

Chapter 2

Extremely Bulky Amido d-Block Metal(II) Halide Complexes

2.1 Introduction

It is perhaps surprising that bulky monodentate amide ligands (-NR_2 , R = an alkyl or aryl group), which have been utilized for decades to stabilize low coordinate d-block metal complexes [1], e.g. two-coordinate $[\text{M}(\text{NR}_2)_2]$ complexes [2], have not been successfully employed in the preparation of related metal(I) dimers. This may result from the fact that reports of the amido d-block metal(II) halide precursor complexes are sparse, despite the many hundreds of structurally characterized amido d-block metal complexes that populate the literature [1].

Though monodentate amido d-block metal(II) halide complexes are limited in number, they are not unknown. However, this complex type usually requires either sterically demanding ligands, or strongly coordinating π -acid ligands such as phosphines or carbon monoxide to be isolated. Examples of amido d-block metal(II) halides with coordinating π -acid ligands include $[\{(\text{dtma})\text{Cu}(\text{PPh}_3)(\mu\text{-Cl})\}_2]$ [3] (dtma = di-*p*-tolylmethylamido) and $[\text{Ni}(\text{PMe}_3)_2(\text{pyr})\text{Cl}]$ [4] (pyr = pyrrolyl). However, in low-coordinate, low oxidation state chemistry, precursor complexes that do not possess strongly coordinating π -acid ligands are desired, as these ligands will likely be present in the final product, increasing the coordination number of the metal centre, thereby lowering its reactivity.

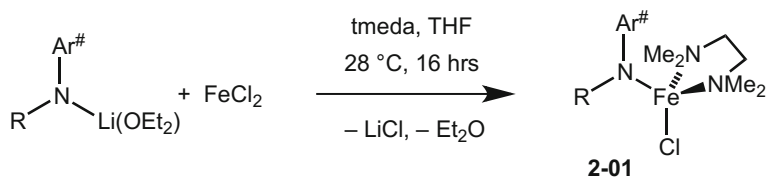
Attempting to prepare a monodentate amido metal(II) halide complex without the use of sterically demanding or π -acid ligands will almost always lead to the formation of the homoleptic species $[\text{M}(\text{NR}_2)_2]$ and the metal(II) halide, via redistribution. However, utilizing steric bulk on its own, without π -acid ligands, has led to a handful of monodentate amido d-block metal(II) halide complexes.

2.1.1 Previously Reported Bulky Amido Transition Metal(II) Halide Complexes

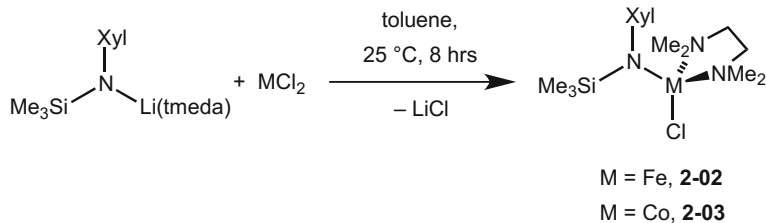
In 1996, the group of Cummins reported the synthesis and isolation of the low valent amido iron(II) chloride complex $[\text{FeCl}\{\text{N}(\text{R})(\text{Ar}^\#)\}(\text{tmeda})]$ [5] **2-01** ($\text{R} = \text{C}(\text{CD}_3)_2\text{CH}_3$, $\text{Ar}^\# = 2,5\text{-FMeC}_6\text{H}_3$). The complex is stabilized by a bulky amide ligand, along with a molecule of chelating tetramethylethylenediamine (tmeda) coordinating to the iron centre. Complex **2-01** was prepared by a salt metathesis reaction between iron(II) bromide and the lithium amide salt $[\text{Ar}^\#(\text{R})\text{NLi}]$, in the presence of tmeda (Scheme 2.1).

The four-coordinate iron(II) complex was found to be monomeric, with the iron(II) centre having a distorted tetrahedral geometry. The four coordination sites of the metal are occupied by the bulky amide ligand, the chloride, and a chelating molecule of tmeda. Complex **2-01** has an effective magnetic moment in solution of $5.29 \mu_{\text{B}}$ at room temperature, determined by the Evans method, which is slightly above the spin only value for a d^6 high spin Fe^{2+} centre ($4.90 \mu_{\text{B}}$). As far as we are aware, no attempts to reduce **2-01**, in order to synthesise a low oxidation state amido iron complex have been reported.

Following this, in 2007, Lee and co-workers reported the synthesis and structure of the similar tmeda stabilised amido iron(II) chloride complex $[\text{FeCl}\{\text{N}(\text{SiMe}_3)(\text{Xyl})\}(\text{tmeda})]$ **2-02** ($\text{Xyl} = 2,6\text{-xylyl}$) and the isostructural cobalt(II) complex $[\text{CoCl}\{\text{N}(\text{SiMe}_3)(\text{Xyl})\}(\text{tmeda})]$ **2-03** [6]. Similar to the synthesis of **2-01**, compounds **2-02** and **2-03** were prepared by reactions of the lithium amide salt $[\text{Xyl}(\text{SiMe}_3)\text{NLi}(\text{tmeda})]$ and the corresponding metal(II) chloride (Scheme 2.2). However, in the synthesis of **2-02** and **2-03**, no tmeda was added to the reaction



Scheme 2.1 Preparation of **2-01**



Scheme 2.2 Preparation of **2-02** and **2-03**

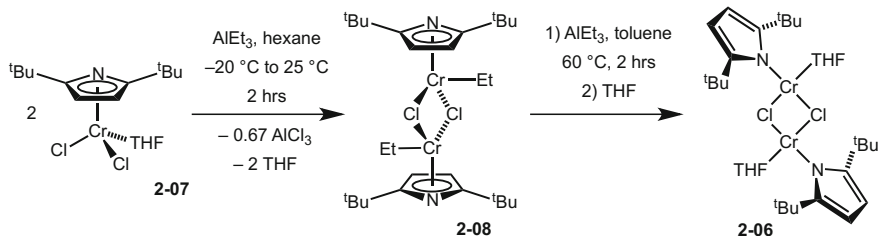
mixture as it was in the synthesis of **2-01**, but was introduced through coordination to the lithium amide reactant.

The structures of **2-02** and **2-03** were determined by X-ray crystallography, and were found to be essentially isostructural to the previously reported amido iron(II) chloride **2-01**. Magnetic measurements were also performed on **2-02** and **2-03**, yielding effective magnetic moments of $4.79 \mu_B$ and $3.77 \mu_B$ respectively, which in both cases are only slightly less than the spin only value for the high spin M^{2+} centre ($4.90 \mu_B$ for high spin Fe^{2+} and $3.87 \mu_B$ for high spin Co^{2+} with Td geometry). Complexes **2-02** and **2-03** were further reacted with methyl lithium, resulting in moderate yields of the corresponding methylated complexes $[Fe(Me)\{N(SiMe_3)(Xyl)\}(tmeda)]$ **2-04** and $[Co(Me)\{N(SiMe_3)(Xyl)\}(tmeda)]$ **2-05** [6]. However, once again, no attempts were made to reduce the complexes, in order to isolate a low oxidation state amido iron or cobalt complex.

In 2011, Duchateau and co-workers reported the bulky amido chromium(II) chloride complex $[Cr(NC_4H_2Bu_{2-2,5})(THF)(\mu-Cl)]_2$ **2-06** [7]. Complex **2-06** was synthesized in a rather unusual way, firstly via the alkylation of the chromium(III) dichloride complex $[Cr(\eta^5-tBu_2C_4H_2N)CrCl_2(THF)]$ **2-07** with triethyl aluminium, to give the alkylated product $[Cr(\eta^5-tBu_2C_4H_2N)CrEt(\mu-Cl)]_2$ **2-08**, which was followed by the reduction of the complex with a further equivalent of $AlEt_3$ (Scheme 2.3). THF was added to aid crystallisation, and **2-06** was isolated in moderate yields.

X-ray crystallography was once again used to determine the structure of **2-06**, which was found to be dimeric in the solid state, with approximately symmetrically bridging chlorides. The metal centres were found to be four-coordinate, and in a distorted square planar geometry. The coordination sites of the chromium centres are occupied by the two bridging chlorides, the bulky amide ligand, and a THF molecule. The square planar geometry of the metal centres in **2-06** differs from that for the three previously reported amido metal(II) chloride complexes **2-01–2-03**, as in all those cases, the metal possessed a distorted tetrahedral environment. However, the coordination geometry of the metal in **2-06** was not unexpected, as numerous four-coordinate square planar chromium(II) complexes have been characterised [8].

Complex **2-06** exhibits an effective magnetic moment in the solid state of $4.95 \mu_B$ at 298 K, which is almost $2.0 \mu_B$ less than the spin only value for two non-interacting



Scheme 2.3 Preparation of **2-06** and **2-08**

Cr^{2+} high spin centres ($6.93 \mu_{\text{B}}$), showing relatively strong antiferromagnetic coupling within the Cr_2Cl_2 core. However, the value of $4.95 \mu_{\text{B}}$ is indicative of two high spin Cr^{2+} centres, as low spin d^4 square planar complexes are expected to be diamagnetic.

Complex **2-06** was tested for catalytic activity in the polymerisation of ethylene, but was found to be inactive. No attempts to reduce **2-06** to a low oxidation state amido chromium complex have been reported.

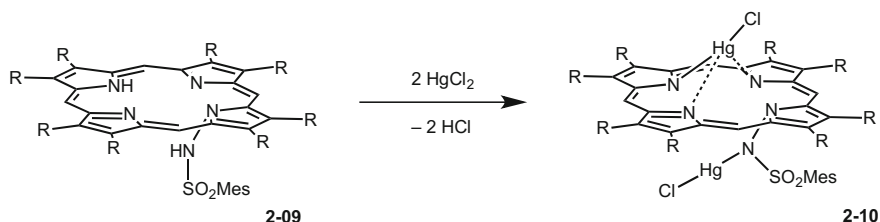
2.1.2 Previously Reported Bulky Amido Group 12 Metal(II) Halide Complexes

To the best of our knowledge, apart from in publications arising from this work, there are no terminal amido zinc(II) halide or amido cadmium(II) halide complexes that have been structurally authenticated. There are however a number of low coordinate zinc metal halide complexes stabilised by bulky N,N' bidentate ligands, e.g. $[(^{\text{Mes}}\text{Nacnac})\text{ZnI}(\text{THF})]$ [9] ($^{\text{Mes}}\text{Nacnac} = [(\text{MesNCMe})_2\text{CH}]^-$) and $[(\text{Giso})\text{ZnI}]$ ($\text{Giso} = [(\text{DippN})_2\text{CNCy}_2]^-$) [10]. There are also multiple zinc and cadmium halide complexes stabilised by amide substituents on tridentate or higher dentate ligands [11]. However, as this chapter is focused primarily on bulky monodentate ligands, these complexes will not be further discussed.

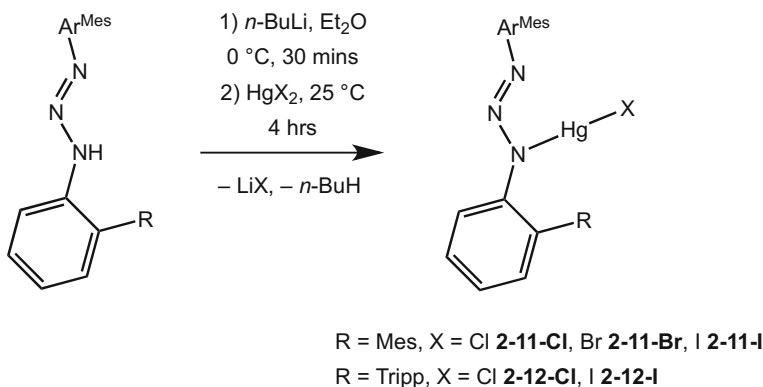
A good number of amido mercury(II) halide complexes are known, the simplest of which is the mercuric amidochloride, $[\text{Hg}(\text{NH}_2)\text{Cl}]$ [12]. However, single crystal X-ray crystallographic analysis of the compound reveals that its solid state structure is actually a salt, consisting of a zig-zag 1-dimensional polymer $(\text{HgNH}_2)_n$ with chloride counterions, and not a sigma bonded complex [13].

Rather surprisingly, the first crystallographically characterised terminal amido mercury(II) halide complex, employed a N-aminoporphyrin compound as a ligand [14]. Porphyrin rings usually act as rigid, dianionic, tetradentate ligands to most metals, forming some extremely stable complexes [15]. However, when the N-aminooctaethyl-porphyrin **2-09** (NAOEP-H_2) [16] is reacted with mercury(II) chloride, two metal centres bond to one aminoporphyrin unit, to give the bis-chloromercury(II)-N-aminoporphyrin complex $[\text{NAOEP}(\text{HgCl})_2]$ **2-10** (Scheme 2.4). The first mercury centre sits above the plane of the ring, bonded to one of the porphyrin pyrrole nitrogen atoms, and loosely coordinated by the two neighbouring pyrrole units. The second metal sits below the ring, and is bonded to the nitrogen atom of the amino group, resulting in a two-coordinate amido mercury(II) chloride moiety.

In 2010, Niemeyer and co-workers reported on a series of mercury(II) halide complexes stabilised by bulky diaryl-substituted triazenide ligands [17]. Triazenide ligands are related to amidinate and guanidinate ligand classes, in that they are N-donor bidentate ligands, which chelate to a metal centre forming a four membered ring. However, triazenide ligands contain a N_3 motif as their backbone, in



Scheme 2.4 Synthesis of bis-chloromercury(II)-N-aminoporphyrin complex [NAOEP(HgCl)₂] **2-10**



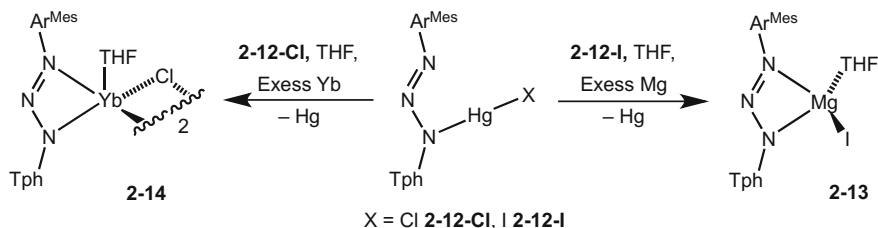
Scheme 2.5 Synthesis of **2-11-X** and **2-12-X**. X = Cl, Br or I

comparison to the amidinates and guanidinates NCN backbone. This subtle change in the ligand's backbone can lead to large electronic differences in a complex.

The complexes were synthesised by a simple deprotonation of the bulky triazenide $\text{Ar}^{\text{Mes}}(\text{Ar})\text{N}_3\text{H}$ ($\text{Ar}^{\text{Mes}} = 2,6\text{-Mes}_2\text{-C}_6\text{H}_3$, Ar = Mph or Tph, Mph = 2-MesC₆H₄, Tph = 2-TrippC₆H₄) with *n*-butyl lithium, followed by a salt metathesis reaction with the corresponding mercury(II) halide, to give the complexes $[\text{Ar}^{\text{Mes}}(\text{Mph})\text{N}_3\text{HgX}]$ (X = Cl **2-11-Cl**, Br **2-11-Br** or I **2-11-I**) and $\text{Ar}^{\text{Mes}}(\text{Tph})\text{N}_3\text{HgX}$ (X = Cl **2-12-Cl** or I **2-12-I**) in moderate to good yields (Scheme 2.5).

All of the triazenide mercury halide complexes (apart from **2-11-I**) were characterised by X-ray crystallography, which revealed that the triazenide is coordinating to the mercury in an η^1 -bonding mode, rather than the more common N,N'-chelating arrangement. This unusual bonding mode makes the mercury two-coordinate, albeit with a weak aryl interaction from one of the flanking phenyl groups.

Further reactivity of the triazenide mercury halide complexes towards a number of alkaline earth metals and lanthanide metals was investigated. When **2-12-I** was reacted with magnesium metal in THF, a redox-transmetallation reaction occurred,



Scheme 2.6 Synthesis of **2-13** and **2-14**

leading to the formation and isolation of $[\text{Ar}^{\text{Mes}}(\text{Tph})\text{N}_3\text{MgI}(\text{THF})]$ **2-13** in good yields (Scheme 2.6). A similar reaction between **2-12-Cl** and ytterbium chips in THF, led to the isolation of the corresponding triazenide ytterbium(II) chloride complex $[\{\text{Ar}^{\text{Mes}}(\text{Tph})\text{N}_3\text{Yb}(\text{THF})(\mu\text{-Cl})\}_2]$ **2-14**, also in high yields.

Apart from the reaction of **2-12-I** with magnesium, which may have initially been an attempt to reduce the triazenide mercury(II) halide to a low oxidation state mercury complex, no other attempts to reduce of the triazenide mercury halide complexes have been reported.

2.1.3 Terphenyl Stabilised D-Block Metal Halide Complexes

The only monodentate ligands that have been successfully applied to the preparation of two-coordinate transition metal(I) dimers, apart from the work presented in this thesis, are the bulky terphenyls, which were introduced in Sect. 1.2.1. This is partly because the precursors to these complexes, terphenyl transition metal(II) halide complexes, e.g. $[\{\text{Ar}^{\text{Dipp}}\text{Cr}(\mu\text{-Cl})\}_2]$ **2-15** ($\text{Ar}^{\text{Dipp}} = 2,6\text{-Dipp}_2\text{-C}_6\text{H}_3$), the precursor complex to the Cr–Cr quintuple bonded complex $[(\text{Ar}^{\text{Dipp}}\text{Cr})_2]$ **1-01**, are readily available and are stable to redistribution reactions [18].

2.1.3.1 Terphenyl Transition Metal(II) Halide Complexes

Power and co-workers have published a range of terphenyl stabilised transition metal(II) halide complexes, including the metals chromium, manganese, iron, and cobalt (Fig. 2.1) [19]. The majority of these complexes were synthesised via salt metathesis reactions between the terphenyl lithium salt and the corresponding metal(II) halide, however a small number have been synthesised by different routes, such as oxidative addition of halogens to metal(I) dimers, and decomposition of terphenyl metal(II) halides during their attempted reductions. X-ray crystallographic studies of the reported terphenyl transition metal(II) halide complexes revealed them all to exist as dimers, with bridging halides in the solid state, in essentially one of four common structural motifs (Fig. 2.1).

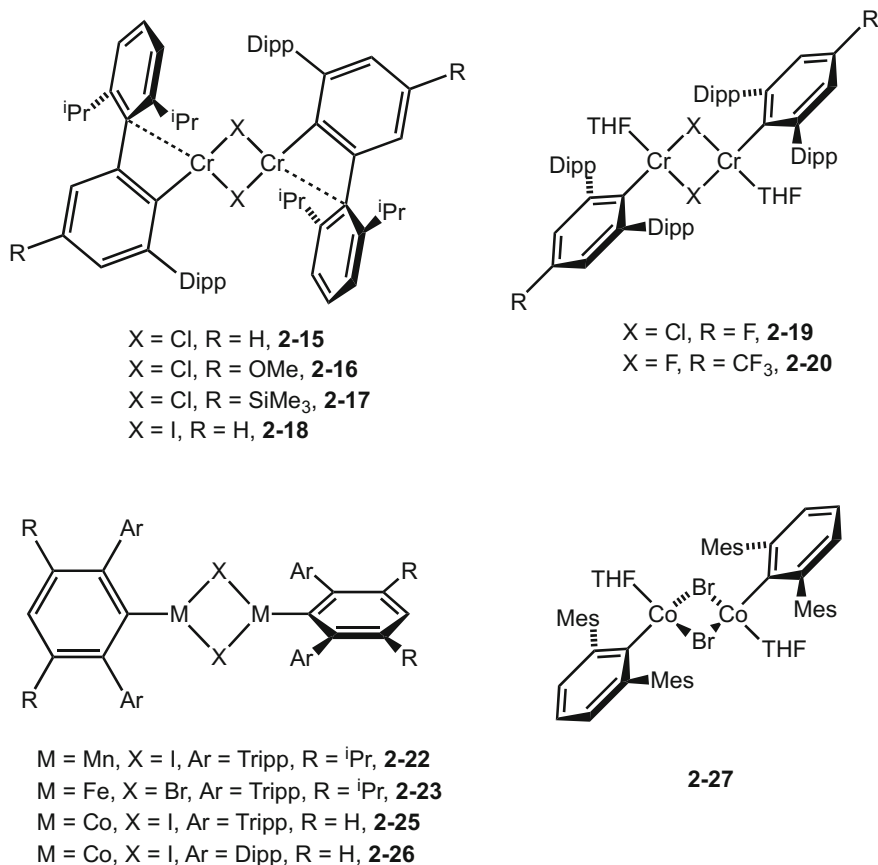


Fig. 2.1 Diagrammatic representations of the structurally characterised terphenyl transition metal(II) halide complexes **2-15–2-20**, **2-22**, **2-23** and **2-25–2-27**

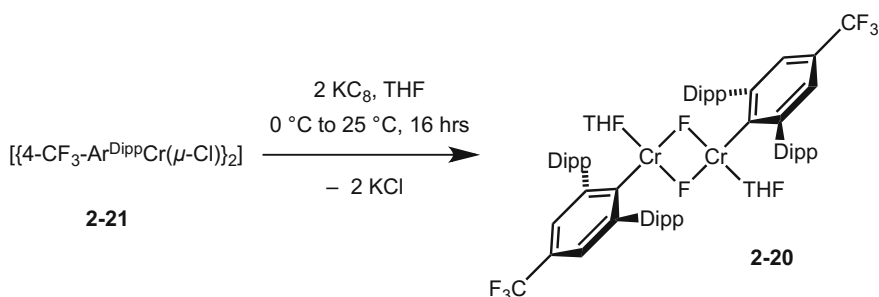
To date, six terphenyl chromium(II) halide complexes have been crystallographically characterised. These are $[\{4\text{-R-Ar}^{\text{Dipp}}\text{Cr}(\mu\text{-Cl})\}_2]$ ($R = \text{H}$ **2-15**, OMe **2-16**, SiMe_3 **2-17**), $[\{\text{Ar}^{\text{Dipp}}\text{Cr}(\mu\text{-I})\}_2]$ **2-18**, $[\{4\text{-F-Ar}^{\text{Dipp}}\text{Cr}(\text{THF})(\mu\text{-Cl})\}_2]$ **2-19** and $[\{4\text{-CF}_3\text{-Ar}^{\text{Dipp}}\text{Cr}(\text{THF})(\mu\text{-F})\}_2]$ **2-20** [19–21]. Complexes **2-15–2-17** are essentially isostructural, differing only by the substituent in the para position of the central ring. The chromium centres in these three complexes exist in distorted square planar geometries, similar to that observed for the amido chromium(II) chloride **2-06**. However, **2-06** contains a molecule of THF coordinating to the Cr centre, whereas in complexes **2-15–2-17**, the four coordination sites occupied by one terphenyl ligand, two bridging chlorides and a relatively strong interaction with the *ipso*-carbon of one of the terphenyl's flanking rings, instead of a coordinating solvent molecule. Complex **2-18** is similar to **2-15–2-17**, but has a slightly different structure in the solid state, in that the bridging halides are iodides rather than

chlorides. Due to the large ionic radius of iodine, the chromium halide bonds in **2-18** are considerably longer than in any of the chromium chloride complexes. As a result, one of the iodides has a weak interaction with one of the ligand's flanking aryl rings.

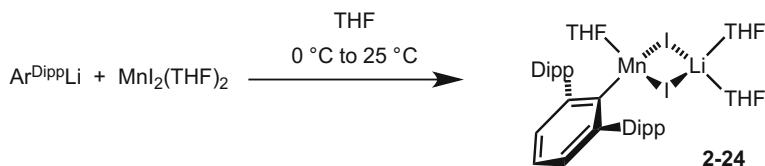
Depending on the steric and/or electronic properties of the metal centre, the coordination of a solvent molecule in the above complexes can be favoured over a ligand interaction. For instance, in **2-19** and **2-20**, a molecule of THF is coordinated to the metal centre, yielding a square planar geometry, similar to **2-06**. This structural change has come about as a result of a fluorine atom in the para position of the terphenyl ligand central ring in **2-19**, or the bridging fluorides in **2-20**. In both cases, the highly electronegative fluorine atoms withdraw electron density from the metal centre, which favours the coordination of a donor molecule, such as THF, rather than an aryl interaction.

Complexes **2-15–2-17** and **2-19** were synthesised via salt metathesis reactions between the appropriate terphenyl lithium salt, such as $[\text{Ar}^{\text{Dipp}}\text{Li}]$ for **2-15**, and chromium(II) chloride THF adduct $[\text{CrCl}_2(\text{THF})_2]$ in diethyl ether at 0 °C [20, 21]. Complex **2-21** was not synthesised by salt metathesis, but via oxidative addition of iodine to the quintuple bonded chromium(I) dimer **1-01**.¹⁹ The synthesis of **2-20** was rather unusual, as it was the decomposition product in the attempted reduction of another terphenyl chromium(II) chloride complex $[\{(4\text{-CF}_3\text{-Ar}^{\text{Dipp}}\text{Cr}(\mu\text{-Cl})\}_2]$ **2-21** with KC_8 (Scheme 2.7) (N.B. No structural analysis of **2-21** has been reported) [20]. Unlike the terphenyl chromium(II) chloride complexes **2-15–2-17**, **2-19** and **2-21**, which are all blue compounds, **2-20** is a pale purple colour.

In contrast to the range of terphenyl chromium(II) halide complexes reported, there is only one terphenyl manganese(II) halide and one terphenyl iron(II) halide complex reported, which are the isostructural complexes $[\{(3,5\text{-}^i\text{Pr}_2\text{-Ar}^{\text{Tripp}}\text{M}(\mu\text{-X})\}_2]$ ($\text{M} = \text{Mn}$, $\text{X} = \text{I}$, **2-22**; $\text{M} = \text{Fe}$, $\text{X} = \text{Br}$, **2-23**; $\text{Ar}^{\text{Tripp}} = 2,6\text{-Tripp}_2\text{-C}_6\text{H}_3$) [22]. Similar to the complexes **2-15–2-17**, **2-19** and **2-21**, complexes **2-22** and **2-23** were synthesised via salt metathesis reactions between the terphenyl lithium salt $[3,5\text{-}^i\text{Pr}_2\text{-Ar}^{\text{Tripp}}\text{Li}]$ and either MnI_2 (for **2-22**) or FeBr_2 (for **2-23**), in diethyl ether. The metal centres in both complexes were found to possess distorted trigonal geometries; the coordination sites being occupied by the terphenyl ligand



Scheme 2.7 Synthesis of **2-20**



Scheme 2.8 Preparation of **2-24**

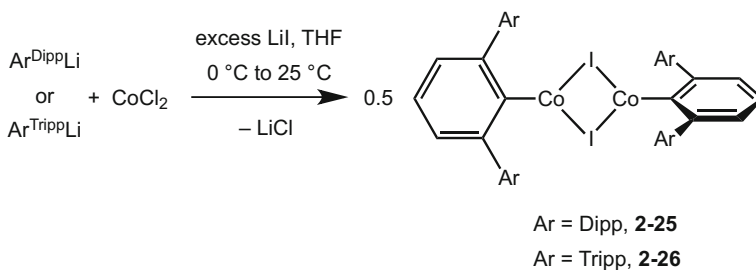
and the two bridging halides, with no strong interactions with the flanking aryl rings. The low coordination number of the metal centres in these compounds is a direct effect of the significant bulk of the $[3,5\text{-}^i\text{Pr}_2\text{-Ar}^{\text{Tripp}}]$ ligands. The related iron(II) chloride complex $[\{3,5\text{-}^i\text{Pr}_2\text{-Ar}^{\text{Tripp}}\text{Fe}(\mu\text{-Cl})\}_2]$ was also targeted by salt metathesis, i.e. the reaction between $[3,5\text{-}^i\text{Pr}_2\text{-Ar}^{\text{Tripp}}\text{Li}]$ and FeCl_2 . However, due to small amounts of the impurity LiI in the terphenyl lithium salt, the complex $[\{3,5\text{-}^i\text{Pr}_2\text{-Ar}^{\text{Tripp}}\text{Fe}(\mu\text{-Cl})\}_2]$ could never be isolated in a pure form, as halogen exchange occurred between LiI and the product. Consequently the crystallised product always contained a percentage of the iron(II) iodide complex $[\{3,5\text{-}^i\text{Pr}_2\text{-Ar}^{\text{Tripp}}\text{Fe}(\mu\text{-I})\}_2]$ [19].

One reason for the lack of terphenyl manganese(II), and iron(II) halide complexes, is that reactions of the smaller terphenyl lithium salts, with manganese(II) or iron(II) halides, often favours the formation of ‘-ate’ complexes, over the elimination of the lithium halide salt. For example, the reaction between $[\text{Ar}^{\text{Dipp}}\text{Li}]$ and manganese(II) iodide in THF, leads to high yields of the manganese iodide lithiate complex $[\text{Ar}^{\text{Dipp}}\text{Mn}(\text{THF})(\mu\text{-I})_2\text{Li}(\text{THF})_2]$ **2-24** (Scheme 2.8) [16]. The extreme bulk of the $3,5\text{-}^i\text{Pr}_2\text{-Ar}^{\text{Tripp}}$ ligands in **2-22** and **2-23** proved to be sufficient to drive the elimination of LiI , and therefore makes their isolation possible [22].

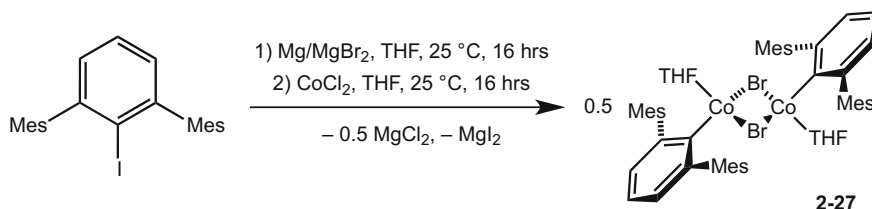
Finally, three terphenyl cobalt(II) halide complexes have been structurally characterised. These are $[\{\text{Ar}^{\text{Dipp}}\text{Co}(\mu\text{-I})\}_2]$ **2-25**, $[\{\text{Ar}^{\text{Tripp}}\text{Co}(\mu\text{-I})\}_2]$ **2-26**, and $[\{\text{Ar}^{\text{Mes}}\text{Co}(\text{THF})(\mu\text{-Br})\}_2]$ **2-27** [23], with a fourth reported $[\{3,5\text{-}^i\text{Pr}_2\text{-Ar}^{\text{Tripp}}\text{Co}(\mu\text{-Cl})\}_2]$ **2-28**, but not structurally characterised [24]. Initially, the terphenyl cobalt(II) chloride complexes were targeted by reactions of the terphenyl lithium salts, $[\text{Ar}^{\text{Dipp}}\text{Li}]$ and $[\text{Ar}^{\text{Tripp}}\text{Li}]$, with CoCl_2 . However, as was found with iron, small amounts of the corresponding terphenyl cobalt(II) iodide complexes were found in the product, formed by halogen exchange with a LiI impurity. However, when the reactions were repeated, adding an excess of LiI to the reaction mixture, the chloride was fully exchanged with iodide, and **2-25** and **2-26** could be isolated cleanly and in good yields (Scheme 2.9) [19].

Complexes **2-25** and **2-26** are essentially isostructural with the previously discussed terphenyl manganese(II) iodide **2-22** and terphenyl iron(II) bromide **2-23**, in that they have three-coordinate metal centres with distorted trigonal geometries.

Along with the two terphenyl cobalt(II) iodide complexes, one terphenyl cobalt(II) bromide complex has also been reported and structurally characterised, viz. $[\{\text{Ar}^{\text{Mes}}\text{Co}(\mu\text{-Br})\}_2]$ **2-27** [23]. The complex was not synthesised from the terphenyl lithium salt, but via a terphenyl Grignard reagent. The terphenyl iodide



Scheme 2.9 Preparation of **2-25** and **2-26**



Scheme 2.10 Preparation of **2-27**

$\text{Ar}^{\text{Mes}}\text{I}$ was reacted with activated magnesium (a mixture of magnesium metal and MgBr_2) and the mixture subsequently treated with CoCl_2 in THF (Scheme 2.10). Once again halogen exchange occurs, this time involving MgBr_2 , and the bromide bridged complex **2-27** is isolated instead of the chloride.

The smaller Ar^{Mes} ligands on **2-27**, compared with Ar^{Dipp} and Ar^{Tripp} on **2-25** and **2-26** respectively, favour the coordination of a molecule of THF to the metal centre, thus increasing the coordination from three in **2-25** and **2-26**, to four in **2-27**. Complex **2-27** bears some resemblance to the chromium(II) halide complexes **2-19** and **2-20**, in that it possesses four coordinate metal centres, with the coordination sites occupied by a terphenyl ligand, two bridging halides and a molecule of THF. However, as the chromium centres in **2-22** and **2-23** were found to be in a distorted square planar geometry, the cobalt centres in **2-27** were found to possess distorted tetrahedral geometries.

2.1.3.2 Terphenyl Group 12 Metal(II) Halide Complexes

In addition to terphenyl transition metal(II) halide complexes, Power, Robinson and co-workers have also isolated and structurally characterised a handful of terphenyl group 12 metal(II) halide complexes, including those of zinc, cadmium and mercury. These are $[\{\text{Ar}^{\text{Dipp}}\text{Zn}(\mu\text{-I})\}_2]$ **2-29**, $[\{\text{Ar}^{\text{Tripp}}\text{Zn}(\mu\text{-I})\}_2]$ **2-30**, $[\{\text{Ar}^{\text{Dipp}}\text{Cd}(\mu\text{-I})\}_2]$ **2-31** and $[\text{Ar}^{\text{Dipp}}\text{HgI}]$ **2-32** (Fig. 2.2) [25, 26].

All four compounds **2-29–2-32** were initially synthesised via salt metathesis reactions between terphenyl lithium salts and the appropriate group 12 metal(II)

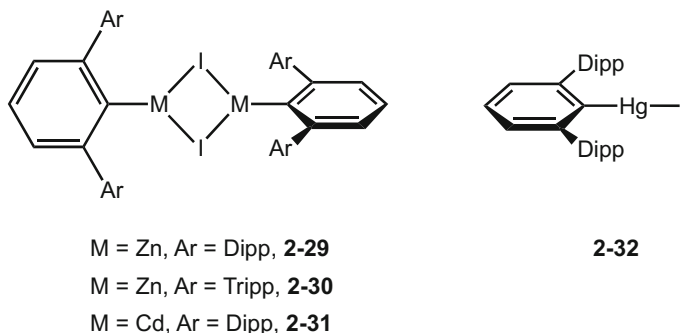


Fig. 2.2 Diagrammatic representations of the structurally characterised terphenyl group 12 metal(II) halide complexes **2-29–2-32**

iodide, which gave moderate yields of all four complexes. However, it was later found that **2-32** could be synthesised in considerably higher yields (92 % compared with 60 %) when the terphenyl Grignard reagent was used in place of the lithium salt [25].

Complexes **2-29–2-31** are essentially isostructural, existing as dimers in the solid state with bridging iodine atoms. The metal centres are three coordinate, in distorted trigonal geometries, with the coordination sites occupied by the two bridging iodine atoms and the terphenyl ligand. The metal centres in all three compounds do not exhibit any close interactions with flanking aryl groups.

The terphenyl mercury(II) iodide complex **2-32** is the only d-block terphenyl metal(II) halide complex reported to date, and is monomeric, two-coordinate in the solid state. However, this was not unexpected, as there are numerous monomeric two-coordinate mercury(II) halide complexes that have been structurally characterised [8]. The majority of these complexes bear much less sterically hindering ligands than terphenyls, e.g. the two-coordinate complex, phenyl mercury(II) iodide, the structure of which was first reported by Pachomov in 1963 [27].

2.1.4 Extremely Bulky Monodentate Amido Ligands

Over the past four years, the Jones group has developed a range of extremely bulky monodentate amide ligands, with the general structure of the secondary amine (or protonated ligand) shown in Fig. 2.3 [28–31].

A large proportion of the bulk, and consequent kinetic protection supplied by these ligands comes from the common pentaaryl substituent [2,6-(Ph₂C(H))₂-4-R'-C₆H₂] bound to the nitrogen atom. The other nitrogen substituent is an R group. This R group is typically either a trisubstituted silyl group or aryl ring, however ligands with alkyl and disubstituted phosphorus substituents have also been synthesised [32]. The overall steric bulk of the ligand can easily be tuned, by changing the size of this

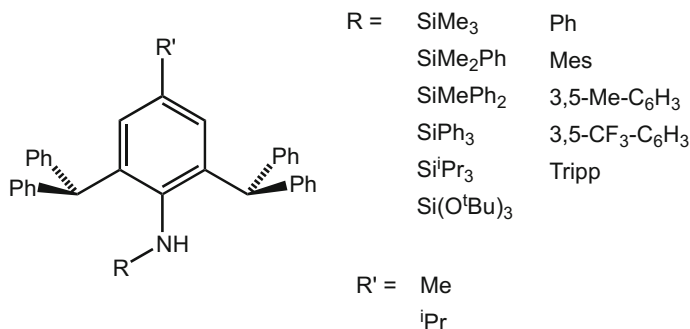


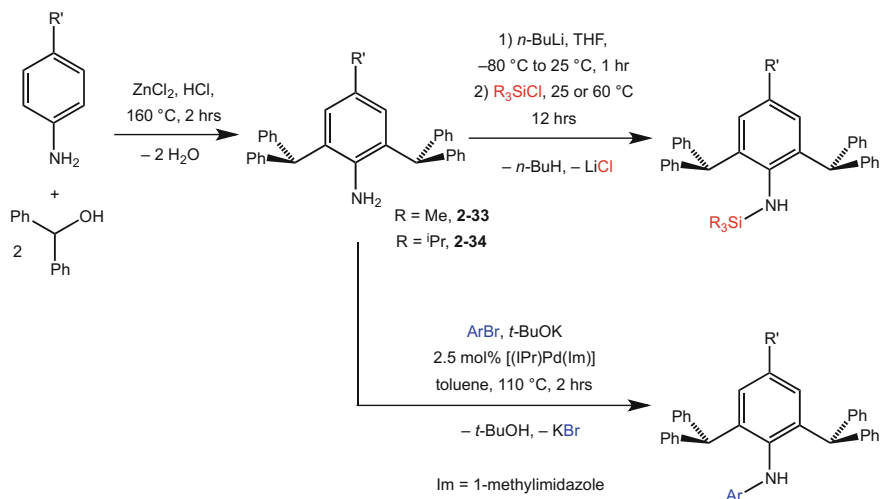
Fig. 2.3 A range of extremely bulky secondary amines

R group, from something relatively small, e.g. a phenyl ring, to an extremely bulky group, such as tri(*tert*butoxy)silyl. The R' group in the *para* position of the central ring is generally either methyl or isopropyl. Changing this R' group from methyl to isopropyl, has little effect on the overall bulk of the ligand, and consequently little effect on the stability of a metal complex bearing it. However, it does influence the solubility and crystallising properties of the ligand itself, as well as derived coordination complexes.

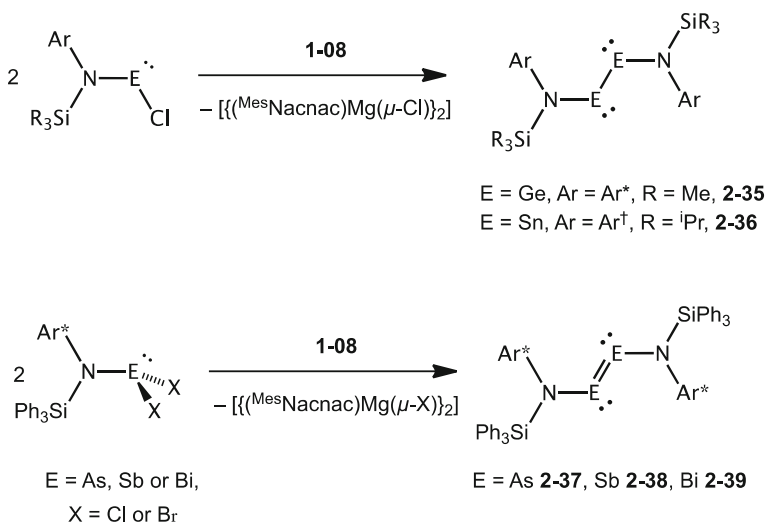
The extremely bulky secondary amines are easily synthesised, in two steps for the bis(aryl) amines, and three steps for the silyl containing ligands (Scheme 2.11). The first step is common to both ligand types, i.e. the synthesis of the bulky aniline, either Ar^{*}NH₂ **2-33** (Ar^{*} = 2,6-(Ph₂CH)₂-4-Me-C₆H₂) or Ar[†]NH₂ **2-34** (Ar[†] = 2,6-(Ph₂CH)₂-4-ⁱPr-C₆H₂). These are prepared via a solvent free Friedel-Crafts alkylation reaction between diphenylmethanol and a *para*-substituted aniline, to give good yields of the corresponding bulky aniline.

The silyl amine pro-ligands are synthesised by deprotonation of the bulky aniline **2-33** or **2-34** with *n*-butyl lithium in THF, followed by the addition of the corresponding silyl chloride, to give the bulky secondary amines in moderate to good yields. The diaryl pro-ligands on the other hand, are synthesised by palladium-catalysed cross-coupling reactions between the bulky aniline, **2-33** or **2-34**, and the corresponding aryl bromide.

These extremely bulky amide ligands have been used to stabilise a number of p-block element(I) dimers, such as the first amido digermene [{Ar^{*}(SiMe₃)NGe}₂] **2-35** [33], the first amido distannylene [{Ar[†](SiⁱPr₃)NSn}₂] **2-36** [34] and a range of dipnictenes [{Ar^{*}(SiPh₃)NE}₂] (E = As **2-37**, Sb **2-38** and Bi **2-39**) [35]. All of these unprecedented p-block compounds were synthesised by reductions of the amido metal halide (or dihalide) precursor complexes with the magnesium(I) reducing agent [{(^{Mes}Nacnac)Mg}₂] **1-08** (Scheme 2.12). The only other monodentate ligand class used to successfully stabilise this range of low oxidation state p-block compounds are the terphenyls.



Scheme 2.11 Preparation of a series of bulky secondary amines



Scheme 2.12 Preparation of 2-35-2-39

2.2 Research Outline

With the recent success that the extremely bulky amide ligands, developed in the Jones group, have had in low oxidation state p-block chemistry, it seemed reasonable that they could also be used to stabilise low coordinate, low oxidation state d-block metal complexes. With this in mind, a range of first row transition metal(II)

halide and group 12 metal(II) halide complexes, stabilised by the bulky amido ligands were targeted. The bulk and the electronic properties of the ligand were proposed to be modified, to investigate how these change the structure of the amido metal(II) halide complex. These complexes would hopefully serve as precursors to novel amide stabilised low oxidation state d-block metal complexes in later studies.

2.3 Results and Discussion

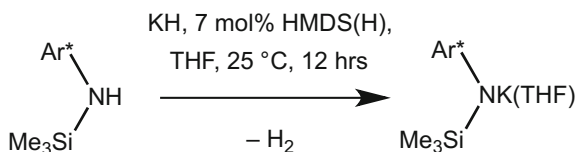
Bulky amido metal(II) halide complexes were initially targeted via salt metathesis reactions between metal(II) halides and bulky lithium amide salts, generated in situ by deprotonation of the bulky secondary amine pro-ligands with *n*-butyl lithium in THF. However, these reactions, e.g. involving $[\text{Ar}^*(\text{SiMe}_3)\text{N}(\text{THF})\text{Li}]$ and $[\text{Ar}^*(\text{SiPh}_3)\text{N}(\text{Li})]$, typically led to complex mixtures of unidentifiable products. That said, one reaction between $[\text{Ar}^*(\text{SiMe}_3)\text{N}(\text{THF})\text{Li}]$ and MnBr_2 in THF, followed by crystallisation from a diethyl ether solution, afforded a very low yield (<5 %) of the “-ate” complex, $[\text{Ar}^*(\text{SiMe}_3)\text{NMn}(\text{THF})(\mu\text{-Br})_2\text{Li}(\text{OEt})_2]$ **2-40**. The complex is reminiscent of **2-24**, the terphenyl manganese(II) bromide lithiate complex, isolated from the reaction of $[\text{Ar}^{\text{Dipp}}\text{Li}]$ and MnI_2 . In an attempt to prevent the formation of these “-ate” complexes, potassium amide salts were chosen as an alternative to lithium amide salts, in the preparation of the amido d-block metal(II) halide complexes, as discussed below.

2.3.1 Preparation of Bulky Potassium Amide Salts

The potassium amide salt $[\text{Ar}^*(\text{SiMe}_3)\text{NK}(\eta^6\text{-toluene})]$ was reported prior to this work, prepared by the deprotonation of the bulky secondary amine $\text{Ar}^*(\text{SiMe}_3)\text{NH}$ with 1.1 equivalents of $[\text{KN}(\text{SiMe}_3)_2]$ (KN'') in THF [36]. After purification by crystallisation from toluene, a modest yield (71 %) of the complex was isolated. However, scaling this reaction up from the reported 2 to 10 g (or above) proved problematic. This was partly due to the reaction not going fully to completion, because it is essentially an equilibrium between the potassium salt of bulky amine and the potassium salt of N'' . Therefore the product was repeatedly contaminated with small amounts of the starting $\text{Ar}^*(\text{SiMe}_3)\text{NH}$ ($\approx 10\%$), even after crystallisation. The equilibrium point of the reaction can be shifted to favour the formation of $[\text{Ar}^*(\text{SiMe}_3)\text{NK}(\eta^6\text{-toluene})]$, by adding a large excess of KN'' , however then the product was found to be contaminated with KN'' . The deprotonation was also attempted with KH , however this does not react with bulky amine $\text{Ar}^*(\text{SiMe}_3)\text{NH}$, even in THF at reflux over the course of several days.

A new and improved synthesis for $[\text{Ar}^*(\text{SiMe}_3)\text{NK}]$ was developed, replacing the use of stoichiometric amounts of KN'' with a cleaner and more atom efficient route. By using a slight excess of KH (1.1–1.3 equiv.) with a catalytic amount of

Scheme 2.13 Improved synthesis of $[\text{Ar}^*(\text{SiMe}_3)\text{NK}(\text{THF})]$



$(\text{Me}_3\text{Si})_2\text{NH}$ (5–10 mol%) in THF, KN'' is generated in situ, by deprotonation of $(\text{Me}_3\text{Si})_2\text{NH}$ with KH. This then deprotonates the bulky secondary amine $\text{Ar}^*(\text{SiMe}_3)\text{NH}$, to give $[\text{Ar}^*(\text{SiMe}_3)\text{NK}(\text{THF})]$, whilst regenerating the catalyst. With the release of H_2 , the reaction is driven to completion over the course 12 h, with no $\text{Ar}^*(\text{SiMe}_3)\text{NH}$ observed in the product by ^1H NMR spectroscopy. Furthermore, workup and purification of the potassium amide is achieved by simply filtering away the remaining KH, removing the solvent *in vacuo*, and finally washing the residue with warm hexane to remove excess KN'' . This gives $[\text{Ar}^*(\text{SiMe}_3)\text{NK}(\text{THF})]$ in significantly higher yields (95 %) (Scheme 2.13).

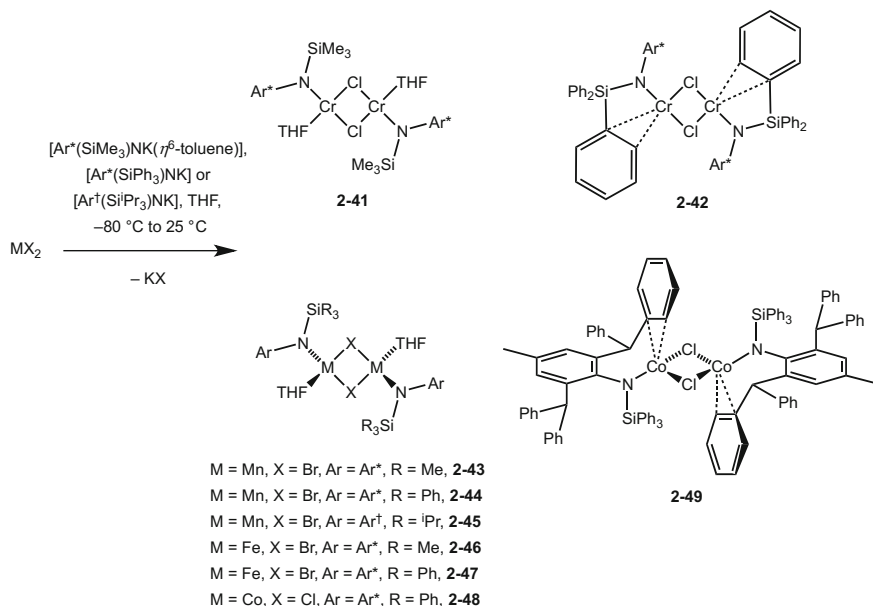
The coordinated THF in $[\text{Ar}^*(\text{SiMe}_3)\text{NK}(\text{THF})]$ is relatively labile, and can be exchanged for other weakly coordinating or aromatic solvent molecules, such as diethyl ether or toluene, by simply dissolving (or suspending in the case of Et_2O) the potassium amide in the appropriate solvent.

The improved synthetic route to $[\text{Ar}^*(\text{SiMe}_3)\text{NK}(\text{THF})]$ was found to be effective for the synthesis of many other bulky potassium amides, such as $[\text{Ar}^*(\text{SiPh}_3)\text{NK}]$ and $[\text{Ar}^\dagger(\text{Si}^i\text{Pr}_3)\text{NK}(\text{THF})]$. However, for the deprotonation of extremely sterically hindered secondary amines, such as $\text{Ar}^\dagger(\text{Si}^i\text{Pr}_3)\text{NH}$ or $\text{Ar}^*(\text{Si}^i\text{Pr}_3)\text{NH}$, the reaction mixtures required heating to $60\text{ }^\circ\text{C}$ for 12 h to proceed. This new route is how all of the potassium amides presented in this work were prepared.

2.3.2 Bulky Amido First Row Transition Metal(II) Halide Complexes

A range of bulky amido transition metal(II) halide complexes were synthesised by the addition of THF solutions of the potassium amides $[\text{Ar}^*(\text{SiMe}_3)\text{NK}(\eta^6\text{-toluene})]$, $[\text{Ar}^*(\text{SiPh}_3)\text{NK}]$ or $[\text{Ar}^\dagger(\text{Si}^i\text{Pr}_3)\text{NK}]$ to a solution (or suspensions) of one equivalent of either CrCl_2 , MnBr_2 , FeBr_2 , or CoCl_2 , in THF and $-80\text{ }^\circ\text{C}$. The reaction mixtures were slowly warmed to room temperature, where they were stirred for between 5 min and 12 h. Work-up, followed by recrystallization of the crude reaction mixture gave moderate to good yields (43–81 %) of the amido metal halide complexes **2-41–2-49** (Scheme 2.14).

Reactions of the three potassium amides with NiBr_2 and CuCl_2 were also attempted. However, in every case these led to intractable mixtures of products, with no amido metal halide complex isolated. Furthermore, reactions of the three potassium amides with CoBr_2 were also targeted, however in every case these led to the recovery of the potassium amide and the reproducible generation of the new

Scheme 2.14 Preparation of **2-41–2-49**

cobalt bromide contact ion-pair complex, [(THF)₄Co(μ-Br)₂CoBr₂] **2-50**. It seems that dissolution of CoBr₂ in THF yields **2-50**, which has a low reactivity towards the potassium amide starting materials. In addition, no identifiable product could be isolated from the reaction of [Ar^{*}(SiMe₃)NK(η⁶-toluene)] with CoCl₂. However, depending on the solvent of crystallization, two amido cobalt(II) chloride complexes **2-48** and **2-49** bearing the same Ar^{*}(SiPh₃)N[−] ligand could be isolated (see structural discussions below for further details).

Unfortunately, in the repeated reactions between the most bulky of the three potassium amides [Ar[†](SiⁱPr₃)NK], and the metal(II) halides CrCl₂, FeBr₂ or CoCl₂, no amido metal halide complex was isolated. The only isolated product from all three reactions was the protonated bulky secondary amine Ar[†](SiⁱPr₃)NH. The only reaction to yield an amido transition metal(II) halide bearing the bulky Ar[†](SiⁱPr₃)N[−] ligand was between [Ar[†](SiⁱPr₃)NK] and MnBr₂, which gave good yields of the amido manganese(II) bromide **2-45**.

All of the complexes **2-41–2-49** were characterised by X-ray crystallography (Figs. 2.4, 2.5 and 2.6), which revealed them to possess varying coordination geometries, depending on the ligand and metal involved. However, they were all found to be dimeric in the solid state, with bridging halides.

The two amido chromium(II) chloride complexes **2-41** and **2-42** differ to the other amido metal(II) halides, in that they both possess distorted square planar metal geometries, whereas complexes **2-43–2-49** all contain metals in distorted tetrahedral environments. The metal coordination sites in **2-41** and **2-42**, are occupied by the

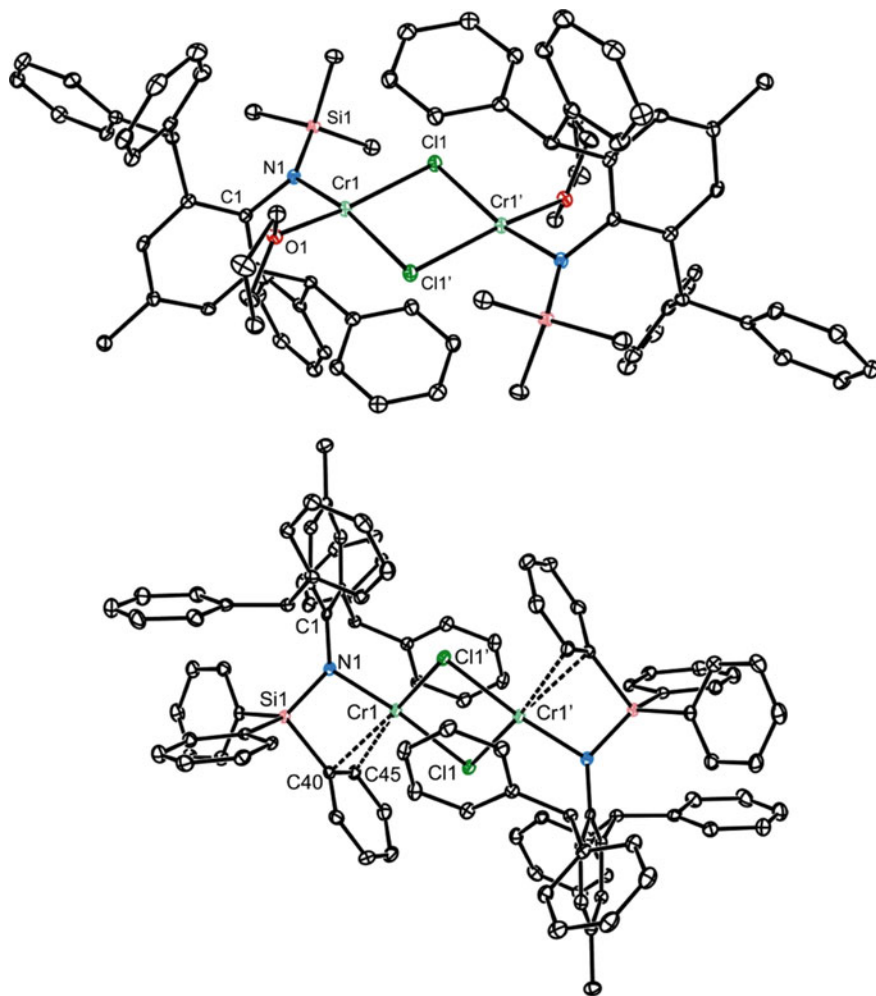


Fig. 2.4 Thermal ellipsoid plots (25 % probability surface) of the molecular structures of **2-41** (top) and **2-42** (bottom). Hydrogen atoms have been omitted for clarity. Selected interatomic distances (Å) and angles (°) for complexes **2-41** and **2-42** can be found in Table 2.1

amide, two approximately symmetrically bridging chlorides and either a molecule of THF in **2-41**, or an η^2 -phenyl interaction to one of the phenyl rings of the triphenyl silyl group in **2-42**. The difference in the chromium coordination sites suggests that there is competition between THF and ligand arene interactions in these complexes, as both complexes were synthesized in THF. The resulting structures can be explained by the bulk of the ligand; the smaller $\text{Ar}^*(\text{SiMe}_3)\text{N}^-$ ligand in **2-41** favours the coordination of a molecule of THF, whereas the more sterically demanding $\text{Ar}^*(\text{SiPh}_3)\text{N}^-$ ligand in **2-42** favours an η^2 -phenyl interaction. The SiPh_3 groups on the $\text{Ar}^*(\text{SiPh}_3)\text{N}^-$ ligands of **2-42** provide the possibility of an

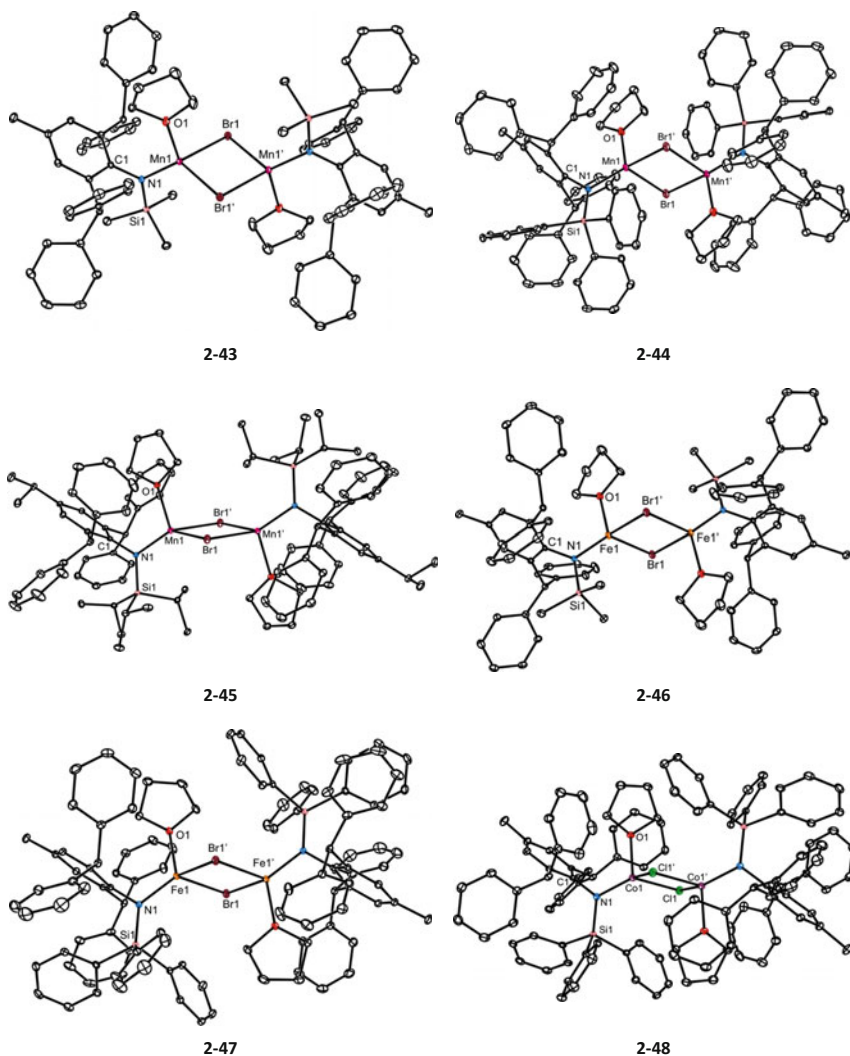


Fig. 2.5 Thermal ellipsoid plots (25 % probability surface) of the molecular structures of **2-43**–**2-48**. Hydrogen atoms have been omitted for clarity. Selected interatomic distances (Å) and angles (°) for complexes **2-43**–**2-48** can be found in Table 2.1

η^2 -phenyl interaction, which is not available in **2-41**. However, as chromium(II) is generally considered a hard acid, the coordination to THF would be favoured over the softer η^2 -phenyl interaction, therefore the steric bulk of the ligand is the main driving force for this change in coordination.

Complex **2-41** closely resembles the previously reported amido chromium(II) complex **2-06**, as well as the two terphenyl chromium(II) halide complexes **2-19** and **2-20**. That is, all four complexes are dimeric, square planar chromium(II) halide

Table 2.1 Selected interatomic distances (Å) and angles (°) for **2-41–2-49**

	2-41 (Cr)	2-42 (Cr)	2-43 (Mn)	2-44 (Mn)	2-45 (Mn)	2-46 (Fe)	2-47 (Fe)	2-48 (Co)	2-49 (Co)
M–N	2.016(2)	2.014(2)	1.9849(13)	2.024(2)	1.924(2)	1.9363(15)	2.0137(17)	1.936(2)	1.909(3)
M–X	2.3654(8)	2.3945(9)	2.5790(3)	2.6196 (5)	2.5514(6)	2.5552(3)	2.6329(4)	2.3500(9)	2.3508(10)
M–X'	2.4248(8)	2.3567(8)	2.5968 (3)	2.5912 (5)	2.5671(5)	2.5455(3)	2.6410(4)	2.3487(8)	2.3209(9)
M–O or M–CC _{mid point}	2.0766(19)	2.423(2)	2.1034(12)	2.127(2)	2.041(2)	2.0507(13)	2.1335(14)	2.027(2)	2.365(2)
M··M'	3.523(1)	3.503(1)	3.574(1)	3.724(1)	3.620(1)	3.685(1)	3.918(11)	3.342(1)	3.310(1)
X–M–X'	85.32(3)	84.99(3)	92.65(1)	88.76(2)	89.98(2)	87.48(1)	84.031(12)	89.34(3)	89.77(3)
M–X–M'	94.68(3)	95.01(3)	87.35(1)	91.24(2)	90.02(2)	92.52(1)	95.969(12)	90.66(3)	90.23(3)
N–M–O or N–M–CC _{mid point}	97.41(8)	81.48(7)	113.28(5)	114.96(8)	118.17(9)	118.71(6)	109.07(6)	108.60(10)	97.14(8)

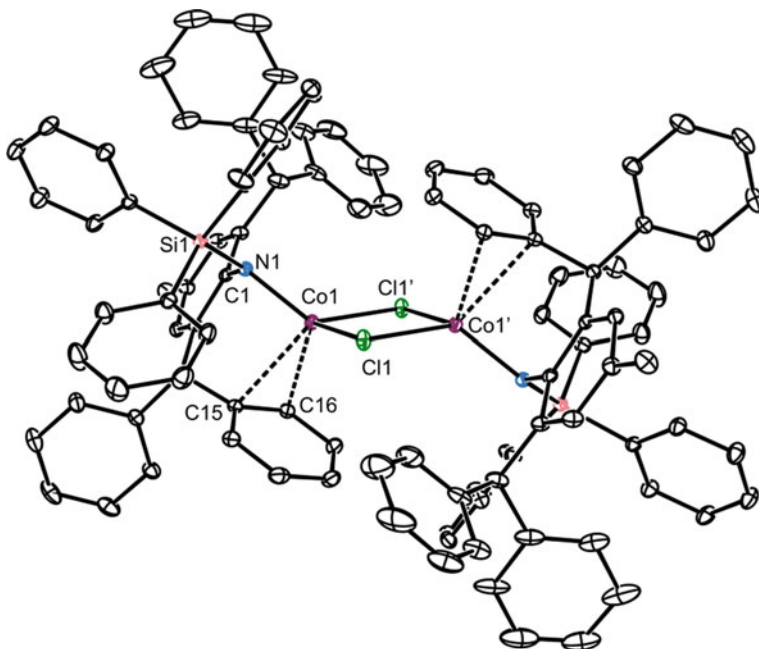


Fig. 2.6 Thermal ellipsoid plot (25 % probability surface) of the molecular structure of **2-49**. Hydrogen atoms have been omitted for clarity. Selected interatomic distances (Å) and angles (°) for complex **2-49** can be found in Table 2.1

complexes in the solid state, with bridging halides and a molecule of THF occupying coordination sites. Complex **2-42** is more closely associated with the terphenyl chromium(II) chloride complexes **2-15–2-18**, which are also dimeric, square planar complexes, but do not possess a coordinating solvent. Instead, the fourth coordination site is occupied by a strong interaction with the *ipso*-carbon of one of the terphenyl flanking aryl groups.

The Cr–N distances in **2-41** and **2-42** are in the normal range for chromium(II) amides [8], but are slightly less than the sum of the covalent radii for Cr and N (2.10 Å) [37]. Although the $\text{Cr}\cdots\eta^2\text{-C-C}_{\text{mid point}}$ distances in **2-42** (2.423(2) Å) are longer than normal Cr–C covalent bonds, e.g. 2.020(7) Å in $[\text{Cr}(\eta^6\text{-benzene})_2]$ [38] and 2.041(3) Å in **2-15** [21], they clearly signify relatively strong Cr $\cdots$ phenyl interactions.

The three amido manganese(II) bromide complexes **2-43**, **2-44** and **2-45**; the two amido iron(II) bromide complexes **2-46** and **2-47**, along with the amido cobalt(II) chloride complex **2-48**, are essentially isostructural in the solid state. All of the metals in complexes **2-43–2-48** possess distorted tetrahedral coordination geometries, with their sites occupied in a similar fashion to **2-41**, i.e. with the terminal amide, two bridging halides and a molecule of THF coordinated to the metal. Rather surprisingly, the amido manganese bromide **2-45**, which bears the most sterically demanding ligand $[\text{Ar}^\dagger(\text{Si}^i\text{Pr}_3)\text{N}]^-$, still possesses this geometry, even

though the extra bulk would be thought to favour a η^2 -phenyl interaction, and not a coordinating THF molecule.

There are no other reported terminal amido manganese(II) halide complexes to compare complexes **2-43–2-45** with, however the manganese complexes reported here contrast to the previously reported monomeric amido iron(II) chloride complexes **2-01** and **2-02**, and the amido cobalt(II) chloride **2-03**. Complexes **2-01–2-03** all contain a bidentate coordinating tmEDA molecule, which occupies two of the four coordination sites; this disfavors dimerisation, therefore **2-01–2-03** are all monomeric in the solid state. There are no equivalent structural types for terphenyl manganese or iron halide complexes either, as the only reported terphenyl manganese(II) halide **2-22** and terphenyl iron(II) halide **2-23** possess one of the most sterically demanding terphenyl ligands 3,5-ⁱPr₂-Ar^{Tripp}. These extremely bulky terphenyl ligands force the metal to occupy a three-coordinate trigonal geometry, with no space for the coordination of a solvent molecule. Comparisons can, however, be made between the cobalt complex **2-49**, and the terphenyl cobalt bromide complex **2-27**, both of which are dimeric, have similar distorted tetrahedral cobalt geometries, with a coordinating molecule of THF.

Within the series of essentially isostructural complexes **2-43–2-48**, there is a general decrease in the M–N and/or M–O distances with increasing relative atomic mass of the metal. This is consistent with the decreasing high spin covalent radii reported for the metal sequence Mn (1.61 Å) > Fe (1.52 Å) > Co (1.50 Å) [37]. Although the N-centers in all of the complexes **2-43–2-48** have planar geometries, none of their M–N distances are especially short, and therefore they do not indicate significant degrees of N → M π -bonding. In addition, their metal-metal separations are not indicative of any substantial metal-metal bonding.

As previously mentioned in the discussion of the amido chromium halide complexes **2-41** and **2-42**, there is a competition in these complexes for the metal's coordination to THF, or the formation of a ligand arene interaction. In the amido cobalt(II) chloride complexes **2-48** and **2-49**, this is apparently a relatively finely balanced competition, as both the THF coordinated complex **2-48** and the THF free, arene interacting complex **2-49** can be isolated with the same Ar*(SiPh₃)N[−] ligand. Complex **2-48** is obtained when the vacuum dried crude reaction product is recrystallized from a toluene/hexane solution. However, if that solution is kept at room temperature for several days before crystallization occurs, only **2-49** is obtained. Moreover, solid samples of **2-48** appear to slowly lose their coordinated THF at ambient temperature, while dissolution of **2-49** in THF leads to the immediate and quantitative regeneration of compound **2-48**.

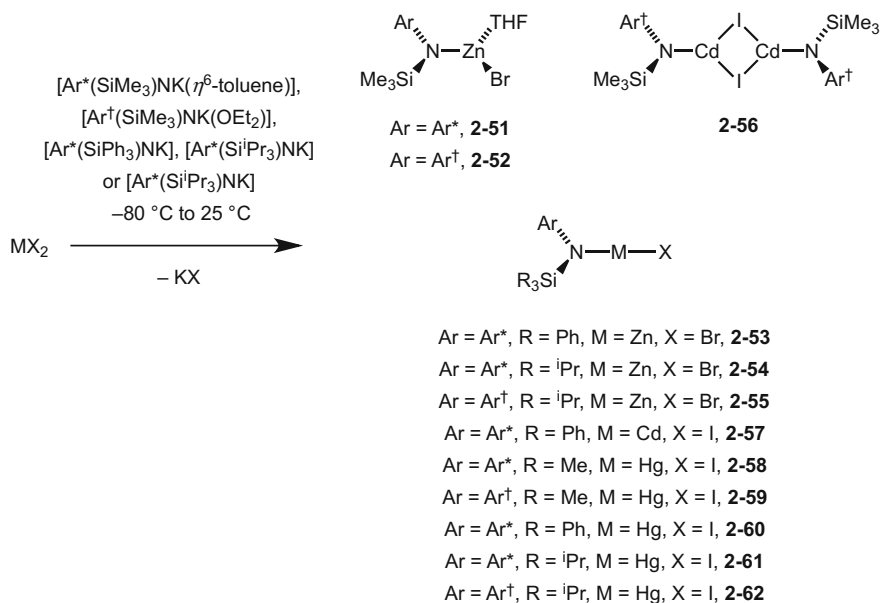
The solid state structure of **2-49** resembles those of **2-43–2-48**, in that it has a distorted tetrahedral cobalt geometry, though the fourth coordination site of the metal is instead taken up by an η^2 -phenyl interaction rather than a coordinating molecule of THF. At first glance, this appears similar to the situation in **2-42**. However, in **2-42** the interaction derives from a phenyl group of the SiPh₃ fragment, whereas in **2-49**, it comes from a phenyl substituent of the Ar* ligand. This difference presumably results from the contrasting metal geometries in the two complexes.

All of the amido transition metal(II) halide compounds reported (except **2-48**) are very thermally stable solids, and are indefinitely stable in solution at ambient temperature. Little information can be gained from their NMR spectroscopic data, due to the paramagnetic nature of the compounds. This gives rise to broad signals in the ^1H NMR spectra, which are typically observed over wide chemical shift ranges, e.g. -53 to 123 ppm for **2-49**.

Solution state effective magnetic moments of the amido transition metal(II) complexes were determined using the Evans method [39]. Unfortunately, the very low solubility of the chromium chloride complex **2-42** in non-coordinating deuterated solvents prevented an accurate magnetic moment determination. The magnetic moment obtained for the amido chromium chloride **2-41** ($\mu_{\text{eff}} = 5.81 \mu_{\text{B}}$ per dimer) is less than the spin-only value for two non-interacting high-spin Cr^{2+} centers ($\mu_{\text{so}} = 6.93 \mu_{\text{B}}$). However, it lies in the range previously reported for related square-planar halide bridged chromium(II) dimers, e.g. the terphenyl chromium fluoride complex **2-20** ($\mu_{\text{eff}} = 6.94 \mu_{\text{B}}$ per dimer) [20] and the previously reported amido chromium(II) chloride complex **2-06** ($\mu_{\text{eff}} = 4.95 \mu_{\text{B}}$ per dimer) [7]. This suggests the compound is high-spin and exhibits a degree of antiferromagnetic coupling over the Cr_2Cl_2 core. Similarly, the magnetic moments obtained for all the tetrahedral dimers, **2-43–2-49**, indicate that they are high-spin complexes, the metal centers of which are antiferromagnetically coupled to varying extents. Specifically, the effective magnetic moments for the manganese complexes, **2-43** ($5.90 \mu_{\text{B}}$ per dimer), **2-44** ($6.85 \mu_{\text{B}}$ per dimer), and **2-45** ($6.90 \mu_{\text{B}}$ per dimer) are markedly less than the spin-only value ($\mu_{\text{so}} = 8.36 \mu_{\text{B}}$). It is difficult to draw comparisons here as we are not aware of any other structurally authenticated tetrahedral, halide bridged manganese(II) dimers that have been the subjects of magnetochemical studies. The only exceptions are several dimeric, tetrahedral manganese dihalide adducts, e.g. $[\{\text{Mn}(\text{NEt}_3)\text{I}(\mu\text{-I})\}_2]$ ($\mu_{\text{eff}} = 6.8 \mu_{\text{B}}$), for which significant antiferromagnetic coupling between the Mn centers was proposed [40]. The magnetic moments obtained for the iron(II) and cobalt(II) dimers, **2-46** ($5.38 \mu_{\text{B}}$ per dimer), **2-47** ($6.61 \mu_{\text{B}}$ per dimer), **2-48** ($4.86 \mu_{\text{B}}$ per dimer) and **2-49** ($5.20 \mu_{\text{B}}$ per dimer), are also somewhat less than the spin-only values (Fe: $6.93 \mu_{\text{B}}$, Co: $5.40 \mu_{\text{B}}$). The observed magnetic moments are, however, comparable to those for related four-coordinate complexes, e.g. the β -diketiminato iron fluoride complex $[\{(\text{Dipp}^{\text{Nacnac}})\text{Fe}(\mu\text{-F})\}_2]$ ($6.2 \mu_{\text{B}}$ per dimer) [41] and the terphenyl cobalt bromide complex **2-27** ($4.7 \mu_{\text{B}}$ per dimer) [23].

2.3.3 Bulky Amido Group 12 Metal(II) Halide Complexes

Bulky amido group 12 halide complexes were prepared here, using similar methods to those for the synthesis of the amido transition metal(II) halide complexes, i.e. via reactions of the bulky potassium amides with metal(II) halides. However, for the group 12 complexes, two additional bulky potassium amides were employed, these are $[\text{Ar}^{\dagger}(\text{SiMe}_3)\text{NK}(\text{OEt}_2)]$ and $[\text{Ar}^*(\text{Si}^i\text{Pr}_3)\text{NK}]$.

**Scheme 2.15** Preparation of **2-51–2-62**

The bulky amido group 12 metal(II) halide complexes were synthesised by the addition of either THF, toluene or diethyl ether solutions of the potassium amides $[\text{Ar}^*(\text{SiMe}_3)\text{NK}(\eta^6\text{-toluene})]$, $[\text{Ar}^*(\text{SiPh}_3)\text{NK}]$, $[\text{Ar}^\dagger(\text{Si}^i\text{Pr}_3)\text{NK}]$, $[\text{Ar}^\dagger(\text{SiMe}_3)\text{NK}(\text{OEt}_2)]$ and $[\text{Ar}^*(\text{Si}^i\text{Pr}_3)\text{NK}]$ to suspensions of one equivalent of either ZnBr_2 , CdI_2 or HgI_2 in the same solvent and -80°C . The reactions were slowly warmed to room temperature, where they were stirred for between 30 min and 4 h. Work-up, followed by recrystallization of the crude reaction mixture gave moderate to excellent yields (53–90 %) of the amido metal halide complexes **2-51–2-62** (Scheme 2.15).

Amido zinc and mercury halide complexes bearing all five ligands have been isolated and characterised. However, reactions between the potassium amides $[\text{Ar}^*(\text{SiMe}_3)\text{NK}(\eta^6\text{-toluene})]$, $[\text{Ar}^*(\text{Si}^i\text{Pr}_3)\text{NK}]$ or $[\text{Ar}^\dagger(\text{Si}^i\text{Pr}_3)\text{NK}]$, and one equivalent of CdI_2 , in THF, toluene or diethyl ether repeatedly lead to the formation of cadmium metal and the corresponding protonated amine.

All of the complexes **2-51–2-62** were crystallographically characterised (Figs. 2.7, 2.8 and 2.9), which once again revealed them to possess varying coordination geometries, depending on the ligand and metal involved. These complexes differ to the equivalent transition metal complexes, in that, with the exception of **2-56**, they are all monomeric in the solid state.

The two amido zinc bromide complex **2-51** and **2-52** are essentially isostructural, and differ from the other amido group 12 metal halide complexes in that they are the only two to possess a coordinating solvent molecule, likely due to the fact that they possess the two least sterically demanding amido ligands. The coordination of THF

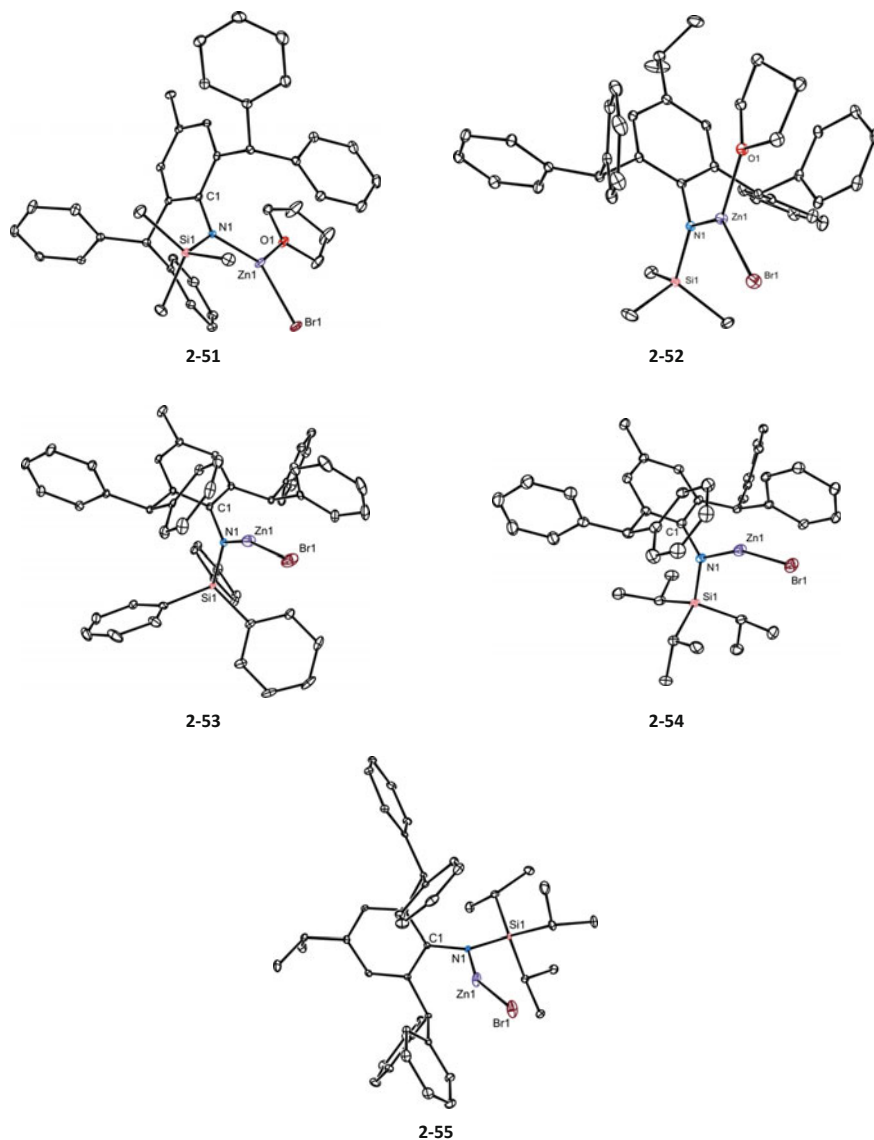


Fig. 2.7 Thermal ellipsoid plots (25 % probability surface) of the molecular structures of **2-51**–**2-55**. Hydrogen atoms have been omitted for clarity. Selected interatomic distances (Å) and angles (°) for complexes **2-51**–**2-55** can be found in Table 2.2

to the zinc centre in **2-51** and **2-52**, results in a three-coordinate zinc centre, in a distorted trigonal geometry. Although in both structures two phenyl rings from the pentaaryl substituent lie above and below the zinc coordination plane, the closest $\text{Zn}\cdots\text{C}_{\text{phenyl}}$ distance (3.048 Å in **2-51**, and 3.109 Å in **2-52**) in both cases is too

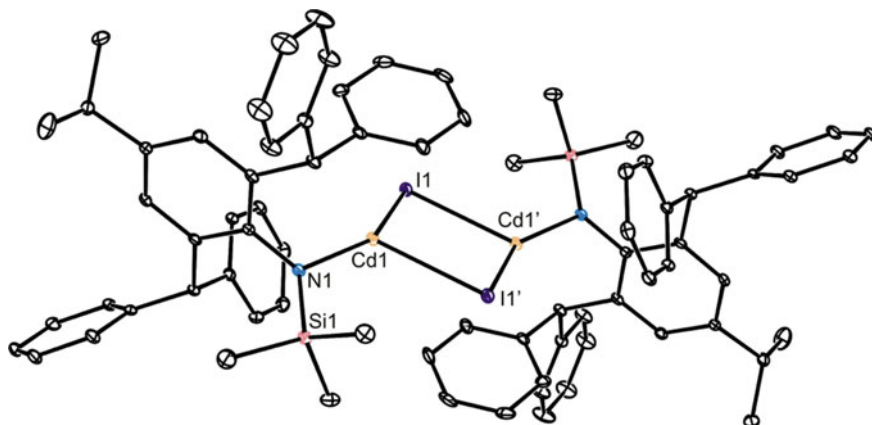


Fig. 2.8 Thermal ellipsoid plot (25 % probability surface) of the molecular structure of **2-56**. Hydrogen atoms have been omitted for clarity. Selected interatomic distances (Å) and angles (°) for complex **2-56** can be found in Table 2.2

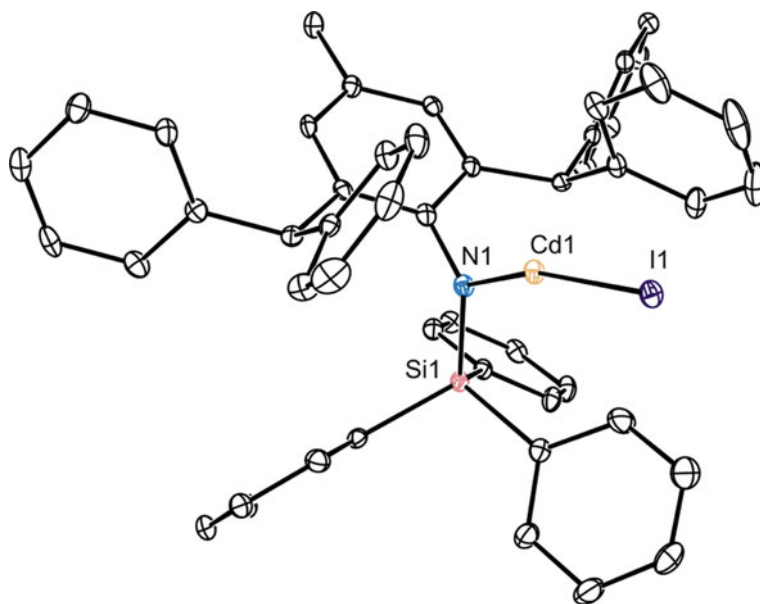


Fig. 2.9 Thermal ellipsoid plot (25 % probability surface) of the molecular structure of **2-57**. Hydrogen atoms have been omitted for clarity. Selected interatomic distances (Å) and angles (°) for complex **2-57** can be found in Table 2.2

long to imply any significant interaction. It is worth noting that the synthesis of amido zinc bromide complexes bearing $[\text{Ar}^*(\text{SiMe}_3)\text{N}]^-$ and $[\text{Ar}^\dagger(\text{SiMe}_3)\text{N}]^-$ without a coordinating molecule of THF was attempted, by carrying out reactions of the potassium amides $[\text{Ar}^*(\text{SiMe}_3)\text{NK}(\eta^6\text{-toluene})]$ and $[\text{Ar}^\dagger(\text{SiMe}_3)\text{NK}(\text{OEt}_2)]$ with ZnBr_2 in toluene, benzene and diethyl ether. However, in every case decomposition occurred, yielding the protonated amine and zinc metal. Therefore it is thought that the steric protection provided by the $\text{Ar}^*(\text{SiMe}_3)\text{N}^-$ and $\text{Ar}^\dagger(\text{SiMe}_3)\text{N}^-$ ligands is not sufficient to stabilise two-coordinate zinc halide complexes.

In contrast to **2-51** and **2-52**, there is no solvent coordinated to the three amido zinc bromide complexes **2-53**, **2-54** and **2-55**, likely due to the increase in ligand bulk. As a result, complexes **2-53–2-55** possess two-coordinate zinc centres. All three structures have slightly bent N–Zn–Br angles (160.41° in **2-53**, 159.37° in **2-54** and 158.63° in **2-55**) which may be due to an interaction between the Zn center and one of the flanking phenyl rings, but as the closest $\text{Zn}\cdots\text{C}_{\text{phenyl}}$ distance is long in all cases ($2.824\text{ \AA}$ in **2-53**, $2.854\text{ \AA}$ in **2-54** and $2.812\text{ \AA}$ in **2-55**), these interactions must be considered weak at best. Compounds **2-53–2-55** represent the first structurally characterised examples of amido zinc halide complexes, and differ from the corresponding terphenyl zinc halide complexes **2-29** and **2-30**, which have three-coordinate zinc centres and are dimeric in the solid state [25, 26].

Two amido cadmium iodide complexes, **2-56** and **2-57**, were also isolated and structurally characterised (Figs. 2.9 and 2.10). Compound **2-56** differs from all of the other amido group 12 metal halide complexes reported here, in that it is the only one to exist as a dimer in the solid state, even though the complex bears the same ligand, and was prepared in the same solvent as the monomeric zinc bromide complex **2-52**. The two cadmium centres are three-coordinate, and have distorted trigonal geometries. Flanking phenyl rings from the $\text{Ar}^\dagger$ substituent lie above and below the cadmium coordination plane, but as the closest $\text{Cd}\cdots\text{C}_{\text{phenyl}}$ distance is $2.952\text{ \AA}$, these distances are considered too long to imply any significant interaction. Complex **2-56** is similar to the corresponding terphenyl cadmium iodide complex **2-31**, which also possesses three-coordinate metal centres, and also exists as a dimer with bridging iodides in the solid state.

In contrast to **2-56**, the amido cadmium iodide complex **2-57** is monomeric in the solid state, due to an increase in ligand bulk, and is also solvent free, resulting in a two-coordinate cadmium centre. The structure of **2-57** is essentially isostructural with the related zinc complex **2-53**, with a slightly bent N–Cd–I fragment (164.8°), which is possibly due to an interaction between the Cd centre and one of the flanking phenyl rings of the $\text{Ar}^\dagger$ substituent. However, as the closest $\text{Cd}\cdots\text{C}_{\text{phenyl}}$ distance is quite long ($2.903\text{ \AA}$), this interaction must once again be considered weak. Compounds **2-56** and **2-57** represent the first examples of amido cadmium halide complexes.

Finally, five amido mercury iodide complexes, **2-58–2-62**, have been synthesised and crystallographically characterised (Fig. 2.10). All complexes were found to be essentially isostructural, monomeric and solvent free in the solid state, resulting in two-coordinate mercury centres. As with the two-coordinate zinc and cadmium

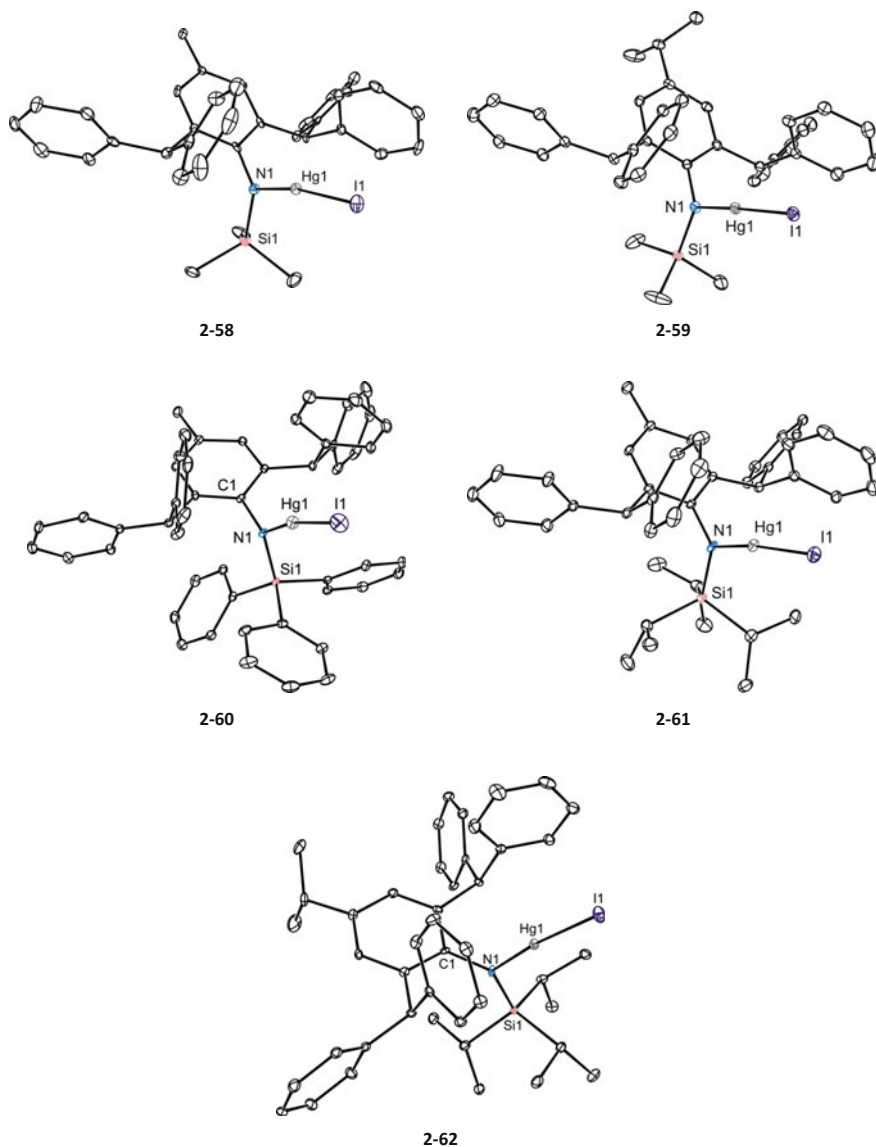


Fig. 2.10 Thermal ellipsoid plots (25 % probability surface) of the molecular structures of **2-58–2-62**. Hydrogen atoms have been omitted for clarity. Selected interatomic distances (Å) and angles (°) for complexes **2-58–2-62** can be found in Table [2.2](#)

structures, **2-53–2-55** and **2-57**, the N-Hg-I angles in the complexes are slightly bent (171.0° (avg) in **2-58**, 174.3° (avg.) in **2-59**, 170.3° in **2-60**, 173.4° in **2-61**, 174.4° in **2-62**) but to a lesser extent than in the related zinc and cadmium complexes. In addition, there are no strong Hg $\cdots$ C interactions with the phenyl groups

Table 2.2 Selected interatomic distances (Å) and angles (°) for 2-51–2-62

	2-51 (Zn)	2-52 (Zn)	2-53 (Zn)	2-54 (Zn)	2-55 (Zn)	2-56 (Cd)	2-57 (Cd)	2-58 (Hg)	2-59 (Hg)	2-60 (Hg)	2-61 (Hg)	2-62 (Hg)
M–N	1.8765(16)	1.8781(19)	1.833(3)	1.867(4) 1.855(4)	1.841(2)	2.099(4)	2.100(4)	2.040(7) 2.040(6)	2.035(5) 2.047(5)	2.049(5)	2.012(4)	2.013(4)
M–X	2.2993(3)	2.2969(7)	2.2180(6)	2.2722(12) 2.2677(10)	2.2218(4)	2.7292(9)	2.6104(7)	2.5629(6) 2.5596(5)	2.5690(8) 2.5638(7)	2.5713(8)	2.5647(9)	2.5570(8)
N–M–X	131.30(5)	130.44(6)	160.41	159.38(11) 160.15(11)	158.62(6)	145.96(10)	164.84(11)	171.16(18) 170.81(17)	177.62(15) 170.90(15)	170.31(13)	173.44(11)	174.40(13)
M–O	1.9936(16)	1.9869(18)	–	–	–	–	–	–	–	–	–	–
N–M–O	119.76(7)	121.73(8)	–	–	–	–	–	–	–	–	–	–
M···M'	–	–	–	–	–	3.822	–	–	–	–	–	–
M–X'	–	–	–	–	–	2.8889(10)	–	–	–	–	–	–
M–X–M'	–	–	–	–	–	85.68(4)	–	–	–	–	–	–
X–M–X'	–	–	–	–	–	94.32(4)	–	–	–	–	–	–

of the ligand (closest $\text{Hg}\cdots\text{C}_{\text{phenyl}} = 3.240 \text{ \AA}$ **2-58**, $3.265 \text{ \AA}$ **2-59**, $3.166 \text{ \AA}$ **2-60**, $3.203 \text{ \AA}$ **2-61** and $3.376 \text{ \AA}$ **2-62**). The complexes mirror the previously reported amido mercury halide complexes, **2-10–2-12**, as well as the corresponding terphenyl mercury iodide compound **2-32**, with no large structural diversity over the series.

2.4 Conclusion

In summary, five extremely bulky amide ligands have been utilized in the preparation of rare examples of monodentate amido first row transition metal(II) halide and group 12 metal halide complexes in moderate to high yields on multigram scales. All prepared complexes have been spectroscopically characterized and their X-ray crystal structures determined. The Cr, Mn, Fe and Co complexes are all high-spin, antiferromagnetically coupled halide bridged dimers, which possess square-planar (Cr) or tetrahedral (Mn, Fe and Co) metal coordination geometries.

The amido group 12 metal halides are almost exclusively monomeric, with the exception of the iodide bridge cadmium complex **2-56**. The amido zinc and cadmium halide complexes were found to display either planar three-coordinate, or distorted linear metal geometries, depending on the steric bulk of the ligand. All of the amido mercury iodide complexes, independent of the ligand size, were found to possess two coordinate metal centres.

2.5 Experimental

General methods. All manipulations were carried out using standard Schlenk and glove box techniques under an atmosphere of high purity dinitrogen. THF, hexane, cyclohexane and toluene were distilled over molten potassium, while diethyl ether and pentane were distilled over sodium/potassium alloy (1:1). ^1H , $^{13}\text{C}\{^1\text{H}\}$, $^{29}\text{Si}\{^1\text{H}\}$, $^{113}\text{Cd}\{^1\text{H}\}$ and $^{199}\text{Hg}\{^1\text{H}\}$ NMR spectra were recorded on either Bruker DPX300, Bruker AvanceIII 400 or Varian Inova 500 spectrometers and were referenced to the resonances of the solvent used, external SiMe_4 , $\text{Cd}(\text{ClO}_4)_2$ or Me_2Hg . Mass spectra were recorded on an Agilent Technologies 5975D inert MSD with a solid-state probe or obtained from the EPSRC National Mass Spectrometric Service at Swansea University. IR spectra were recorded using a Perkin-Elmer RX1 FT-IR spectrometer as Nujol mulls between NaCl plates or recorded as solid samples using an Agilent Cary 630 attenuated total reflectance (ATR) spectrometer. Microanalyses were carried out by the Science Centre, London Metropolitan University. A reproducible microanalysis for **2-44** could not be obtained because of its highly air sensitive nature, and because total removal of the hexane and THF of crystallization proved difficult by vacuum drying the compound at elevated temperature. A reproducible microanalysis for **2-48** could also not be obtained as it

slowly loses its THF of coordination in the solid state, yielding **2-49**. Melting points were determined in sealed glass capillaries under dinitrogen and are uncorrected. Solution state effective magnetic moments were determined by the Evans method [39]. The potassium amides $[\text{Ar}^*(\text{SiMe}_3)\text{NK}(\eta^6\text{-toluene})]$, $[\text{Ar}^*(\text{SiPh}_3)\text{NK}]$, and $[\text{Ar}^\dagger(\text{Si}^i\text{Pr}_3)\text{NK}]$ were prepared as discussed in Sect. 2.3.1. All other reagents were used as received.

Preparation of $[\text{Ar}^*(\text{Si}^i\text{Pr}_3)\text{NH}]$. To a suspension of Ar^*NH_2 (10.0 g, 22.7 mmol) in THF (100 mL) was added $n\text{BuLi}$ (14.9 mL of a 1.6 M solution in hexanes) at -80°C over 10 min. The reaction mixture was warmed to room temperature and stirred for a further 2 h, producing a white precipitate. Subsequently, neat triisopropylsilyl chloride (4.82 g, 25.0 mmol) was added, and the reaction mixture was warmed to 60°C and stirred for 12 h, whereupon volatiles were removed *in vacuo*. The residue was extracted with toluene (100 mL), the extract filtered and volatiles removed *in vacuo* to give an off white solid, which was washed with hexane (3×25 mL) to give $[\text{Ar}^*(\text{Si}^i\text{Pr}_3)\text{NH}]$ as an off white powder (9.80 g, 73 %). Mp: $224\text{--}226^\circ\text{C}$; ^1H NMR (499 MHz, C_6D_6 , 298 K): $\delta = 1.05$ (d, $^3J_{\text{HH}} = 7.5$ Hz, 18H, $\text{CH}(\text{CH}_3)_2$), 1.31 (sept, $^3J_{\text{HH}} = 7.5$ Hz, 3H, $\text{CH}(\text{CH}_3)_2$), 1.83 (s, 3H, ArCH_3), 6.28 (s, 2H, Ph_2CH), 6.89 (s, 2H, *o*- ArH), 7.01–7.21 (m, 20H, ArH); $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, C_6D_6): $\delta = 14.9$ ($\text{Si}\{\text{CH}(\text{CH}_3)_2\}_3$), 19.1 ($\text{Si}\{\text{CH}(\text{CH}_3)_2\}_3$), 21.2 (ArCH_3), 52.5 (CHPh_2), 126.6, 128.6, 130.1, 130.3, 132.5, 141.0, 141.1, 144.9 (Ar-C); $^{29}\text{Si}\{^1\text{H}\}$ NMR (80 MHz, C_6D_6): $\delta = 3.3$ (s); IR ν/cm^{-1} (Nujol): 1598(m), 1493(m), 1443(s), 1354(m), 1255(m), 1128(m), 1076(m), 1030(m), 914(m), 879(s), 762(m), 721(s), 698(s), 661(s); MS/EI m/z (%): 595.5 (M^+ , 41), 552.4 ($\text{M}^+ - ^i\text{Pr}$, 100), 167.1 (Ph_2CH^+ , 84); acc. mass MS/ESI calc. for $\text{C}_{42}\text{H}_{50}\text{NSi}(\text{Ar}^*\text{N}(\text{H})\text{Si}^i\text{Pr}_3 + \text{H}^+)$: 596.3713, found: 596.3701.

Preparation of $[\text{Ar}^\dagger(\text{SiMe}_3)\text{NK}(\text{OEt}_2)]$. To a suspension of KH (0.557 g, 13.9 mmol) in THF (40 mL) was added a solution of $\text{Ar}^\dagger(\text{SiMe}_3)\text{NH}$ (5.00 g, 9.26 mmol) in THF (40 mL) at room temperature. To the reaction mixture was added 7 mol% of hexamethyldisilazane (0.10 mL, 0.62 mmol), and the mixture warmed to 60°C , where the evolution of hydrogen gas was observed. The reaction was stirred for a further 12 h at 60°C , whereupon it was cooled to room temperature, filtered and volatiles removed *in vacuo*. The brown red residue was washed with hot hexane (2×30 mL) and diethyl ether (2×30 mL) to give $[\text{Ar}^\dagger(\text{SiMe}_3)\text{NK}(\text{OEt}_2)]$ as an off white powder (5.10 g, 84 %). Mp: $241\text{--}244^\circ\text{C}$; ^1H NMR (499 MHz, C_6D_6 , 298 K): $\delta = 0.41$ (s, 9H, $\text{Si}(\text{CH}_3)_3$), 1.12 (d, $^3J_{\text{HH}} = 6.9$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 2.67 (sept, $^3J_{\text{HH}} = 6.9$ Hz, 1H, $\text{CH}(\text{CH}_3)_2$), 6.51–7.39 (m, 24H, Ph_2CH and ArH); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, C_6D_6): $\delta = 5.5$ ($\text{Si}(\text{CH}_3)_3$), 25.0 ($\text{ArCH}(\text{CH}_3)_2$), 33.9 ($\text{ArCH}(\text{CH}_3)_2$), 53.6 (CHPh_2), 124.6, 125.8, 125.9, 126.6, 127.5, 128.6, 130.1, 130.3, 130.6, 131.2, 139.2, 144.9, 146.6, 151.3, 155.4 (Ar-C); $^{29}\text{Si}\{^1\text{H}\}$ NMR (80 MHz, C_6D_6): $\delta = -32.8$ (s); IR ν/cm^{-1} (Nujol): 1596(m), 1491(m), 1428(s), 1328(s), 1230(m), 1103(m), 1070(m), 1028(m), 979(s), 955(s), 860(m), 827(s), 811(s), 761(s), 704(s); MS/EI m/z (%): 577.5 ($\text{Ar}^\dagger\text{N}(\text{K})\text{SiMe}_3^+$, 9), 539.5 ($\text{Ar}^\dagger\text{N}(\text{H})\text{SiMe}_3^+$, 100), 466.4 ($\text{Ar}^\dagger\text{NH}^+$, 22), 167.2 (Ph_2CH^+ , 41), 73.2 (Me_3Si^+ , 53); anal. calc. for $\text{C}_{42}\text{H}_{50}\text{KNOSi}$: C 77.37 %, H 7.73 %, N 2.15 %, found: C 77.28 %, H 7.78 %, N 2.24 %.

Preparation of $[\text{Ar}^*(\text{Si}^i\text{Pr}_3)\text{NK}(\text{OEt}_2)]$. To a suspension of KH (0.505 g, 12.6 mmol) in THF (40 mL) was added a solution of $\text{Ar}^*(\text{Si}^i\text{Pr}_3)\text{NH}$ (5.00 g, 8.40 mmol) in THF (40 mL) and hexamethyldisilazane (0.10 mL, 0.62 mmol, 7 mol%) at ambient temperature. The reaction mixture was warmed to 60 °C, whereupon the evolution of hydrogen gas was observed. The mixture was stirred for a further 12 h. It then was allowed to cool to ambient temperature before it was filtered, and volatiles removed from the filtrate *in vacuo*. The red brown residue was washed with hot hexane (2×30 mL) and ice cold diethyl ether (2×20 mL) to give $[\text{Ar}^*(\text{Si}^i\text{Pr}_3)\text{NK}(\text{OEt}_2)]$ as an off white powder (5.30 g, 89 %). Mp: >260 °C; N.B. diethyl ether resonances appear at the same chemical shifts as for uncoordinated Et_2O in C_6D_6 ; ^1H NMR (499 MHz, C_6D_6 , 298 K): $\delta = 1.34$ (d, $^3J_{\text{HH}} = 7.4$ Hz, 18H, $\text{CH}(\text{CH}_3)_2$), 1.52 (sept, $^3J_{\text{HH}} = 7.4$ Hz, 3H, $\text{CH}(\text{CH}_3)_2$), 2.10 (s, 3H, ArCH_3), 6.60–7.41 (m, 24H, Ph_2CH and ArH); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, C_6D_6): $\delta = 17.7$ ($\text{CH}(\text{CH}_3)_2$), 21.1 ($\text{CH}(\text{CH}_3)_2$), 21.4 (ArCH_3), 52.7 (Ph_2CH), 119.8, 125.4, 125.9, 127.5, 128.5, 129.0, 130.5, 130.9, 139.2, 147.0, 150.9, 156.9 (Ar-C); $^{29}\text{Si}\{^1\text{H}\}$ NMR (80 MHz, C_6D_6): $\delta = -23.4$ (s); IR ν/cm^{-1} (Nujol): 1599 (m), 1492(m), 1421(s), 1308(s), 1075(m), 1030(m), 997(m), 946(m), 910(m), 880 (m), 764(m), 700(s), 674(m); MS/EI m/z (%): 633.5 ($\text{Ar}^*\text{N}(\text{K})\text{Si}^i\text{Pr}_3^+$, 5), 595.5 ($\text{Ar}^*\text{N}(\text{H})\text{Si}^i\text{Pr}_3^+$, 33), 552.4 ($\text{Ar}^*\text{N}(\text{H})\text{Si}^i\text{Pr}_2^+$, 64), 167.1 (Ph_2CH^+ , 100); anal. calc. for $\text{C}_{46}\text{H}_{58}\text{KNOSi}$: C 78.02 %, H 8.26 %, N 1.98 %, found: C 77.91 %, H 8.26 %, N 2.01 %.

Preparation of $[\{\text{Ar}^*(\text{SiMe}_3)\text{NCr}(\text{THF})(\mu\text{-Cl})\}_2]$, **2-41.** To a solution of CrCl_2 (0.096 g, 0.779 mmol) in THF (30 mL) was added a solution of $[\text{Ar}^*(\text{SiMe}_3)\text{NK}(\eta^6\text{-toluene})]$ (0.500 g, 0.779 mmol) in THF (10 mL) at -80 °C over 5 min. The reaction mixture was warmed to room temperature and stirred for a further 2 h, whereupon volatiles were removed *in vacuo*. The residue was extracted with warm toluene (40 mL), the extract filtered and volatiles removed from the filtrate *in vacuo* to give **2-41** as a turquoise solid (0.38 g, 73 %). N.B. X-ray quality crystals of **2-41** were obtained by recrystallizing this solid from warm THF. Mp: 305–308 °C (248–250° C decomp.); ^1H NMR (499 MHz, C_6D_6 , 298 K): $\delta = -11.71$, $-4.42(\text{br.})$, 6.72, 10.15(br.), 10.94(br.), 16.61(br.), 36.09(br.); IR ν/cm^{-1} (Nujol): 1597(m), 1491(s), 1346(m), 1254(s), 1207(m), 1067(s), 1030(m), 1015(m), 917(s), 857(s), 829(s), 748(m), 716(m), 702(s), 603(m), 559(m); MS/EI m/z (%): 511.3 ($\text{Ar}^*\text{N}(\text{H})\text{SiMe}_3^+$, 87), 439.2 (Ar^*NH_2^+ , 79), 167.0 (Ph_2CH^+ , 33), 73.0 (Me_3Si^+ , 20); μ_{eff} (Evans, C_6D_6 , 298 K): 5.81 μ_{B} ; anal. calc. for $\text{C}_{80}\text{H}_{88}\text{Cl}_2\text{Cr}_2\text{N}_2\text{O}_2\text{Si}_2$: C 71.67 %, H 6.62 %, N 2.09 %, found: C 71.82 %, H 6.51 %, N 2.13 %.

Preparation of $[\{\text{Ar}^*(\text{SiPh}_3)\text{NCr}(\mu\text{-Cl})\}_2]$, **2-42.** To a solution of CrCl_2 (0.092 g, 0.747 mmol) in THF (30 mL) was added a solution of $[\text{Ar}^*(\text{SiPh}_3)\text{NK}]$ (0.500 g, 0.679 mmol) in THF (10 mL) at -80 °C over 5 min. The reaction mixture was warmed to room temperature and stirred for a further 2 h, whereupon volatiles were removed *in vacuo*. The residue was extracted with toluene (40 mL), the extract filtered and volatiles removed from the filtrate *in vacuo* to give **2-42** as a green solid (0.41 g, 81 %). N.B. X-ray quality crystals of **2-42** were obtained by recrystallizing this solid from toluene. Mp: 156–159 °C; ^1H NMR (499 MHz, d_8 -toluene, 298 K): $\delta = -12.88$, 0.89, 1.23, 1.83, 3.02(br.), 6.00, 6.75, 7.51, 10.05

(br.), 14.97(br.); IR ν/cm^{-1} (Nujol): 1597(m), 1491(s), 1283(m), 1263(s), 1138(m), 1103(s), 1087(m), 1076(m), 1029(m), 944(m), 790(m), 720(s), 700(s), 604(m), 560(m), 539(m), 507(m); MS/EI m/z (%): 697.4 ($\text{Ar}^*\text{N}(\text{H})\text{SiPh}_3^+$, 81), 439.2 (Ar^*NH_2^+ , 83), 259.1 (Ph_3Si^+ , 100) 167.0 (Ph_2CH^+ , 17); anal. calc. for $\text{C}_{102}\text{H}_{84}\text{Cl}_2\text{Cr}_2\text{N}_2\text{Si}_2$: C 78.09 %, H 5.40 %, N 1.79 %, found: C 77.99 %, H 5.49 %, N 1.83 %.

Preparation of $[\{\text{Ar}^*(\text{SiMe}_3)\text{NMn}(\text{THF})(\mu\text{-Br})\}_2]$, 2-43. To a suspension of MnBr_2 (0.184 g, 0.857 mmol) in THF (30 mL) was added a solution of $[\text{Ar}^*(\text{SiMe}_3)\text{NK}(\eta^6\text{-toluene})]$ (0.500 g, 0.779 mmol) in THF (10 mL) at -80°C over 5 min. The reaction mixture was warmed to room temperature and stirred for a further 2 h, whereupon volatiles were removed *in vacuo*. The residue was extracted with warm toluene (40 mL), the extract filtered and slowly cooled to 5°C overnight to give **2-43** as pink crystals (0.42 g, 75 %). Mp: $222\text{--}224^\circ\text{C}$; ^1H NMR (499 MHz, C_6D_6 , 298 K): δ = 0.92(br.), 1.36(br.), 7.54(br.), 34.45(br.), 41.06(br.); IR ν/cm^{-1} (Nujol): 1598(m), 1493(m), 1260(s), 1241(s), 1208(m), 1130(m), 1076(m), 1030(m), 1013(m), 916(s), 906(s), 856(s), 832(s), 727(s), 700(s), 674(m), 622(m), 606(m), 554(m), 531(m); MS/EI m/z (%): 511.2 ($\text{Ar}^*\text{N}(\text{H})\text{SiMe}_3^+$, 100), 438.2 (Ar^*NH^+ , 23), 167.0 (Ph_2CH^+ , 25); μ_{eff} (Evan's, C_6D_6 , 298 K): $5.90 \mu_{\text{B}}$; anal. calc. for $\text{C}_{80}\text{H}_{88}\text{Br}_2\text{Mn}_2\text{N}_2\text{O}_2\text{Si}_2$: C 66.94 %, H 6.18 %, N 1.95 %, found: C 66.84 %, H 6.26 %, N 1.98 %.

Preparation of $[\{\text{Ar}^*(\text{SiPh}_3)\text{NMn}(\text{THF})(\mu\text{-Br})\}_2]$, 2-44. To a suspension of MnBr_2 (0.143 g, 0.747 mmol) in THF (30 mL) was added a solution of $[\text{Ar}^*(\text{SiPh}_3)\text{NK}]$ (0.500 g, 0.679 mmol) in THF (10 mL) at -80°C over 5 min. The reaction mixture was warmed to room temperature and stirred for a further 2 h, whereupon volatiles were removed *in vacuo*. The residue was extracted with toluene (40 mL), the extract filtered and volatiles removed from the filtrate *in vacuo* to give **2-44** as a pale pink solid (0.38 g, 62 %). N.B. X-ray quality crystals were obtained from crystallizing this solid from a mixture of toluene and hexane. Mp: $296\text{--}299^\circ\text{C}$ (decomp. on melting); ^1H NMR (499 MHz, C_6D_6 , 298 K): δ = -34.71 (br) 0.87, 0.93, 1.37, 33.04(br), 40.81(br); IR ν/cm^{-1} (Nujol): 1597(m), 1492(s), 1425(s), 1260(m), 1229(m), 1207(m), 1128(m), 1101(s), 1029(m), 903(s), 798(m), 736(m), 729(s), 702(s), 605(m), 577(m), 556(m), 540(m), 504(m); MS/EI m/z (%): 697.3 ($\text{Ar}^*\text{N}(\text{H})\text{SiPh}_3^+$, 54), 439.2 (Ar^*NH_2^+ , 18), 259.0 (Ph_3Si^+ , 100), 167.0 (Ph_2CH^+ , 11); μ_{eff} (Evans, C_6D_6 , 298 K): $6.85 \mu_{\text{B}}$.

Preparation of $[\{\text{Ar}^+(\text{Si}^i\text{Pr}_3)\text{NMn}(\text{THF})(\mu\text{-Br})\}_2]$, 2-45. To a suspension of MnBr_2 (0.160 g, 0.747 mmol) in THF (30 mL) was added a solution of $[\text{Ar}^+(\text{Si}^i\text{Pr}_3)\text{NK}(\text{OEt}_2)]$ (0.500 g, 0.679 mmol) in THF (10 mL) at -80°C over 5 min. The reaction mixture was warmed to room temperature and stirred for a further 12 h, whereupon volatiles were removed *in vacuo*. The residue was extracted with warm benzene (40 mL), the extract filtered and slowly cooled to 6°C overnight to give **2-45** as pink crystals (0.365 g, 65 %). Mp: $191\text{--}194^\circ\text{C}$; ^1H NMR (499 MHz, C_6D_6 , 298 K): δ = 2.47 (br.), 15.51 (br.); IR ν/cm^{-1} (Nujol): 1595(m), 1491(s), 1227(s), 1205(m), 1166(m), 1120(m), 1070(m), 1032(m), 1013(m), 891(s), 863(m), 850(m), 798(m), 764(m), 726(s), 702(s), 679(s), 658(m), 604(m), 594(m); MS/EI m/z (%): 715.2 ($\text{Ar}^+(\text{Si}^i\text{Pr}_2)\text{NMnBr}^+$, 1), 623.4 ($\text{Ar}^+\text{N}(\text{H})\text{Si}^i\text{Pr}_3^+$, 46), 580.4 ($\text{Ar}^+\text{N}(\text{H})\text{Si}^i\text{Pr}_2^+$, 100), 467.3 (Ar^+NH_2^+ , 80), 167.0 (Ph_2CH^+ , 48); μ_{eff} (Evan's, C_6D_6 ,

298 K): 6.9 μ_B ; anal. calc. for $C_{96}H_{120}Br_2Mn_2N_2O_2Si_2$: C 69.47 %, H 7.29 %, N 1.69 %, found: C 69.53 %, H 7.33 %, N 1.73 %.

Preparation of $[Ar^*(SiMe_3)NFe(THF)(\mu-Br)]_2$, 2-46. To a suspension of $FeBr_2$ (0.185 g, 0.857 mmol) in THF (30 mL) was added a solution of $[Ar^*(SiMe_3)NK(\eta^6\text{-toluene})]$ (0.500 g, 0.779 mmol) in THF (10 mL) at $-80^\circ C$ over 5 min. The reaction mixture was warmed to room temperature and stirred for a further 2 h, whereupon volatiles were removed from the filtrate *in vacuo*. The residue was extracted with toluene (40 mL), the extract filtered and volatiles removed from the filtrate *in vacuo* to give **2-46** as a yellow solid (0.32 g, 57 %). N.B. X-ray quality crystals of **2-46** were obtained by crystallizing this solid from a mixture of THF and hexane. Mp: $210\text{--}212^\circ C$ ($88\text{--}92^\circ C$ decomp.); 1H NMR (400 MHz, C_6D_6 , 298 K): $\delta = -21.01(\text{br.}), -4.07, 3.99, 13.36, 15.19, 21.35, 28.35(\text{br.}), 71.19(\text{br.})$; IR ν/cm^{-1} (Nujol): 1598(m), 1493(s), 1260(s), 1242(s), 1208(m), 1129(m), 1077(m), 1030(m), 1015(m), 917(m), 902(s), 860(s), 836(s), 766(m), 749(m), 730(s), 703(s), 605(m), 555(m), 535(m); MS/CI m/z (%): 647.0 ($\{M/2 - THF\}^+$, 100), 435.1 ($Ar^*NH_2^+$, 17); μ_{eff} (Evans, C_6D_6 , 298 K): 5.38 μ_B ; anal. calc. for $C_{80}H_{88}Br_2Fe_2N_2O_2Si_2$: C 66.85 %, H 6.17 %, N 1.95 %, found: C 66.92 %, H 6.25 %, N 2.06 %.

Preparation of $[Ar^*(SiPh_3)NFe(THF)(\mu-Br)]_2$, 2-47. To a suspension of $FeBr_2$ (0.161 g, 0.747 mmol) in THF (30 mL) was added a solution of $[Ar^*(SiPh_3)NK]$ (0.500 g, 0.679 mmol) in THF (10 mL) at $-80^\circ C$ over 5 min. The reaction mixture was warmed to room temperature and stirred for a further 2 h, whereupon volatiles were removed *in vacuo*. The residue was extracted with toluene (40 mL), the extract filtered and volatiles removed from the filtrate *in vacuo* to give **2-47** as a yellow solid (0.43 g, 70 %). N.B. X-ray quality crystals of **2-47** were obtained from crystallizing this solid from a mixture of toluene and hexane. Mp: $276\text{--}279^\circ C$; 1H NMR (400 MHz, C_6D_6 , 298 K): $\delta = -41.70(\text{br.}), 3.50(\text{br.}), 5.57(\text{br.}), 12.64(\text{br.}), 64.17(\text{br.}), 73.59(\text{br.})$; IR ν/cm^{-1} (Nujol): 1596(m), 1492(m), 1237(m), 1209(m), 1130(m), 1105(s), 1030(m), 918(m), 903(s), 884(m), 852(m), 791(m), 743(m), 725(s), 696(s), 604(m), 579(m), 558(m), 548(m), 506(m); MS/EI m/z (%): 833.3 ($Ar^*(SiPh_3)NFeBr^+$, <1), 697.3 ($Ar^*N(H)SiPh_3^+$, 82), 439.2 ($Ar^*NH_2^+$, 20), 259.0 (Ph_3Si^+ , 100), 167.0 (Ph_2CH^+ , 10); μ_{eff} (Evans, C_6D_6 , 298 K): 6.61 μ_B ; anal. calc. for $C_{110}H_{100}Br_2Fe_2N_2O_2Si_2$: C 73.01 %, H 5.57 %, N 1.55 %, found: C 72.96 %, H 5.41 %, N 1.57 %.

Preparation of $[Ar^*(SiPh_3)NCo(THF)(\mu-Cl)]_2$, 2-48. Compound **2-49** (0.100 g, 0.063 mmol) was dissolved in THF (5 mL) and stirred for 5 min at room temperature to give a blue/green solution. Volatiles were removed *in vacuo* to yield **2-48** as a green solid (0.107 g, 99 %). N.B. X-ray quality crystals of **2-48** were obtained by recrystallizing this solid from a mixture of toluene and hexane. Mp: $239\text{--}243^\circ C$ ($118\text{--}121^\circ C$ turns orange/brown); 1H NMR (499 MHz, $C_6D_6/d_8\text{-THF}$, 298 K): $\delta = -22.13, -14.11, -0.99, 5.10, 10.22, 11.88, 18.07, 49.56, 54.56$; IR ν/cm^{-1} (Nujol): 1597(m), 1492(m), 1260(s), 1100(s), 1076(s), 1018(s), 896(m), 880(m), 799(s), 738(m), 697(s), 604(m), 542(m), 504(m); μ_{eff} (Evans, $C_6D_6/d_8\text{-THF}$, 298 K): 5.20 μ_B .

Preparation of $[\text{Ar}^*(\text{SiPh}_3)\text{NCo}(\mu\text{-Cl})_2]$, 2-49. To a suspension of CoCl_2 (0.088 g, 0.679 mmol) in THF (30 mL) was added a solution of $[\text{Ar}^*(\text{SiPh}_3)\text{NK}]$ (0.500 g, 0.679 mmol) in THF (10 mL) at -80°C over 5 min. The reaction mixture was warmed to room temperature and stirred for a further 2 h, whereupon volatiles were removed *in vacuo*. The residue was extracted with toluene (40 mL), the extract filtered and volatiles removed *in vacuo* and washed with hexane (20 mL) to give **2-49** as an orange solid (0.23 g, 43 %). N.B. X-ray quality crystals of **2-49** were obtained from crystallizing this solid from a mixture of toluene and hexane. Mp: $241\text{--}244^\circ\text{C}$; ^1H NMR (499 MHz, $\text{C}_6\text{D}_6/\text{d}_8\text{-THF}$, 298 K): $\delta = -52.82$, -49.44 , -40.48 , 1.37 , 7.01 , 7.58 , 12.11 , 14.29 , 16.29 , 25.62 , 59.17 , 75.70 , $123.04(\text{br})$; IR ν/cm^{-1} (Nujol): $1598(\text{m})$, $1425(\text{s})$, $1257(\text{m})$, $1216(\text{m})$, $1130(\text{m})$, $1100(\text{s})$, $1029(\text{m})$, $895(\text{s})$, $797(\text{m})$, $722(\text{s})$, $708(\text{s})$, $697(\text{s})$, $624(\text{m})$, $574(\text{m})$, $557(\text{m})$, $540(\text{m})$, $502(\text{m})$; MS/EI m/z (%): 790.3 ($\text{Ar}^*(\text{SiPh}_3)\text{NCoCl}^+$, 1), 755.3 ($\text{Ar}^*(\text{SiPh}_3)\text{NCo}^+$, 5), 697.4 ($\text{Ar}^*\text{N}(\text{H})\text{SiPh}_3^+$, 76), 438.2 (Ar^*NH^+ , 10), 259.1 (Ph_3Si^+ , 100), 167.0 (Ph_2CH^+ , 13); μ_{eff} (Evans, C_6D_6 , 298 K): $4.86 \mu_{\text{B}}$; anal. calc. for $\text{C}_{102}\text{H}_{84}\text{Cl}_2\text{Co}_2\text{N}_2\text{Si}_2$: C 77.40 %, H 5.35 %, N 1.77 %, found: C 77.31 %, H 5.37 %, N 1.80 %.

Preparation of $[\text{Ar}^*(\text{SiMe}_3)\text{NZnBr}(\text{THF})]$, 2-51. To a suspension of ZnBr_2 (0.192 g, 0.857 mmol) in THF (30 mL) was added a solution of $[\text{Ar}^*(\text{SiMe}_3)\text{NK}(\eta^6\text{-toluene})]$ (0.500 g, 0.779 mmol) in THF (10 mL) at -80°C over 5 min. The reaction mixture was warmed to room temperature and stirred for a further 2 h, whereupon volatiles were removed *in vacuo*. The residue was extracted with toluene (40 mL), the extract filtered and volatiles removed from the filtrate *in vacuo* to give **2-51** as an off white solid (0.43 g, 76 %). N.B. X-ray quality crystals of **2-51** were obtained by recrystallizing this solid from a mixture of THF and hexane. Mp: $176\text{--}180^\circ\text{C}$; ^1H NMR (400 MHz, C_6D_6 , 298 K): $\delta = 0.52$ (s, 9H, $\text{Si}(\text{CH}_3)_3$), 0.83 (m, 4H, CH_2), 1.98 (s, 3H, ArCH_3), 2.66 (m, 4H, CH_2O), 6.54 (s, 2H, Ph_2CH), 6.91 (t, $J = 7.6$ Hz, 2H, ArH), $7.02\text{--}7.18$ (m, 12H, ArH), 7.35 (d, $J = 8.0$ Hz, 4H, ArH), 7.50 (d, $J = 6.8$ Hz, 4H, ArH); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, C_6D_6): $\delta = 4.0$ ($\text{Si}(\text{CH}_3)_3$), 21.3 (ArCH_3), 24.6 (CH_2), 52.0 (Ph_2CH), 70.1 (CH_2O), 126.4 , 126.8 , 128.5 , 129.4 , 129.7 , 129.8 , 130.2 , 130.4 , 141.7 , 144.7 , 145.4 , 150.2 (Ar-C); $^{29}\text{Si}\{^1\text{H}\}$ NMR (80 MHz, C_6D_6): $\delta = 1.0$ (s); IR ν/cm^{-1} (Nujol): $1597(\text{m})$, $1492(\text{s})$, $1262(\text{s})$, $1244(\text{s})$, $1207(\text{m})$, $1125(\text{m})$, $1075(\text{m})$, $1032(\text{m})$, $1014(\text{m})$, $931(\text{s})$, $860(\text{s})$, $849(\text{s})$, $829(\text{s})$, $767(\text{m})$, $733(\text{s})$, $709(\text{s})$, $697(\text{s})$, $604(\text{m})$, $554(\text{m})$; MS/CI m/z (%): 656.1 ($\text{M}^+ - \text{THF}$, 2), 512.3 ($\text{Ar}^*\text{N}(\text{H})\text{SiMe}_3 + \text{H}^+$, 100), 440.2 ($\text{Ar}^*\text{NH}_2 + \text{H}^+$, 35), 167.0 (Ph_2CH^+ , 19); anal. calc. for $\text{C}_{40}\text{H}_{44}\text{BrNOSiZn}$: C 65.98 %, H 6.09 %, N 1.92 %, found: C 66.07 %, H 6.13 %, N 2.06 %.

Preparation of $[\text{Ar}^+(\text{SiMe}_3)\text{NZnBr}(\text{THF})]$, 2-52. To a suspension of ZnBr_2 (0.190 g, 0.844 mmol) in THF (30 mL) was added a solution of $[\text{Ar}^+(\text{SiMe}_3)\text{NK}(\text{OEt}_2)]$ (0.500 g, 0.767 mmol) in THF (10 mL) at -80°C over 5 min. The reaction mixture was warmed to room temperature and stirred for a further 2 h, whereupon volatiles were removed *in vacuo*. The residue was extracted with toluene (40 mL), the extract filtered and concentrated *in vacuo* (to ca. 10 mL). Hexane (50 mL) was added, and stirred for a further 10 min producing a white precipitate, which was filtered and dried to give **2-52** as a white powder (0.370 g, 64 %). X-ray quality crystals of **2-52** were obtained by recrystallizing this solid from hot toluene. Mp:

176–178 °C; ^1H NMR (499 MHz, C_6D_6 , 298 K): δ = 0.50 (s, 9H, $\text{Si}(\text{CH}_3)_3$), 0.80 (br., 4H, CH_2), 0.98 (d, $^3J_{\text{HH}}$ = 6.9 Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 2.51 (br., 4H, CH_2O), 2.54 (sept., $^3J_{\text{HH}}$ = 6.9 Hz, 1H, $\text{CH}(\text{CH}_3)_2$), 6.55 (s, 2H, Ph_2CH), 6.92–7.54 (m, 22H, ArH); $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, C_6D_6): δ = 4.0 ($\text{Si}(\text{CH}_3)_3$), 24.4 ($\text{CH}(\text{CH}_3)_2$), 24.6 (CH_2), 33.8 ($\text{CH}(\text{CH}_3)_2$), 52.1 (Ph_2CH), 70.3 (CH_2O), 126.4, 126.7, 126.8, 128.4, 129.7, 129.9, 130.2, 141.5, 141.6, 145.0, 145.5, 150.6 (Ar-C); $^{29}\text{Si}\{^1\text{H}\}$ NMR (80 MHz, C_6D_6): δ = 1.2 (s); IR ν/cm^{-1} (Nujol): 1599(m), 1493(m), 1446(s), 1247 (s), 1223(m), 1031(m), 1016(m), 923(s), 849(s), 831(s), 767(m), 731(s), 699(s); MS/CI m/z (%): 683.3 ($\text{M}^+ - \text{THF}$, <1), 539.5 ($\text{Ar}^+\text{N}(\text{H})\text{SiMe}_3^+$, 69), 467.4 (Ar^+NH_2^+ , 100), 167.0 (Ph_2CH^+ , 31), 73.1 ($\text{THF} + \text{H}^+$, 11); anal. calc. for $\text{C}_{42}\text{H}_{48}\text{BrNOSiZn}$: C 66.71 %, H 6.40 %, N 1.85 %, found: C 66.61 %, H 6.48 %, N 1.91 %.

Preparation of $[\text{Ar}^*(\text{SiPh}_3)\text{NZnBr}]$, 2-53. To a suspension of ZnBr_2 (0.168 g, 0.747 mmol) in THF (30 mL) was added a solution of $[\text{Ar}^*(\text{SiPh}_3)\text{NK}]$ (0.500 g, 0.679 mmol) in THF (10 mL) at -80 °C over 5 min. The reaction mixture was warmed to room temperature and stirred for a further 2 h, whereupon volatiles were removed *in vacuo*. The residue was extracted with toluene (40 mL), the extract filtered and volatiles removed from the filtrate *in vacuo* to give **2-53** as an off white solid (0.45 g, 79 %). N.B. X-ray quality crystals of **2-53** were obtained by recrystallizing this solid from a mixture of toluene and hexane. Mp: 248–250 °C; ^1H NMR (400 MHz, C_6D_6 , 298 K): δ = 1.89 (s, 3H, ArCH_3), 6.14 (s, 2H, Ph_2CH), 6.45 (d, $^3J_{\text{HH}}$ = 7.0 Hz, 4H, ArH), 6.73 (s, 2H, ArH), 6.81 (d, J = 7.0 Hz, 2H, ArH), 6.94–7.27 (m, 23H, ArH), 7.66 (d, $^3J_{\text{HH}}$ = 8.0 Hz, 6H, ArH); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, C_6D_6): δ = 21.3 (ArCH_3), 53.0 (Ph_2CH), 126.5, 128.4, 128.5, 128.6, 129.1, 129.8, 130.2, 130.4, 130.5, 131.3, 132.5, 136.8, 142.3, 144.6, 144.7 (Ar-C); $^{29}\text{Si}\{^1\text{H}\}$ NMR (80 MHz, C_6D_6): δ = -18.9 (s); IR ν/cm^{-1} (Nujol): 1597(m), 1586 (m), 1489(m), 1237(s), 1216(s), 1136(m), 1105(s), 1076(m), 1031(m), 924(s), 909 (s), 879(m), 849(s), 763(m), 756(m), 737(s), 700(s), 602(s), 575(m), 555(s), 506(s); MS/EI m/z (%): 841.2 (M^+ , 7), 697.4 ($\text{Ar}^*\text{N}(\text{H})\text{SiPh}_3^+$, 100), 439.2 (Ar^*NH_2^+ , 81), 259.1 (Ph_3Si^+ , 71), 167.0 (Ph_2CH^+ , 16); anal. calc. for $\text{C}_{51}\text{H}_{42}\text{BrNSiZn}$: C 72.73 %, H 5.03 %, N 1.66 %, found: C 72.84 %, H 5.13 %, N 1.56 %.

Preparation of $[\text{Ar}^*(\text{Si}^i\text{Pr}_3)\text{NZnBr}]$, 2-54. To a suspension of ZnBr_2 (0.350 g, 1.55 mmol) in diethyl ether (25 mL) was added a fine suspension of $[\text{Ar}^*(\text{Si}^i\text{Pr}_3)\text{NK}(\text{OEt}_2)]$ (1.00 g, 1.41 mmol) in diethyl ether (25 mL) at -80 °C over 5 min. The reaction mixture was warmed to room temperature and stirred for a further 12 h, whereupon volatiles were removed *in vacuo*. The residue was extracted with pentane (40 mL), the extract filtered, concentrated (to ca. 10 mL) and slowly cooled to -30 °C overnight to give **2-54** as colourless crystals (0.690 g, 66 %). Mp: 107–110 °C; ^1H NMR (499 MHz, C_6D_6 , 298 K): δ = 1.25 (d, $^3J_{\text{HH}}$ = 7.5 Hz, 18H, $\text{Si}\{\text{CH}(\text{CH}_3)_2\}_3$), 1.53 (sept, $^3J_{\text{HH}}$ = 7.5 Hz, 3H, $\text{Si}\{\text{CH}(\text{CH}_3)_2\}_3$), 1.87 (s, 3H, ArCH_3), 6.43 (s, 2H, Ph_2CH), 6.81–7.22 (m, 22H, ArH); $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, C_6D_6): δ = 15.6 ($\text{Si}\{\text{CH}(\text{CH}_3)_2\}_3$), 19.1 ($\text{Si}\{\text{CH}(\text{CH}_3)_2\}_3$), 21.2 (ArCH_3), 52.8 (CHPh_2), 126.8, 128.4, 128.9, 129.4, 129.5, 130.5, 131.5, 131.8, 142.5, 144.5, 144.7 (Ar-C); $^{29}\text{Si}\{^1\text{H}\}$ NMR (80 MHz, C_6D_6): δ = 2.5 (s); IR ν/cm^{-1} (Nujol): 1598(m), 1493(m), 1439(s), 1233(s), 1212(m), 1133(m), 1075(m), 914(m), 899(s), 879(s), 842(s), 762(m), 746(s), 699(s), 657(s); MS/EI m/z (%):

595.5 ($\text{Ar}^*\text{N}(\text{H})\text{Si}^i\text{Pr}_3^+$, 36), 552.5 ($\text{Ar}^*\text{N}(\text{H})\text{Si}^i\text{Pr}_2^+$, 100), 439.3 (Ar^*NH_2^+ , 39), 167.1 (Ph_2CH^+ , 88); anal. calc. for $\text{C}_{42}\text{H}_{48}\text{BrNSiZn}$: C 68.15 %, H 6.54 %, N 1.89 %, found: C 68.08 %, H 6.63 %, N 1.87 %.

Preparation of $[\text{Ar}^+(\text{Si}^i\text{Pr}_3)\text{NZnBr}]$, 2-55. To a suspension of ZnBr_2 (0.336 g, 1.49 mmol) in diethyl ether (20 mL) was added a fine suspension of $[\text{Ar}^+(\text{Si}^i\text{Pr}_3)\text{NK}(\text{OEt}_2)]$ (1.00 g, 1.36 mmol) in diethyl ether (20 mL) at -80°C over 5 min. The reaction mixture was warmed to room temperature and stirred for a further 12 h, whereupon volatiles were removed *in vacuo*. The residue was extracted with pentane (40 mL), the extract filtered, concentrated (to *ca.* 10 mL) and slowly cooled to -30°C overnight to give **2-55** as pale orange crystals (0.81 g, 78 %). Mp: $178\text{--}181^\circ\text{C}$; ^1H NMR (499 MHz, C_6D_6 , 298 K): δ = 0.93 (d, $^3J_{\text{HH}}$ = 7.0 Hz, 6H, $\text{ArCH}(\text{CH}_3)_2$), 1.24 (d, $^3J_{\text{HH}}$ = 7.5 Hz, 18H, $\text{Si}\{\text{CH}(\text{CH}_3)_2\}_3$), 1.53 (sept, $^3J_{\text{HH}}$ = 7.5 Hz, 3H, $\text{Si}\{\text{CH}(\text{CH}_3)_2\}_3$), (sept, $^3J_{\text{HH}}$ = 7.0 Hz, 1H, $\text{ArCH}(\text{CH}_3)_2$), 6.44 (s, 2H, Ph_2CH), 6.85–7.23 (m, 22H, ArH); $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, C_6D_6): δ = 15.6 ($\text{Si}\{\text{CH}(\text{CH}_3)_2\}_3$), 19.8 ($\text{Si}\{\text{CH}(\text{CH}_3)_2\}_3$), 24.2 ($\text{ArCH}(\text{CH}_3)_2$), 33.8 ($\text{ArCH}(\text{CH}_3)_2$), 53.0 (CHPh_2), 126.6, 126.7, 126.8, 128.4, 128.6, 128.9, 129.4, 130.1, 130.3, 131.5, 142.4, 142.9, 144.6, 144.8, 145.0, 146.6 (Ar-C); $^{29}\text{Si}\{^1\text{H}\}$ NMR (80 MHz, C_6D_6): δ = 2.53 (s); IR ν/cm^{-1} (Nujol): 1599(m), 1492(m), 1437 (s), 1382(m), 1259(m), 1234(m), 1158(m), 1125(m), 1074(m), 1031(m), 897(s), 883(s), 867(s), 839(s), 750(s), 699(s), MS/EI m/z (%): 767.2 (M^+ , 2), 724.2 ($\text{M}^+ - ^i\text{Pr}$, 10), 623.5 ($\text{Ar}^+\text{N}(\text{H})\text{Si}^i\text{Pr}_3^+$, 39), 580.4 ($\text{Ar}^+\text{N}(\text{H})\text{Si}^i\text{Pr}_2^+$, 100), 467.3 (Ar^+NH_2^+ , 14), 167.0 (Ph_2CH^+ , 35); anal. calc. for $\text{C}_{44}\text{H}_{52}\text{BrNSiZn}$: C 68.79 %, H 6.82 %, N 1.82 %, found: C 68.66 %, H 6.90 %, N 1.78 %.

Preparation of $[\{\text{Ar}^+(\text{SiMe}_3)\text{NCd}(\mu\text{-I})\}_2]$, 2-56. To a solution of CdI_2 (0.62 g, 1.69 mmol) in THF (30 mL) was added a solution of $[\text{Ar}^+(\text{SiMe}_3)\text{NK}(\text{OEt}_2)]$ (1.00 g, 1.53 mmol) in THF (10 mL) at -80°C over 5 min. The reaction mixture was slowly warmed to room temperature and stirred for a further 30 min, whereupon volatiles were removed *in vacuo*. The residue was extracted with toluene (40 mL), the extract filtered and concentrated (to *ca.* 10 mL). Hexane (50 mL) was added to the stirring solution producing a white precipitate, which was filtered and dried *in vacuo* to give **2-56** as a white powder (0.79 g, 66 %). N.B. X-ray quality crystals of **2-56** were grown by crystallizing this powder from hot cyclohexane. Mp: $205\text{--}208^\circ\text{C}$ (180–190 $^\circ\text{C}$ decomp.); ^1H NMR (499 MHz, C_6D_6 , 298 K): δ = 0.37 (s, 18H, $\text{Si}(\text{CH}_3)_3$), 0.94 (d, $^3J_{\text{HH}}$ = 6.9 Hz, 12H, $\text{ArCH}(\text{CH}_3)_2$), 2.49 (sept, $^3J_{\text{HH}}$ = 6.9 Hz, 2H, $\text{ArCH}(\text{CH}_3)_2$), 6.34 (s, 4H, Ph_2CH), 6.89–7.21 (m, 44H, ArH); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, C_6D_6): δ = 4.0 ($\text{Si}(\text{CH}_3)_3$), 24.2 ($\text{ArCH}(\text{CH}_3)_2$), 33.8 ($\text{ArCH}(\text{CH}_3)_2$), 53.2 (CHPh_2), 126.6, 126.7, 127.0, 128.7, 128.8, 129.3, 130.1, 130.3, 131.2, 141.7, 141.8, 144.5, 144.9 (Ar-C); $^{29}\text{Si}\{^1\text{H}\}$ NMR (80 MHz, C_6D_6): δ = -1.3(s); $^{113}\text{Cd}\{^1\text{H}\}$ NMR (89 MHz, C_6D_6): δ = 110.2(s); IR ν/cm^{-1} (Nujol): 1597(m), 1493(m), 1437(s), 1256(s), 1238(s), 1162(m), 1126(m), 1075(m), 1031 (m), 927(s), 894(m), 831(s), 751(s), 720(m), 697(s), 676(s); MS/EI m/z (%): 539.5 ($\text{Ar}^+\text{N}(\text{H})\text{SiMe}_3^+$, 75), 467.4 (Ar^+NH_2^+ , 100), 452.4 ($\text{Ar}^+\text{NH}_2^+ - \text{CH}_3$, 74), 167.0 (Ph_2CH^+ , 37); anal. calc. for $\text{C}_{76}\text{H}_{80}\text{Cd}_2\text{I}_2\text{N}_2\text{Si}_2$: C 58.65 %, H 5.18 %, N 1.80 %, found: C 58.72 %, H 5.27 %, N 1.74 %.

Preparation of $[\text{Ar}^*(\text{SiPh}_3)\text{NCdI}]$, 2-57. To a suspension of CdI_2 (0.274 g, 0.747 mmol) in THF (30 mL) was added a solution of $[\text{Ar}^*(\text{SiPh}_3)\text{NK}]$ (0.500 g, 0.679 mmol) in THF (10 mL) at -80°C over 5 min. The reaction mixture was warmed to room atmospheric temperature and stirred for a further 2 h, whereupon volatiles were removed *in vacuo*. The residue was extracted with benzene (40 mL), the extract filtered and volatiles removed from the filtrate *in vacuo* to give **2-57** as a pale yellow solid (0.420 g, 72 %). N.B. X-ray quality crystals of **2-57** were obtained by recrystallizing this solid from diethyl ether. Mp: $255\text{--}258^\circ\text{C}$ (decomp. $203\text{--}205^\circ\text{C}$); ^1H NMR (400 MHz, C_6D_6 , 298 K): $\delta = 1.92$ (s, 3H, ArCH_3), 6.20 (s, 2H, Ph_2CH), 6.44–7.69 (m, 37H, ArH); $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, C_6D_6): $\delta = 21.4$ (ArCH_3), 52.9 (Ph_2CH), 128.4, 128.5, 128.7, 129.7, 130.2, 130.4, 130.6, 131.2, 131.9, 136.7, 142.2, 144.4, 144.7, 146.3 (Ar-C); $^{29}\text{Si}\{^1\text{H}\}$ NMR (80 MHz, C_6D_6): $\delta = -20.1$ (s); $^{113}\text{Cd}\{^1\text{H}\}$ NMR (C_6D_6 , 89 MHz): $\delta = 104.8$; IR ν/cm^{-1} (Nujol): 1597(m), 1490(m), 1447(m), 1426(s), 1257(m), 1232(m), 1103(s), 1030(m), 926(s), 910(m), 835(m), 799(m), 765(m), 745(s), 733(s), 697(s); MS/CI m/z (%): 937.4 (M^+ , 2), 697.6 ($\text{Ar}^*\text{N}(\text{H})\text{SiPh}_3^+$, 10), 438.3 (Ar^*NH^+ , 3), 259.1 (SiPh_3^+ , 100), 167.1 (Ph_2CH^+ , 17); anal. calc. for $\text{C}_{51}\text{H}_{42}\text{CdINSi}$: C 65.42 %, H 4.52 %, N 1.50 %, found: C 65.36 %, H 4.57 %, N 1.53 %.

Preparation of $[\text{Ar}^*(\text{SiMe}_3)\text{NHgI}]$, 2-58. To a suspension of HgI_2 (0.389 g, 0.857 mmol) in THF (30 mL) was added a solution of $[\text{Ar}^*(\text{SiMe}_3)\text{NK}(\eta^6\text{-toluene})]$ (0.500 g, 0.779 mmol) in THF (10 mL) at -80°C over 5 min. The reaction mixture was warmed to room temperature and stirred for a further 2 h, whereupon volatiles were removed *in vacuo*. The residue was extracted with toluene (20 mL), the extract filtered and volatiles removed from the filtrate *in vacuo* to give **2-58** as an orange solid (0.308 g, 79 %). N.B. X-ray quality crystals of **2-58** were obtained by recrystallizing this solid from hot toluene. Mp: $181\text{--}182^\circ\text{C}$; ^1H NMR (400 MHz, C_6D_6 , 298 K): $\delta = 0.32$ (s, 9H, $\text{Si}(\text{CH}_3)_3$), 1.87 (s, 3H, ArCH_3), 6.31 (s, 2H, Ph_2CH), 6.82–7.18 (m, 22H, ArH); $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, C_6D_6): $\delta = 3.4$ ($\text{Si}(\text{CH}_3)_3$), 21.2 (ArCH_3), 52.8 (Ph_2CH), 126.7, 128.7, 128.9, 129.5, 129.8, 130.0, 130.2, 130.3, 133.4, 143.0, 143.3, 143.4, 145.1 (Ar-C); $^{29}\text{Si}\{^1\text{H}\}$ NMR (80 MHz, C_6D_6): $\delta = 2.9$ (s); $^{199}\text{Hg}\{^1\text{H}\}$ NMR (C_6D_6 , 107.4 MHz): $\delta = -2001.6$ (br.); IR ν/cm^{-1} (Nujol): 1598(m), 1492(s), 1442(s), 1247(s), 1215(m), 1075(m), 1030(m), 932(s), 846(s), 829(s), 754(s), 697(s); MS/EI m/z (%): 511.4 ($\text{Ar}^*\text{N}(\text{H})\text{SiMe}_3^+$, 100), 438.3 (Ar^*NH^+ , 47), 167.0 (Ph_2CH^+ , 53), 73.1 (Me_3Si^+ , 42); anal. calc. for $\text{C}_{36}\text{H}_{36}\text{HgINSi}$: C 51.58 %, H 4.33 %, N 1.67 %, found: C 51.62 %, H 4.32 %, N 1.76 %.

Preparation of $[\text{Ar}^+(\text{SiMe}_3)\text{NHgI}]$, 2-59. To a solution of HgI_2 (0.77 g, 1.69 mmol) in THF (30 mL) was added a solution of $[\text{Ar}^+(\text{SiMe}_3)\text{NK}(\text{OEt}_2)]$ (1.00 g, 1.53 mmol) in THF (10 mL) at -80°C over 5 min. The reaction mixture was slowly warmed to room temperature and stirred for a further 2 h, whereupon volatiles were removed *in vacuo*. The residue was extracted with toluene (40 mL), the extract filtered and concentrated (to ca. 10 mL). Hexane (50 mL) was added to the stirring solution producing a white precipitate, which was filtered and dried *in vacuo* to give **2-59** as a white powder (0.71 g, 53 %). N.B. X-ray quality crystals of **2-59** were obtained by recrystallizing this powder from a concentrated solution of

hot benzene. Mp: 202–204 °C; ^1H NMR (300 MHz, C_6D_6 , 298 K): δ = 0.31 (s, 9H, $\text{Si}(\text{CH}_3)_3$), 0.90 (d, $^3J_{\text{HH}}$ = 6.9 Hz, 6H, $\text{ArCH}(\text{CH}_3)_2$), 2.45 (sept, $^3J_{\text{HH}}$ = 6.9 Hz, 1H, $\text{ArCH}(\text{CH}_3)_2$), 6.33 (s, 2H, Ph_2CH), 6.90–7.22 (m, 22H, ArH); $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, C_6D_6): δ = 3.5 ($\text{Si}(\text{CH}_3)_3$), 24.2 ($\text{ArCH}(\text{CH}_3)_2$), 33.8 ($\text{ArCH}(\text{CH}_3)_2$), 53.0 (Ph_2CH), 126.6, 126.7, 128.9, 127.1, 127.3, 128.6, 128.7, 128.8, 128.9, 129.4, 130.0, 130.2, 130.3, 140.8, 141.7, 143.1, 143.2, 143.4, 143.7, 144.3, 144.9, 145.2 (Ar-C); $^{29}\text{Si}\{^1\text{H}\}$ NMR (80 MHz, C_6D_6): δ = 3.2 (s); $^{199}\text{Hg}\{^1\text{H}\}$ NMR (72 MHz, C_6D_6): δ = –2002.9; IR ν/cm^{-1} (Nujol): 1599(m), 1492(s), 1438(s), 1246(s), 1161(m), 1126(m), 1075(m), 1030(m), 927(s), 857(m), 830(s), 756(s), 734(m), 697(s); MS/EI m/z (%): 852.5 ($\text{M}^+ - \text{Me}$, <1), 539.5 ($\text{Ar}^+\text{N}(\text{H})\text{SiMe}_3^+$, 100), 167.2 (Ph_2CH^+ , 48), 73.2 (SiMe_3^+ , 72); anal. calc. for $\text{C}_{38}\text{H}_{40}\text{HgINSi}$: C 52.68 %, H 4.65 %, N 1.62 %, found: C 52.71 %, H 4.71 %, N 1.64 %.

Preparation of $[\text{Ar}^*(\text{SiPh}_3)\text{NHgI}]$, 2-60. To a suspension of HgI_2 (0.340 g, 0.747 mmol) in toluene (30 mL) was added a solution of $[\text{Ar}^*(\text{SiPh}_3)\text{NK}]$ (0.500 g, 0.679 mmol) in toluene (10 mL) at –80 °C over 5 min. The reaction mixture was warmed to room temperature and stirred for a further 4 h, whereupon volatiles were removed *in vacuo*. The residue was extracted with benzene (40 mL), the extract filtered and volatiles removed from the filtrate *in vacuo* to give **2-60** as an orange solid (0.440 g, 63 %). N.B. X-ray quality crystals of **2-60** were obtained by recrystallizing this solid from hexane and benzene layer. Mp: 210–213 °C; ^1H NMR (400 MHz, C_6D_6 , 298 K): δ = 1.89 (s, 3H, ArCH_3), 6.40 (s, 2H, Ph_2CH), 6.44–7.71 (m, 37H, ArH); $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, C_6D_6): δ = 21.3 (ArCH_3), 52.3 (Ph_2CH), 126.4, 128.6, 128.9, 129.3, 130.2, 130.4, 130.5, 136.8, 143.6, 143.8, 144.3, 145.1 (Ar-C); $^{29}\text{Si}\{^1\text{H}\}$ NMR (80 MHz, C_6D_6): δ = –16.6 (s); $^{199}\text{Hg}\{^1\text{H}\}$ NMR (C_6D_6 , 107.4 MHz): δ = –2092.7 (br.); IR ν/cm^{-1} (Nujol): 1597(m), 1491 (s), 1438(s) 1426(s), 1259(m), 1238(m), 1212(m), 1107(s) 1030(m), 928(s), 912(s) 881(m), 837(m) 737(s), 697(s) 676(s); MS/EI m/z (%): 697.5 ($\text{Ar}^+\text{N}(\text{H})\text{SiPh}_3^+$, 20), 439.2 (Ar^+NH_2^+ , 10), 259.1 (SiPh_3^+ , 100), 167.0 (Ph_2CH^+ , 45); anal. calc. for $\text{C}_{51}\text{H}_{42}\text{HgINSi}$: C 59.79 %, H 4.13 %, N 1.37 %, found: C 59.89 %, H 4.17 %, N 1.33 %.

Preparation of $[\text{Ar}^*(\text{Si}^i\text{Pr}_3)\text{NHgI}]$, 2-61. To a suspension of HgI_2 (0.706 g, 1.55 mmol) in toluene (30 mL) was added a solution of $[\text{Ar}^*(\text{Si}^i\text{Pr}_3)\text{NK}(\text{OEt}_2)]$ (1.00 g, 1.41 mmol) in toluene (10 mL) at –80 °C over 5 min. The reaction mixture was warmed to room temperature and stirred for a further 2 h, whereupon volatiles were removed *in vacuo*. The residue was extracted with hexane (40 mL), the extract filtered and volatiles removed from the filtrate *in vacuo* to give **2-61** as a pale orange solid (0.75 g, 58 %). N.B. X-ray quality crystals of **2-61** were obtained by recrystallizing this solid from pentane. Mp: 235–238 °C; ^1H NMR (400 MHz, C_6D_6 , 298 K): δ = 1.24 (d, $^3J_{\text{HH}}$ = 7.5 Hz, 18H, $\text{CH}(\text{CH}_3)_2$), 1.54 (sept, $^3J_{\text{HH}}$ = 7.5 Hz, 3H, $\text{CH}(\text{CH}_3)_2$), 1.88 (s, 3H, ArCH_3), 6.58 (s, 2H, Ph_2CH), 6.88–7.28 (m, 22H, ArH); $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, C_6D_6): δ = 15.2 ($\text{CH}(\text{CH}_3)_2$), 19.6 ($\text{CH}(\text{CH}_3)_2$), 21.2 (ArCH_3), 51.9 (Ph_2CH), 126.7, 128.6, 128.9, 129.1, 129.5, 130.2, 130.4, 143.6, 143.7, 145.3 146.2 (Ar-C); $^{29}\text{Si}\{^1\text{H}\}$ NMR (80 MHz, C_6D_6): δ = 5.6 (s); $^{199}\text{Hg}\{^1\text{H}\}$ NMR (C_6D_6 , 107.4 MHz): δ = –1943.8; IR ν/cm^{-1} (Nujol): 1597(m), 1490(m), 1435(s), 1231(m), 1126(m), 1074(m), 1029(m), 883(s),

830(m), 809(m), 733(s), 698(s); MS/EI m/z (%): 880.5 ($M^+ - ^i\text{Pr}$, 2) 595.5 ($\text{Ar}^*\text{NSi}^i\text{Pr}_3^+$, 42), 552.5 ($\text{Ar}^*\text{N(H)Si}^i\text{Pr}_2^+$, 79), 167.0 (Ph_2CH^+ , 100); anal. calc. for $\text{C}_{42}\text{H}_{48}\text{HgINSi}$: C 54.69 %, H 5.25 %, N 1.52 %, found: C 54.80 %, H 5.30 %, N 1.58 %.

Preparation of $[\text{Ar}^+(\text{Si}^i\text{Pr}_3)\text{NHgI}]$, **2-62.** To a suspension of HgI_2 (0.679 g, 1.49 mmol) in toluene (30 mL) was added a solution of $[\text{Ar}^+(\text{Si}^i\text{Pr}_3)\text{NK}(\text{OEt}_2)]$ (1.00 g, 1.36 mmol) in toluene (10 mL) at -80°C over 5 min. The reaction mixture was warmed to room temperature and stirred for a further 2 h, whereupon volatiles were removed *in vacuo*. The residue was extracted with hexane (40 mL), the extract filtered and volatiles removed from the filtrate *in vacuo* to give **2-62** as a pale orange solid (1.29 g, 90 %). N.B. X-ray quality crystals of **2-62** were obtained by recrystallizing this solid from hot hexane. Mp: $188\text{--}192^\circ\text{C}$; ^1H NMR (400 MHz, C_6D_6 , 298 K): δ = 0.92 (d, $^3J_{\text{HH}}$ = 6.9 Hz, 6H, $\text{ArCH}(\text{CH}_3)_2$), 1.22 (d, $^3J_{\text{HH}}$ = 7.5 Hz, 18H, $\text{Si}\{\text{CH}(\text{CH}_3)_2\}_3$), 1.54 (sept, $^3J_{\text{HH}}$ = 7.5 Hz, 3H, $\text{Si}\{\text{CH}(\text{CH}_3)_2\}_3$), 2.49 (sept, $^3J_{\text{HH}}$ = 6.9 Hz, 1H, $\text{ArCH}(\text{CH}_3)_2$), 6.59 (s, 2H, Ph_2CH), 6.93–7.29 (m, 22H, ArH); $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, C_6D_6): δ = 15.2 ($\text{Si}\{\text{CH}(\text{CH}_3)_2\}_3$), 19.6 ($\text{Si}\{\text{CH}(\text{CH}_3)_2\}_3$), 24.2 ($\text{ArCH}(\text{CH}_3)_2$), 33.8 ($\text{ArCH}(\text{CH}_3)_2$), 52.0 (Ph_2CH), 126.7, 127.0, 128.6, 128.8, 129.1, 129.5, 130.1, 130.3, 143.6, 143.7, 145.4 (Ar-C); $^{29}\text{Si}\{^1\text{H}\}$ NMR (80 MHz, C_6D_6): δ = 5.6 (s); $^{199}\text{Hg}\{^1\text{H}\}$ NMR (C_6D_6 , 107.4 MHz): δ = -2017.1 ; IR ν/cm^{-1} (Nujol): 1598(m), 1491(s), 1448(s), 1426(s), 1379(m), 1233(s), 1098(m), 1075(m), 1031(m), 910(s), 835(m), 757(m), 736(s), 697(s); MS/EI m/z (%): 951.4 (M^+ , < 1) 908.5 ($M^+ - ^i\text{Pr}$, 3) 622.5 ($\text{Ar}^*\text{NSi}^i\text{Pr}_3^+$, 86), 580.5 ($\text{Ar}^*\text{N(H)Si}^i\text{Pr}_2^+$, 24), 167.0 (Ph_2CH^+ , 100); anal. calc. for $\text{C}_{44}\text{H}_{52}\text{HgINSi}$: C 55.60 %, H 5.51 %, N 1.47 %, found: C 55.80 %, H 5.40 %, N 1.52 %.

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