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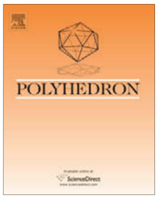

Molecular structures of three coordinate zinc and cadmium complexes that feature β-diketiminato and anilido-imine ligands

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A series of zinc and cadmium complexes of the β-diketiminato and anilido-imine classes of ligands, namely [BDI^{Ar}], [AI^{Ar}] and [AI$^{Ar,NPr^i_2}$], have been synthesized and structurally characterized by X-ray diffraction. For example, the zinc and cadmium alkyl compounds [AI^{Ar}]ZnEt and [AI^{Ar}]CdMe have been synthesized via the reactions of [AI^{Ar}]H with Et_2Zn and Me_2Cd, respectively, while [AI^{Ar}]ZnN$(SiMe_3)_2$ has been obtained by treatment of [AI^{Ar}]H with Zn$[N(SiMe_3)_2]_2$. Single crystal X-ray diffraction studies establish that the metal centers in each of these complexes are trigonal planar. Comparison of the molecular structures of [AI^{Ar}]CdMe and [BDI^{Ar}]CdMe demonstrates that the cadmium methyl moiety lies in the plane of the annulated [AI^{Ar}] ligand, whereas there is considerable displacement for [BDI^{Ar}]CdMe. [AI$^{Ar,NPr^i_2}$]Li, an anilido-imine ligand that incorporates a $CH_2CH_2NPr^i_2$ tether, has been synthesized via a sequence involving condensation of 2-fluorobenzaldehyde with $H_2NCH_2CH_2NPr^i_2$, followed by treatment with ArNHLi. X-ray diffraction demonstrates that the lithium has a T-shaped coordination environment which is supplemented by an agostic interaction with a C–H bond of one of the isopropyl groups of the NPr^i_2 moiety. However, while the NPr^i_2 group of the tether coordinates to lithium in [AI$^{Ar,NPr^i_2}$]Li, it does not coordinate to the zinc center of [AI$^{Ar,NPr^i_2}$]ZnMe. The structure of [AI$^{Ar,NPr^i_2}$]ZnMe is also in marked contrast to that reported for [AI^{Ar,NMe_2}]ZnMe, in which the NMe_2 group does coordinate to the zinc center. The M–C bonds of [AI$^{Ar,NPr^i_2}$]ZnMe, [BDI^{Ar}]ZnEt and [BDI^{Ar}]CdMe are cleaved by $B(C_6F_5)_3$ to give the perfluorophenyl derivatives [AI$^{Ar,NPr^i_2}$]ZnC_6F_5, [BDI^{Ar}]ZnC_6F_5 and [BDI^{Ar}]CdC_6F_5. Interestingly, the C_6F_5 groups are almost orthogonal to the planes of the chelating ligands in the zinc complexes, [AI$^{Ar,NPr^i_2}$]ZnC_6F_5 and [BDI^{Ar}]ZnC_6F_5, whereas the C_6F_5 and [BDI^{Ar}] ligands of [BDI^{Ar}]CdC_6F_5 reside in the same plane. In addition to 1:1 [AI$^{Ar,NPr^i_2}$]ZnX complexes, it is also possible to synthesize the 2:1 complex [AI$^{Ar,NPr^i_2}$]$_2$Zn which is consistent with the [AI$^{Ar,NPr^i_2}$] ligand being less sterically demanding than the [BDI^{Ar}] ligand.

1. Introduction

Although initially developed in the 1960s [1–6], there has recently been a resurgence in activity concerned with the β-diiminate class of ligands [R′C{C(R″)NR}$_2$], as shown in the protonated form in Fig. 1 [7–12]. In large part, this revival is due to the advent of derivatives in which the nitrogen atoms feature bulky substituents and, in particular, 2,6-diisopropylphenyl groups, i.e. the [HC{C(Me)NAr}$_2$] ligand ([BDI^{Ar}]) [13–15].[1] For example, with respect to zinc chemistry, the [BDI^{Ar}] ligand has enabled the isolation of the zinc–zinc bonded complex, [BDI^{Ar}]Zn–Zn[BDI^{Ar}] [16,17], the monomeric zinc hydride complex [BDI^{Ar}]ZnH [18], and a variety of other three- and four-coordinate zinc compounds (e.g. [BDI^{Ar}]ZnX, X = Et, OAc, OMe, OPr^i, N$(SiMe_3)_2$, Cl, and Br) [15,19,20], some of which have found applications as catalysts for (i) the copolymerization of cyclohexene oxide and CO_2, and (ii) the polymerization of lactides [15,20–25]. In view of the many successful applications of the [BDI^{Ar}] ligand, it is, therefore, not surprising that a variety of modifications of this ligand system have been introduced. For example, Piers reported the anilido-imine ligand [AI^{Ar}] (Ar = 2,6-$Pr^i_2C_6H_3$) [26–29],[2] while others have described variants that feature additional donor groups [30–32], as illustrated in Fig. 2. Here, we describe structural aspects of zinc and cadmium complexes derived from β-diketiminato and anilido-imine classes of ligands, namely [BDI^{Ar}]ZnC_6F_5, [BDI^{Ar}]CdC_6F_5, [BDI^{Ar}]CdMe, [AI^{Ar}]ZnEt, [AI^{Ar}]CdMe, [AI^{Ar}]ZnN$(SiMe_3)_2$, [AI$^{Ar,NPr^i_2}$]ZnMe, [AI$^{Ar,NPr^i_2}$]ZnC_6F_5, {[AI$^{Ar,NPr^i_2}$]Zn(μ-OH)}$_2$ and [AI$^{Ar,NPr^i_2}$]$_2$Zn.

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[1] Other abbreviations have also been used for the [HC{C(Me)NAr}$_2$] ligand (Ar = 2,6-$Pr^i_2C_6H_3$), including BDI, BDI-1 and (dipp)NacNac.

[2] *o*-Phenylene-bridged bis(anilido-imine) ligands have also been reported. See Refs. [28,29].

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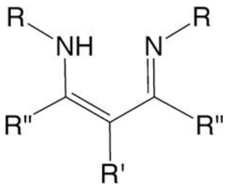


Fig. 1. $[R'C\{C(R'')NR\}_2]H$.

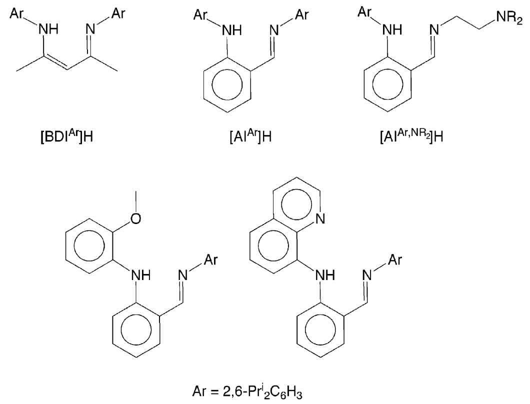
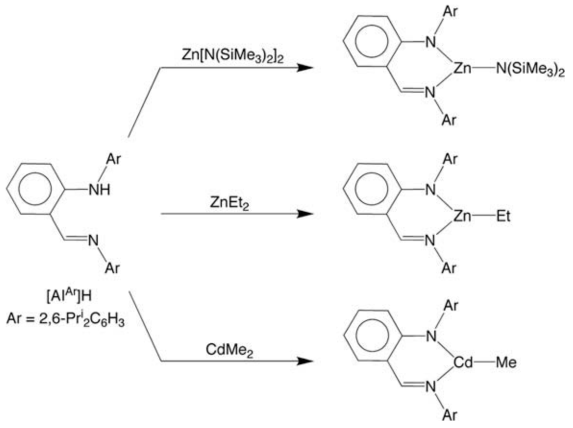


Fig. 2. Examples of β-diketiminate and anilido-imine ligands (in their protonated forms).



Scheme 1.

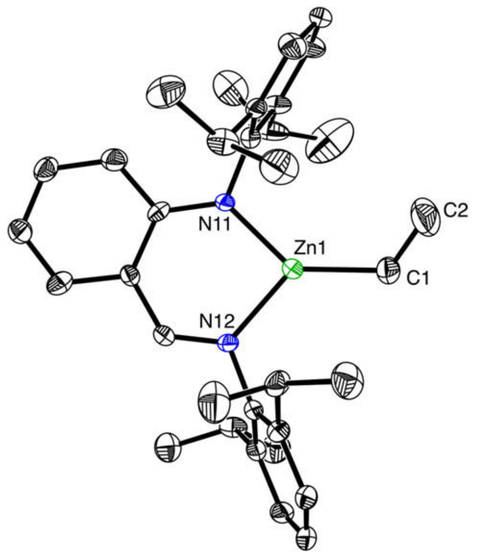


Fig. 3. Molecular structure of $[AI^{Ar}]ZnEt$.

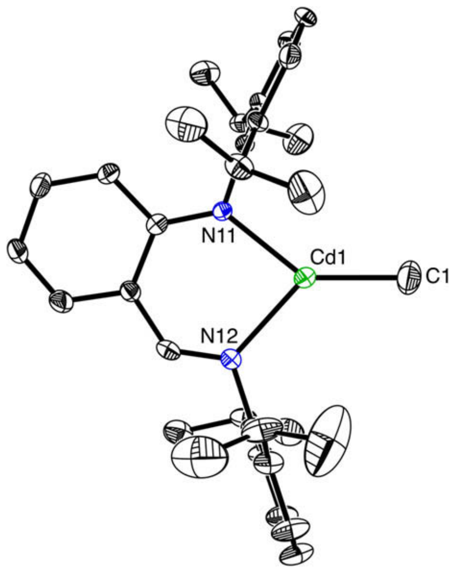


Fig. 4. Molecular structure of $[AI^{Ar}]CdMe$.

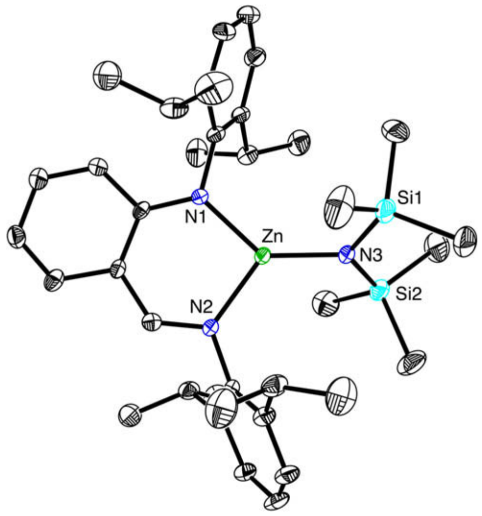


Fig. 5. Molecular structure of $[AI^{Ar}]ZnN(SiMe_3)_2$.

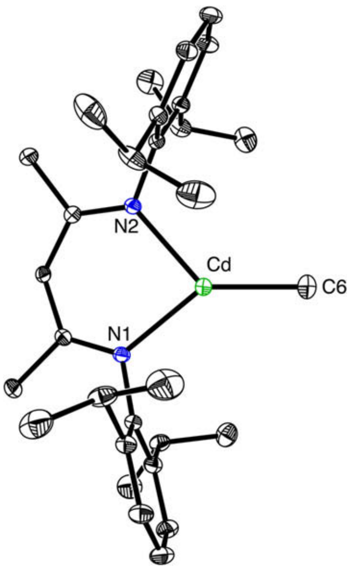


Fig. 6. Molecular structure of $[BDI^{Ar}]CdMe$.

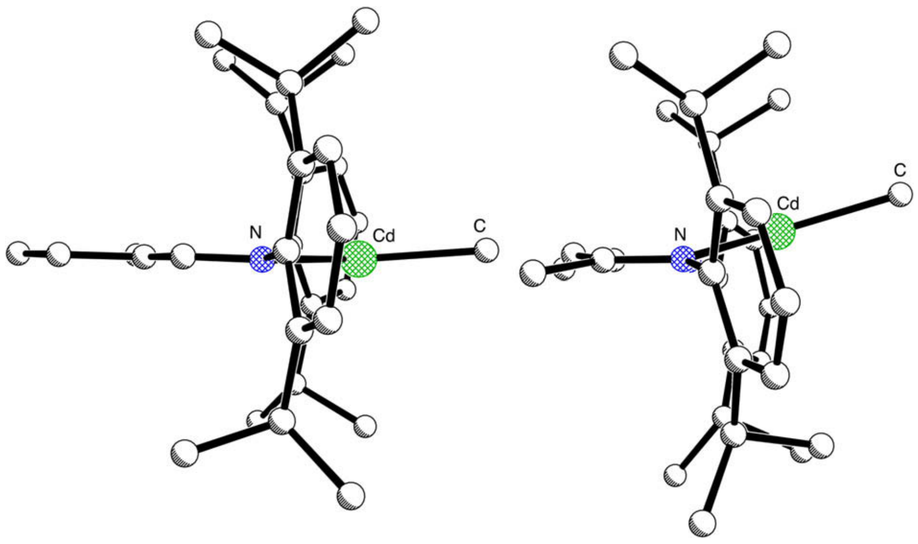
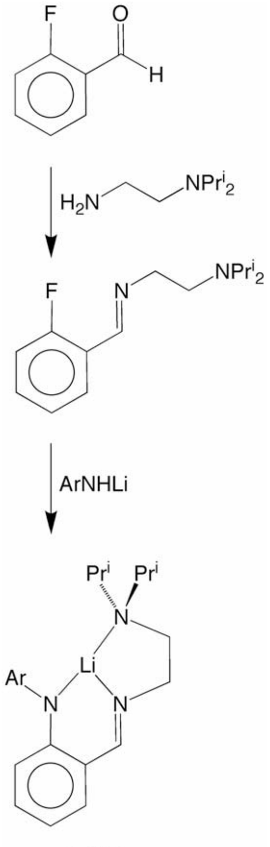


Fig. 7. Comparison of the structures of $[\mathrm{AI}^{\mathrm{Ar}}]\mathrm{CdMe}$ (left) and $[\mathrm{BDI}^{\mathrm{Ar}}]\mathrm{CdMe}$ (right).



$[\mathrm{AI}^{\mathrm{Ar,NPr^i_2}}]\mathrm{Li}$
$\mathrm{Ar} = 2,6\text{-}\mathrm{Pr^i_2C_6H_3}$

Scheme 2.

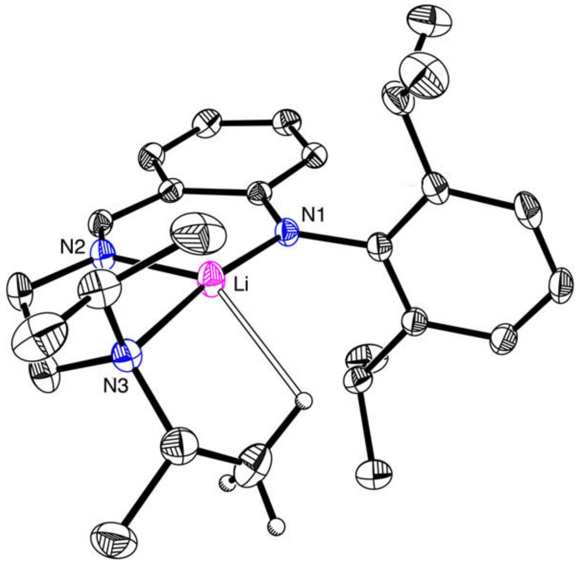


Fig. 8. Molecular structure of $[\mathrm{AI}^{\mathrm{Ar,NPr^i_2}}]\mathrm{Li}$.

1.1. Synthesis and structures of $[\mathrm{AI}^{\mathrm{Ar}}]\mathrm{MX}$ (M = Zn, Cd) derivatives

The zinc and cadmium alkyl complexes, $[\mathrm{AI}^{\mathrm{Ar}}]\mathrm{ZnEt}$ and $[\mathrm{AI}^{\mathrm{Ar}}]\mathrm{CdMe}$, are conveniently synthesized via the reactions of $[\mathrm{AI}^{\mathrm{Ar}}]\mathrm{H}$ [26] with $\mathrm{Et_2Zn}$ and $\mathrm{Me_2Cd}$, respectively (Scheme 1). In addition, the reaction between $[\mathrm{AI}^{\mathrm{Ar}}]\mathrm{H}$ and $\mathrm{Zn[N(SiMe_3)_2]_2}$ yields the bis(trimethylsilyl)amido complex $[\mathrm{AI}^{\mathrm{Ar}}]\mathrm{ZnN(SiMe_3)_2}$ (Scheme 1). The molecular structures of $[\mathrm{AI}^{\mathrm{Ar}}]\mathrm{ZnEt}$, $[\mathrm{AI}^{\mathrm{Ar}}]\mathrm{CdMe}$ and $[\mathrm{AI}^{\mathrm{Ar}}]\mathrm{ZnN(SiMe_3)_2}$ have been determined by X-ray diffraction, as illustrated in Figs. 3–5, which demonstrate that the metal center in each complex adopts a three-coordinate trigonal planar geometry.

The trigonal planar geometries of these $[\mathrm{AI}^{\mathrm{Ar}}]\mathrm{ZnX}$ complexes are similar to those of the $[\mathrm{BDI}^{\mathrm{Ar}}]\mathrm{ZnX}$ counterparts, namely $[\mathrm{BDI}^{\mathrm{Ar}}]\mathrm{ZnEt}$ [15] and $[\mathrm{BDI}^{\mathrm{Ar}}]\mathrm{ZnN(SiMe_3)_2}$ [15,33,34].[3] In contrast to zinc, however, few $[\mathrm{BDI}^{\mathrm{Ar}}]\mathrm{CdX}$ compounds have been reported [34,35]. Therefore, for comparison with $[\mathrm{AI}^{\mathrm{Ar}}]\mathrm{CdMe}$, the molecular structure of $[\mathrm{BDI}^{\mathrm{Ar}}]\mathrm{CdMe}$ is illustrated in Fig. 6 and the Cd–Me bond length [2.126(3) Å] is similar to that in $[\mathrm{AI}^{\mathrm{Ar}}]\mathrm{CdMe}$ [2.098(5) Å and 2.105(5) Å]. Furthermore, the Cd–Me bond lengths of $[\mathrm{AI}^{\mathrm{Ar}}]\mathrm{CdMe}$ and $[\mathrm{BDI}^{\mathrm{Ar}}]\mathrm{CdMe}$ are comparable to that for $[\mathrm{Tp}^{\mathrm{Bu^t,Me}}]\mathrm{CdMe}$ which has a tetrahedral geometry [2.07(2) Å] [36].

While both $[\mathrm{AI}^{\mathrm{Ar}}]\mathrm{CdMe}$ and $[\mathrm{BDI}^{\mathrm{Ar}}]\mathrm{CdMe}$ have a similar trigonal planar geometry, a notable structural difference is that the cadmium methyl moiety of $[\mathrm{AI}^{\mathrm{Ar}}]\mathrm{CdMe}$ lies in the plane of the annulated $[\mathrm{AI}^{\mathrm{Ar}}]$ ligand, whereas there is considerable displacement

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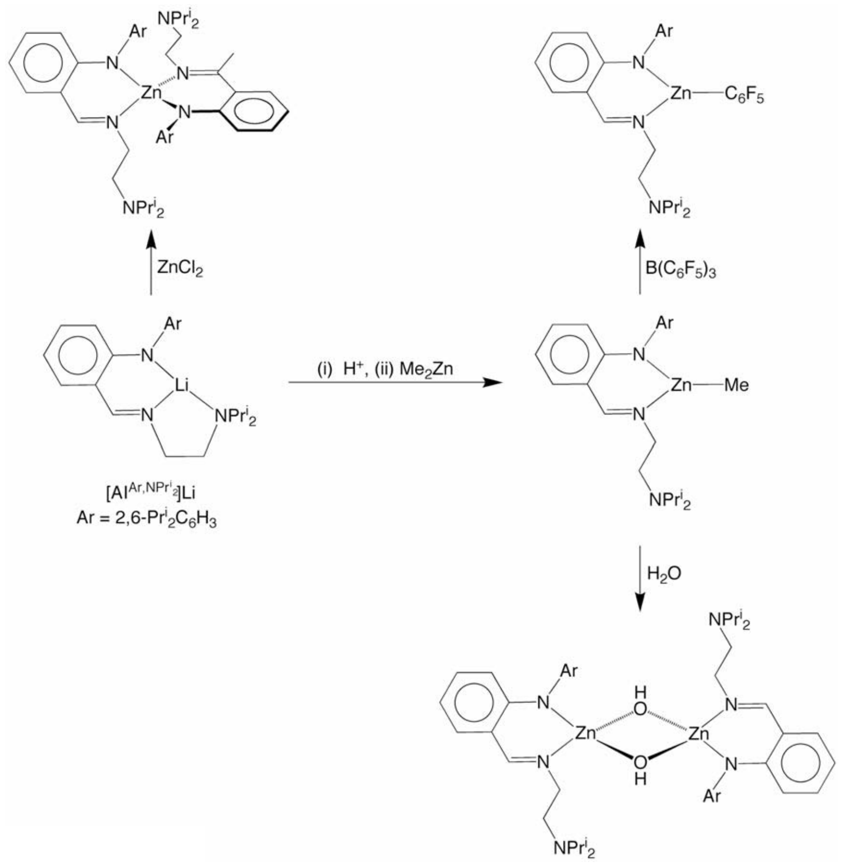
[3] For other examples of trigonal planar $[\mathrm{BDI}^{\mathrm{Ar}}]\mathrm{ZnX}$ complexes, see Refs. [33,34].



Scheme 3.

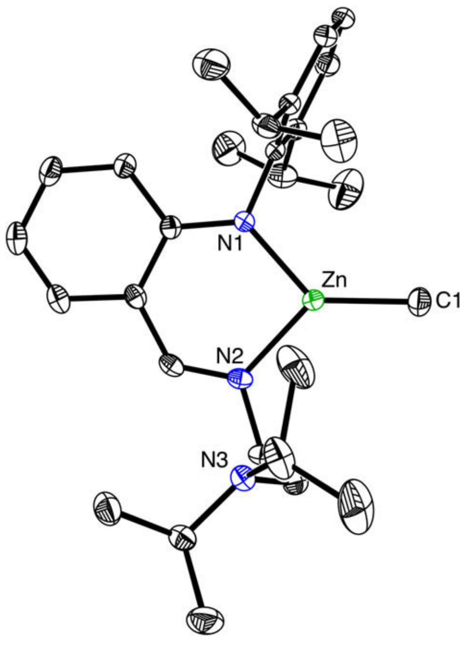


Fig. 9. Molecular structure of $[\mathrm{AI}^{\mathrm{Ar,NPr^i_2}}]\mathrm{ZnMe}$.

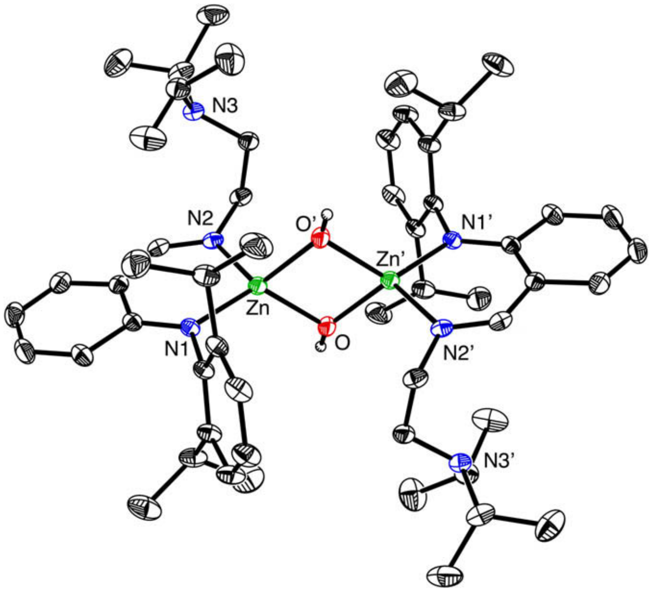
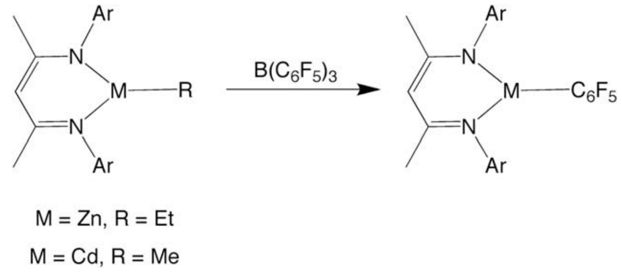


Fig. 10. Molecular structure of $\{[\mathrm{AI}^{\mathrm{Ar,NPr^i_2}}]\mathrm{Zn}(\mu\text{-OH})\}_2$.

for $[\mathrm{BDI}^{\mathrm{Ar}}]$CdMe (Fig. 7). For example, the dihedral angle between the $[\mathrm{N_2CdC}]$ and $[\mathrm{N_2C_3}]$ planes is 18.6° for $[\mathrm{BDI}^{\mathrm{Ar}}]$CdMe, but only 2.8° for $[\mathrm{AI}^{\mathrm{Ar}}]$CdMe. Interestingly, the displacement observed for $[\mathrm{BDI}^{\mathrm{Ar}}]$CdMe is not observed for $[\mathrm{BDI}^{\mathrm{Ar}}]$ZnEt [15].

1.2. Synthesis and structures of $[\mathrm{AI}^{\mathrm{Ar,NPr^i_2}}]$ZnX derivatives

A variety of tethers that feature donor groups have been incorporated into diiminate and anilido-imine ligands as part of an effort to influence the catalytic ring-opening polymerization of lactide by changing the Lewis acidity of the metal center [30–



Scheme 4.

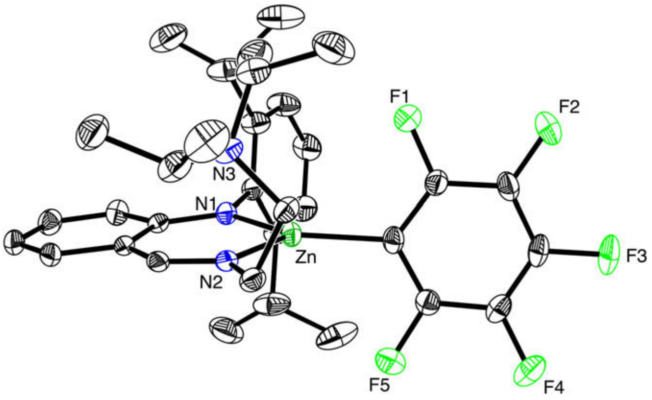


Fig. 11. Molecular structure of [AI$^{\mathrm{Ar,NPr^i_2}}$]ZnC_6F_5.

32,37]. For example, the $CH_2CH_2NMe_2$ tether has been attached to the anilido-imine ligand and the resulting [AI$^{\mathrm{Ar,NMe_2}}$]ZnEt complex adopts a distorted tetrahedral geometry due to the coordination of the NMe_2 group [31], in marked contrast to the trigonal planar structure of [AI$^{\mathrm{Ar}}$]ZnEt described above (Fig. 3). Since the ability of the tether to interact with the metal center would be expected to be dependent on the nature of the substituents on nitrogen, we were prompted to synthesize the counterpart with more bulky Pr^i groups to determine the extent to which such modification modulates structure and reactivity.

Access to the desired anilido-imine ligand that incorporates a $CH_2CH_2NPr^i_2$ tether, [AI$^{\mathrm{Ar,NPr^i_2}}$]Li, is provided via a sequence analo-

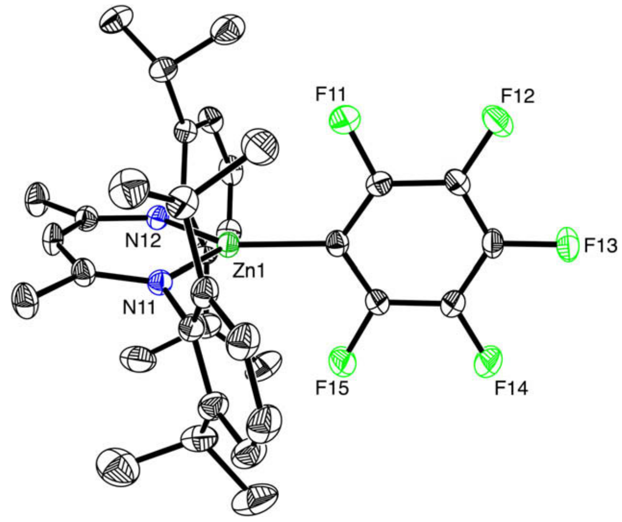


Fig. 12. Molecular structure of [BDI$^{\mathrm{Ar}}$]ZnC_6F_5.

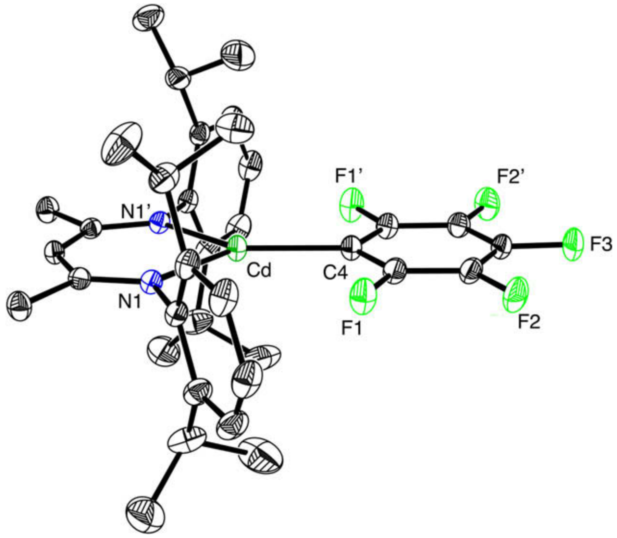


Fig. 13. Molecular structure of [BDI$^{\mathrm{Ar}}$]CdC_6F_5.

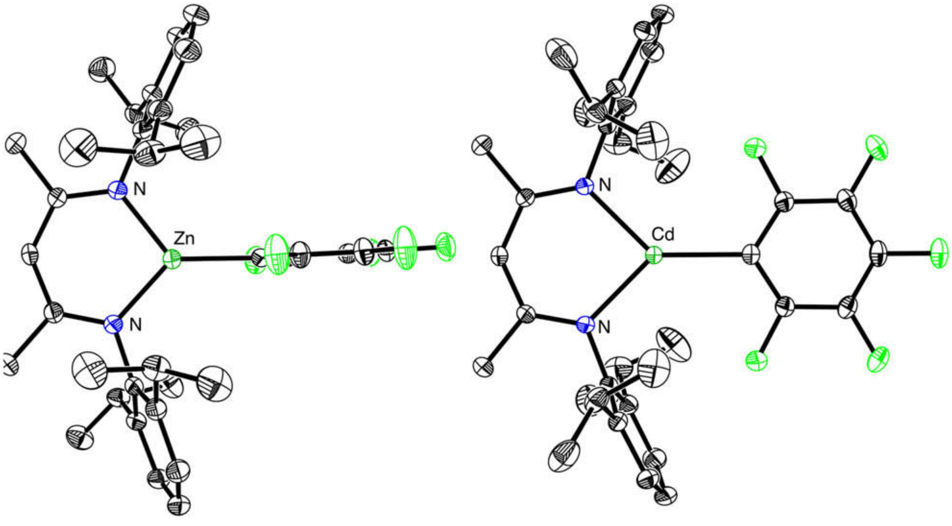


Fig. 14. Comparison of [BDI$^{\mathrm{Ar}}$]ZnC_6F_5 (left) and [BDI$^{\mathrm{Ar}}$]CdC_6F_5 (right).

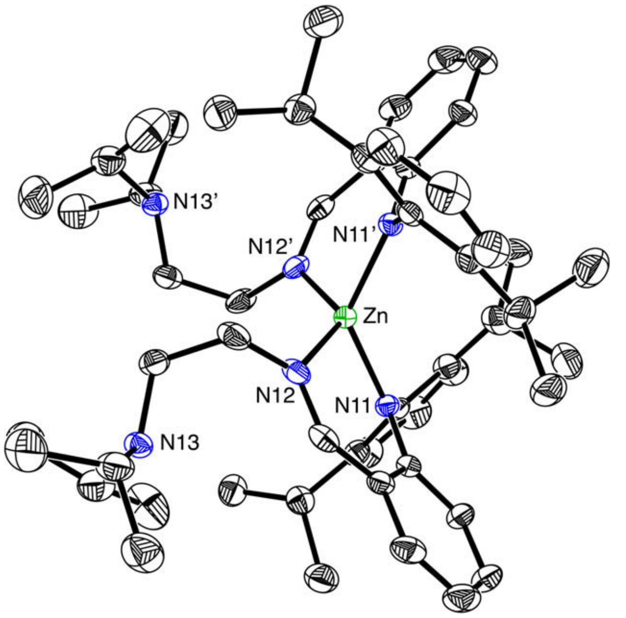


Fig. 15. Molecular structure of $[\mathrm{Al^{Ar,NPr^i_2}}]_2\mathrm{Zn}$.

gous to that for $[\mathrm{Al^{Ar,NMe_2}}]\mathrm{H}$ [31], namely condensation of 2-fluorobenzaldehyde with $\mathrm{H_2NCH_2CH_2NPr^i_2}$, followed by treatment with ArNHLi (Scheme 2). The molecular structure of $[\mathrm{Al^{Ar,NPr^i_2}}]\mathrm{Li}$ has been determined by X-ray diffraction, as illustrated in Fig. 8, thereby demonstrating that the lithium has a T-shaped coordination environment. While three-coordinate lithium with a T-shaped geometry is unusual, it is, nevertheless, precedented [38–41].[4] The coordination geometry of lithium in $[\mathrm{Al^{Ar,NPr^i_2}}]\mathrm{Li}$ is, however, supplemented by an agostic interaction [42] with a C–H bond of one of the isopropyl groups of the $\mathrm{NPr^i_2}$ moiety, with a Li···H distance of 2.3 Å [43–49].[5]

The zinc methyl complex $[\mathrm{Al^{Ar,NPr^i_2}}]\mathrm{ZnMe}$ may be obtained by treatment of the protonated ligand $[\mathrm{Al^{Ar,NPr^i_2}}]\mathrm{H}$ with $\mathrm{Me_2Zn}$ (Scheme 3). X-ray diffraction demonstrates that the nitrogen of the $\mathrm{NPr^i_2}$ does not coordinate to the zinc center of $[\mathrm{Al^{Ar,NPr^i_2}}]\mathrm{ZnMe}$, such that it is 3-coordinate and planar (Fig. 9). In this regard, the molecular structure of $[\mathrm{Al^{Ar,NPr^i_2}}]\mathrm{ZnMe}$ is quite distinct from that of $[\mathrm{Al^{Ar,NMe_2}}]\mathrm{ZnEt}$, which adopts a distorted tetrahedral geometry due to the coordination of the $\mathrm{NMe_2}$ group [22].

The Zn–C bond of $[\mathrm{Al^{Ar,NPr^i_2}}]\mathrm{ZnMe}$ is a site of facile reactivity. For example, the Zn–C bond is cleaved by water to give the dinuclear hydroxide-bridged compound $\{[\mathrm{Al^{Ar,NPr^i_2}}]\mathrm{Zn}(\mu\text{-OH})\}_2$, as illustrated in Fig. 10. The zinc methyl compound $[\mathrm{Al^{Ar,NPr^i_2}}]\mathrm{ZnMe}$ also reacts with $\mathrm{B(C_6F_5)_3}$ to give the perfluorophenyl complex $[\mathrm{Al^{Ar,NPr^i_2}}]\mathrm{ZnC_6F_5}$. The formation of $[\mathrm{Al^{Ar,NPr^i_2}}]\mathrm{ZnC_6F_5}$ involves the exchange of alkyl and perfluorophenyl groups between zinc and boron, a class of transformation that has precedent [50–55]. Furthermore, $[\mathrm{BDI^{Ar}}]\mathrm{ZnEt}$ and $[\mathrm{BDI^{Ar}}]\mathrm{CdMe}$ also react with $\mathrm{B(C_6F_5)_3}$ to give $[\mathrm{BDI^{Ar}}]\mathrm{ZnC_6F_5}$ and $[\mathrm{BDI^{Ar}}]\mathrm{CdC_6F_5}$ (Scheme 4), although these compounds have been previously synthesized via the reaction of $[\mathrm{BDI^{Ar}}]\mathrm{H}$ with $\mathrm{Zn(C_6F_5)_2{\cdot}2EtCN}$ and $\mathrm{Cd(C_6F_5)_2{\cdot}2MeCN}$, respectively [34].

The molecular structure of $[\mathrm{Al^{Ar,NPr^i_2}}]\mathrm{ZnC_6F_5}$ has been determined by X-ray diffraction which demonstrates that the zinc adopts a three-coordinate trigonal planar coordination environment in which the planes of the $[\mathrm{Al^{Ar,NPr^i_2}}]$ and $\mathrm{C_6F_5}$ ligands are almost orthogonal to each other (Fig. 11). This type of structure is analogous to that of $[\mathrm{BDI^{Ar}}]\mathrm{ZnC_6F_5}$ (Fig. 12), but is very different to that of the cadmium counterpart $[\mathrm{BDI^{Ar}}]\mathrm{CdC_6F_5}$ (Fig. 13) in which the $[\mathrm{BDI^{Ar}}]$ and $\mathrm{C_6F_5}$ ligands reside in the same plane (Fig. 14). Of these two structures, it is the cadmium structure that is the more unusual on the basis that a perpendicular arrangement would have been anticipated to minimize steric interactions. In this regard, it is worth noting that the structure of a different crystalline form of $[\mathrm{BDI^{Ar}}]\mathrm{CdC_6F_5}$ [34] exhibits a similar structure to that described here and so it is not likely that the coplanarity can be attributed to crystal packing forces. One possible explanation is that the longer Cd–N and Cd–C bonds, relative to the Zn–N and Zn–C bonds, result in the ortho fluorine substituents being further away from the Ar groups so that the energetic steric penalty for coplanarity is not as severe as that for the zinc counterpart.

Finally, we note that it is also possible to synthesize the 2:1 complex $[\mathrm{Al^{Ar,NPr^i_2}}]_2\mathrm{Zn}$ via treatment of $[\mathrm{Al^{Ar,NPr^i_2}}]\mathrm{Li}$ with $\mathrm{ZnCl_2}$ (Scheme 3), which has been shown by X-ray diffraction to adopt a pseudo tetrahedral coordination environment (Fig. 15). The $[\mathrm{BDI^{Ar}}]_2\mathrm{Zn}$ counterpart is unknown and ability to isolate the 2:1 complex $[\mathrm{Al^{Ar,NPr^i_2}}]_2\mathrm{Zn}$ is in accord with $[\mathrm{Al^{Ar,NPr^i_2}}]$ being less sterically demanding than the $[\mathrm{BDI^{Ar}}]$ ligand.

2. Conclusions

In summary, the three coordinate alkyl compounds, $[\mathrm{Al^{Ar}}]\mathrm{ZnEt}$ and $[\mathrm{Al^{Ar}}]\mathrm{CdMe}$, have been synthesized via the reactions of $[\mathrm{Al^{Ar}}]\mathrm{H}$ with $\mathrm{Et_2Zn}$ and $\mathrm{Me_2Cd}$, respectively. The related complex $[\mathrm{Al^{Ar,NPr^i_2}}]\mathrm{ZnMe}$, in which the $[\mathrm{Al^{Ar,NPr^i_2}}]$ ligand features an additional donor group, also possesses a trigonal planar zinc center, which is in marked contrast to the tetrahedral geometry observed for $[\mathrm{Al^{Ar,NMe_2}}]\mathrm{ZnMe}$. It is, therefore, evident that the additional bulk associated with the $\mathrm{CH_2CH_2NPr^i_2}$ tether reduces its tendency to coordinate to the zinc center, as compared to that for the $\mathrm{CH_2CH_2NMe_2}$ variant. The Zn–C bond of $[\mathrm{Al^{Ar,NPr^i_2}}]\mathrm{ZnMe}$ is cleaved by $\mathrm{B(C_6F_5)_3}$ to give the perfluorophenyl complex $[\mathrm{Al^{Ar,NPr^i_2}}]\mathrm{ZnC_6F_5}$, a transformation that is also observed for $[\mathrm{BDI^{Ar}}]\mathrm{ZnEt}$ and $[\mathrm{BDI^{Ar}}]\mathrm{CdMe}$. Interestingly, the $\mathrm{C_6F_5}$ groups are almost orthogonal to the planes of the $[\mathrm{Al^{Ar,NPr^i_2}}]$ and $[\mathrm{BDI^{Ar}}]$ ligands in the zinc complexes, $[\mathrm{Al^{Ar,NPr^i_2}}]\mathrm{ZnC_6F_5}$ and $[\mathrm{BDI^{Ar}}]\mathrm{ZnC_6F_5}$, whereas the $\mathrm{C_6F_5}$ and $[\mathrm{BDI^{Ar}}]$ ligands of $[\mathrm{BDI^{Ar}}]\mathrm{CdC_6F_5}$ reside in the same plane. In addition to 1:1 $[\mathrm{Al^{Ar,NPr^i_2}}]\mathrm{ZnX}$ complexes, it is also possible to synthesize the 2:1 complex $[\mathrm{Al^{Ar,NPr^i_2}}]_2\mathrm{Zn}$, a compound that has no precedent in the $\{[\mathrm{BDI^{Ar}}]\mathrm{Zn}\}$ system.

3. Experimental

3.1. General considerations

All manipulations were performed using a combination of glovebox, high-vacuum and Schlenk techniques under a nitrogen or argon atmosphere, except where otherwise stated. Solvents were purified and degassed by standard procedures. NMR spectra were measured on Bruker 300 DRX and Bruker 400 DRX spectrometers. For solutions in organic solvents, ^{1}H NMR spectra are reported in ppm relative to $\mathrm{SiMe_4}$ ($\delta = 0$) and were referenced internally with respect to the protio solvent impurity (δ 7.16 for $\mathrm{C_6D_5H}$) [56]. ^{13}C NMR spectra are reported in ppm relative to $\mathrm{SiMe_4}$ ($\delta = 0$) and were referenced internally with respect to the solvent (δ 128.06 for $\mathrm{C_6D_6}$) [56]. Coupling constants are given in hertz. IR spectra were recorded as KBr pellets on a Nicolet Avatar DTGS spectrometer, and the data are reported in reciprocal centimeters. Combustion analyses were carried out by Robertson Microlit Laboratories, Madison, NJ, USA. $[\mathrm{Al^{Ar}}]\mathrm{H}$ [26] and $[\mathrm{BDI^{Ar}}]\mathrm{H}$ [14] were synthesized as previously reported.

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[4] For other examples of three-coordinate lithium, see Refs. [38–41].

[5] For other examples of lithium compounds with agostic interactions, see Refs. [43–49].

3.2. X-ray structure determinations

Single crystal X-ray diffraction data were collected on a Bruker P4 diffractometer equipped with a SMART CCD detector. Crystal data, data collection and refinement parameters are summarized in Table 1. The structures were solved using direct methods and standard difference map techniques, and were refined by full-matrix least-squares procedures on F^2 with SHELXTL (Version 6.10) [57,58]. The crystallographic data for [AI^{Ar}]CdMe, [AI^{Ar}]ZnEt, [AI^{Ar}]ZnN(SiMe$_3$)$_2$, [AI$^{Ar,NPr^i_2}$]Li, [AI$^{Ar,NPr^i_2}$]ZnMe, [AI$^{Ar,NPr^i_2}$]ZnC$_6$F$_5$, {[AI$^{Ar,NPr^i_2}$]Zn(μ–OH)}$_2$, [AI$^{Ar,NPr^i_2}$]$_2$Zn, [BDI^{Ar}]CdMe, [BDI^{Ar}]ZnC$_6$F$_5$, and [BDI^{Ar}]CdC$_6$F$_5$ have been deposited with the Cambridge Crystallographic Data Centre (CCDC 762879–762890). The unit cells of [BDI^{Ar}]ZnC$_6$F$_5$·0.25C$_5$H$_{12}$ and [AI$^{Ar,NPr^i_2}$]$_2$Zn·C$_5$H$_{12}$, respectively contain 3 and 4 pentane molecules which were treated as diffuse contributions to the overall scattering without specific atom positions by use of SQUEEZE/PLATON [59,60].

3.3. Synthesis of [AI^{Ar}]ZnEt

A solution of [AI^{Ar}]H (1.0 g, 2.3 mmol) in benzene (30 mL) was cooled in an ice/water bath and treated with a solution of Et$_2$Zn in hexanes (5.0 mL of 1.0 M, 5.0 mmol). The resulting solution was stirred at room temperature for 1 h and then refluxed for 1 day. After this period, an additional quantity of Et$_2$Zn in hexanes (2.0 mL of 1.0 M, 2.0 mmol) was added and the resulting solution was refluxed for an additional day to afford a yellow-green solution. The volatile components were removed by lyophilization and the yellow solid residue was extracted into pentane (20 mL). The solvent was removed in vacuo to give [AI^{Ar}]ZnEt as a yellow powder (1.1 g, 90%). ^{1}H NMR (C$_6$D$_6$): 0.40 [q, $^3J_{H-H} = 8$, 2H of CH_2CH$_3$], 1.01 [t, $^3J_{H-H} = 8$, 3H of CH$_2$CH_3], 1.06 [d, $^3J_{H-H} = 7$, 6H of CH(CH_3)$_2$], 1.14 [d, $^3J_{H-H} = 7$, 6H of CH(CH_3)$_2$], 1.22 [d, $^3J_{H-H} = 7$, 6H of CH(CH_3)$_2$], 1.29 [d, $^3J_{H-H} = 7$, 6H of CH(CH_3)$_2$], 3.11 [septet, $^3J_{H-H} = 7$, 2H of CH(CH$_3$)$_2$], 3.35 [septet, $^3J_{H-H} = 7$, 2H of CH(CH$_3$)$_2$], 6.36 [t, $^3J_{H-H} = 9$, 1H of aromatic ring], 6.54 [d, $^3J_{H-H} = 9$, 1H of aromatic ring], 6.93 [m, 2H of aromatic ring], 7.12 [m, protons of aromatic ring], 7.26 [m, protons of aromatic ring], 7.99 [s, 1H of C$_6$H$_4$CH=NAr].

3.4. Synthesis of [AI^{Ar}]CdMe

A mixture of [AI^{Ar}]H (46 mg, 0.10 mmol) and Me$_2$Cd (40 μL, 0.56 mmol) in benzene (0.5 mL) was heated at 110 °C for 3 days. After this period, the volatile components were removed by lyophilization and the resulting residue was extracted into pentane (0.5 mL). Colorless crystals of [AI^{Ar}]CdMe were obtained by slow evaporation at −15 °C (25 mg, 44%). ^{1}H NMR (C$_6$D$_6$): −0.35 [s, 3H of CdCH_3], 1.10 [d, $^3J_{H-H} = 7$, 6H of CH(CH_3)$_2$], 1.14 [d, $^3J_{H-H} = 7$, 6H of CH(CH_3)$_2$], 1.17 [d, $^3J_{H-H} = 7$, 6H of CH(CH_3)$_2$], 1.24 [d, $^3J_{H-H} = 7$, 6H of CH(CH_3)$_2$] 3.18 [septet, $^3J_{H-H} = 7$, 2H of CH(CH$_3$)$_2$], 3.43 [septet, $^3J_{H-H} = 7$, 2H of CH(CH$_3$)$_2$], 6.33 [t, $^3J_{H-H} = 9$, 1H of aromatic ring], 6.47 [d, $^3J_{H-H} = 9$, 1H of aromatic ring], 6.88 [t, $^3J_{H-H} = 9$, 1H of aromatic ring], 6.94 [d, $^3J_{H-H} = 9$, 1H of aromatic ring], 7.10 [m, protons of aromatic ring], 7.24 [m, protons of aromatic ring], 8.06 [s, 1H of C$_6$H$_4$CH=NAr].

3.5. Synthesis of [AI^{Ar}]ZnN(SiMe$_3$)$_2$

A solution of [AI^{Ar}]H (3.0 g, 6.8 mmol) and Zn[N(SiMe$_3$)$_2$]$_2$ (2.6 g, 6.7 mmol) in toluene (30 mL) was refluxed under N$_2$ for 6 days, resulting in the formation of [AI^{Ar}]ZnN(SiMe$_3$)$_2$ as a yellow precipitate which was separated by filtration and washed with pentane (30 mL). The filtrate was refluxed for an additional 12 days, after which period the volatile components were removed in vacuo to give a yellow residue, which was washed with pentane (30 mL) to give an additional crop of [AI^{Ar}]ZnN(SiMe$_3$)$_2$ as a yellow powder (combined yield: 1.2 g, 27%). Anal. Calc. for C$_{37}$H$_{57}$N$_3$Si$_2$Zn: C, 66.8; H, 8.6; N, 6.3. Found: C, 67.4; H, 8.4; N, 4.8%. ^{1}H NMR (C$_6$D$_6$): −0.01 [s, 18H of Si(CH_3)$_3$], 1.04 [d, $^3J_{H-H} = 7$, 6H of CH(CH_3)$_2$], 1.11 [d, $^3J_{H-H} = 7$, 6H of CH(CH_3)$_2$], 1.27 [d, $^3J_{H-H} = 7$, 6H of CH(CH_3)$_2$], 1.44 [d, $^3J_{H-H} = 7$, 6H of CH(CH_3)$_2$], 3.23 [septet, $^3J_{H-H} = 7$, 2H of CH(CH$_3$)$_2$], 3.43 [septet, $^3J_{H-H} = 7$, 2H of CH(CH$_3$)$_2$], 6.34 [t, $^3J_{H-H} = 9$, 1H of aromatic ring], 6.53 [d, $^3J_{H-H} = 9$, 1H of aromatic ring], 6.82 [t, $^3J_{H-H} = 9$, 1H of aromatic ring], 6.94 [d, $^3J_{H-H} = 9$, 1H of aromatic ring], 7.12 [m, protons of aromatic ring], 7.29 [m, protons of aromatic ring], 8.14 [s,1H of C$_6$H$_4$CH=NAr]. IR Data (KBr pellet, cm^{-1}): 2961 (s), 2926 (w), 2868 (m), 1622 (s), 1573 (s), 1510 (m), 1462 (s), 1436 (m), 1328 (m), 1173 (w), 1160 (m), 913 (w), 793 (w), 745 (m).

3.6. Synthesis of [BDI^{Ar}]CdMe

Me$_2$Cd (0.15 mL, 2.1 mmol) was added to a solution of [BDI^{Ar}]H (0.84 g, 2.0 mmol) in benzene (10 mL) and refluxed under N$_2$ for 16 h. After this period, an additional quantity of Me$_2$Cd (0.15 mL, 2.1 mmol) was added and the reaction mixture was refluxed under N$_2$ for a further 16 h. The volatile components were removed in vacuo to give a white solid. The solid was extracted into benzene and the extract was lyophilized to give [BDI^{Ar}]CdMe as a white powder (0.93 g, 85%). ^{1}H NMR (C$_6$D$_6$): −0.37 [s, satellite peaks: $^2J_{^{111}Cd-H} = 74$, $^2J_{^{113}Cd-H} = 77$, 3H of CdCH_3], 1.20 [d, $^3J_{H-H} = 7$, 12H of CH(CH_3)$_2$], 1.25 [d, $^3J_{H-H} = 7$, 12H of CH(CH_3)$_2$] 1.74 [s, 6 H of CHC(NAr)CH_3], 3.34 [septet, $^3J_{H-H} = 7$, 4H of CH(CH$_3$)$_2$], 4.92 [s, 1H of CHC(NAr)CH$_3$], 7.10 [s, 6H of Pr$^i_2$C$_6$$H_3$]. ^{13}C NMR (C$_6D_6$): −15.6 [q, $^1J_{C-H} = 129$, satellite peaks: $^1J_{^{111}Cd-C} = 886$, $^1J_{^{113}Cd-C} = 927$, 1C of CdCH$_3$], 23.3 [q, $^1J_{C-H} = 125$, 4C of CH(CH$_3$)$_2$], 24.1 [q, $^1J_{C-H} = 127$, 2C of CHC(NAr)CH$_3$], 24.6 [q, $^1J_{C-H} = 125$, 4C of CH(CH$_3$)$_2$], 28.2 [d, $^1J_{C-H} = 127$, 4C of CH(CH$_3$)$_2$], 94.4 [d, $^1J_{C-H} = 155$, 1C of (NAr)CCHC (NAr)], 123.9 [d, $^1J_{C-H} = 154$, 4C of NAr], 125.6 [d, $^1J_{C-H} = 158$, 2C of NAr], 141.0 [s, C of NAr], 146.5 [s, C of NAr], 167.6 [s, 2C of (NAr)CCHC(NAr)].

3.7. Synthesis of [AI$^{Ar,NPr^i_2}$]Li

(a) 2-fluorobenzaldehyde (10.5 mL, 0.10 mol) and solid MgSO$_4$ (10.0 g, 0.08 mol) was added to a solution of *N*,*N*-diisopropylethylenediamine (17.4 mL, 0.10 mol) in hexanes (100 mL). The resulting mixture was stirred at room temperature for 2 h and filtered. The volatile components were removed in vacuo to give 2-F-C$_6$H$_4$CH = NCH$_2$CH$_2$NPr$^i_2$ as yellowish oily liquid (21.0 g, 84%), which was used in the next step without further purification. ^{1}H NMR (C$_6$D$_6$): 0.93 [d, $^3J_{H-H} = 7$, 12H of CH(CH_3)$_2$], 2.75 [t, $^3J_{H-H} = 7$, 2H of CH_2CH$_2$], 2.89 [septet, $^3J_{H-H} = 7$, 12H of CH(CH_3)$_2$], 3.60 [t, $^3J_{H-H} = 7$, 2H of CH$_2$CH_2], 6.7–6.9 [m, 3H on aromatic ring], 8.29 [m, 1H on aromatic ring], 8.60 [s, 1H of CH=NCH$_2$CH$_2$]. (b) A solution of diisopropylaniline (6.4 mL, 34 mmol) in THF (20 mL) at −78 °C was treated with Bu^{n}Li (1.6 M in hexanes, 24 mL, 38 mmol). The solution was allowed to warm to room temperature and stirred overnight. After this period, 2-F-C$_6$H$_4$CH=NCH$_2$CH$_2$NPr^i_2 (3.8 g, 15 mmol) was added and the resulting mixture was stirred at room temperature for 1 day. The reaction was quenched with an aqueous solution of NH$_4$Cl (10% w/w, 50 mL) and the product was extracted into hexanes (2 × 40 mL). The hexane extracts were washed with water (80 mL) and dried over MgSO$_4$. The solvent was then removed and the resulting oily residue was dissolved in pentane (30 mL) and treated with Bu^{n}Li (1.6 M in hexanes, 12 mL, 19 mmol) at −78 °C. The resulting mixture was allowed to stir at room temperature for 1 h to yield [AI$^{Ar,NPr^i_2}$]Li as a yellow solid precipitate, which was isolated by filtration, washed with cold pentane at −78 °C (2 × 30 mL) and dried in vacuo (5.8 g, 65%). ^{1}H NMR spectroscopy

Table 1
Crystal, intensity collection and refinement data.

	$[\mathrm{AI}^{\mathrm{Ar}}]\mathrm{CdMe}$	$[\mathrm{AI}^{\mathrm{Ar}}]\mathrm{ZnEt}$	$[\mathrm{AI}^{\mathrm{Ar}}]\mathrm{ZnN(SiMe_3)_2}$	$[\mathrm{AI}^{\mathrm{Ar,NPr^i_2}}]\mathrm{Li}$	$[\mathrm{AI}^{\mathrm{Ar,NPr^i_2}}]\mathrm{ZnMe}$	$[\mathrm{AI}^{\mathrm{Ar,NPr^i_2}}]\mathrm{ZnC_6F_5}$	$\{[\mathrm{AI}^{\mathrm{Ar,NPr^i_2}}]\mathrm{Zn}(\mu\text{–}\mathrm{OH})\}_2$	$[\mathrm{AI}^{\mathrm{Ar,NPr^i_2}}]_2\mathrm{Zn}\cdot\mathrm{C_5H_{12}}$	$[\mathrm{BDI}^{\mathrm{Ar}}]\mathrm{CdMe}$	$[\mathrm{BDI}^{\mathrm{Ar}}]\mathrm{ZnC_6F_5}\cdot0.25\mathrm{C_5H_{12}}$	$[\mathrm{BDI}^{\mathrm{Ar}}]\mathrm{CdC_6F_5}$
Lattice	triclinic	orthorhombic	triclinic	orthorhombic	triclinic	monoclinic	triclinic	monoclinic	orthorhombic	monoclinic	monoclinic
Formula	$C_{32}H_{42}N_2Cd$	$C_{33}H_{44}N_2Zn$	$C_{37}H_{57}N_3Si_2Zn$	$C_{27}H_{40}N_3Li$	$C_{28}H_{43}N_3Zn$	$C_{33}H_{40}F_5N_3Zn$	$C_{54}H_{82}N_6O_2Zn_2$	$C_{59}H_{92}N_6Zn$	$C_{30}H_{44}N_2Cd$	$C_{36.25}H_{44}F_5N_2Zn$	$C_{35}H_{41}F_5N_2Cd$
Formula weight	567.08	534.07	665.41	413.56	487.02	639.05	978.00	950.76	545.07	668.10	697.10
Space group	$P\bar{1}$	$Pca2_1$	$P\bar{1}$	$P2_12_12_1$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$C2/c$	$P2_12_12_1$	$P2_1/n$	$P2_1/m$
a (Å)	9.3452(6)	34.1012(19)	10.6606(11)	11.1407(6)	10.8479(6)	14.2013(6)	10.9646(8)	16.0843(9)	8.7658(5)	18.7547(9)	8.7794(16)
b (Å)	18.0141(14)	9.2401(5)	11.4633(12)	13.8524(8)	11.3562(7)	10.8744(4)	11.2787(8)	18.2035(11)	14.5902(9)	18.4198(10)	20.962(4)
c (Å)	18.6853(14)	19.4152(9)	16.5666(16)	16.6396(9)	11.5527(7)	21.8665(9)	11.4634(8)	22.2659(14)	21.9488(13)	32.8588(17)	9.9476(19)
α (°)	76.6850(10)	90	84.949(2)	90	91.5780(10)	90	77.4830(10)	90	90	90	90
β (°)	88.626(2)	90	81.293(3)	90	94.1800(10)	104.5100(10)	86.6050(10)	105.3330(10)	90	91.4200(10)	108.675(3)
γ (°)	87.245(2)	90	74.453(2)	90	100.4410(10)	90	76.9260(10)	90	90	90	90
V (Å^3)	3057.2(4)	6117.7(6)	1925.6(3)	2567.9(2)	1394.69(14)	3269.1(2)	1347.99(17)	6287.2(7)	2807.1(3)	11347.8(10)	1734.3(6)
Z	4	8	2	4	2	4	1	4	4	12	2
T (K)	243(2)	243(2)	243(2)	243(2)	243(2)	243(2)	243(2)	243(2)	243(2)	243(2)	243(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
ρ (g cm$^{-3)}$	1.232	1.160	1.148	1.070	1.160	1.298	1.205	1.004	1.290	1.173	1.335
μ (mm^{-1})	0.734	0.825	0.727	0.062	0.899	0.805	0.933	0.427	0.797	0.698	0.681
θ (°)	28.31	28.31	28.30	28.31	28.38	28.35	28.38	28.31	28.31	28.34	28.29
Number of data collected	21 504	41 094	13 775	18 339	10 055	22 887	9492	22 403	19 593	78 687	11 958
Number of data used	13 582	9609	8683	3457	6321	7719	6032	7408	6523	26 471	4096
Number of parameters	631	668	389	289	298	379	292	276	313	1192	207
R_1 [$I > 2\sigma(I)$]	0.0603	0.0469	0.0669	0.0486	0.0341	0.0408	0.0363	0.0565	0.0278	0.0464	0.0293
wR_2 [$I > 2\sigma(I)$]	0.0638	0.0786	0.1116	0.1308	0.0818	0.0946	0.0941	0.1070	0.0520	0.0981	0.0733
R_1 [all data]	0.1960	0.1437	0.1832	0.0697	0.0473	0.0820	0.0480	0.1349	0.0369	0.1155	0.0396
wR_2 [all data]	0.0779	0.0954	0.1350	0.1464	0.0886	0.1119	0.1017	0.1182	0.0543	0.1068	0.0770
Goodness-of-fit (GOF) on F^2	1.000	1.004	1.004	1.056	1.024	1.008	1.043	1.013	1.004	1.011	1.025

shows that the product contains ca. 5% 2,6-diisopropylaniline as impurity. Crystals of $[\mathrm{Al}^{\mathrm{Ar,NPr^i_2}}]$Li suitable for X-ray diffraction were obtained by slow evaporation of pentane solution. ^{1}H NMR (C_6D_6): 0.57 [d, $^3J_{H-H}$ = 7, 12H of $N[CH(CH_3)_2]_2$], 1.24 [d, $^3J_{H-H}$ = 7, 6H of $C_6H_3[CH(CH_3)_2]_2$], 1.27 [d, $^3J_{H-H}$ = 7, 6H of $C_6H_3[CH(CH_3)_2]_2$], 2.13 [t, $^3J_{H-H}$ = 6, 2H of CH_2CH_2], 2.53 [septet, $^3J_{H-H}$ = 6, 2H of $CH(CH_3)_2$], 3.07 [t, $^3J_{H-H}$ = 6, 2H of CH_2CH_2], 3.53 [septet, $^3J_{H-H}$ = 6, 2H of $CH(CH_3)_2$], 6.42–6.48 [m, 2H on aromatic ring], 7.00–7.37 [m, 5H on aromatic ring], 8.12 [s, 1H of $CH{=}NCH_2CH_2$]. IR Data (KBr pellet, cm^{-1}): 2962 (vs), 2927 (w), 2868 (m), 1630 (s), 1577 (s), 1511 (m), 1456 (s), 1382 (w), 1362 (w), 1329 (m), 796 (w), 747 (m).

3.8. Synthesis of $[\mathrm{Al}^{\mathrm{Ar,NPr^i_2}}]$ZnMe

$[\mathrm{Al}^{\mathrm{Ar,NPr^i_2}}]$Li (1.9 g, 4.6 mmol) was added to an aqueous solution of NH_4Cl (10% w/w, 20 mL) and the generated $[\mathrm{Al}^{\mathrm{Ar,NPr^i_2}}]$H was extracted into hexanes (50 mL). The hexanes extract was washed with water (30 mL) and dried over $MgSO_4$. The volatile components were removed in vacuo to give a yellow oil which was dissolved in toluene (40 mL), cooled in an ice bath, and treated with a solution of Me_2Zn in toluene (5.0 mL of 2.0 M, 10.0 mmol). The resulting solution was allowed to warm to room temperature, stirred for 4 h, and then stirred at 75 °C for 16 h. The volatile components were removed in vacuo to give $[\mathrm{Al}^{\mathrm{Ar,NPr^i_2}}]$ZnMe as a yellow solid (1.8 g, 80%). Crystals of $[\mathrm{Al}^{\mathrm{Ar,NPr^i_2}}]$ZnMe suitable for X-ray diffraction were obtained by slow evaporation of a benzene solution. Anal. Calc. for $C_{28}H_{43}N_3Zn$: C, 69.1; H, 8.9; N, 8.6. Found: C, 67.9; H, 9.3; N, 8.5%. ^{1}H NMR (C_6D_6): −0.30 [s, 3H of Zn–CH_3], 0.82 [d, $^3J_{H-H}$ = 7, 12H of $N[CH(CH_3)_2]_2$], 1.15 [d, $^3J_{H-H}$ = 7, 6H of $C_6H_3[CH(CH_3)_2]_2$], 1.25 [d, $^3J_{H-H}$ = 7, 6H of $C_6H_3[CH(CH_3)_2]_2$], 2.51 [t, $^3J_{H-H}$ = 6, 2H of CH_2CH_2], 2.72 [septet, $^3J_{H-H}$ = 6, 2H of $CH(CH_3)_2$], 3.23 [t, $^3J_{H-H}$ = 6, 2H of CH_2CH_2], 3.32 [septet, $^3J_{H-H}$ = 6, 2H of $CH(CH_3)_2$], 6.40–6.50 [m, 2H on aromatic ring], 6.89–7.30 [m, 5H on aromatic ring], 7.85 [s, 1H of $CH{=}NCH_2CH_2$]. ^{13}C NMR (C_6D_6): −16.6 [q, $^1J_{C-H}$ = 121, 1C of Zn–CH_3], 21.0 [q, $^1J_{C-H}$ = 123, 4C of $N[CH(CH_3)_2]_2$], 24.3 [q, $^1J_{C-H}$ = 128, 4C of $N[CH(CH_3)_2]_2$], 24.9 [q, $^1J_{C-H}$ = 128, 4C of $N[CH(CH_3)_2]_2$], 28.2 [d, $^1J_{C-H}$ = 129, 2C of $CH(CH_3)_2$], 46.4 [t, $^1J_{C-H}$ = 131, 1C of CH_2CH_2], 48.2 [d, $^1J_{C-H}$ = 132, 2C of $CH(CH_3)_2$], 61.0 [t, $^1J_{C-H}$ = 137, 1C of CH_2CH_2], 113.2 [d, $^1J_{C-H}$ = 162, 1C on aromatic ring], 114.8 [s, 1C on aromatic ring], 116.6 [d, $^1J_{C-H}$ = 159, 1C on aromatic ring], 124.4 [d, $^1J_{C-H}$ = 155, 1C on aromatic ring], 125.7 [d, $^1J_{C-H}$ = 159, 1C on aromatic ring], 128.4 [d, $^1J_{C-H}$ = 159, 1C on aromatic ring], 133.9 [d, $^1J_{C-H}$ = 156, 1C on aromatic ring], 137.5 [d, $^1J_{C-H}$ = 155, 1C on aromatic ring], 144.2 [s, 1C on aromatic ring], 145.1 [s, 1C on aromatic ring], 157.8 [s, 1C on aromatic ring], 170.3 [d, $^1J_{C-H}$ = 159, 1C of N=CH]. IR Data (KBr pellet, cm^{-1}): 2961 (s), 2927 (w), 2866 (m), 1616 (s), 1532 (m), 1470 (s), 1440 (s), 1408 (w), 1381 (w), 1359 (w), 1335 (m), 1244 (w), 1197 (m), 1162 (m), 1036 (w), 793 (w), 757 (m), 748 (w).

3.9. Synthesis of $\{[\mathrm{Al}^{\mathrm{Ar,NPr^i_2}}]\mathrm{Zn}(\mu\text{-}OH)\}_2$

Crystals of $\{[\mathrm{Al}^{\mathrm{Ar,NPr^i_2}}]\mathrm{Zn}(\mu\text{-}OH)\}_2$ were obtained from a benzene solution *via* reaction of $[\mathrm{Al}^{\mathrm{Ar,NPr^i_2}}]$ZnMe with adventitious water. ^{1}H NMR (C_6D_6): −0.06 [s, 1H of OH (assignment tentative)], 0.88 [d, $^3J_{H-H}$ = 7, 12H of $N[CH(CH_3)_2]_2$], 1.16 [d, $^3J_{H-H}$ = 7, 6H of $C_6H_3[CH(CH_3)_2]_2$], 1.33 [d, $^3J_{H-H}$ = 7, 6H of $C_6H_3[CH(CH_3)_2]_2$], 2.18 [m, 2H of CH_2CH_2], 2.74 [septet, $^3J_{H-H}$ = 7, 2H of $CH(CH_3)_2$], 2.87 [m, 2H of CH_2CH_2], 3.49 [septet, $^3J_{H-H}$ = 7, 2H of $CH(CH_3)_2$], 6.35 [m, 2H on aromatic ring], 6.8–7.3 [m, 5H on aromatic ring], 7.75 [s, 1H of $CH{=}NCH_2CH_2$].

3.10. Synthesis of $[\mathrm{Al}^{\mathrm{Ar,NPr^i_2}}]ZnC_6F_5$

A solution of $[\mathrm{Al}^{\mathrm{Ar,NPr^i_2}}]$ZnMe in C_6D_6 (0.6 mL) was treated with $B(C_6F_5)_3$ (10 mg, 0.020 mmol). The reaction was monitored by ^{1}H NMR spectroscopy which demonstrated that $[\mathrm{Al}^{\mathrm{Ar,NPr^i_2}}]ZnC_6F_5$ was formed over a period of 1 day at 60 °C. ^{1}H NMR (C_6D_6): 0.74 [d, $^3J_{H-H}$ = 7, 12H of $N[CH(CH_3)_2]_2$], 1.10 [d, $^3J_{H-H}$ = 7, 6H of $C_6H_3[CH(CH_3)_2]_2$], 1.27 [d, $^3J_{H-H}$ = 7, 6H of $C_6H_3[CH(CH_3)_2]_2$], 2.38 [m, 2H of CH_2CH_2], 2.62 [septet, $^3J_{H-H}$ = 7, 2H of $CH(CH_3)_2$], 3.19 [m, 2H of CH_2CH_2], 3.46 [septet, $^3J_{H-H}$ = 7, 2H of $CH(CH_3)_2$], 6.40-6.53 [m, 2H on aromatic ring], 6.88 [m, 1H on aromatic ring], 7.03 [m, 1H on aromatic ring], 7.22 [m, 3H on aromatic ring], 7.80 [s, 1H of $CH{=}NCH_2CH_2$].

3.11. Synthesis of $[\mathrm{BDI}^{\mathrm{Ar}}]ZnC_6F_5$

A mixture of $[\mathrm{BDI}^{\mathrm{Ar}}]$ZnEt (20 mg, 0.039 mmol) and $B(C_6F_5)_3$ (10 mg, 0.020 mmol) was dissolved in benzene (*ca.* 0.5 mL) and heated at 80 °C for 1 h. After this period, the volatile components were removed by lyophilization to give a white solid residue. The residue was extracted into pentane (ca. 0.5 mL) and colorless crystals of composition $[\mathrm{BDI}^{\mathrm{Ar}}]ZnC_6F_5\cdot 0.25(C_5H_{12})$ were obtained by slow evaporation at −15 °C (15 mg, 59%). Anal. Calc. for $C_{36.25}H_{44}F_5N_2Zn$: C, 65.2; H, 6.6; N, 4.2. Found: C, 65.6; H, 7.4; N, 4.6%. ^{1}H NMR (C_6D_6): 1.11 [d, $^3J_{H-H}$ = 7, 12H of $CH(CH_3)_2$], 1.26 [d, $^3J_{H-H}$ = 7, 12H of $CH(CH_3)_2$], 1.67 [s, 6 H of $CHC(NAr)CH_3$], 3.23 [septet, $^3J_{H-H}$ = 7, 4H of $CH(CH_3)_2$], 5.06 [s, 1H of $CHC(NAr)CH_3$], 7.02 [s, 6H of $Pr^i_2C_6H_3$].

3.12. Synthesis of $[\mathrm{BDI}^{\mathrm{Ar}}]CdC_6F_5$

A mixture of $[\mathrm{BDI}^{\mathrm{Ar}}]$CdMe (25 mg, 0.046 mmol) and $B(C_6F_5)_3$ (11 mg, 0.021 mmol) was dissolved in benzene (ca. 0.5 mL) and allowed to stand at room temperature for 2 h. After this period, the volatile components were removed by lyophilization to give a white solid residue. The residue was extracted into pentane (0.5 mL) and colorless crystals of $[\mathrm{BDI}^{\mathrm{Ar}}]CdC_6F_5$ were obtained by slow evaporation at −15 °C (ca. 5 mg, 16%). Anal. Calc. for $C_{35}H_{41}CdF_5N_2$: C, 60.3; H, 5.9; N, 4.0. Found: C, 61.8; H, 7.7; N, 4.3%. ^{1}H NMR (C_6D_6): 1.15 [d, $^3J_{H-H}$ = 7, 12H of $CH(CH_3)_2$], 1.24 [d, $^3J_{H-H}$ = 7, 12H of $CH(CH_3)_2$], 1.68 [s, 6 H of $CHC(NAr)CH_3$], 3.30 [septet, $^3J_{H-H}$ = 7, 4H of $CH(CH_3)_2$], 4.94 [s, 1H of $CHC(NAr)CH_3$], 7.05 [s, 6H of $Pr^i_2C_6H_3$].

3.13. Synthesis of $[\mathrm{Al}^{\mathrm{Ar,NPr^i_2}}]_2$Zn

A solution of $[\mathrm{Al}^{\mathrm{Ar,NPr^i_2}}]$Li (1.2 g, 2.9 mmol) in THF (20 mL) was added to a solution of $ZnCl_2$ (0.28 g, 2.1 mmol) in THF (30 mL). The mixture was stirred at room temperature for 1 day and after this period the volatile components were removed in vacuo. The residue was extracted with pentane (2 × 40 mL). The pentane extract was concentrated to ca. 20 mL and placed at −5 °C, thereby depositing yellow crystals of $[\mathrm{Al}^{\mathrm{Ar,NPr^i_2}}]_2\mathrm{Zn}\cdot C_5H_{12}$ which were isolated by filtration, washed with cold pentane (−78 °C, 10 mL) and dried in vacuo (0.29 g, 23%). Anal. Calc. for $C_{54}H_{80}N_6Zn$: C, 73.8; H, 9.2; N, 9.6. Found: C, 74.0; H, 9.5; N, 9.3%. ^{1}H NMR (C_6D_6): 0.68 [d, $^3J_{H-H}$ = 7, 6H of $C_6H_3[CH(CH_3)_2]_2$], 0.83[d, $^3J_{H-H}$ = 7, 12H of $N[CH(CH_3)_2]_2$], 0.90 [d, $^3J_{H-H}$ = 7, 12H of $N[CH(CH_3)_2]_2$], 1.03 [d, $^3J_{H-H}$ = 7, 6H of $C_6H_3[CH(CH_3)_2]_2$], 1.22 [d, $^3J_{H-H}$ = 7, 6H of $C_6H_3[CH(CH_3)_2]_2$], 1.34 [d, $^3J_{H-H}$ = 7, 6H of $C_6H_3[CH(CH_3)_2]_2$], 2.60 [m, 2H of CH_2CH_2], 2.72 [m, 2H of CH_2CH_2],2.78 [septet, $^3J_{H-H}$ = 7, 4H of $CH(CH_3)_2$], 3.10 [m, 2H of CH_2CH_2], 3.30 [septet, $^3J_{H-H}$ = 7, 2H of $CH(CH_3)_2$], 3.53 [septet, $^3J_{H-H}$ = 7, 2H of $CH(CH_3)_2$], 3.85 [m, 2H of CH_2CH_2], 6.28 [m, 4H on aromatic ring], 6.72 [m, 2H on aromatic ring], 6.90 [m, 2H on aromatic ring], 7.04–7.27 [m, 6H on aromatic ring], 7.98 [s, 2H of $CH{=}NCH_2CH_2$].

4. Supplementary data

CCDC 762879–762890 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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