2 and XXXVIII.

	$[(BDI_{DIPP})Cd(\mu-CI)_2Li(THF)_2] \ \textbf{2}$	$[(BDI_{DIPP})Cd(\mu\text{I})_2Li(OEt_2)_2]\mathbf{XXXVIII}$
	Selected bond lengths (Å)	
Cd-N(1)	2.1674(14)	2.188(2)
Cd-N(2)	2.1965(13)	2.196(2)
Cd-X(1)	2.4792(5)	2.7920(7)
Cd-X(2)	2.4805(4)	2.7518(7)
X(1)–Li	2.373(4)	2.816(6)
X(2)–Li	2.380(4)	2.975(6)
Li–O(1)	1.936(4)	1.899(6)
Li–O(2)	1.926(4)	1.962(6)
N(1)-C(1)	1.326(2)	1.322(4)
C(1)-C(2)	1.408(2)	1.407(4)
C(2)–C(3)	1.411(2)	1.410(4)
C(3)–N(2)	1.327(2)	1.332(4)
Cd–Li	3.204(3)	3.683
	Selected bond angles (°)	
N(1)-Cd-N(2)	90.09(5)	91.46(9)
N(1)-Cd-X(1)	114.05(4)	113.31(7)
N(1)-Cd-X(2)	122.48(4)	121.77(7)
N(2)-Cd-X(1)	124.99(4)	112.92(7)
N(2)-Cd-X(2)	114.40(4)	116.92(7)
X(1)-Cd-X(2)	93.756(16)	101.13(3)
X(1)–Li–X(2)	99.21(13)	95.33(15)
Cd-N(1)-C(1)	122.38(11)	120.13(19)
N(1)-C(1)-C(2)	125.10(15)	125.7(3)

C(1)-C(2)-C(3)	131.44(16)	132.7(3)
C(2)-C(3)-N(2)	125.25(15)	124.9(3)
C(3)–N(2)–Cd	121.70(11)	120.23(19)

The ratio of **1** and **2** can be manipulated to favour **1** by changing the reaction solvent in the second step (addition  $BDI_{DIPP}$ -H to  $[Cd(HMDS)_2]$ ) from THF to toluene (equation 14). This results in precipitation of lithium chloride which can be removed by filtration, however the synthesis of  $[Cd(HMDS)_2]$  gives better yields in THF as [Li(HMDS)] is less soluble in toluene. This results in an increase for the yield of **1** to 63 %.

#### 1.9 Synthesis of β-Diketiminato-cadmium Chloride

In an attempt to generate a monomeric  $\beta$ -diketiminato-cadmium chloride, trimethylsilyl chloride, TMS-Cl, was added to a solution of **1**. After stirring the reaction overnight at room temperature, no reaction was observed. The reaction mixture was then heated to 90 °C and monitored by <sup>1</sup>H NMR spectroscopy over 10 days. An evolution of two resonances at  $\delta$  4.64 ppm and  $\delta$  4.41 ppm were observed, corresponding to two new  $\gamma$ –CH protons on the BDI<sub>DIPP</sub> backbone and potentially two new products (equation 15). After 10 days, no evidence of **1** was seen in the <sup>1</sup>H NMR spectrum. The solution was allowed to cool to room temperature, filtered, and the volatiles removed by vacuum. The white solid was then dissolved in a minimum amount of THF and colourless crystals were observed after 48 hours at -30 °C.



The <sup>1</sup>H NMR spectrum of the crystals showed that the product with a resonance at  $\delta$  4.64 ppm had crystallised out of THF. The spectrum was almost identical to  $[(BDI_{DIPP})Cd(\mu-CI)_2Li(THF)_2]$  **2**, although without the resonances corresponding to the two coordinated THF molecules. An X-ray diffraction study revealed the structure to be  $[(BDI_{DIPP})Cd(\mu-CI)]_2$  (**3**) (Figure 11), in which two cadmium centres are bridged by two chlorine atoms. Selected bond distances and angle are reported in Table 3.



*Figure 11* ORTEP diagram of [{(BDI<sub>DIPP</sub>)CdCl}<sub>2</sub>] **3**. Thermal elipsoids are shown at 30 %. Structure solved by Associate Professor Martyn Coles.

The cadmium centres possess a distorted tetrahedral geometry, similar to other 4 coordinate cadmium complexes such as  $[(BDI_{DIPP})Cd(\mu-CI)_2Li(THF)_2]$  **2**, with the cadmium lying in a six membered ring with the  $\beta$ -diketiminato ligand and a four membered ring created by the two bridging chlorides. The structure is highly symmetrical with two planes of symmetry, one running along the Z axis, along the Cd(1)–Cl(1)–Cd(1')–Cl(1') plane and the other perpendicular running through the two chlorine atoms. The bite angle created by the  $\beta$ -diketiminato ligand is 92.86(8)°. The metallocycle lies in a boat conformation, as observed for the other tetrahedral cadmium species, **2** and **XXXVIII**, although the cadmium lies closer to the N(1)C(1)C(3)N(2) plane (0.378 Å). The bond lengths for Cd–Cl(1), 2.5074(6) Å and Cd–Cl(1'), 2.5199(6) Å are shorter than analogous bridging chlorides in Zompa's [Cd<sub>2</sub>([9]aneN<sub>3</sub>)<sub>2</sub>( $\mu$ –Cl)<sub>2</sub>Cl<sub>2</sub>], 2.669(6) Å and 2.747(7) Å respectively.<sup>28</sup> The Cl(1)–Cd–Cl(1') bond angle is 89.43(2)°, which is significantly less than the Cl(1)–Cd–Cl(1') bond angle for **2**, 93.756(16)°. One compound was observed in the <sup>1</sup>H NMR spectrum when **2** and **3** were added to the same NMR tube, indicating that they both exist as [BDI<sub>DIPP</sub>CdCl], in solution.

Selected bond lengths (Å)				
Cd(1)-Cl(1)	2.5074(6)	N(1)-C(1)	1.322(3)	
Cd(1)-Cl(2)	2.5199(6)	C(1)-C(2)	1.415(3)	
Cd(1)-N(1)	2.1618(19)	C(2)–C(3)	1.407(3)	
Cd(1)-N(2)	2.1514(19)	C(3)–N(2)	1.330(3)	
Selected bond angles (°)				
Cl(1)-Cd(1)-Cl(2)	89.43(2)	N(1)-Cd(1)-N(2)	92.86(8)	

Table 3 Selected bond lengths (Å) and angles (deg) for compound 3.

The second product from the addition of TMS-Cl to [(BDI<sub>DIPP</sub>)Cd(HMDS)] **1** was isolated from subsequent recrystallizations from THF. The <sup>1</sup>H NMR spectrum of the colourless crystals possessed four separate doublet resonances at  $\delta$  1.24 ppm,  $\delta$  1.18 ppm,  $\delta$  1.12 ppm and  $\delta$  1.07 ppm, corresponding to the *iso*-propyl methyl groups on the *N*-aryl group. Two resonances were also observed at  $\delta$  3.59 ppm and  $\delta$  3.12 ppm for the corresponding *iso*-propyl methane carbons. An X-Ray diffraction study revealed the structure to be N(2,6–*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)C(Me)C(H)C(Me)N(2,6–*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)SiMe<sub>3</sub> **4** (equation 15). A trimethylsilyl group is directly bound to a nitrogen atom of a former  $\beta$ –diketiminato ligand. This compound had previously been synthesised by Lappert from the addition of TMS-Cl to potassiated ligand, K–BDI<sub>Dipp</sub>.<sup>29</sup>

Although we were able to generate **3**, the poor yields (58%) and long reaction conditions were not ideal. As such other chlorinating reagents were investigated in an attempt to discover a more facile synthesis of  $[(BDI_{DIPP})Cd(\mu-CI)]_2$  **3** from  $[(BDI_{DIPP})Cd(HMDS)]$  **1**. The formation of **4** revealed that the  $[SiMe_3^+]$  cation, formed from the loss of nucleophilic chloride in TMS-CI, is reactive towards the  $\beta$ -diketiminato cadmium complexes, resulting in relatively lower yields of **3**.

#### 1.9.1 Alternate Syntheses of β-Diketiminato-cadmium Chloride

A reaction was fortuitously observed when [( $BDI_{DIPP}$ )Cd(HMDS)] **1** was heated in CDCl<sub>3</sub> in a sealed NMR tube. After two hours of heating to 55 °C, two products were observed in the <sup>1</sup>H NMR spectrum, protonated H-HMDS and [( $BDI_{DIPP}$ )Cd( $\mu$ –Cl)]<sub>2</sub> **3**. Crystals of **3** were grown overnight from CDCl<sub>3</sub> at -30 °C. Chloroform is used in organic synthesis as a source of the dichlorocarbene group, CCl<sub>2</sub>. A mechanism for the formation of **3** was proposed, (Scheme 2) based on this chemistry. The HMDS ligand of **1** acts as a base and removes the acidic hydrogen of the CHCl<sub>3</sub>, forming the CCl<sub>3</sub><sup>-</sup> anion. This decomposes into dichlorocarbene and a nucleophilic chloride ion which attacks the cadmium centre, leading to the formation of **3**. Cyclohexene was added to the reaction mixture to trap dichlorocarbene by forming 7,7 dichlorobicyclo[4.1.0]heptane. Unfortunately no evidence of this trapping product was observed in the <sup>1</sup>H NMR spectrum and, as such, the mechanism for this transformation is still under investigation.



Scheme 2 Suggested mechanism for the formation of 3 from the addition of CHCl<sub>3</sub>.

When 200 mg [(BDI<sub>DIPP</sub>)Cd(HMDS)] **1** was stirred in CHCl<sub>3</sub> at room temperature, decomposition of **1** occurred and protonated ligand, BDI<sub>DIPP</sub>–H, was observed in the <sup>1</sup>H NMR spectrum. When complex **1** was treated with one equivalent of CHCl<sub>3</sub> in toluene, the reaction time significantly increased to 72 hours and [(BDI<sub>DIPP</sub>)Cd( $\mu$ –Cl)]<sub>2</sub> **3** was isolated in a 74 % yield. This latter reaction was further scaled to 500 mg of complex **1**. The conversion to **3** was 58%, with BDI<sub>DIPP</sub>-H the other observable product. Although this route to **3** looked promising on a smaller scale, decomposition was observed on a larger scale, giving similar yields of **3** to reaction with TMS-Cl. A reaction was also attempted between **1** and dichloromethane at 40 °C, however, only trace amounts of **3** were observed after 72 hours.

One equivalent of triethylaminehydrochloride, Et<sub>3</sub>NHCl was added to [(BDI<sub>DIPP</sub>)Cd(HMDS)] **1** on an NMR tube scale. An instantaneous reaction was observed by <sup>1</sup>H NMR spectroscopy revealing three products, [(BDI<sub>DIPP</sub>)Cd( $\mu$ -Cl)]<sub>2</sub> **3**, H-HMDS and free triethylamine (equation 16). The reaction also proved facile on a larger scale, 200 mg, in toluene with the reaction going to completion in one hour at room temperature with just one  $\beta$ -diketiminato containing product, **3**, observable by a <sup>1</sup>H NMR spectrum of the reaction mixture. Upon work up of the entire reaction mixture, only protonated ligand and a white insoluble precipitate, presumably CdCl<sub>2</sub> was isolated. The reaction was attempted in THF and diethylether, yielding similar outcomes.



#### 1.10 Synthesis of $\beta$ -Diketiminato-cadmium Anilide

A solution of  $[(BDI_{DIPP})Cd(HMDS)]$  in THF was treated with 2,6–di-*iso*-propylaniline at room temperature, producing  $[(BDI_{DIPP})Cd(2,6-Pr_2NHC_6H_3)(THF)]$  (6) (equation 17). The NMR spectrum of 6 revealed two multiplets at  $\delta$  3.57 and  $\delta$  1.41 ppm, which integrated for four protons each and was attributed to coordinated THF. Three resonances are observed for the *iso*-propyl methyl groups on the N-aryl groups at  $\delta$  1.58 ppm,  $\delta$  1.27 ppm and  $\delta$  1.07 ppm, integrating to twelve hydrogens each. Two of these resonances can be assigned to the  $\beta$ -diketiminate ligand, the third can be assigned to the anilido ligand. The *iso*-propyl methine carbon on the *N*-aryl groups overlaps with the *iso*-propyl methine resonance from the  $\beta$ -diketiminato ligand to give one multiplet at  $\delta$  3.00 ppm, integrating to six hydrogens. Crystals suitable for an X-ray diffraction study were grown from THF over 48 hours at – 30 °C, the ORTEP diagram is shown in Figure 12. Recrystallisation from a non-coordinating solvent, such as toluene, in order to generate a THF free molecule, proved unsuccessful.



The cadmium centre in [(BDI<sub>DIPP</sub>)Cd(2,6–<sup>*i*</sup>Pr<sub>2</sub>NHC<sub>6</sub>H<sub>3</sub>)(THF)] **6** has a distorted tetrahedral geometry, lying in 6-membered metallocycle with the  $\beta$ -diketiminato ligand, and a N(1)–Cd(1)–N(2) bite angle of 91.01(4) °. Selected bond lengths and angles are reported in Table 4. The metallocycle possesses a boat conformation with cadmium at the prow, similar to the bridged 4 coordinate cadmium species; however, the cadmium lies closer to the N(1)C(1)C(3)N(2) plane than the bridged species at 0.323 Å. The NH(2,6–<sup>*i*</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) ligand coordinates through the nitrogen with a Cd–N(3)–C(30) bond angle of 123.29 °. The Cd–N(3) bond length, 2.1081(13) Å is slightly shorter than the Cd–N(1) and Cd–N(2) bond lengths, 2.1628(12) Å and 2.2159(12) Å respectively. The Cd–O bond length of the THF ligand is 2.3734(11) Å, similar to other cadmium complexes with THF ligands, such as Darensbourg's [Cd{2,6–(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>](THF)<sub>2</sub>] and Guo's [{HB(3–Me–5–PhPz)<sub>3</sub>}Cd(NO<sub>3</sub>)(THF)], 2.321 Å and 2.391 Å respectively.


*Figure 12* ORTEP diagram of [(BDI<sub>DIPP</sub>)Cd(2,6–<sup>i</sup>Pr<sub>2</sub>NHC<sub>6</sub>H<sub>3</sub>)(THF)] **6**. Thermal elipsoids are shown at 30 %. Structure solved by Associate Professor Martyn Coles.

Table 4 Selected bond lengths (Å) and angles (deg) for compound 6.

Selected bond lengths (Å)				
Cd-N(1)	2.1628(12)	2.1628(12) N(1)-C(1)		
Cd-N(2)	2.2159(12)	C(1)-C(2)	1.405(2)	
Cd-N(3)	2.1081(13)	C(2)–C(3)	1.416(2)	
Cd–O	2.3734(11)	C(3)–N(2)	1.3226(18)	
O-C(42)	1.452(2)	N(3)–C(30)	1.3858(18)	
O–C(45)	1.451(2)			
	Selected bo	ond angles (°)		
N(1)-Cd-N(2)	91.01(4)	Cd-N(1)-C(1)	121.75(10)	
N(1)-Cd-N(3)	139.05(5)	N(1)-C(1)-C(2)	125.75(13)	
N(2)-Cd-N(3)	110.30(5)	C(1)-C(2)-C(3)	132.22(13)	
N(1)-Cd-O	103.66(4)	C(2)–C(3)–N(2)	124.85(13)	
N(2)–Cd–O	103.85(4)	C(3)–N(2)–Cd	121.51(10)	
N(3)-Cd-O	104.41(4)	C(42)–O–Cd	123.91(9)	
Cd-N(3)-C(30)	123.29(10)	C(45)–O–Cd	126.44(9)	
		C(42)–O–C(45)	109.61(12)	

#### 1.11 Synthesis of β-Diketiminato-cadmium Alkoxide Complexes

Treatment of [(BDI<sub>DIPP</sub>)Cd(HMDS)] **1** with a solution of 2,6–di-*tert*-butyl phenol in toluene produced a single product, [(BDI<sub>DIPP</sub>)Cd(2,6–<sup>t</sup>BuOC<sub>6</sub>H<sub>3</sub>)] (**7**) (equation 18). A <sup>1</sup>H NMR spectrum of **7** revealed the *tert*-butyl groups on the aryloxide ligand to be a singlet resonance integrating to 18 hydrogens, at  $\delta$  1.18 ppm, upfield to that of 2,6–di-*tert*-butyl phenol ( $\delta$  1.40 ppm). There are no resonance below  $\delta$  0 ppm, associated with a coordinated HMDS group, however H-HMDS was observed in the <sup>1</sup>H NMR spectrum, with a resonance at  $\delta$  0.06 ppm. Crystals suitable for X-ray analysis were grown from toluene at –30 °C over 24 hours, the ORTEP diagram is shown in Figure 13.



The cadmium in [(BDI<sub>DIPP</sub>)Cd(2,6–<sup>t</sup>BuOC<sub>6</sub>H<sub>3</sub>)] **7** is three coordinate with a distorted trigonal planar geometry, caused by the N(1)–Cd–N(2) fixed bite angle of the  $\beta$ –diketiminato ligand, 94.47(4) °. Selected bond lengths and angles are reported in Table 5. The O–C(30) bond also lies on this plane, however the aromatic ring of the (2,6–<sup>t</sup>BuOC<sub>6</sub>H<sub>3</sub><sup>-1</sup>) ligand lies perpendicular to the metallocycle, with a Cd–O–C(30) bond angle of 122.03 °. The metallocycle lies in a boat conformation with cadmium at the prow, in contrast to other 3 coordinate planar  $\beta$ -diketiminato-cadmium complexes, such as [(BDI<sub>DIPP</sub>)Cd(HMDS)] **1** and [(BDI<sub>DIPP</sub>)Cd(C<sub>6</sub>F<sub>5</sub>)] **XXXIII**. The cadmium is 0.354 Å from the N(1)C(1)C(3)N(2) plane, less puckered than the four coordinate  $\beta$ –diketiminato-cadmium complexes **2** and **3**. Cd–O bond distance for **7** is 2.0480(9) Å, which is very similar to the Cd–O bond distance in the terminal (2,6–<sup>t</sup>BuOC<sub>6</sub>H<sub>3</sub>) ligands in Darensbourg's [Cd<sub>2</sub>(2,6–<sup>t</sup>BuOC<sub>6</sub>H<sub>3</sub>)<sub>4</sub>], 2.0422(5) Å.<sup>32</sup>



*Figure 13* ORTEP diagram of  $[(BDI_{DIPP})Cd(2,6-^{t}BuOC_{6}H_{3})]$  **7.** Thermal elipsoids are shown at 30 %. Structure solved by Associate Professor Martyn Coles.

Selected bond lengths (Å)				
N(1)Cd	2.1549(10)	N(1)-C(1)	1.3330(16)	
N(2)–Cd	2.1399(10)	C(1)-C(2)	1.4082(17)	
O–Cd	2.0480(9)	C(2)–C(3)	1.4082(17)	
O-C(30)	1.3485(15)	C(3)–N(2)	1.3317(16)	
	Selected bo	ond angles (°)		
N(1)-Cd-N(2)	94.47(4)	Cd-N(1)-C(1)	118.76(8)	
N(1)-Cd-O	121.82(4)	N(1)-C(1)-C(2)	125.70(11)	
N(2)–Cd–O	143.34(4)	C(1)-C(2)-C(3)	132.12(11)	
Cd-O-C(30)	122.03(8)	C(2)-C(3)-N(2)	125.67(11)	
O-C(30)-C(31)	119.62(12)	C(3)–N(2)–Cd	118.84(8)	
O–C(30)–C(35)	119.74(12)			

Table 5 Selected bond lengths (Å) and angles (deg) for compound 7.

Addition of one equivalent of *tert*-butanol to a stirred solution of [(BDI<sub>DIPP</sub>)Cd(HMDS)] **1** in toluene at room temperature produced H-BDI<sub>DIPP</sub> as the major product. A similar decomposition of **1** to H-BDI<sub>DIPP</sub> was observed when *tert*-butanol was added to Coate's [(BDI<sub>DIPP</sub>)Zn(HMDS)] **XXXII**.<sup>23</sup> The reaction temperature was cooled to 0 °C and two products containing the  $\beta$ -diketiminato ligand were observed in the <sup>1</sup>H NMR spectrum, BDI<sub>DIPP</sub>-H and a new product with a  $\gamma$ -CH resonance at  $\delta$  4.48 ppm. This product was not the expected [(BDI<sub>DIPP</sub>)Cd(O<sup>t</sup>Bu)] as the <sup>1</sup>H NMR spectrum revealed only resonances from the  $\beta$ -diketiminato ligand, with no resonances associated with a *tert*-butoxide or HMDS ligand. An X-ray diffraction study determined the product to be a dimer [{(BDI<sub>DIPP</sub>)Cd(OH)}<sub>2</sub>] **7** (equation 19), very similar to Coate's [{(BDI<sub>DIPP</sub>)Zn(OH)}<sub>2</sub>].<sup>31</sup> As with the zinc system, the *tert*-butoxide product in our cadmium system is very sensitive to hydrolysis from trace amounts of water in the atmosphere or from the alcohol starting material.



The cadmium centre in [{(BDI<sub>DIPP</sub>)Cd(OH)}<sub>2</sub>] (**8**) has a distorted tetrahedral geometry and lies in a 6membered metallocycle with the  $\beta$ -diketiminato ligand backbone and a 4-membered ring, bridged by two hydroxyl ligands, The ORTEP diagram is shown in Figure 14. Selected bond lengths and angles are reported in Table 6. The metallocycle lies in a boat conformation, similar to other 4 coordinate cadmium complexes, with the cadmium at the prow lying 0.471 Å above the N(1)C(1)C(3)N(2) plane and a N(1)–Cd–N(2) bite angle of 91.64(5)°. The hydroxyl ligands lie perpendicular to the N(1)C(1)C(3)N(2) plane with an O(1)–Cd(1)–O(2) bond angle of 82.74(5)°, slightly larger than the analogous bond angle in [{(BDI<sub>DIPP</sub>)Zn(OH)}<sub>2</sub>], 80.01°. The M–M distance is greater for the cadmium atoms in **7**, than the smaller zinc atoms in [{(BDI<sub>DIPP</sub>)Zn(OH)}<sub>2</sub>], 3.324(2) Å and 3.056 Å, respectively. The Cd(1)–O(1) bond length in **7** is 2.2359(13) Å which is equal within experimental error to the Cd(1)– O(1) bond length in Berreau's [{(bmnpa)Cd(µ-OH)}<sub>2</sub>] complex, 2.237(5) Å.<sup>33</sup> The Cd(1)–O(2) bond lengths of **7**, 2.1936(12) Å, and [{(bmnpa)Cd(µ-OH)}<sub>2</sub>], 2.215(4) Å, are also very similar.



*Figure 14* ORTEP diagram of [{(BDI<sub>DIPP</sub>)Cd(OH)}<sub>2</sub>] **8.** Thermal elipsoids are shown at 30 %. Structure solved by Associate Professor Martyn Coles

Table 6 Selected bond lengths (Å) and angles (deg) for compound 8.

Selected bond lengths (Å)				
Cd(1)-O(1)	2.2359(13)	N(1)-C(1)	1.329(2)	
Cd(1)-O(2)	2.1936(12)	C(1)-C(2)	1.403(2)	
Cd(1)-N(1)	2.1805(13)	C(2)–C(3)	1.410(2)	
Cd(1)-N(2)	2.1828(14)	C(3)–N(2)	1.325(2)	
Cd(1)–Cd(1')	3.3242(2)			
	Selected b	oond angles (°)		
N(1)-Cd(1)-N(2)	91.64(5)	Cd(1)-N(1)-C(1)	119.86(11)	
N(1)-Cd(1)-O(1)	119.78(5)	N(1)-C(1)-C(2)	125.88(14)	
N(1)-Cd(1)-O(2)	126.00(5)	C(1)-C(2)-C(3)	131.99(15)	
N(2)-Cd(1)-O(1)	117.04(5)	C(2)-C(3)-N(2)	125.77(15)	
N(2)-Cd(1)-O(2)	122.79(5)	C(3)-N(2)-Cd(1)	119.71(11)	
O(1)-Cd(1)-O(2)	82.74(5)	Cd(1)-O(1)-Cd(1')	97.26(5)	
N(1)-Cd(1)-N(2) N(1)-Cd(1)-O(1) N(1)-Cd(1)-O(2) N(2)-Cd(1)-O(1) N(2)-Cd(1)-O(2) O(1)-Cd(1)-O(2)	Selected b 91.64(5) 119.78(5) 126.00(5) 117.04(5) 122.79(5) 82.74(5)	Cd(1)-N(1)-C(1) N(1)-C(1)-C(2) C(1)-C(2)-C(3) C(2)-C(3)-N(2) C(3)-N(2)-Cd(1) Cd(1)-O(1)-Cd(1')	119.86(11) 125.88(14) 131.99(15) 125.77(15) 119.71(11) 97.26(5)	

[(BDI<sub>DIPP</sub>)Cd(HMDS)] **1** was treated with one equivalent of *iso*-propanol in toluene at room temperature producing BDI<sub>DIPP</sub>–H as the major product. A similar result is observed when the reaction is cooled to 0 °C, however when the reaction is done at -77 °C, multiple  $\beta$ –diketiminato containing products are observed in the <sup>1</sup>H NMR spectrum. The major product of the reaction has a  $\gamma$ –CH resonance at  $\delta$  4.61 ppm and no resonance is observed at  $\delta$  4.48 ppm, corresponding to [{(BDI<sub>DIPP</sub>)Cd(OH)}<sub>2</sub>] **8**. Recrystallisation in toluene was attempted at -30 °C, however the solid obtained was not crystalline and impurities were observed in the <sup>1</sup>H NMR spectrum.

#### 1.12 Initial Reactivity Study with Heterocumulenes

A preliminary insertion reaction was performed between cadmium alkoxide  $[(BDI_{DIPP})Cd(2,6-$ <sup>t</sup>BuOC<sub>6</sub>H<sub>3</sub>)] **7**, and phenyl *iso*-cyanate was added to a solution of **7** in C<sub>6</sub>D<sub>6</sub>. An immediate colour change was observed from yellow to colourless and the <sup>1</sup>H NMR spectrum showed one major product with a BDI<sub>DIPP</sub> backbone resonance at  $\delta$  4.97 ppm. Two resonances associated with the methine hydrogen on the *iso*-propyl groups are observed at  $\delta$  3.11 ppm and  $\delta$  2.68 ppm integrating for two hydrogens each, indicating that the complex is no longer symmetrical. The desired insertion product is shown in equation 20.



Treatment of the cadmium amides [(BDI<sub>DIPP</sub>)Cd(HMDS)] **1**, [(BDI<sub>DIPP</sub>)Cd(2,6–<sup>*i*</sup>Pr<sub>2</sub>NHC<sub>6</sub>H<sub>3</sub>)(THF)] **6** with phenyl *iso*-cyanate on an NMR scale gave multiple products, which were unable to be separated. Further research is required to isolate products from these reactions.

### 1.13 Attempted Synthesis of β–Diketiminato-cadmium Cation Complexes

[(BDI<sub>DIPP</sub>)Cd( $\mu$ -Cl)]<sub>2</sub> **3** was treated with NaBPh<sub>4</sub> in toluene, giving one BDI<sub>dipp</sub> containing product. The <sup>1</sup>H NMR spectrum in C<sub>6</sub>D<sub>6</sub> revealed multiple overlapping peaks between  $\delta$  7.65 – 7.25 ppm, integrating for 20 hydrogens, as well as peaks from the  $\beta$ -diketiminato ligand including a  $\gamma$ -CH resonance at  $\delta$  4.90 ppm, which suggest the product [(BDI<sub>DIPP</sub>)CdBPh<sub>4</sub>] (equation 21). The same product was observed in the <sup>1</sup>H NMR spectrum when NEt<sub>3</sub>BPh<sub>4</sub> was added to [(BDI<sub>DIPP</sub>)Cd(HMDS)] **1** along with H-HMDS and free triethylamine. Recrystallisation from THF and toluene did not produce crystals suitable for an X-ray diffraction study and further spectroscopic data is required to fully assign this complex.



A slurry of AlCl<sub>3</sub> in toluene was added to  $[(BDI_{DIPP})Cd(\mu-Cl)]_2$  **3** and the reaction was stirred overnight at room temperature to give one product. The <sup>1</sup>H NMR spectrum shows resonances associated with a  $\beta$ -diketiminato ligand, with a backbone  $\gamma$ -CH resonance at  $\delta$  4.27 ppm and a splitting of the methine hydrogen on the *iso*-propyl groups, which are observed at  $\delta$  3.08 ppm and  $\delta$  2.71 ppm integrating for two hydrogens each. Recrystallisation from toluene at -30 °C produced colourless crystals, however an X-ray diffraction study revealed these to be [AlCl<sub>2</sub>(THF)<sub>4</sub>][AlCl<sub>4</sub>], previously reported by Atwood, as seen in equation 22.<sup>34</sup> Further attempts to isolate a BDI containing complex from this reaction are underway.



### 1.14 Attempted Synthesis of Complexes containing a Homonuclear Cd–Cd Bond

When 100 mg of  $[(BDI_{DIPP})Cd(\mu-CI)]_2$  **3** was stirred in toluene in the presence of a potassium mirror, H-BDI<sub>DIPP</sub> and a new BDI<sub>DIPP</sub> containing product were observed in the <sup>1</sup>H NMR spectrum at a 1:1 ratio. The complex, however, was unable to be isolated and subsequent recrystallisations produced a mixture of products. The reaction were performed on a larger scale, 500 mg, however the ratio of BDI<sub>DIPP</sub>-H became greater. No reaction was observed when **3** was treated with 2 equivalents of NaH in toluene, a method previously reported in the formation of  $[\{C_6H_3-2,6-(C_6H_3-2,6-Pr_2)_2\}CdH]$  **XXIII** and  $[\{C_6H_3-2,6-(C_6H_3-2,6-Pr_2)_2]CdH]$  **XIII** and  $[\{C_6H_3-2,6-(C_6H_3-2,6-Pr_2)_2]CdH]$  and  $[\{C_6H_3-2,6-Pr_2)_2]CdH]$  and

When[(BDI<sub>DIPP</sub>)Cd( $\mu$ –CI)]<sub>2</sub> **3** was treated with SuperHydride, LiHBEt<sub>3</sub>, at room temperature, a black precipitate, BDI<sub>DIPP</sub>-H as well as a  $\beta$ –diketiminato containing product was formed, the latter of which was crystallised from THF. Only resonances from the BDI<sub>DIPP</sub> ligand were observed in the <sup>1</sup>H NMR spectrum with a BDI<sub>DIPP</sub> backbone  $\gamma$ –CH resonance at  $\delta$  4.90 ppm. An X-Ray diffraction study showed the product to be sodiated BDI<sub>DIPP</sub>, [(BDI<sub>DIPP</sub>)Na(THF)] (**9**). The origin of the sodium is unknown, however it is assumed to have come from impurities in the SuperHydride. Further investigations into this reaction are ongoing.



*Figure 15* ORTEP diagram of [(BDI<sub>DIPP</sub>)Na(THF)] **9.** Thermal elipsoids are shown at 30 %. Structure solved by Associate Professor Martyn Coles.

Although crystal structures of lithiated and potassiated BDI<sub>DIPP</sub> are known, this is the first reported crystal structure of the sodiated ligands, the ORTEP diagram is shown in Figure 15. Selected bond lengths and angles are reported in Table 7. The geometry of the sodium in **9** is distorted trigonal planar, the distortion arising from the fixed  $\beta$ -diketiminato bite angle of 82.87(4) °. This bite angle is highly dependent on the size of the alkalai metal with the N(1)–M–N(2) angle of Power's [(BDI<sub>DIPP</sub>)Li(THF)] and Hitchcock's [BDI<sub>DIPP</sub>K] at 95.5(3) ° and 67.6(3) ° respectively.<sup>35,36</sup> The Na–O bond length for **8** is 1.437(4) Å, significantly shorter than the Li – O seen in [(BDI<sub>DIPP</sub>)Li(THF)] (1.790(7) Å).

Table 7 Selected bond lengths (Å) and angles (deg) for compound 9.

#### Selected bond lengths (Å)

N(1)–Na	2.201(3)	C(1)-C(2)	1.410(3)
N(2)–Na	2.201(3)	C(2)–C(3)	1.410(3)
Na–O	1.437(4)	C(3)–N(2)	1.321(4)
N(1)-C(1)	1.321(4)		
	Selected bo	ond angles (°)	
N(1)–Na–N(2)	82.87(4)	N(1)-C(1)-C(2)	123.83(3)
N(1)–Na–O	138.56(7)	C(1)-C(2)-C(3)	128.38(4)
N(2)–Na–O	138.56(7)	C(2)-C(3)-N(2)	123.83(3)
Na–N(1)–C(1)	130.32(3)	C(3)–N(2)–Na	130.32(3)

#### 1.15 Concluding Remarks

The novel  $\beta$ -diketiminato-cadmium amide complex, [(BDI<sub>DIPP</sub>)Cd(HMDS)] **1**, was synthesised from the addition of BDI<sub>DIPP</sub>-H to the known complex [Cd(HMDS)<sub>2</sub>]. From further reactions with **1**, the cadmium anilide [(BDI<sub>DIPP</sub>)Cd(2,6-<sup>*i*</sup>Pr<sub>2</sub>NHC<sub>6</sub>H<sub>3</sub>)(THF)] **6** and cadmium alkoxide [(BDI<sub>DIPP</sub>)Cd(2,6-<sup>*i*</sup>BuOC<sub>6</sub>H<sub>3</sub>)] **7** were also synthesised. An initial reactivity study of **7** with phenyl *iso*-cyanate revealed one new BDI containing product as observed in the <sup>1</sup>H NMR spectrum, however further characterisation of this product is required. Attempted syntheses of cadmium alkoxides using *iso*-propanol and *tert*-butanol is still underway however both of these syntheses generate significant amounts of protonated ligand (BDI<sub>DIPP</sub>-H). The two alcohols have relatively high *pK*<sub>a</sub> values, 30.3 and 32.2 in dimethylsulfoxide respectively, compared to 2,6-di-*tert*-butylphenol (16.8). It is presumed that the greater acidity of the phenol leads to a more facile protonation of the (HMDS) ligand and therefore a more facile synthesis. A possible method for the synthesis of [(BDI<sub>DIPP</sub>)CdCl]<sub>2</sub>] **3**, driving the reaction forward through the formation of lithium alkoxide LiOR to [{(BDI<sub>DIPP</sub>)CdCl]<sub>2</sub>] **3**, driving the reaction forward through the formation of **1** with *tert*-

butanol, highlighting the sensitivity of the *tert*-butoxide product to trace amounts of water in the alcohol or atmosphere.

[{(BDI<sub>DIPP</sub>)CdCl}<sub>2</sub>] **3** was synthesised through the treatment of **1** with TMS-Cl. This synthesis was found to have a long reaction time and produced relatively low yields (58%), leading to the investigation of different chlorinating agents. Although CHCl<sub>3</sub> was promising as a chlorinating agent on a small scale, BDI<sub>DIPP</sub>-H was observed on a larger scale, leading to similar yields as with TMS-Cl. The formation of cadmium cations was investigated though treatment of **3** with AlCl<sub>3</sub> and NaBPh<sub>4</sub> and a single product was isolated for both of these reactions; however, further spectroscopic evidence and X-ray analysis is required to confirm the structure of these products. **3** was treated with a variety of different reducing agents in an attempt to form a homonuclear cadmium–cadmium bond. The results ranged from no reaction to over-reduction, generating protonated ligand. A single product is observed from the addition of LiBHEt<sub>3</sub>, however the product surprisingly was [(BDI<sub>Dipp</sub>)Na(THF)]. This reaction is to be repeated in a further investigation, with a different source of LiBHEt<sub>3</sub>.

# Chapter 2 Synthesis of Lead Selenide Nanoparticles for Use in Solar Cells

## Introduction

#### 2.1 Lead Coordination Chemistry

Lead is the heaviest group 14 element in the periodic table. It is a borderline soft metal and can have a wide variety of co-ordination numbers. Lead chemistry is dominated by two main oxidation states, lead(II) which can bind as few as two and as many as 10 ligands, and lead(IV) which is known to have co-ordination numbers between 4 and 8.<sup>37</sup> Lead(II) has an electronic configuration of [Xe]4f<sup>14</sup>5d<sup>10</sup>6s<sup>2</sup> and like other post transition metal elements exhibits the inert pair effect. This refers to a lone pair of electrons held by the relevant atom which resists forming covalent and hydrogen bonds. The lone pair has directionality, resulting in hemidirected ligand geometry in lead(II) complexes, as opposed to the holodirected ligand geometry in lead(VI) complexes (Figure 16).<sup>38</sup> Lead(II) can be stabilised with both soft and hard donor ligands, although it has a greater affinity for softer sulfur and selenium containing ligands than oxygen or nitrogen based ligands.





HemidirectedHolodirectedLone pair is stereochemically activeLone pair is stereochemically inactive



#### 2.2 Background to Group 14-16 Materials

Group 14-16 materials, such as lead chalcogenides, have been researched extensively as practical photovoltaic materials. These materials are p-type IV–VI semi-conductors and have the potential to replace current expensive silicon based photovoltaics.<sup>39</sup> When a photon is absorbed by a semiconducting material, an electron is excited from the valence band into the conduction band. This leaves behind a positively charged hole, which is attracted to the promoted electron by the Coulomb force. This state, of a promoted electron and the remaining hole, is called an exciton. The separation of charge can be manipulated to form a circuit, thereby generating electricity. A p-type semiconductor uses the positively charged holes of the exciton as charge carriers and so generally has an excess of positively charged holes. Group IV–VI semiconductors typically have a narrow band gap width at an energy within the optimal band gap values to absorb solar photons, between 1.0–1.5 eV.<sup>40</sup> Many group IV–VI semiconductors also have good absorption coefficients and transport properties.

In 1985, the first results of using IV–VI semiconducting nanoparticles for nano-electronic devices was published by Novik.<sup>41</sup> Lead selenide colloidal nanoparticles between 20 and 100 nm were synthesised by bubbling H<sub>2</sub>Se through a solution of lead acetate, Pb(CH<sub>3</sub>COO)<sub>2</sub>. These crystals showed quantum confinement effects at lengths of less than 50 nm, namely the optical absorption edge was blue shifted to higher frequencies. These quantum confinement effects stem from a large Bohr exciton radii,<sup>42</sup> an approximation of the average distance between the electron and the hole of an exciton. This distance can be confined by a nanoparticle, similar to the particle in a box model. The manipulation of the distance between an electron and a hole will have an effect on how much coulombic attraction there is between the exciton pair. This gives one the ability to tailor the band gap energies as well as the absorption wavelength. Thus, there has been a large amount of interest since 1985 in controlling crystal size and morphology of group 14-16 nanomaterials. Recently, the focus has shifted to multiple exciton generation (MEG) in lead selenide and lead sulfide nanomaterials, which involves the generation of multiple electron-hole pairs from a single absorbed photon. The mechanism for this remains unknown, however MEG has the potential to considerably increase the quantum efficiencies of nanocrystal based photovoltaics. Stable solution-processed lead selenide photovoltaic cells have reached 46% external quantum efficiencies in the infrared and 70% across the visible region, compared to silicon based solar cells which have not exceeded 30%. <sup>39,43</sup>

The main components in the synthesis of group 14-16 nanomaterials have remained largely unchanged since Novik's synthesis in 1985. A chalcogen source, typically a tertiary phosphine chalcogenide, is added to a reactive metal salt at high temperatures, typically around 200 °C (equation 24).<sup>44</sup> Advances in this multiple precursor approach include the design of ligands with a greater control

over nanopartical size, size distribution, morphology, shape and removing the need for pyrophoric compounds. However, most of these syntheses still require high temperatures.

$$PbL_{x} + \begin{array}{c} E \\ P \\ R \\ R \\ R \\ R \\ R \end{array} \xrightarrow{\frown} \left( \begin{array}{c} E \\ P \\ P \\ P \\ P \\ P \\ \end{array} \right)$$
(24)

#### 2.3 Transmission Electron Microscopy

Transmission electron microscopy (TEM) involves passing an electron beam, controlled using condenser and objective lenses, through a sample.<sup>45</sup> The electrons are deflected by positive nuclei and negative electron clouds in the sample, which causes a nonuniform distribution of electron energies. This generates an image of the sample, based on the interaction of the electron beam, at a resolution far greater than traditional optical microscopes. It can provide structural information for particles on the nanoscale (with at least one dimension less than 100 nanometres).

In this project the transmission electron microscope, TEM, was used to determine the size, shape, distribution, and morphology of lead selenide nanoparticles. Low resolution images gave information for agglomerations of particles on a scale greater than 50 nm, whereas high resolution images revealed the structure and crystallinity of individual particles. Electron dispersive spectroscopy, EDS was also performed on the TEM, which provided insight into the elemental composition of the sample. EDS focuses a high energy beam of X-rays into the sample, exciting and promoting an electron from an inner shell. This is replaced by an electron from a higher energy shell, omitting an X-ray in the process. This X-ray is able to be characterised as each element has a unique atomic structure which allows for a unique set of peaks on its X-Ray spectrum.

## 2.4 Synthesis of Lead Selenide Nanoparticles via Single Source Precursors

A single source precursor is an inorganic molecule which contains the elements required in the growth of the target compound. In the growth of a lead chalcogenide such as PbS, PbSe or PbTe, it is a stable molecule which generally contains a lead chalcogen bond. The decomposition of a single source precursor to form a desired compound can have many advantages over a multiple precursor approach. Single source precursors are often much easier to handle and incorporate clean, low temperature decomposition routes. The chance of defects may be less due to the bond between the two elements already present in the precursor. It becomes much simpler to manage the temperature and conditions of flow in common decomposition techniques such as chemical vapour deposition (CVD). There have been various single source precursors which have been synthesised to form lead chalcogenide nanostructures. These have been shown to produce nanocrystals under mild conditions with good control over size and morphology.

The synthesis of lead bisdiselenocarbamate,  $[Pb(Se_2CNEt_2)_2]$  **XXXIX**, and its use as a single source precursor for lead selenide nanocrystals was reported by Trindale and coworkers.<sup>43</sup> The complex  $[Zn(Se_2CNEt_2)_2]$  was dissolved in 50 ml of CH<sub>2</sub>Cl<sub>2</sub> and shaken vigorously with aqueous Pb(NO<sub>3</sub>)<sub>2</sub> to form **XXXIX** with a yield of 69%. The lead atom is coordinated to four selenium atoms in a distorted trigonal bipyramidal geometry, with the lone pair of electrons occupying one of the equatorial positions (equation 25).



The bond lengths of the axial Pb–Se bonds are longer than the equatorial Pb–Se bond, due to electronic repulsion effects from the lone pair of electrons (Table 8). This is also shown in the Se–Pb–Se angle of the two axial selenium atoms (142°) which has deviated significantly from the 180° found in a regular trigonal bipyramid. A second lead bisselenocarbamate complex, [Pb(Se<sub>2</sub>CNMeHx)<sub>2</sub>] **XL**, was synthesised in a similar fashion from [Na(Se<sub>2</sub>CNMeHx)<sub>2</sub>] and Pb(NO<sub>3</sub>)<sub>2</sub>, although the crystal structure was not reported.

Table 8 Pb–Se bond lengths for [Pb(Se<sub>2</sub>CNEt<sub>2</sub>)<sub>2</sub>] XXXIX.

Se(1) equatorial	Se(3) equatorial	Se(2) axial	Se(4) axial
2.849(3) Å	2.827(3) Å	3.013(3) Å	2.952(3) Å

A solution of **XXXIX** in trioctylphosphine, TOP, was injected into a hot solution of trioctylphosphine oxide TOPO. A mixture of lead selenide nanocrystals and elemental selenium was observed, identified by X-ray powder diffraction. However pure cubic-type lead selenide was obtained from the decomposition of **XL** under the same conditions. TEM imaging revealed that circular nanocrystals, ca. 16  $\pm$  5 nm in diameter, were formed from the decomposition of **XL**. An onset of absorption in the visible region was observed in the absorption spectrum of the lead selenide nanocrystals dispersed in toluene compared to macrocrystalline lead selenide. This blue shift is a result of the three-dimensional confinement of the charge carriers in lead selenide nanocrystals. The absorption spectrum of the nanocrystals remained basically unchanged over 6 days suggesting that the nanocrystals were not agglomerating over time.

The bis(diphenylselenophosphoryl)amide ligand has been successfully coordinated to lead as a single source precursor for lead selenide nanocrystals.<sup>46</sup> It is a bidentate ligand which co-ordinates through two selenium atoms. Cea-Olivares synthesised the 4 coordinate  $[Pb{N(PPh_2Se)_2}_2]$  **XLI** by adding a solution of K[N(PPh\_2Se)\_2] in methanol to a stirred aqueous solution of Pb(O\_2CMe)\_2·3H\_2O (equation 26). The coordination geometry of **XLI** is a distorted trigonal bipyramidal where the two ligands form sixmembered chelate rings and a vacant equatorial position, suggesting the presence of the sterically active lone pair. Comparison with the free ligand reveals the P–Se bond lengths for **XLI** are greatly increased, 3.092(8) Å, whilst the P–N bond lengths are shortened, 1.682(4) Å, suggesting delocalisation of the  $\pi$ -electrons. The PbSe<sub>2</sub>P<sub>2</sub>N chelate rings are arranged in a boat conformation with the lead and nitrogen atoms at the apices, common for bis(diphenylselenophosphoryl)amido complexes.

$$Ph_{2}P^{/N}PPh_{2} + \{Pb(O_{2}CMe)_{2}\}.3H_{2}O \longrightarrow NP=Se^{V}Pb_{1}/Se=P^{/N}Se=P^{/N}Se=P^{/N}Se^{-Ph_{2}}Se^{-P$$

A lead imidodiselenodiphosphinato complex,  $[Pb\{N(P'Pr_2Se)_2\}_2]$  **XLII**, has been reported recently by Ritch.<sup>47</sup> It was synthesised from the addition of solvent to a solid mixture of  $[(TMEDA)Na\{(SeP'Pr_2)_2N\}_2]$ and Pbl<sub>2</sub> (equation 27). Crystals suitable for X-ray diffraction of **XLII** were grown from ether, revealing a square based pyramidal geometry at lead, with different Se(2)–Pb(1)–Se(3) and Se(4)–Pb(1)–Se(3) bond angles, 99.07(2) ° and 159.87(1) ° respectively. The lone pair of electron on the lead once again takes up a vacant equatorial position. The complex is observed to be dimeric with secondary bonding noted between lead and an equatorial selenium. The Pb–Se bond lengths in **XLII** are comparable to those in **XLI**, (R = 'Pr, 2.777(1)–3.099(1) Å, R = Ph, 2.874(3)–2.997(2) Å), with a partial Pb–Se bond observed intermolecularly for **XLII** with a bond length of 3.574(2) Å. Spectral studies also indicate that a dimeric structure is favoured for **XLII** in solution. When grown from a different solvent system, a dimeric structure was isolated, rather than a square based pyramid. The geometry at lead is best described as distorted trigonal bipyramidal, as evident from the Se(2)–Pb(1)–Se(3) and Se(4)–Pb(1)– Se(3) bond angles, 138.84(3)° and 120.91(2)° respectively. The intermolecular Pb–Se distances found to be 3.709(1) Å, 0.14 Å longer than in the non-solvated crystals.



Lead selenide nanowires have been synthesised from **XLII** via a solution-liquid-solid growth procedure, which is a method used to generate one dimensional structures, such as nanowires.<sup>48</sup> It involves the use of low concentrations of a catalytic liquid alloy phase, in this case BiCl<sub>3</sub>, which supersaturates the solution at the liquid solid interface, promoting linear crystal growth. Various solvents and reaction temperatures were examined, however the best results were obtained when a mixture of **XLII** and BiCl<sub>3</sub> in TOP were injected into a solution of TOPO at 210 °C. The diameter of the nanowires was dependant on the concentration of BiCl<sub>3</sub> used (Table 9). Higher concentrations of BiCl<sub>3</sub> have been previously reported to lead to larger nanoparticles, in turn resulting in nanowires with larger diameters.<sup>10</sup>

Conc(BiCl₃)	$BiCl_3$ : $Pb\{N(P'Pr_2Se)_2\}_2$ ratio	Diameter of nanowires
25 nmol	1:784	9 ± 1 nm (± 11 %)
50 nmol	1:392	11 ± 2 nm (± 18 %)
100 nmol	1:196	13 ± 2 nm (± 15 %)
200 nmol	1:98	15 ± 2 nm (± 13 %)

Table 9 Diameters of PbSe nanowires based on the concentration of BiCl<sub>3</sub>

Another potential single source precursor for lead selenide nanomaterials are the lead diselenophosphato complexes, [Pb{PSe<sub>2</sub>(OR)Ph<sub>2</sub>], where R = Me **XLIII**, Et **XLIV**, <sup>*i*</sup>Pr **XLV**.<sup>49</sup> The synthesis of the complexes involves the addition the sodiated disselenophosphato ligand, [Na{PSe<sub>2</sub>(OR)Ph<sub>2</sub>], to a stirred solution of lead acetate and the corresponding alcohol ROH. X-ray diffraction studies were performed on **XLIII** and **XLIV**, showing the diselenophosphato ligand is bidentate, co-ordinating through two selenium atoms. The geometry of **XLIV** is a distorted trigonal bipyramidal with a vacant equatorial site, providing a site for weak Pb–Se secondary bonding. Thus there are two molecules in the unit cell with axial and equatorial Pb–Se bond lengths of 2.9249(12) Å and 2.93335(9) Å respectively, and an intermolecular Pb–Se bond length of 3.39(1) Å. The crystal structure of **V** reveals an alternate dimeric structure, based on a central Pb<sub>2</sub>Se<sub>2</sub> unit, where each lead atom is coordinated to

a bridging selenium and a terminal selenium. The difference, highlighted in Figure 17, is caused by the secondary Pb–Se bonding in **XLIV** becoming formal covalent bonds in **XLIII**, with the Pb–Se bonds in the Pb<sub>2</sub>Se<sub>2</sub> unit ranging from 3.133 Å to 3.269 Å.



Figure 17 Intermolecular bonding in [Pb{PSe<sub>2</sub>(OMe)Ph}<sub>2</sub>] XLIII and [Pb{PSe<sub>2</sub>(OEt)Ph}<sub>2</sub>] XLIV

## 2.5 Synthesis of $\beta$ –Diketiminato-germanium Selenide Single Source

#### Precursors

The addition of a tertiary phosphines chalcogen (TOPSe) to a group 14 metal complex at high temperatures is a well established synthesis for the nucleation of group 14–16 nanomaterials.<sup>44, 50</sup> Metal phosphinato,  $[L_nMPR_2]$  and metal phosphinochalcogenito  $[L_nMEPR_2]$  complexes have been suggested as intermediates in these syntheses, due to observed dialkylphosphine impurities. Previously in this group we have reported syntheses for stable group 14 phosphinato  $[L_nMEPR_2]$  complexes, stabilised by the  $\beta$ -diketiminato ligand, and explored their relative stabilities and reactivity with chalcogen sources.

The synthesis of  $[(BDI_{DIPP})GePCy_2]$  **XLVI**, recently reported by Fulton, proceeds via addition of the lithium phosphanide, [Li-PCy\_2], to  $\beta$ -diketiminato germanium chloride,  $[(BDI_{DIPP})GeCI]$ .<sup>51</sup> This strategy previously had been used to synthesise the diphenylphosphide,  $[(BDI_{DIPP})GePPh_2]$  **XLVII** and bistrimethylsilylphosphide  $[(BDI_{DIPP})GeP(SiMe_3)_2]$  **XLVIII** analogues.<sup>52</sup> The crystal structures of **XLVI** and **XLVII** reveal the coordination at the germanium is pyramidal, with a terminal phosphanide ligands and an *exo* conformation, where the germanium and the chloride lie on opposite sides of the plane as defined by the N–C–C–C–N atoms in the  $\beta$ -diketiminate ligand (NCCCN plane), (Figure 18). In comparison, an *endo* conformation is observed for **XLVIII**, presumably due to sterics as the P(SiMe\_3)\_3 ligand can adopt a planar geometry allowing it to fit between the two *N*-Aryl groups in the  $\beta$ -diketiminate ligand. The Ge–P bond length for **XLVIII** is shorter, 2.3912(8) Å, than for either **XLVI** or **XLVII**, 2.4724(8) and 2.4746(11) respectively.



Figure 18 Exo and Endo conformations of β-diketiminato germanium phosphanide complexes

In an attempt to synthesise a single source precursor for nanocrystalline GeSe, [(BDI<sub>DIPP</sub>)GePCy<sub>2</sub>] XLVI was treated with elemental selenium (Scheme 3).<sup>53</sup> Oxidation by selenium of both germanium(II) complexes and phosphines has been well established.<sup>54</sup> Surprisingly, addition of one equivalent of selenium XLVI gives β–diketiminato germanium dicyclohexyl-selenophosphonite to [(BDI<sub>DIPP</sub>)GeSePCy<sub>2</sub>] XLIX, in which the selenium has inserted into the Ge–P bond. The crystal structure reveals that the P–Se bond length, 2.2602(9) Å and the Ge–Se bond length, 2.4498(5) Å are both single bonds with a Ge–Se–P bond angle of 94.07(3)°. DFT calculations confirmed that XLIX was energetically more favourable than either oxidation on germanium, + 55.3 kJ mol<sup>-1</sup> or phosphorus, + 98.4 kJ mol<sup>-1</sup>. A similar reaction was observed for [(BDIDIPP)GePPh2] XLVII under identical reaction conditions, resulting in formation of the  $\beta$ -diketiminato germanium diphenylselenophosphanite [(BDI<sub>DIPP</sub>)GeSePPh<sub>2</sub>] I. The crystal structure revealed a distorted trigonal bipyramidal geometry and an exo conformation. The Ge-Se bond length is 2.4490(4) Å, within experimental error of Ge-Se bond length reported for XLIX and the P–Se bond length, 2.2524(7) Å is only slightly shorter than the P–Se bond length for XLIX. The Ge–Se–P bond angle is also acute, 90.27(2) ° revealing the similarity of these structures.



Scheme 3 Reactivity of [BDI<sub>DIPP</sub>GePCy<sub>2</sub>] **XLVI** with 1 equivalent and excess selenium.

The mechanism resulting in the insertion of selenium into the Ge–P bond remains unknown. One mechanism proposed by Tam involves coordination of the selenium to either the germanium centre (Route A) or the phosphorus (Route B).<sup>55</sup> This is followed by the formation of a three membered

heterocycle, which breaks down to give an overall insertion of selenium into the Ge–P bond (Scheme 4).



*Scheme 4* Proposed mechanism for selenium insertion into a germanium phosphorus bond via a 3membered heterocycle.

When excess selenium was added to **XLVI** the phosphinodiselenoato complex, [(BDI<sub>DIPP</sub>)GeSeP{Se}Cy<sub>2</sub>] **LI** was observed with a bridging selenium and oxidisation on the phosphorus (Scheme 3). The bridging Ge–Se(1) distance, 2.4613(4) Å was similar to that in **XLIX**, whereas the terminal Ge–Se(2) has a distance of 3.7109(4) Å. This value does lies within the sum of their Van der Waals radii, however the calculated Wiberg bond index for the two atoms is 0.05 suggesting no coordination. The relative stability of the germanium (IV) complex [(BDI<sub>DIPP</sub>)Ge{Se}SePCy<sub>2</sub>] was calculated to be only 9.9 kJ mol<sup>-1</sup> less stable than the phosphinodiselenoato complex **LI**. An atom transfer reaction was also seen upon the addition of **LI** to the phosphanide **XLVI** with the <sup>31</sup>P NMR spectrum revealing the formation of the phosphinoselenoito **XLIX**. This suggests that an atom transfer mechanism is plausible in the nucleation of GeSe nanomaterials.

The addition of excess selenium to **XLVII** resulted in a similar product,  $[(BDI_{DIPP})GeSeP{Se}Ph_2]$  **LII** with a bridging selenium and an oxidation on the phosphorus atom.<sup>56</sup> An *endo* conformation is observed however, with the germanium displaced out of the  $\beta$ -diketiminate backbone plane by just 0.020 Å compared to the diphenylselenophosphinite complex **L** which has an *exo* conformation and is displaced by 0.986 Å (Figure 19). It has been observed for the  $[(BDI)Ge]^+$  cation that a cationic germanium centre results in a relatively planar GeNCCCN metalacycle.<sup>20</sup> The diphenylphosphine ligand is better able to stabilise negative charge than the corresponding dialkylphosphine  $[PCy_2^-]$ , resulting in a more stable anion, which may explain the difference in conformations. Unfortunately, initial attempts of using **LI** as a single source precursor were unsuccessful.



*Figure 19* [(BDI<sub>DIPP</sub>)GeSeP{Se}Cy<sub>2</sub>] **LI** and [(BDI<sub>DIPP</sub>)GeSeP{Se}Ph<sub>2</sub>] **LII** showing exo and endo conformations.

#### 2.6 Synthesis of $\beta$ -Diketiminato-lead Selenide Single Source Precursors

A series of  $\beta$ -diketiminato lead phosphanide complexes, [(BDI<sub>DIPP</sub>)PbPR<sub>2</sub>] R = Cy LIII, Ph LIV and SiMe<sub>3</sub> LV were also recently synthesised, from the addition of a lithium phosphanide LiPR<sub>2</sub> to  $\beta$ -diketiminato lead chloride, [(BDI<sub>DIPP</sub>)PbCl].<sup>55</sup> The complex [(BDI<sub>DIPP</sub>)PbP(SiMe<sub>3</sub>)<sub>2</sub>] LV had previously been reported by Driess.<sup>57</sup> An *exo* conformation is observed in all three lead complexes with similar Pb-P bond lengths ranging from 2.6945(9) Å to 2.715(2) Å. The N(1)-Pb-N(2) bond angles (average 80.7 °) are significantly reduced in comparison to the N(1)-Ge-N(2) angles (average 88.15 °) causing less steric interaction between the *N*-Aryl groups on the  $\beta$ -diketiminato ligand and the terminal phosphinide, resulting in the preferred *exo* conformation.

Similar to the germanium system, addition of one equivalent of elemental selenium to  $\beta$ -diketiminato lead dicyclohexylphosphonide [(BDI<sub>DIPP</sub>)PbPCy<sub>2</sub>] **LIII** gives the insertion product,  $\beta$ -diketiminato lead dicyclohexyl-selenophosphonite [(BDI<sub>DIPP</sub>)PbSePCy<sub>2</sub>] **LVI**, which gives a single peak with lead and selenide coupling in the <sup>31</sup>P NMR spectrum at  $\delta$  23.9 ppm, <sup>1</sup>J<sub>PSe</sub> =192 Hz <sup>2</sup>J<sub>PPb</sub> = 1469 Hz. The structure is isomorphous with the germanium dicyclohexyl-selenophosphonite complex **XLIX**, adopting an *exo* conformation with a pyramidal geometry around the lead atom. The Se–P bond length, 2.2543(9) is within experimental error of the analogous bond length in **XLIX**, 2.2524(7). The Pb–Se bond length, 2.6811(4) Å, is comparable to other Pb–Se bond lengths stabilised with phosphines, Ritch's [Pb{N(P<sup>i</sup>Pr<sub>2</sub>Se)<sub>2</sub>}<sub>2</sub>], 2.777(1) - 3.099(1) Å, and Pb{N(PPh<sub>2</sub>Se)<sub>2</sub>}<sub>2</sub>, 2.874(3)–2.997(2) Å.<sup>47</sup>

Reaction of the lead phosphinde  $[(BDI_{DIPP})PbPCy_2]$  LIII with excess selenium yielded the lead phosphinodiselenoato complex  $[(BDI_{DIPP})PbSeP{Se}Cy_2]$  LVII. These lead complexes were found to be thermally sensitive, although if stored at – 30 ° C, no decomposition was observed for several weeks. An *exo* conformation was observed for LVII with a pyramidal geometry around the lead atom. The Pb–

Se bond length is 2.7417(4) Å, slightly longer than that in the dicyclohexylphosphinoselenoite **LVI**, 2.6811(4) Å. The bridging P–Se(1) bond length, 2.2094(10) Å is longer than the terminal P–Se(2) bond length 2.1287(11) Å, which is similar to previously synthesised P=Se double bond lengths, 2.071(3) Å.<sup>58</sup> No formal Pb–Se(2) bond is observed with the Pb–Se(2) distance, 3.396 Å, being significantly longer than the sum of the covalent radii of lead and selenium, 2.66 Å. The lead phosphinodiselenoato complex [(BDI<sub>DIPP</sub>)PbSeP{Se}Cy<sub>2</sub>] **LVII** has not yet been tested for use as a single source precursor.

#### 2.7 Synthesis of bis- $\beta$ -Diketiminato-Lead Complexes

Synthesis of two bis- $\beta$ -diketiminato-lead complexes,  $[Pb(BDI_{Ph})_2]$  **LVIII** and  $[Pb(BDI_{PP})_2]$  **LIX**, were reported by Tam. These were generated when attempting to synthesise a range of lead alkoxide complexes,  $[(BDI_y)PbO^tBu]$ , with different  $\beta$ -diketiminato ligands from  $\beta$ -diketiminato-lead chloride  $[(BDI_y)PbCl]$  (y = Ph or IPP, 4-*i*PrC<sub>6</sub>H<sub>4</sub>).<sup>55</sup> The expected lead alkoxide complexes were unable to be stabilised with the relatively smaller  $[BDI_{Ph}^{--}]$  and  $[BDI_{IPP}^{--}]$  ligands, instead the bis- $\beta$ -diketiminatolead complexes were observed (equation 27). The treatment of lead dichloride with two equivalents of  $[(BDI_{Ph})-Li]$  also gave  $[Pb(BDI_{Ph})_2]$  **LVIII** in high yields. Attempts to synthesise  $[(BDI_{DMP})_2Pb]$  (DMP = 2,6- $Me_2C_6H_3$ ) and  $[(BDI_{DIPP})_2Pb]$  were unsuccessful suggesting that substituents at the *ortho* position of the *N*-substituted aryl rings interact with neighbouring  $\beta$ -diketiminato ligands.



A distorted pseudo trigonal bipyramidal geometry was observed with the lone pair of the lead in an empty coordination site. The two  $\beta$ -diketiminato ligands are not arranged symmetrically, with the axial Pb–N(1), 2.482(3) Å, and Pb–N(4), 2.466(3) Å, longer than the equatorial Pb–N(2), 2.362(3) Å, and Pb–N(3), 2.338(3) Å. The N(1)–Pb–N(4) bond angle (151.05(11) °) is also wider than the N(2)–Pb–N(3) bond angle, 89.87(11)°. There is evidence also for weak C–H–aryl<sub>centre</sub> interactions between the *ortho* hydrogen of the *N*-substituted aryl group and the aryl ring of the other ligand (Figure 20). A toluene molecule is weakly coordinated  $\eta^6$  to the lead centre at a distance of 3.616 Å,



*Figure 20* ORTEP diagram of [(BDI<sub>Ph</sub>)<sub>2</sub>Pb] **LVIII**, showing H(11)-Aryl<sub>ring</sub>, H(34)-Aryl<sub>ring</sub> and Pb-toluene interactions as dashed lines.<sup>55</sup>

#### 2.8 Project Aims

The aim of this project was to synthesise the previously reported lead phosphinodiselenato,  $[(BDI_{DIPP})PbSeP{Se}Cy_2]$  **LVII** and test its usefulness as a single source precursor for lead selenide nanoparticles. A second aim was to synthesise the  $\beta$ -diketiminato-lead complex  $[(BDI_{Ph})_2Pb]$  **LVIII** and test its reactivity with selenium as a phosphorus free route to lead selenide nanoparticles.

## **Results and Discussion**

2.9 Reactivity of Bis-β-diketiminato-lead with Selenium

#### 2.9.1 Results from 2012

Initial work for this project was completed last year as part of a Postgraduate Diploma in Chemistry, however because results of that work were reinvestigated this year, I have included them in this results section.

A solution of H-BDI<sub>Ph</sub> in THF was cooled to -30 °C and treated with a solution of n-butyllithium in hexane to form Li-BDI<sub>Ph</sub>. Two equivalents were added *in situ* to a slurry of PbCl<sub>2</sub>, the mixture was stirred over 24 hours and [(BDI<sub>Ph</sub>)<sub>2</sub>Pb] **LVIII** was isolated in a 77 % yield (Scheme 5).<sup>55</sup>





#### Scheme 5 Synthesis of [Pb(BDI<sub>Ph</sub>)<sub>2</sub>] LVIII.

The <sup>1</sup>H NMR spectrum of [(BDI<sub>Ph</sub>)<sub>2</sub>Pb] **LVIII** showed three resonances at  $\delta$  7.09 ppm, 6.93 ppm and 6.51 ppm which are assigned to the *ortho-, meta-* and *para-* positions on the phenyl ring, respectively. Two resonances were observed from the BDI backbone with the  $\gamma$ -CH proton at  $\delta$  4.85 ppm and the methyl groups at  $\delta$  1.86 ppm. These values agreed with previous literature.<sup>55</sup>

The reactivity of [(BDI<sub>Ph</sub>)<sub>2</sub>Pb] **LVIII** with selenium was investigated as a route to a single source precursor for nanocrystalline lead selenide (Scheme 6). Toluene was added to elemental grey selenium and the slurry was sonicated at room temperature for 20 minutes. A toluene solution of [(BDI<sub>Ph</sub>)<sub>2</sub>Pb] **LVIII** was added and the reaction was stirred for 30 minutes before a black precipitate, lead selenide, was observed. A <sup>1</sup>H NMR spectrum of the solution revealed H-BDI<sub>Ph</sub> as the major product, with no evidence of **LVIII**. The solution was allowed to settle and the toluene was removed leaving the black precipitate, which was washed with hexane to remove traces of the protonated ligand. After four days a TEM sample was prepared by sonicating the black precipitate in toluene to break up any aggregates, before being loaded onto a copper TEM grid.



Scheme 6 Proposed route to lead selenide nanoparticles via a single source precursor route

TEM images at low and high resolution were taken and the elemental composition was analysed by energy dispersive spectroscopy. Layers of particles with distinct edges were observed at low resolution with differing shapes and sizes and an average size of 20 nm (Figure 21). Several particles have rounded edges although they are not perfectly spherical, with many others adopting hexagonal based shapes. At high resolution the crystal lattice fringes are observable as shading around the edges of the particles, indicating a crystalline morphology. EDS was taken at various points on the grid, indicating that nanocrystals of lead selenide had been formed at an approximate 1:1 ratio of Pb:Se.



*Figure 21 A)* Low resolution images of a PbSe nanocrystal cluster. *B)* High resolution image of PbSe nanocrystal cluster. *C)* High resolution image of a hexagonal PbSe nanocrystal showing crystal lattice fringes.

#### 2.9.2 Results from 2013

 $[Pb(BDI_{Ph})_2]$  **XLIX** was synthesised with the same method as previously used in 2012. A similar reactivity was observed with elemental selenium leading to the formation of H-BDI<sub>Ph</sub> and a black precipitate. The black precipitate was observed to be nanoparticles of lead selenide under the TEM, aggregating together to form high and low density areas (figure 22). This is presumably due to trace amounts of organic material, which hold the nanoparticles together in solution. The nanoparticles tended to be around 5 ± 3 nm in diameter, significantly smaller than the nanoparticles synthesised previously using a similar methodology. The nanoparticles do not have a uniform shape, although this is difficult to determine as the edges of the particles are not distinct. At high resolution, crystal lattice fringes are observed, running the length of the particle, indicating that the particles are crystalline.



*Figure 22 A & B)* Low resolution images of nanocrystalline PbSe. *C)* High resolution image of nanocrystalline PbSe showing crystal lattice fringes. *D)* High resolution image of a PbSe nanocrystal cluster

Energy dispersive spectroscopy was performed at different areas to assess the elemental composition of the particles (Table 10). The EDS images indicate that the product is lead selenide and the ratio of lead to selenium is 1:1, however there are discrepancies between different areas. This is due to the random nature of the heterogeneous reaction between Pb(BDI<sub>Ph</sub>)<sub>2</sub>, **20** and selenium, where there is no control over how the reactants will react and therefore how the crystals will nucleate and grow. This also accounts for the differences in the size and morphology of particles synthesised previously using an identical method.

	Selenium		Lead	
	Mass %	Atomic %	Mass%	Atomic %
Area 1	41.77	65.31	58.23	34.69
Area 2	32.08	55.35	67.92	44.65
Area 3	27.97	50.47	72.03	49.53
Area 4	22.11	42.69	77.89	57.31
Area 5	24.82	46.42	75.18	53.58

*Table 10* EDS elemental analysis of PbSe nanocrystals through decomposition of Pb(BDI<sub>Ph</sub>)<sub>2</sub> **LVIII** at room temperature.

Macrocrystalline lead selenide typically has a direct band gap at 4275 nm (0.29 eV) at room temperature. The optical absorption spectrum of the synthesised nanocrystalline lead selenide dispersed in toluene was measured (Figure 23), and a blue shift is observed with an absorption peak between 295 nm and 380 nm. This is caused by the quantum confinement of the charge carriers in the lead selenide nanocrystals. The peak in the optical absorption spectrum has a tail which suggests a distribution of particle size when dispersed in toluene, which may be caused by particle aggregation. The absorption peak is observed to reduce in intensity when the sample is allowed to settle over an hour and completely disappear after 24 hours without sonication, suggesting the lead selenide nanoparticles agglomerate readily in toluene.



Figure 23 Optical absorption spectrum of nanodispersed PbSe in toluene.

#### 2.10 Reacitivty of bis- $\beta$ -Diketiminato-lead with Selenium at 80 °C

Elemental grey selenium in toluene was sonicated for 20 minutes before being added to a solution of Pb(BDI<sub>Ph</sub>)<sub>2</sub> **LVIII** in toluene at 80 °C and stirred for 30 minutes. A <sup>1</sup>H NMR spectrum of the solution revealed H-BDI<sub>Ph</sub> as the major product, with no evidence of **LVIII.** The toluene was removed leaving a black precipitate, which was washed with hexane to remove traces of protonated ligand the sample was loaded onto a copper TEM grid.

Distinct nanoparticles were not observed under the TEM, which instead revealed areas of solid product held together by organic material, shown in Figure 24. Crystal lattice fringes, aligned in differing directions, are observed at higher resolution on various areas of the solid. This suggests that the product is at least partially crystalline, or contains nanocrystals; however, these cannot be individually identified.



*Figure 24* A) Low resolution image of lead precipitate, surrounded by organic material. B) High resolution image of lead precipitate, showing crystal lattice fringes.

EDS spectra of different areas on the grid revealed that the product is largely made up of lead, reported in Table 11. This indicates that Pb(BDI<sub>Ph</sub>)<sub>2</sub> **LVIII** thermally decomposed before reacting with the selenium. An optical absorption spectrum of the black precipitate dispersed in toluene revealed no peak in the UV-visable range, confirming that lead selenide nanocrystals were not formed.

	Selenium		Lead	
	Mass %	Atomic %	Mass %	Atomic %
Area 1	2.25	5.70	97.75	94.30
Area 2	4.14	10.18	95.86	89.82
Area 3	0.08	0.21	99.92	99.79

Table 11 EDS elemental analysis of Pb precipiate through decomposition of Pb(BDI<sub>Ph</sub>)<sub>2</sub> LVIII at 80 °C

## 2.11 Formation of Lead Selenide Nanoparticles via a Single Source Precursor

A solution of  $BDI_{DIPP}$ -H in THF was cooled to -30 °C and treated with a solution of n-butyllithium in hexane to form Li-BDI<sub>DIPP</sub>. One equivalent was added *in situ* to a slurry of PbCl<sub>2</sub> and the reaction was stirred over 24 hours to form [(BDI<sub>DIPP</sub>)PbCl] (Scheme 7).<sup>55</sup>



Scheme 7 Synthesis of [(BDI<sub>DIPP</sub>)PbCI]

A solution of dicyclohexylphosphine, HPCy<sub>2</sub>, in toluene was stirred with a solution of n-butyllithium in hexane for two hours to form LiPCy<sub>2</sub>. 1.5 equivalents of LiPCy<sub>2</sub> were added to a solution of (BDI<sub>DIPP</sub>)PbCl in toluene and the reaction was stirred over 48 hours to form [(BDI<sub>DIPP</sub>)PbPCy<sub>2</sub>] LIII, with a single resonance in the <sup>31</sup>P NMR spectrum at  $\delta$  26.9 ppm. A solution of LIII in toluene was stirred with an excess of elemental grey selenium over 24 hours to form [(BDI<sub>DIPP</sub>)PbSeP{Se}Cy<sub>2</sub>] LVII, shown in Scheme 8, observed as a singlet resonance with selenium satellites in the <sup>31</sup>P NMR spectrum at  $\delta$  57.0 ppm and a J<sub>PbSe</sub> value of 521 Hz.





No decomposition was observed when a solution of lead phosphinodiselenoato **LVII** in toluene was stirred at 80 °C for 30 minutes. After five days of heating, a black precipitate formed and a resonance corresponding to BDI<sub>DIPP</sub>-H was observed in the <sup>1</sup>H NMR spectrum. The black precipitate was isolated, however no dispersion into hexane was observed after sonication and therefore it was unable to be analysed by the TEM. Lead phosphinodiselenoato **LVII** was dissolved in *ortho*-xylene and heated to 130 °C. After an hour, a black precipitate was observed and a <sup>1</sup>H NMR spectrum revealed that **LVII** had decomposed into BDI<sub>DIPP</sub>-H. The solution was allowed to settle and the toluene was removed, leaving a black precipitate which was washed with hexane to remove traces of protonated ligand. A TEM sample was prepared by sonicating the black precipitate in toluene in order to break up any aggregates, before being loaded onto a copper TEM grid.

TEM images revealed the black precipitate to be nanoparticles, around  $4 \pm 3$  nm in diameter (Figure 25). A good distribution across the copper grid was observed and minimal organic material was observed. The shape of the nanoparticles was hard to determine as the edges of particles are not distinct. Crystal lattice fringes running along the particles are observed at high resolution, indicating that the particles are crystalline.



*Figure 25 A)* Low resolution TEM image of PbSe nanocrystals *B)* high resolution TEM image showing a cluster of nanocrystals *C)* High resolution TEM image showing crystal lattice fringes on PbSe nanocrystals *D)* EDS spectrum showing peaks for Se and Pb from the nanocrystals, and Cu and O from the copper grid.

EDS spectra were taken on different areas to assess the elemental composition of the nanocrystals. The spectra revealed that the nanocrystals are lead selenide with a ratio of 1:1 (Table 12). The discrepancies between the different EDS specta were significantly lower than the nanocrystals synthesised with [Pb(BDI<sub>Ph</sub>)<sub>2</sub>] **LVIII**. This is presumably due to the lead selenide bond existing in the starting material before decomposition. Unfortunately Uv-vis analysis was not performed on the nanocrystals.

Table 12 EDS elemental analysis of PbSe nanocrystals through decomposition of[(BDIDIPP)PbSeP{Se}Cy2] LVII at 130 °C

	Selenium		Lead	
	Mass %	Atomic %	Mass %	Atomic %
Area 1	27.39	49.75	72.61	50.25
Area 2	27.82	50.28	72.18	49.72
Area 3	22.47	43.20	77.53	56.80
Area 4	27.52	49.90	72.48	50.10

#### 2.12 Concluding remarks

No addition product ([(BDI<sub>Ph</sub>)<sub>2</sub>PbSe]) was observed through the treatment of [(BDI<sub>Ph</sub>)<sub>2</sub>Pb] with elemental selenium, instead decomposition of the lead complex with concurrent formation of lead selenide nanoparticles was observed. It is presumed that the lead complex reacts with selenium before decomposing, suggesting that the addition product may have formed, but was unstable. Stabilisation of this product remains a synthetic challenge and further research could investigate altering the reaction conditions and ligand environment around the lead centre to achieve this.

(BDI<sub>Ph</sub>-H) was chosen for this project, due to its smaller steric influence, compared to (BDI<sub>IPP</sub>), however different results may be observed through slight changes of the electronic or steric properties of the ligand. The nanoparticles synthesised in this project had a different size and shape to nanoparticles synthesised in 2012 using a similar method. This suggests that the nucleation and growth of these nanoparticles is occurring in an uncontrolled manner, which is affecting the reproducibility of this method. This is perhaps not unexpected as little effort is being made in this synthesis to control in what manner the product decomposes. When the reaction temperature was raised from room temperature to 80 °C, thermal decomposition of  $[(BDI_{Ph})_2Pb]$  was observed and lead selenide nanoparticles were not formed. Further research to control the size and shapes of the nanoparticles could involve the addition of a surfactant, addition of a catalyst to aid decomposition, such as a metal nuclei, or changes to the reaction time and temperature.

Decomposition of the single source precursor [(BDI<sub>DIPP</sub>)PbSeP{Se}Cy<sub>2</sub>] was achieved at 130 °C and produced nanoparticles slightly smaller than those observed in 2013 from the decomposition of

[(BDI<sub>Ph</sub>)<sub>2</sub>Pb] with selenium. EDS revealed that the nanoparticles from [(BDI<sub>DIPP</sub>)PbSeP{Se}Cy<sub>2</sub>] were lead selenide at a ratio of 1:1, with less discrepancies between different spectra than the previous method. This method does have drawbacks however, with a much more time consuming synthesis and poor atom efficiency. The phosphanide ligand is required to stabilise the lead selenide bond and must be thermally decomposed to form lead selenide nanoparticles. This requires high temperatures in comparison with the previous method which can be performed at room temperature.

# Chapter 3 Experimental

All manipulations were carried out under dry nitrogen using standard Schlenk-line and cannula techniques, or in an inert atmosphere glovebox. Solvents were dried using a PureSolv. system (Innovative Technologies) and stored over 4 Å sieves. <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR spectra were recorded in  $C_6D_6$  at 298 K, using a Varian INOVA system at 300 MHz (<sup>1</sup>H), 75 MHz (<sup>13</sup>C{<sup>1</sup>H}) or 121 MHz (<sup>31</sup>P{<sup>1</sup>H}). <sup>1</sup>H and <sup>13</sup>C chemical shifts were referenced internally to residual solvent resonances. Elemental analyses were performed by S. Boyer at London Metropolitan University. TEM images were taken on a JEOL 2010 microscope with an acceleration voltage of 200 kV.

[CH{(CH<sub>3</sub>)CN-2,6<sup>-i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>5</sub>}<sub>2</sub>], [BDI<sub>Dipp</sub>-H] This compound was prepared following the literature procedure.<sup>55</sup> 12M HCl (5.6 mL) was added dropwise to a mixture of acetylacetone (7 ml, 68 mmol) and 2,6 diisopropylaniline (28.2 mL, 150 mmol) in ethanol (200 mL) whilst stirring. The reaction was refluxed at 70 °C for 72 h until precipitation was seen. The precipitate was filtered off and was washed with cold petroleum ether (30 mL). Dichloromethane (30 mL) and saturated sodium carbonate solution (200 mL) were added to the solid and the aqueous layer was extracted using dichloromethane (2 x 30 mL). The organic layer was dried over magnesium sulfate and volatiles were removed *in vacuo*. The residue was washed with cold methanol and dried under reduced pressure. <sup>1</sup>H NMR data is in agreement with the literature values. (16.48 g, 58%) [lit.: 73%]<sup>ref 1</sup>H NMR (299.741 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  12.41 (*s*, 1*H*, N*H*), 7.12 (*s*, 6*H*, Ar*H*), 4.85 (*s*, 1*H*,  $\gamma$ -C*H*), 3.27 (*m*, 4*H*, C*H*(CH<sub>3</sub>)<sub>2</sub>), 1.63 (*s*, 6*H*, NC*Me*), 1.18(*d*, 12*H*, *J* = 6.9 Hz, CH*Me*<sub>2</sub>), 1.12 (*d*, 12*H*, *J* = 6.8 Hz, CH*Me*<sub>2</sub>) (299.741 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$  12.12 (*s*, 1*H*, N*H*), 7.12 (*s*, 10*H*, Ar*H*), 4.87 (*s*, 1*H*,  $\gamma$ -C*H*), 3.11 (*m*, 4*H*, C*H*(CH<sub>3</sub>)<sub>2</sub>), 1.72 (*s*, 6*H*, NC*Me*), 1.21 (*d*, 12*H*, *J* = 7.22 Hz, CH*Me*<sub>2</sub>)

[CH{(CH<sub>3</sub>)CN-2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>5</sub>}<sub>2</sub>CdN{SiMe<sub>3</sub>}<sub>2</sub>], [(BDI<sub>dipp</sub>)Cd-HMDS] (1) LiN(SiMe<sub>3</sub>)<sub>2</sub> (1.82 g, 11.0 mmol) was dissolved in THF (10 mL) and added dropwise to a suspension of CdCl<sub>2</sub> (1.00 g, 5.5 mmol) in THF (10 mL). This mixture was stirred overnight at room temperature. The solvent was then removed *in vacuo* to give a brown oil containing Cd(HMDS)<sub>2</sub> as identified by <sup>1</sup>H NMR spectroscopy. Toluene (20 mls) was added to the precipitate and the resulting suspension was filtered through a pad of Celite. To this was added a toluene (10 mL) solution of BDI<sub>DIPP</sub>-H (1.83 g, 4.4 mmol). The mixture was stirred at 55 °C for
72 h. Volatiles were removed *in vacuo* and the product was washed with hexane (3 x 5 mL). Colourless crystals were obtained by crystallisation from toluene at -30 °C. (1.92 g, 63%) <sup>1</sup>H NMR (299.741 MHz, CDCl<sub>3</sub>, 298 K): δ 7.12 (*t*, 4H, *J* = 7.6 Hz, Ar-*H*), 6.94 (*d*, 2H, *J* = 7.6 Hz, Ar-*H*), 4.79 (*s*, 1H, γ-CH), 3.00 (*m*, 4H, CHMe<sub>2</sub>), 1.78 (*s*, 6H, NCMe), 1.27 (*d*, 12H, *J* = 6.7 Hz, CHMe<sub>2</sub>), 1.20 (*d*, 12H, *J* = 6.8 Hz, CHMe<sub>2</sub>), -0.31 (*s*, 18H, SiMe<sub>3</sub>) (299.741 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K) δ7.11 (*t*, 4H, *J* = 7.6 Hz, Ar-*H*), 7.00 (*d*, 2H, *J* = 7.6 Hz, Ar-*H*), 4.75 (*s*, 1H, γ-CH), 3.32 (*m*, 4H, CHMe<sub>2</sub>), 1.67 (*s*, 6H, NCMe), 1.37 (*d*, 12H, *J* = 6.7 Hz, CHMe<sub>2</sub>), 1.17 (*d*, 12H, *J* = 6.8 Hz, CHMe<sub>2</sub>), 0.00 (*s*, 18H, SiMe<sub>3</sub>). <sup>13</sup>C NMR (75.378 MHz, CDCl<sub>3</sub>, 298K) δ 169.6 NC, 146.0 *ipso-C*, 141.5 *o*-Ar, 125.4 *p*-Ar, 123.9 *m*-Ar, 93.9 γ-C, 28.5 CH(CH<sub>3</sub>)<sub>2</sub>, 25.2 CH(CH<sub>3</sub>)<sub>2</sub>, 24.6 C(CH<sub>3</sub>), 5.5 Si(Me)<sub>3</sub>. Anal. calcd for C<sub>35</sub>H<sub>59</sub>CdN<sub>3</sub>Si<sub>2</sub>: C, 60.88; H, 8.61; N, 6.09. Found: C, 60.75; H, 8.79; N, 6.00

[(CH{(CH<sub>3</sub>)CN-2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>5</sub>}<sub>2</sub>)<sub>2</sub>CdCl<sub>2</sub>Li(THF)<sub>2</sub>] [(BDI<sub>DIPP</sub>)CdCl<sub>2</sub>Li(THF)<sub>2</sub>] (2) LiN(SiMe<sub>3</sub>)<sub>2</sub> (0.91 g, 5.5 mmol) was dissolved in THF (10 mL) and added dropwise to a suspension of CdCl<sub>2</sub> (0.50 g, 2.8 mmol) in THF (10 mL). This mixture was stirred overnight at room temperature. A THF (10 mL) solution of BDI<sub>DIPP</sub>-H (0.92 g, 2.2 mmol) was added dropwise and the reaction was stirred at 60 degrees for 72 hours. The solution was then filtered through a pad of Celite and the solvent was then reduced to 10 mL *in vacuo*. Colourless crystals were obtained by crystallization at -30 °C. (400 g, 24%) <sup>1</sup>H NMR (299.741 MHz, CDCl<sub>3</sub>, 298 K) δ 7.12 (*t*, 4H, J = 7.6 Hz, Ar-H), 6.94 (*d*, 2H, J = 7.6 Hz, Ar-H), 4.58 (*s*, 1H, γ-CH), 3.48 (*m*, 8H, THF) 3.00 (*m*, 4H, CHMe<sub>2</sub>), 1.58 (*s*, 6H, NCMe), 1.26 (*m*, 8H, THF) 1.07 (*d*, 12H, J = 6.7 Hz, CHMe<sub>2</sub>), 0.74 (*d*, 12H, J = 6.8 Hz, CHMe<sub>2</sub>). <sup>13</sup>C NMR (75.378 MHz, CDCl<sub>3</sub>, 298K) δ 169.6 NC, 144.9 *ipso-C*, 141.7 *o*-Ar, 125.4 *p*-Ar, 123.7 *m*-Ar, 92.9 γ-C, 68.1 THF, 27.7 CH(CH<sub>3</sub>)<sub>2</sub>, 25.7 THF, 24.6 CH(CH<sub>3</sub>)<sub>2</sub>, 24.5 C(CH<sub>3</sub>)<sub>3</sub>. Anal. calcd for C<sub>37</sub>H<sub>57</sub>CdLiN<sub>2</sub>Cl<sub>2</sub>O<sub>2</sub>: C, 59.09; H, 7.64; N, 3.72. Found: C, 58.88; H, 7.64; N, 3.83

[(CH{(CH<sub>3</sub>)CN-2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>5</sub>}<sub>2</sub>)<sub>2</sub>Cd<sub>2</sub>Cl<sub>2</sub>] [{(BDI<sub>DIPP</sub>)CdCl}<sub>2</sub>] (3) Trimethylsilylchloride (0.027 g, 2.50 mmol) was added to a toluene (40 mL) solution of [(BDI<sub>DIPP</sub>)Cd(HMDS)] **1** (1.20 g, 1.70 mmol) and the reaction was stirred for 10 days at 90 °C. The mixture was then filtered through a pad of celite and the solvent was reduced to 10 ml *in vacuo*. Colourless crystals were obtained by crystallization at -30 °C. (0.55 g, 57%)

Alternate Synthesis: Chloroform (0.130 g, 1.08 mmol) was added dropwise to a toluene (20 mL) solution of [(BDI<sub>DIPP</sub>)Cd(HMDS)] (0.500 g, 0.73 mmol) and the reaction was stirred 72 hours at 50 °C. The volatiles were removed *in vacuo* and the product was washed with hexane (3 mL) to give a white powder, which was used without further purification. (0.24 g, 58%) <sup>1</sup>H NMR (299.741 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$  7.12 (*t*, 4H, J = 7.6 Hz, Ar-H), 6.94 (*d*, 2H, J = 7.6 Hz, Ar-H), 4.58 (*s*, 1H,  $\gamma$  -CH), 3.00 (*m*, 4H, CHMe<sub>2</sub>),

1.58 (*s*, *6H*, NC*Me*), 1.07 (*d*, *12H*, *J* = 6.7 Hz, CH*Me*<sub>2</sub>), 0.74 (*d*, *12H*, *J* = 6.8 Hz, CH*Me*<sub>2</sub>). <sup>13</sup>C NMR (75.378 MHz, CDCl<sub>3</sub>, 298K)  $\delta$  169.6 N*C*, 144.9 *ipso-C*, 141.7 *o-Ar*, 125.4 *p-Ar*, 123.7 *m-Ar*, 92.9 *y-C*, 27.7 *C*H(CH<sub>3</sub>)<sub>2</sub>, 24.6 CH(*C*H<sub>3</sub>)<sub>2</sub>, 24.5 C(*C*H<sub>3</sub>). Anal. calcd for C<sub>58</sub>H<sub>82</sub>Cd<sub>2</sub>N<sub>4</sub>Cl<sub>2</sub>: C, 61.59; H, 7.31; N, 4.95. Found: C, 61.72; H, 7.29; N, 5.03

[CH{(CH<sub>3</sub>)CN-2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>5</sub>}<sub>2</sub>Cd(N-2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)(THF)] [(BDI<sub>DIPP</sub>)Cd(NAr)(THF)] (6) 2,6-di-*iso*-propyl aniline (0.075 g, 0.42 mmol) was dissolved in THF (5 mL) and added dropwise to a THF (10 mL) solution of [(BDI<sub>DIPP</sub>)Cd(HMDS)] **1** (0.300 g, 0.42 mmol). This was stirred at room temperature for 20 h. The mixture was filtered through a pad of Celite and then volatiles were removed *in vacuo*. Colourless crystals were obtained by crystallisation from THF at -30 °C. (0.19g, 62%) <sup>1</sup>H NMR (299.741 MHz, CDCl<sub>3</sub>, 298 K) δ 7.09 – 6.94 (*m*, *9*H, Ar-H), 4.57 (*s*, *1H*, *γ*-CH), 3.59 (*m*, *8*H, *THF*), 3.00 (*m*, *6*H, CHMe<sub>2</sub>), 1.58 (*s*, *6*H, NCMe), 1.41 (*m*, *4*H, *THF*), 1.27 (*d*, *12*H, *J* = 7.3 Hz, CHMe<sub>2</sub>) 1.07 (*d*, *12*H, *J* = 7.9 Hz, CHMe<sub>2</sub>), 0.74 (*d*, *12*H, *J* = 6.6 Hz, CHMe<sub>2</sub>). (299.741 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K) δ 7.21 – 7.08 (*m*, *9*H, Ar-H), 4.85 (*s*, *1*H, *γ*-CH), 3.60(*m*, *8*H, *THF*), 3.30 (*m*, *6*H, CHMe<sub>2</sub>), 1.09 (*d*, *12*H, *J* = 7.9 Hz, CHMe<sub>2</sub>). <sup>13</sup>C NMR (75.378 MHz, C<sub>6</sub>D<sub>6</sub>, 298K) δ 168.8 NC, 151.1 *o*-NAr, 145.9 *ipso*-C, 141.2 *o*-Ar, 133.3 *p*-NAr, 125.9 *p*-Ar, 124.4 *m*-NAr, 122.5 *m*-Ar, 114.9 NHC, 93.9 *γ*-C, 68.4 *THF*, 28.9 *C*H(CH<sub>3</sub>)<sub>2</sub>, 28.4 *C*H(CH<sub>3</sub>)<sub>2</sub>, 24.5 CH(CH<sub>3</sub>)<sub>2</sub>, 24.4 *THF*, 23.8 C(CH<sub>3</sub>). 23.3 CH(CH<sub>3</sub>)<sub>2</sub>.

[CH{(CH<sub>3</sub>)CN-2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>5</sub>}<sub>2</sub>CdO-2,6-<sup>t</sup>Bu<sub>2</sub>C<sub>6</sub>H<sub>3</sub>] [(BDI<sub>DIPP</sub>)Cd-OAr] (7) 2,6-di-*tert*-butyl phenol (0.088 g, 0.42 mmol) was dissolved in toluene (5 mL) and added dropwise to a toluene (10 mL) solution of [BDI<sub>DIPP</sub>)Cd(HMDS)] **1** (0.300 g, 0.42 mmol). This was stirred at room temperature for 20 h. The mixture was filtered through a pad of Celite and then volatiles were removed *in vacuo*. Colourless crystals were obtained by crystallisation from toluene at -30 °C. Yield 0.21 g, 68% <sup>1</sup>H NMR (299.741 MHz, CDCl<sub>3</sub>, 298 K) δ: 7.10 – 6.89 (*m*, *9H*, Ar-*H*), 4.84 (*s*, *1H*, γ-C*H*), 3.08 (*m*, *4H*, C*H*Me<sub>2</sub>), 1.77 (*s*, *6H*, NC*Me*), 1.20 (*s*, *12H*, CH*Me*<sub>2</sub>), 1.18 (*s*, *18H*, C*Me*<sub>3</sub>) 1.08 (*d*, *12H*, *J* = 6.7 Hz, CH*Me*<sub>2</sub>), 1.20 (*s*, *12H*, CH*Me*<sub>2</sub>). <sup>13</sup>C NMR (75.378 MHz, CDCl<sub>3</sub>, 298K) δ 171.0 N*C*, 145.0 *ipso*-*C*, 141.4 *o*-*Ar*, 138.8 *o*-O*Ar*, 129.2 *p*-O*Ar*, 125.8 *p*-*Ar*, 124.7 *m*-O*Ar*, 123.9 *m*-*Ar*, 114.9 O*C*, 94.3 γ-*C*, 35.2 *C*(CH<sub>3</sub>)<sub>3</sub>, 31.0 *C*H(CH<sub>3</sub>)<sub>2</sub>, 28.5 C(*C*H<sub>3</sub>)<sub>3</sub>, 25.4 CH(*C*H<sub>3</sub>)<sub>2</sub>, 24.3 C(*C*H<sub>3</sub>). Anal. calcd for C<sub>43</sub>H<sub>62</sub>CdN<sub>2</sub>O: C, 70.23; H, 8.50; N, 3.81. Found: C, 70.16; H, 8.45; N, 3.98.

[CH{(CH<sub>3</sub>)CN-2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>5</sub>}<sub>2</sub>CdOH] [(BDI<sub>DIPP</sub>)Cd-OH] (8) *tert*-Butanol (0.022 g, 0.28 mmol) in toluene (5 mL) was added dropwise to a toluene (15 mL) solution of [(BDI<sub>DIPP</sub>)Cd(HMDS)] **1** (0.20 g, 0.28 mmol) at 0 °C for 30 minutes. The mixture was filtered through a pad of Celite and then volatiles were removed *in vacuo*. Colourless crystals were obtained by crystallisation from toluene at -30 °C. (0.85g, 54%) <sup>1</sup>H NMR (299.741 MHz, CDCl<sub>3</sub>, 298 K) 7.09 (*t*, *4H*, *J* = 7.7 Hz, Ar-*H*), 6.92 (*d*, *2H*, *J* = 8.0 Hz, Ar-*H*), 4.48 (*s*, *1H*,  $\gamma$ -CH), 3.02 (*m*, *4H*, CHMe<sub>2</sub>), 1.50 (*s*, *6H*, NCMe), 1.08 (*d*, 12H, *J* = 6.7 Hz, CHMe<sub>2</sub>), 0.70 (*t*, 12H, *J* = 7.2 Hz, CHMe<sub>2</sub>). <sup>13</sup>C NMR (75.378 MHz, CDCl<sub>3</sub>, 298K)  $\delta$  168.7 NC, 141.5 *ipso*-C, 141.3 *o*-Ar, 128.4 *p*-Ar, 123.7 *m*-Ar, 92.0  $\gamma$ -C, 27.7 CH(CH<sub>3</sub>)<sub>2</sub>, 24.2 CH(CH<sub>3</sub>)<sub>2</sub>, 22.8 C(CH<sub>3</sub>),

[CH{(CH<sub>3</sub>)CN-2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>5</sub>}<sub>2</sub>Cd{B(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>}] [(BDI<sub>DIPP</sub>)CdBPh<sub>4</sub>] NaBPh<sub>4</sub> (0.120 g, 0.35 mmol) was dissolved in THF (5 mL) and added dropwise to a THF (10 mL) solution of (BDI<sub>DIPP</sub>)CdCl (0.200 g, 0.35 mmol). This was stirred at 50 °C for 20 h. The mixture was filtered through a pad of Celite and then volatiles were removed *in vacuo*. (0.21g, 70%)

Alternate synthesis: NEt<sub>3</sub>HBPh<sub>4</sub> (0.122 g, 0.29 mmol) was dissolved in toluene (5 mL) and added dropwise to a toluene (10 mL) solution of (BDI<sub>DIPP</sub>)Cd(HMDS) (0.200 g, 0.29 mmol). This was stirred at room temperature for 20 h. The mixture was filtered through a pad of Celite and then volatiles were removed *in vacuo*. (0.20g, 82%) <sup>1</sup>H NMR (299.741 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K)  $\delta$  7.69 – 6.96 (*m*, 26H, Ar-H) 4.94 (*s*, 1H,  $\gamma$ -CH), 3.36 (*m*, 6H, CHMe<sub>2</sub>), 1.75 (*s*, 6H, NCMe), 1.24 (*d*, 12H, J = 7.6, CHMe<sub>2</sub>) 1.19 (*d*, 12H, J = 7.1 Hz, CHMe<sub>2</sub>), 0.98 (*d*, 12H, J = 6.6 Hz, CHMe<sub>2</sub>)

[CH{(CH<sub>3</sub>)CN-C<sub>6</sub>H<sub>5</sub>}<sub>2</sub>], [BDI<sub>Ph</sub>-H] This compound was prepared following the literature procedure.<sup>55</sup> Concentrated HCI (8.3mL) was added dropwise to a mixture of acetylacetone (9.8 ml, 100 mmol) and aniline (19.0 mL, 200 mmol) at 0 °C whilst stirring. The reaction was left for 24 h until precipitation was seen. The precipitate was filtered off and was washed with cold petroleum spirit (~ 30 mL). Dichloromethane (~ 30 mL) and saturated sodium carbonate solution (~200 mL) were added to the solid and the aqueous layer was extracted using dichloromethane (2 x 30 mL). The organic layer was dried over magnesium sulfate and volatiles were removed *in vacuo*. The residue was washed with cold methanol and dried under reduced pressure. <sup>1</sup>H NMR data is in agreement with the literature values. (15.88 g, 64%) <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  13.163 (*s*, 1H, NH), 7.11-6.87 (*m*, 10H, N-Ar), 4.78 (*s*, 1H,  $\gamma$ -CH), 1.80 (*s*, 6H, NCMe)

[CH{(CH<sub>3</sub>)CN-C<sub>6</sub>H<sub>5</sub>}<sub>2</sub>Pb] [(BDI<sub>Ph</sub>)<sub>2</sub>Pb] This compound was prepared following the literature procedure.<sup>55</sup> A THF (5 mL) solution of (BDI<sub>Ph</sub>-H) (0.18 g, 0.72 mmol) was cooled to -30 °C and added

to a solution of n-Buli in hexane (0.43 mL, 0.86 mmol) also cooled to -30 °C. The mixture is added to a suspension of PbCl<sub>2</sub> (0.10 g, 0.36 mmol) in THF (10 mL). The mixture was stirred at room temperature for 20 h. The mixture was filtered through a pad of Celite and volatile material was removed from the filtrate *in vacuo*. The residue was washed with pentane (~3 ml) and dissolved in a minimum amount of toluene. <sup>1</sup>H NMR data is in agreement with the literature values. (0.32 g, 77%) <sup>1</sup>H NMR (299.714 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  7.09 (*m*, 8H, o-H), 6.93(*m*, 4H, p-H), 6.51 (*d*, 8H, J = 7.5 Hz, *m*-H), 4.85 (*s*, 2H,  $\gamma$ -CH), 1.86 (*s*, 12H, NC**Me**)

**Reaction** [CH{(CH<sub>3</sub>)CN-C<sub>6</sub>H<sub>5</sub>}<sub>2</sub>Pb] [(BDI<sub>Ph</sub>)<sub>2</sub>Pb] with elemental selenium. A suspension of selenium (0.010 g, 0.14 mmol) in toluene (5 mL) was sonicated for 20 minutes at room temperature. A solution of [(BDI<sub>Ph</sub>)<sub>2</sub>Pb] (0.1 g, 0.14 mmol) in toluene (5 mL) was added and the mixture stirred for 30 minutes at room temperature. The volatiles were removed *in vacuo* and the residue was washed with hexane (3 x 3 mL), generating a black precipitate. [BDI<sub>Ph</sub>-H] is observed in the <sup>1</sup>H NMR spectrum

[CH{(CH<sub>3</sub>)CN-2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>}<sub>2</sub>]<sub>2</sub>PbCl], [(BDI<sub>DIPP</sub>)PbCl] This compound was prepared following the literature procedure.<sup>55</sup>[BDI<sub>DIPP</sub>-H] (1.40 g, 3.58 mmol) was dissolved in THF (15 mL) and a solution of *n*-BuLi in *n*-hexane 1.99 mL, 4.30 mmol) was added. The mixture was stirred at room temperature for 45 minutes and transferred dropwise to a THF (10 mL) slurry of PbCl<sub>2</sub> (1.00 g, 3.58 mmol). The mixture was stirred at room temperature for 20 h and the volatiles were removed *in vacuo*. Toluene (3 × 15 mL) was added and filtered through a pad of Celite. The solvent was removed from the filtrate under reduced pressure, and the residue was washed with hexane (3 × 15 mL). The yellow [(BDI<sub>DIPP</sub>)PbCl] (2) was collected and used without further purification. <sup>1</sup>H NMR data is in agreement with the literature values. (1.86 g, 79%). <sup>1</sup>H NMR (299.741 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  7.21 (*dd*, *2H*, *J* = 7.5, 1.5 Hz, *m*-H), 7.12 (*t*, *2H*, *J* = 7.5 Hz, *p*-H), 7.06 (*dd*, *2H*, *J* = 7.5, 1.5 Hz, *m*-H), 4.87 (s, 1H, γ-CH), 3.96 (*m*, *2H*, CH(CH<sub>3</sub>)<sub>2</sub>), 3.05 (*m*, *2H*, CH(CH<sub>3</sub>)<sub>2</sub>), 1.68 (*s*, *6H*, NCMe), 1.50 (*d*, *6H*, *J* = 7.5 Hz, CHMe<sub>2</sub>), 1.24 (*d*, *6H*, *J* = 7.5 Hz, CHMe<sub>2</sub>), 1.16 (*d*, *6H*, *J* = 7.5 Hz, CHMe<sub>2</sub>), 1.08 (*d*, *6H*, *J* = 7.5 Hz, CHMe<sub>2</sub>).

[CH{(CH<sub>3</sub>)CN-2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>5</sub>}<sub>2</sub>]<sub>2</sub>PbP(C<sub>6</sub>H<sub>11</sub>)<sub>2</sub>)] [(BDI<sub>DIPP</sub>)PbPCy<sub>2</sub>] This compound was prepared following the literature procedure.<sup>55</sup> [(BDI<sub>DIPP</sub>)PbCl] (0.50 g, 0.79 mmol) in toluene (15 mL) was added to a toluene (10 mL) suspension of LiPCy<sub>2</sub> (0.16 g, 0.79 mmol). The mixture was stirred at room temperature for 24 h. The red mixture was filtered through a pad of Celite and the volatiles were removed from the filtrate *in vacuo*. The deep red solid residue was crystallised from a minimum amount of toluene at –30 °C. <sup>1</sup>H NMR data is in agreement with the literature values. (0.47 g, 75%) <sup>1</sup>H NMR (299.741 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  7.21 (*dd*, 2H, J = 7.6, 1.6 Hz, *m*-H), 7.05 (*t*, 2H, J = 7.6 Hz, *p*-H), 7.02 (*dd*, 2H, J = 7.6, 1.6 Hz, *m*-H), 4.61 (s, 1H,  $\gamma$ -CH), 3.95 (*m*, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 3.25 (*m*, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.73 (*s*, 6H, NC**Me**), 1.68 (*d*, 6H, J = 7.5 Hz, CH**Me**<sub>2</sub>), 1.62 (*br*, 6H, Cy-CH<sub>2</sub>), 1.26 (*d*, 6H, J = 7.5 Hz, CH**Me**<sub>2</sub>), 1.23 (*d*, 6H, J = 7.5 Hz, CH**Me**<sub>2</sub>), 1.18 (*d*, 6H, J = 7.5 Hz, CH**Me**<sub>2</sub>), 1.00 (*br*, 6H, Cy-CH<sub>2</sub>). <sup>31</sup>P NMR (121.318 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  26.9.

[CH{(CH<sub>3</sub>)CN-2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>5</sub>}<sub>2</sub>]<sub>2</sub>PbSeP(=Se)(C<sub>6</sub>H<sub>11</sub>)<sub>2</sub>)] [(BDI<sub>DIPP</sub>)PbSeP{Se}Cy<sub>2</sub>] This compound was prepared following literature procedure.[(BDI<sub>DIPP</sub>)PbPCy<sub>2</sub>] (0.13 g, 0.16 mmol) in toluene (10 mL) was added to an excess of elemental selenium (0.06 g, 0.78 mmol) suspended in toluene (5 mL). The mixture was stirred at room temperature for 20 h. The mixture was filtered through a pad of Celite. Volatiles were removed from the filtrate *in vacuo* and the residue was washed with hexane (3 × 5 mL). Orange crystals of [(BDI<sub>DIPP</sub>)PbSeP{Se}Cy<sub>2</sub>] were obtained by recrystallisation from toluene at -30 °C. <sup>1</sup>H NMR data is in agreement with the literature values. (0.10 g, 63%)%) <sup>1</sup>H NMR (299.741 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  7.18 (*s*, *2H*, *p*-*H*), 7.14-7.01 (*m*, *4H*, *Ar*-*H*), 4.58 (*s*, 1H, *y*-CH), 3.36 (*sept*, *4H*, *J* = 6.8 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.72 (*br*, 6H, *Cy*-CH<sub>2</sub>), 1.65 (*s*, 6H, NCMe), 1.57 (*d*, 6H, *J* = 6.8 Hz, CHMe<sub>2</sub>), 1.47(*br*, 2H, *Cy*-CH<sub>2</sub>), 1.34(*br*, 4H, *Cy*-CH<sub>2</sub>), 1.22 (*d*, 6H, *J* = 6.8 Hz, CHMe<sub>2</sub>, *Cy*-CH<sub>2</sub>), 1.02 (*br*, 6H, *Cy*-CH<sub>2</sub>).<sup>31</sup>P NMR (121.318 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  57.0

**Decomposition of [(BDI**<sub>DIPP</sub>)**PbSeP{Se}Cy**<sub>2</sub>] An *ortho*-xylene (5 mL) solution of [(BDI<sub>DIPP</sub>)PbSeP{Se}Cy<sub>2</sub>] (0.05 g, 0.05 mmol) was added via syringe to a solution of *ortho*-xylene (20 mL) at 130 °C. This mixture was stirred at 130 °C for 30 minutes. The volatiles were removed via filtration and the residue was washed with hexane (3 x 3 mL), generating a black precipitate. BDI<sub>DIPP</sub>-H is observed in the <sup>1</sup>H NMR spectrum.

## Appendix A: NMR spectra of novel compounds

<sup>1</sup>H NMR spectrum of [(BDI<sub>DIPP</sub>)Cd(HMDS)] **1** (299.741 MHz, C<sub>6</sub>D<sub>6</sub>)





<sup>13</sup>C NMR spectrum of [(BDI<sub>DIPP</sub>)Cd(HMDS)] **1** (75.378 MHz, C<sub>6</sub>D<sub>6</sub>)



<sup>1</sup>H NMR spectrum of [(BDI<sub>DIPP</sub>)CdCl<sub>2</sub>Li(THF)<sub>2</sub>)] **2** (299.741 MHz, C<sub>6</sub>D<sub>6</sub>)



 $^{13}\text{C}$  NMR spectrum of [(BDI\_{DIPP})CdCl\_2Li(THF)\_2)] **2** (75.378 MHz, C\_6D\_6)



<sup>1</sup>H NMR spectrum of [(BDI<sub>DIPP</sub>)Cd( $\mu$ -Cl)]<sub>2</sub> **3** (299.741 MHz, CDCl<sub>3</sub>)



 $^{13}\text{C}$  NMR spectrum of [(BDI\_{DIPP})Cd( $\mu\text{-CI})]_2\,\textbf{3}$  (75.378 MHz, CDCl\_3)



<sup>1</sup>H NMR spectrum of [(BDI<sub>DIPP</sub>)Cd(2,6–<sup>i</sup>Pr<sub>2</sub>NHC<sub>6</sub>H<sub>3</sub>)(THF)] **6** (299.741 MHz, C<sub>6</sub>D<sub>6</sub>)



<sup>13</sup>C NMR spectrum of [(BDI<sub>DIPP</sub>)Cd(2,6-iPr<sub>2</sub>NHC<sub>6</sub>H<sub>3</sub>)(THF)] **6** (75.378 MHz, C<sub>6</sub>D<sub>6</sub>)



<sup>1</sup>H NMR spectrum of [(BDI<sub>DIPP</sub>)Cd(2,6–<sup>t</sup>BuOC<sub>6</sub>H<sub>3</sub>)] 7 (299.741 MHz, CDCl<sub>3</sub>)



## $^{13}\text{C}$ NMR spectrum of [(BDI\_{DIPP})Cd(2,6-^tBuOC\_6H\_3)] 7 (75.378 MHz, CDCl\_3)



<sup>1</sup>H NMR spectrum of [{(BDI<sub>DIPP</sub>)Cd(OH)}<sub>2</sub>] **8** (299.741 MHz, CDCl<sub>3</sub>)



 $^{13}\text{C}$  NMR spectrum of [{(BDI\_{DIPP})Cd(OH)}\_2] **8** (75.378 MHz, CDCl\_3)



<sup>1</sup>H NMR spectrum of [(BDI<sub>DIPP</sub>)Na(THF)] **9** (299.741 MHz, C<sub>6</sub>D<sub>6</sub>)

## Appendix B: Bibliography

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