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Low-Coordinate Monomeric Zinc Hydride Complexes with Encapsulating Dipyrromethene Ligands and Reactivity with $B(C_6F_5)_3$

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Dedicated to Professor Manfred Scheer on the Occasion of his 65th Birthday

Abstract. The dipyrromethene (DPM) ligand is the key to isolation of monomeric Zn hydride complexes with tricoordinate zinc centers. A range of ^RDPM ligands with various substituents in the pole position (1,9-positions) were prepared: R = tBu, adamantyl (Ad), mesityl (Mes), 2,6-diisopropylphenyl (DIPP), 2,4,6-triphenylphenyl (Mes*), or 9-anthracenyl (Anth). Reaction of the ligands with Et₂Zn gave a series of (^RDPM)ZnEt complexes, which were converted with I₂ to the corresponding (^RDPM)ZnI compounds. The latter reacted by salt metathesis with KN(*i*Pr)HBH₃ to the series of Zn hydride complexes (^RDPM)

Introduction

In contrast to the high reactivity and rich reduction chemistry of hydrides from the s- and p-block, the development of ZnH₂ chemistry always lagged behind. Although already prepared in 1951 by Schlesinger,^[1] its poor solubility in organic solvents and especially its very low thermal stability precluded major applications. A convenient route to ZnH₂ has been reported by van der Kerk.^[2] who converted Et₂Zn with LiAlH₄ to obtain a white powder that at room temperature already turned grey on account of decomposition into its elements. The latter problem is clearly related to the more noble character of Zn which, combined with the low stability of hydride (H_2 + $2e^- \rightleftharpoons 2 \text{ H}^- E^0 = -2.23 \text{ V}$,^[3] is easily reduced. The recognition that heteroleptic RZnH complexes are much more stable initiated great interest in this compound class.^[4,5] Especially bulky R groups were found to preserve Zn hydride complexes by blocking redox decomposition (e.g. I).^[6] Also use of multidentate ligands led to isolation of a large variety of stable Zn hydride complexes among which the scorpionate complex II.^[7] Although the solid-state structure of ZnH_2 is currently still unknown, Okuda and co-workers recently demonstrated that decomposition of this labile metal hydride can be pre-

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ZnH. For ligands with the larger Mes* and Anth substituents, (^RDPM) ZnEt was converted to (^RDPM)ZnOSiPh₃, which after reaction with PhSiH₃ gave the hydrides. While Zn hydride complexes with R = *t*Bu or Ad are dimeric, all complexes with aryl-substituents are monomeric. The aryl groups span a cavity around the metal, blocking dimerization and causing a high-field shift of the ¹H NMR signals due to the ASIS effect. Attempted abstraction of the hydride with B(C₆F₅)₃ led to cleavage of the B-C₆F₅ bond.

vented by addition of bulky, strongly coordinating, NHC ligands which led to structural characterization of a sub unit of $(ZnH_2)_{\infty}$ (III).^[8]

We and others contributed to Zn hydride chemistry by introducing its first β -diketiminate complexes which especially for bulky ligands led to unusual low-coordinate Zn hydride complexes (**IV**).^[9] In solution, however, even complex **IV** shows strong tendency to aggregate: dissolved in toluene it is in a monomer-dimer equilibrium. We recently found that Zn hydride complexes seem to become less stable with increasing cluster size: the coupled β -diketiminate Zn hydride complex **V** decomposes at 80 °C, i.e. at a significantly lower temperature than **IV** (150 °C).^[10] For stability it is crucial that short H•••H distances and therefore H–Zn–H bridges are avoided. This explains the generally high stability of monomeric Zn hydride complexes.

Monomeric zinc hydrides or complexes with terminal Zn– H functionalities are of interest as model systems for zinc enzymes,^[7,11] or as precursors in material chemistry.^[12] Welldefined Zn hydride complexes also found their way in the field of catalysis.^[13] Being generally more covalent than early main group metal hydride catalysts, their mild reactivity has clear advantages for functional group tolerance. Several groups have found that cationic Zn hydride complexes show a very versatile reactivity in catalysis.^[14] The high reactivity of cationic species may be explained by an increased Lewis acidity of the metal center.

It is for this reason that we became interested in low-coordinate Zn hydride complexes, in which the metal center should be considerably more Lewis-acidic than in complexes with higher coordination numbers. We recently introduced a "true" tricoordinate Zn hydride complex (VI) which, in contrast to the β -diketiminate complex IV, is also in solution mono-

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meric.^[15] The key to control mononuclearity is the dipyrromethene ligand which we abbreviate in here as ^{DIPP}DPM (DIPP = 2, 6-diisopropylphenyl). Although this ligand has close similarity to β -diketiminate ligands, there are two main differences. First of all, the bulky aryl substituents in the pole positions (1,9-positions) are arranged differently, resulting in a defined cavity for the metal center. We could show in a previous publication that even highly labile heteroleptic Ba complexes can be stabilized effectively by the dipyrromethene ligand.^[16] Secondly, electron density calculations suggest that the central backbone carbon in dipyrromethene is much less negatively charged compared to that in β -diketiminate ligands.^[15] Therefore, the DPM ligands may be more inert and more appropriate spectator ligands.

We introduce here a comprehensive series of (^RDPM)ZnH complexes and evaluate the influence of the ligand substituent R on complex nuclearity and the metal coordination number. In order to boost the reactivity of these complexes, we also discuss attempts to isolate cationic complexes by abstraction of the hydride using the strong Lewis acid $B(C_6F_5)_3$.



Results and Discussion

Syntheses

All dipyrromethene ligands were prepared by the general route developed by *Betley* and co-workers (Scheme 1) and are strongly colored compounds. The *t*Bu and adamantyl (Ad) substituted ligands are yellow-brown powders.^[17] The mesityl (Mes)^[18] and 2,4,6-triphenyl-phenyl (Mes*)^[17] substituted ligands are bright yellow and red, respectively. Dipyrromethene

ligands with DIPP^[15] and 9-anthracenyl^[16] substituents have been introduced by us and are orange and red, respectively.

For the synthesis of Zn hydride complexes we chose a pathway previously introduced for the preparation of complex **IV** (Scheme 1).^[9b] The first step is the conversion of the ligands to (^RDPM)ZnEt (**2-R**) complexes which can be simply achieved in quantitative yields by reaction of the ligand with Et₂Zn in benzene at 60 °C but for increased purity the complexes have been recrystallized from toluene at -20 °C. The latter alkylzinc complexes react smoothly with I₂ to give a series of (^RDPM)ZnI (**3-R**) complexes in quantitative yields. Complexes were recrystallized from yields varying from 48% to 95% (lower recrystallization yields are generally due to high solubility). Starting from the iodide complexes, the Zn hydrides (**4-R**) are accessible by salt metathesis with KN(*i*Pr) HBH₃. For this particular step the yields are generally lower.

We presume that the intermediate Zn amidoborane complexes, (RDPM)ZnN(iPr)HBH3, are highly labile and after βhydride elimination give (RDPM)ZnH and [N(iPr)HBH2]n. Due to the low solubility of (AnthDPM)ZnI and (Mes*DPM) ZnI, the Zn hydride complexes of these ligands were not easily accessible via the salt metathesis route. In these cases the ethvlzinc intermediates were first reacted with Ph₃SiOH to give (^RDPM)ZnOSiPh₃ (**5-R**), which reacted in a second step with PhSiH₃ to give the hydrides. This route has previously been shown successful by the groups of Williams and Okuda.^[19] Like the related (^RDPM)BF₂ complexes (BODIPY),^[20] all Zn hydride complexes are highly colored and fluorescent crystalline products. While alkyl-, Mes- and DIPP-substituted Zn hydride complexes are orange the Mes* and Anth-substituted complexes are red. The melting/decomposition points of the Zn hydride complexes are all relatively high and vary from 187-281 °C. The highest stabilities have been found for the Mes* and Anth-substituted Zn hydride complexes, i.e. the complexes with the most shielded Zn-H units.

Crystal Structures

The Zn hydride complexes (**4-R**) as well as the Zn ethyl (**2-R**) and Zn iodide (**3-R**) intermediates along the path have been characterized by single-crystal X-ray diffraction (Figure 1, Figure 2, and Table 1). Whereas all the Zn ethyl complexes are monomeric, some of the iodides and hydrides form loosely bound dimers in the solid state. In these dimers, the H⁻ or I⁻ anions bridge asymmetrically: bonds within the N₂Zn plane are considerably shorter than those perpendicular on this plane.

The tendency to form dimers increases from Zn ethyl (never dimer) > iodide (dimer for R = tBu) > hydride (dimer for R = tBu and Ad). All complexes with aryl-substituted ligands are monomeric, whereas ligands with bulky alkyl substituents tend to form dimeric complexes. This is due to the fact that *tBu* or adamantyl substituents restrict the space for metal coordination. Consequently, for the alkyl-substituted DPM ligands, the Zn atom is always situated 0.8–1.0 Å out of the NCCCN plane. Since aryl substituents extend mainly in two dimensions, they are less bulky and allow for binding of the Zn metal in or close to the NCCCN plane, thus providing substantially better

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Scheme 1. Syntheses of dipyrromethene ligands (1-R) and the Zn hydride complexes (4-R). Yields relate to crystallized products.



Figure 1. Crystal structures of dipyrromethene Zn hydride complexes; for clarity only the hydride H is shown and the mesityl group in the backbone has been reduced to its C_{ipso} . (a) [(^{HBu}DPM)ZnH]₂, (b) [(^{Ad}DPM)ZnH]₂, (c) (^{Mes}DPM)ZnH, (d) (^{DIPP}DPM)ZnH, ^[15] (e) ($^{Mes*}DPM$)ZnH, and (f) (^{Anth}DPM)ZnH.

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Figure 2. Crystal structures of the dipyrromethene Zn iodide complexes: (a) (^{Ad}DPM)ZnI (3-Ad) and (b) (^{DIPP}DPM)ZnI (3-DIPP).^[15]

shielding of the metal. This is nicely illustrated by comparison of the structures of (^{Ad}DPM)ZnI and (^{DIPP}DPM)ZnI (Figure 2).

For the adamantyl-substituted ligand the Zn and I centers strongly bend out-of-plane due to space limitation. Very short C–H···Zn agostic interactions (striped lines in Figure 1a; 2.382 and 2.435 Å) illustrate the enormous steric pressure in (^{Ad}DPM)ZnI. Similar out-of-plane bonding and short agostic interactions are found in the dimeric complexes. In contrast, the ligand with DIPP-substituents enables in-plane bonding of the Zn–I unit (Figure 2b). The DIPP-plane makes a nearly perpendicular angle of 87.26(7)° with the NC₄ ring. Both DIPP-substituents form a cavity around the metal center which fits the Zn-I unit but there is no Zn–aryl contact: the shortest Zn···C distances measure 3.325(2)–3.419(2) Å. As we mentioned previously,^[15] it should also be noted that the Zn–N

distances to DPM ligands are in general longer than those to comparable BDI ligands. This has been related to the somewhat lower negative charge on the N atoms in DMP ligands compared to those in BDI.

It was anticipated that the extended 2,4,6-triphenyl-phenyl substituents (Mes^{*}) would span a large cavity for the metal center. However, the crystal structures with the ^{Mes*}DPM ligand all show cavities that to a certain extent collapsed. The NC₄ rings and the attached aryl rings in (^{Mes*}DPM)ZnH (Figure 1e) are not perpendicular to each other but angles of $60.8(1)^{\circ}$ and $69.4(1)^{\circ}$ are found. This is likely attributed to C– H··· π interactions between the Mes* substituents.

Within the series of monomeric (^RDPM)ZnEt complexes, there is hardly any influence of the substituent R on the Zn coordination arrangement. The Zn–N bonds vary from 1.977(1) Å to 2.000(1) Å, the Zn–C distances are in the narrow range of 1.953(2)–1.974(3) Å and the N–Zn–N' angles have values between 93.21(7)° and 94.54(6)°. Similar observations are made within the series of monomeric (^RDPM)ZnI and (^RDPM)ZnH complexes. This means that the substitution pattern is irrelevant to Zn coordination but at most changes the size and form of the ligand's cavity and determines the aggregation state.

Data in Table 1 also clearly show that the ligand bite angles, N–Zn–N', in Zn iodide complexes are somewhat larger than those in the Zn ethyl or hydride complexes. These larger bite angles are directly related to the shorter Zn–N bonds in the iodide series. The latter is due to the fact that the iodide ligand is much softer and weakly coordinating than ethyl or hydride ligands, thus strengthening the Zn–N bonds and increasing the bite angles.

Solution Studies

All Zn hydride complexes are soluble in C_6D_6 except for (^{Anth}DPM)ZnH•(THF), which was dissolved in [D₈]THF. Diffusion-Ordered-Spectroscopy (DOSY) shows that most complexes are monomeric in benzene (Table S19, Supporting Information). This includes the loosely bound dimer [(^{Ad}DPM) ZnH]₂ but not [(^{Bu}DPM)ZnH]₂ which is in a dimer-monomer equilibrium. Not surprisingly, complex (^{Anth}DPM)ZnH•(THF) in [D₈]THF was also found to be monomeric.

The Zn–Et and Zn–H chemical shifts deserve special attention. The ¹H NMR shifts for the Et groups lie in a very broad range (Table 1). The Zn–CH₂ chemical shifts vary from +1.11 to -1.95 ppm while the CH₃ groups are scattered between +1.66 to -1.01 ppm. The same holds for the Zn-H signals which can be found in the range of +5.75 to +2.57 ppm. The large variance in these values can be related to the ASIS effect (Aromatic-Solvent-Induced-Shift)^[21] in which nuclei positioned above an aromatic ring experience a strong upfield shift. Consequently, the Zn–H moieties in complexes with alkyl-substituted ligands do not experience any ASIS effect and feature the highest chemical shifts (5.45–5.75 ppm). With increasing encapsulation, the hydride resonances shift to lower ppm values. It is noteworthy that the Zn–H shift for (^{DIPP}DPM)ZnH (δ =3.78 ppm)^{I[15]} is substantially lower than that for the β - meine Chemie

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(^R DPM)ZnEt	Aggregation	Zn–N	Zn-Et	N–Zn–N'	NCCCN/Zn ^{a)}	δ Et /ppm
R = tBu	monomer	1.990(2)	1.974(3)	93.21(7)	0.839(1)	1.60 / 0.97
R = Ad	monomer	1.993(1)	1.969(3)	93.86(5)	0.869(1)	1.66 / 1.11
R = Mes	monomer	1.991(2)	1.973(2)	94.07(6)	0.219(1)	0.64 / -0.20
R = DIPP [15]	monomer	1.989(2)	1.965(2)	93.40(6)	0.033(1)	0.46 / -0.31
$R = Mes^*$	monomer	1.977(1)	1.953(2)	94.21(5)	0.003(1)	0.86 / 0.16
R = Anth	monomer	2.000(2)	1.965(2)	94.54(6)	0.040(1)	-1.01 /
						-1.95
(^R DPM)ZnI	Aggregation	Zn–N	Zn–I	N–Zn–N'	NCCCN/Zn ^{a)}	·
R = tBu	dimer	1.983(2)	2.5928(4) /	95.42(8)	0.883(1)	
			2.8483(4) b)			
R = Ad	monomer	1.939(2)	2.4655(5)	96.22(8)	0.799(1)	
R = Mes	monomer	1.940(2)	2.4478(5)	98.09(7)	0.027(1)	
R = DIPP [15]	monomer	1.945(2)	2.4428(4)	98.37(8)	0.151(1)	
$R = Mes^*$	monomer	1.941(2)	2.4655(6)	97.46(9)	0.010(1)	
(^R DPM)ZnH	Aggregation	Zn–N	Zn-Et	N–Zn–N'	NCCCN/Zn ^{a)}	δ H /ppm
R = tBu	dimer	1.976(2)	1.50(4) / 2.00(4) ^{b)}	93.28(9)	0.980(1)	5.45
R = Ad	dimer	1.973(2)	1.46(3) / 1.99(3) ^{b)}	96.41(6)	0.889(1)	5.73
R = Mes	monomer	1.973(2)	1.51(3)	95.1(1)	0.013(1)	3.96
R = DIPP[15]	monomer	1.973(1)	1.49(3)	93.68(5)	0.101(1)	3.78
$R = Mes^*$	monomer	1.970(2)	1.43(3)	92.33(7)	0.155(1)	4.03
$R = Anth^{c}$	monomer	2.025(2)	1.55(3)	93.27(6)	0.046(1)	2.57

Table 1. Selected geometric parameter for the crystal structures (average bond lengths in Å and angles in °) and ¹H NMR chemical shifts (ppm).

a) Defined as the distance between the least-squares-plane NCCCN and the Zn atom in Å. b) Asymmetric bridging. The shorter bond length lies in the N₂Zn plane while the longer bond length is perpendicular to this plane. c) The arrangement for the THF adduct (^{Anth}DPM)ZnH•(THF) is given. The Zn–O distance is 2.127(2) Å.

diketiminate complex (^{DIPP}BDI)ZnH (δ = 4.39 ppm).^{][9b]} This can be attributed to the more pronounced encapsulation of the Zn–H unit in the diypyrromethene ligand.

As we reported earlier, the angles between the DIPP-planes in ^{DIPP}DPM [46.7(1)°] and those in ^{DIPP}BDI [126.4(1)°] are quite different.^[15] The highest upfield shift, i.e. largest ASIS effect, was found for the anthracenyl-substituted Zn hydride complex: (^{Anth}DPM)ZnH•(THF). The ¹H NMR chemical shifts for the Zn-Et groups follow the same order and also (^{Anth}DPM) ZnEt features unusually low chemical shifts for the Et group.

Attempted Conversion to Cationic Complexes

Cationic Zn hydride complexes show increased activity in catalysis.^[4,14] There is also growing awareness that Zn hydride complexes in combination with either $BPh_3^{[14c]}$ or $B(C_6F_5)_3^{[22]}$ generate efficient catalysts for CO₂ hydrosilylation.

In order to isolate cationic Zn complexes, (^{DIPP}DPM)ZnH in C₆D₆ was reacted with B(C₆F₅)₃ at room temperature. Within minutes full conversion into two new species in a 1/1 ratio was observed (Figure S37) but surprisingly only 0.5 equivalent of B(C₆F₅)₃ had been consumed. Both products dissolve well in hexane and crystallization at low temperature gave a few crystals which were identified as (^{DIPP}DPM)ZnC₆F₅ (Figure 3a). Although we did not manage to obtain good quality crystals of the second species, a similar experiment with (^{Mes}DPM)ZnH gave after reaction with B(C₆F₅)₃ crystals of (^{Mes}DPM)Zn[H₂B(C₆F₅)₂] (Figure 3b). Although both species could not be obtained pure, the stoichiometry of the reaction combined with NMR analysis of the raw reaction mixtures (Figures S36 and S37, Supporting Information) and identification of some

of the reaction products by X-ray diffraction led us to propose the reactivity as shown in Scheme 2.

Instead of hydride abstraction, a cleavage of the B–C₆F₅ bond by Zn-H occurred. Reaction of a second equivalent of the Zn hydride complex with the Piers borane HB(C₆F₅)₂^[23] gave the salt with H₂B(C₆F₅)₂⁻ anion. Cleavage of the B–C bond in B(C₆F₅)₃ is relatively rare and generally observed for species with highly Lewis acidic metal centers (e.g. Ti⁴⁺ or Al³⁺).^[24] We presume that the low coordination number of Zn in the Zn hydride complexes presented here makes the Zn centers also unusually Lewis acidic, explaining why attempted isolation of cationic dipyrromethene Zn complexes resulted in B–C₆F₅ bond cleavage.

Conclusions

Monomeric low-coordinate Zn hydride complexes are accessible by use of dipyrromethene ligands. It is essential that the substituents in the pole positions are aryl groups. Alkyl substituents restrict the space available for metal coordination, which results in a shift of the metal out of the NCCCN plane. Consequently, Zn hydride complexes with alkyl-substituted dipyrromethene ligands crystallize as dimeric entities with four-coordinate Zn centers. These dimers are, however, loosely bound. This is indicated by asymmetric bridging of the hydride ligands with two short and two long Zn–H bonds of circa 1.5 and 2.0 Å, respectively, and is also in agreement with monomer-dimer equilibria in solution.

The Zn hydride complexes with aryl-substituted dipyrromethene ligands are truly monomeric and feature tricoordinate Zn centers, in the solid state as well as in solution. The aryl und allgemeine Chemie

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Figure 3. (a) Crystal structure of (^{DIPP}DPM)ZnC₆F₅. Selected bond lengths /Å: Zn–N1 1.946(2), Zn–N2 1.956(2), Zn–C1 1.956(2). (b) Crystal structure of (^{Mes}DPM)Zn[H₂B(C₆F₅)₂]. Selected bond lengths / Å: Zn–N1 1.929(2), Zn–N2 1.938(2), Zn•··B 2.221(2), Zn-H1 1.84(2), Zn-H2 1.77(2).



Scheme 2. Reaction of (^RDPM)ZnH complexes (R = DIPP or Mes) with 0.5 equivalent of B(C₆F₅) gives a 1/1 mixture of (^RDPM)ZnC₆F₅ and (^RDPM)Zn[H₂B(C₆F₅)₂].

substituents span a cavity around the Zn metal and successfully block dimerization. This is also evident from the ¹H NMR chemical shifts of the Zn-Et and Zn-H groups which are unusually shifted to higher field on account of the ASIS effect. Attempted synthesis of cationic Zn complexes by abstraction of the hydride ligand with $B(C_6F_5)_3$ led to an unexpected cleavage of the B- C_6F_5 bond and formation of (DPM)Zn C_6F_5 and (DPM)Zn[H₂B($C_6F_5)_2$] complexes. This reactivity is likely related to the high Lewis acidity of tricoordinate Zn centers.

Experimental Section

General Experimental Procedures: All experiments were carried out in dry glassware in a N2 atmosphere using standard Schlenk techniques and freshly dried and degassed solvents (all solvents were dried with a column except for THF, which was dried with Na and redistilled). Starting materials and research chemicals were obtained from commercial suppliers, where appropriate and used without further purification. Diethylzinc,^[25] $K[(iPr)NHBH_3]$,^[26] $t^{Bu}DPM-H$,^[17] AdDPM-H,^[17] MesDPM-H,^[18] DIPPDPM-H,^[15] Mes*DPM-H,^[17] AnthDPM-H^[16] and (DIPPDPM)ZnH^[15] were synthesized following literature known procedures. NMR spectra were measured on Bruker Avance III HD 400 MHz and Bruker Avance III HD 600 MHz spectrometers. Chemical shifts (δ) are given in ppm (parts per million) values, coupling constants (J) in Hz (Hertz). For describing signal multiplicities common abbreviations were used: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and br (broad). Spectra were referenced due to solvent residual signal. Elemental analysis was performed with a Hekatech Eurovector EA3000 analyzer. All crystal structures have been measured on a SuperNova (Agilent) diffractometer with dual Cu and Mo microfocus sources and an Atlas S2 detector.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-1944426 for (1BuDPM)ZnEt, CCDC-1944427 for (^{tBu}DPM)ZnI, CCDC-1944428 for (^{tBu}DPM)ZnH, CCDC-1944429 for (AdDPM)ZnEt, CCDC-1944430 for (AdDPM)ZnI, CCDC-1944431 for (AdDPM)ZnH, CCDC-1944432 for (MesDPM)ZnEt, CCDC-1944433 for (MesDPM)ZnI, CCDC-1944434 for (MesDPM)ZnH, CCDC-1944435 for (Mes*DPM)ZnEt, CCDC-1944436 for (Mes*DPM)ZnI, CCDC-1944437 for (Mes*DPM)ZnH, CCDC-1944438 for (Mes*DPM) ZnOSiPh₂, CCDC-1944439 for (AnthDPM)ZnEt, CCDC-1944440 for (AnthDPM)ZnEt·(THF), CCDC-1944441 for (AnthDPM)ZnH·(THF), CCDC-1944442 for (DIPPDPM)ZnC₆F₅, and CCDC-1944443 for (MesDPM)Zn[H2B(C6F5)2] (Fax: +44-1223-336-033; E-Mail: deposit-@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk)

Synthesis of ("BuDPM)ZnEt (2-tBu): In a 25 mL Schlenk flask ^{tBu}DPM-H (712 mg, 1.900 mmol) was dissolved in benzene (10 mL). Neat Et₂Zn (234 µL, 2.279 mmol, 1.2 equiv.) was added to the stirred yellow solution resulting in a color change to orange. The reaction mixture was heated to 60 °C overnight and the solvent was removed in vacuo yielding an orange powder in quantitative yield. Recrystallization from *n*-hexane at -20 °C yielded orange crystalline blocks. Yield: 782 mg (1.677 mmol; 88%). ¹H NMR (600 MHz, C₆D₆, 25 °C): $\delta = 6.75$ (s, 2 H, Mes-aryl-CH), 6.68 (d, J = 4.1 Hz, 2 H, pyrrole-CH), 6.35 (d, J = 4.1 Hz, 2 H, pyrrole-CH), 2.18 [s, 3 H, $C_6H_2(CH_3)_3$], 2.12 [s, 6 H, $C_6H_2(CH_3)_3$], 1.60 (t, J = 8.1 Hz, 3 H, $ZnCH_2CH_3$), 1.41 (s, 18 H, *t*Bu-CH₃), 0.97 (q, J = 8.1 Hz, 2 H, ZnCH₂CH₃) ppm. ¹³C{¹H} NMR (151 MHz, C₆D₆, 25 °C): δ = 173.0 $(C_{\text{arom}}), 145.5 \ (C_{\text{arom}}), 139.1 \ (C_{\text{arom}}), 137.2 \ (C_{\text{arom}}), 137.0 \ (C_{\text{arom}}),$ 136.1 (C_{arom}), 132.4 (C_{arom}), 128.1 (C_{arom}), 115.5 (C_{arom}), 34.1 (C_{aliph}), 30.8 (Caliph), 21.5 (Caliph), 20.1 (Caliph), 12.3 (Caliph), 6.2 (Caliph) ppm. C₂₈H₃₈N₂Zn (466.23 g·mol⁻¹): calcd. C 71.86, H 8.18, N 5.99; found: C 71.44, H 8.14, N 5.53%.

Synthesis of (tBuDPM)ZnI (3-tBu): In a 50 mL Schlenk flask (1BuDPM)ZnEt (413 mg, 0.886 mmol) was dissolved in benzene (15 mL). A solution of elemental iodine (247 mg, 0.975 mmol, 1.1 equiv.) in *n*-heptane (10 mL) was added at room temperature. The reaction mixture was stirred at room temperature overnight and the solvent and excess of iodine were removed in vacuo yielding an orange powder in quantitative yield. Trituration with pentane $(2 \times 6 \text{ mL})$ and recrystallization in a toluene/n-hexane mixture at -20 °C yielded crystalline orange blocks. Yield: 380 mg (0.674 mmol; 76%). ¹H NMR (600 MHz, C₆D₆, 25 °C): δ = 6.72 (s, 2 H, Mes-aryl-CH), 6.62 (d, J = 4.0 Hz, 2 H, pyrrole-CH), 6.28 (br., 2 H, pyrrole-CH), 2.16 [s, 3 H, C₆H₂(CH₃)₃], 2.03 [s, 6 H, C₆H₂(CH₃)₃], 1.48 (s, 18 H, tBu-CH₃) ppm. ¹³C{¹H} NMR (151 MHz, C₆D₆, 25 °C): δ = 173.9 (C_{arom}), 145.5 (C_{arom}), 139.0 (C_{arom}), 137.6 (C_{arom}), 136.9 (C_{arom}), 135.4 (C_{arom}), 133.6 (C_{arom}), 128.1 (C_{arom}), 116.3 (C_{arom}), 34.3 (C_{aliph}), 31.1 (C_{aliph}), 21.1 (C_{aliph}), 19.9 (C_{aliph}) ppm. $C_{26}H_{33}N_2ZnI$ (564.10 g·mol⁻¹): calcd. C 55.19, H 5.88, N 4.95; found: C 55.74, H 5.53, N 4.82%.

Synthesis of ("BuDPM)ZnH (4-tBu): In a 50 mL Schlenk flask (^{tBu}DPM)ZnI (380 mg, 0.674 mmol) was dissolved in benzene (20 mL) and K[(iPr)NHBH₃] (112 mg, 1.009 mmol, 1.5 equiv.) was added. The milky orange suspension was stirred at room temperature overnight and filtered through a syringe filter to give an orange solution. Removal of solvent in vacuo gave the crude product as orange solid. Recrystallization in a concentrated pentane solution at -20 °C yielded crystalline orange blocks. Yield: 213 mg (0.486 mmol; 72%). M.p.: 187 °C – 192 °C (dec.) ¹H NMR (600 MHz, C₆D₆, 25 °C): δ = 6.78 (s, 2 H, Mes-aryl-CH), 6.65 (d, J = 4.1 Hz, 2 H, pyrrole-CH), 6.34 (d, J = 4.1 Hz, 2 H, pyrrole-CH), 5.45 (s, 1 H, ZnH), 2.20 [s, 3 H, C₆H₂(CH₃)₃], 2.16 [s, 6 H, C₆H₂(CH₃)₃], 1.48 (s, 18 H, tBu-CH₃) ppm. ¹³C{¹H} NMR (151 MHz, C₆D₆, 25 °C): δ = 174.0 (C_{arom}), 145.3 (Carom), 139.7 (Carom), 137.3 (Carom), 137.1 (Carom), 136.3 (Carom), 132.8 (Carom), 128.2 (Carom), 116.0 (Carom), 34.8 (Caliph), 31.5 (Caliph), 21.2 (C_{aliph}), 20.2 (C_{aliph}) ppm. $C_{26}H_{34}N_2Zn$ (438.20 g·mol⁻¹): calcd. C 70.98, H 7.79, N 6.37; found: C 71.49, H 7.85, N 6.40%.

Synthesis of (AdDPM)ZnEt (2-Ad): In a 50 mL Schlenk flask ^{Ad}DPM-H (775 mg, 1.50 mmol) was dissolved in benzene (20 mL). Neat Et₂Zn (185 µL, 1.801 mmol, 1.2 equiv.) was added to the stirred vellow ochre solution resulting in a color change to orange. The reaction mixture was heated to 60 °C overnight and the solvent was removed in vacuo yielding an orange powder in quantitative yield. Recrystallization from n-hexane at -20 °C yielded orange crystalline blocks. Yield: 859 mg (1.38 mmol; 92%). ¹H NMR (600 MHz, C₆D₆, 25 °C): $\delta = 6.76$ (s, 2 H, Mes-aryl-CH), 6.73 (d, J = 4.2 Hz, 2 H, pyrrole-CH), 6.42 (d, J = 4.2 Hz, 2 H, pyrrole-CH), 2.19 [br., 15 H, C₆H₂(CH₃)₃ and Ad-α-CH₂], 2.13 [s, 6 H, C₆H₂(CH₃)₃], 1.97 (br., 6 H, Ad-CH), 1.77-1.73 (m, 6 H, Ad-CH), 1.68-1.63 (m, 9 H, Ad-CH and ZnCH₂CH₃), 1.11 (q, J = 8.1 Hz, 2 H, ZnCH₂CH₃) ppm. ¹³C{¹H} **NMR** (151 MHz, C₆D₆, 25 °C): δ = 173.0 (C_{arom}), 145.4 (C_{arom}), 139.0 (C_{arom}), 137.2 (C_{arom}), 137.0 (C_{arom}), 136.2 (C_{arom}), 132.2 (C_{arom}), 128.0 (C_{arom}), 115.1 (C_{arom}), 42.7 (C_{aliph}), 36.9 (C_{aliph}), 36.4 (C_{aliph}), 29.1 (C_{aliph}), 21.2 (C_{aliph}), 20.1 (C_{aliph}), 12.5 (C_{aliph}) ppm. C₄₀H₅₀N₂Zn (622.33 g·mol-1): calcd. C 76.96, H 8.07, N 4.49; found: C 77.00, H 8.09, N 4.08%.

Synthesis of (^{Ad}**DPM**)**ZnI** (3-Ad): In a 50 mL Schlenk flask (^{Ad}DPM) ZnEt (880 mg, 1.41 mmol) was dissolved in benzene (12 mL). A solution of elemental iodine (395 mg, 1.56 mmol, 1.1 equiv.) in *n*-heptane (15 mL) was added at room temperature. The reaction mixture was stirred at room temperature overnight and the solvent and excess of iodine were removed in vacuo yielding an orange powder in quantitative yield. Trituration with *n*-hexane (2 × 4 mL) and recrystallization in a toluene/pentane mixture at -20 °C yielded crystalline orange blocks. Yield: 969 mg (1.35 mmol; 95%). ¹H NMR (600 MHz, C₆D₆, 25 °C): $\delta = 6.73$ (s, 2 H, Mes-aryl-CH), 6.67 (br., 2 H, pyrrole-CH), 6.37 (br., 2 H, pyrrole-CH), 2.31 (s, 12 H, Ad- α -CH₂), 2.17 [s, 3 H, C₆H₂(CH₃)₃], 2.02 [s, 12 H, C₆H₂(CH₃)₃], 2.00 (br., 6 H, Ad-CH), 1.86–1.84 (m, 6 H, Ad-CH), 1.62–1.60 (m, 6 H, Ad-CH) ppm. ¹³C{¹H} NMR (151 MHz, C₆D₆, 25 °C): $\delta = 173.9$ (C_{arom}), 145.5 (C_{arom}), 139.0 (C_{arom}), 137.6 (C_{arom}), 137.0 (C_{arom}), 135.5 (C_{arom}), 133.4 (C_{arom}), 128.2 (C_{arom}), 115.8 (C_{arom}), 42.2 (C_{aliph}), 36.6 (C_{aliph}), 36.6 (C_{aliph}), 29.0 (C_{aliph}), 21.1 (C_{aliph}), 19.9 (C_{aliph}) ppm. C₃₈H₄₅N₂ZnI (720.19 g·mol⁻¹): calcd. C 63.21, H 6.28, N 3.88; found: C 63.15, H 6.35, N 3.82%.

Synthesis of (AdDPM)ZnH (4-Ad): In a 50 mL Schlenk flask (AdDPM)ZnI (650 mg, 0.903 mmol) was dissolved in benzene (20 mL) and K[(iPr)NHBH₃] (150 mg, 1.35 mmol, 1.5 equiv.) was added. The milky orange suspension was stirred at room temperature overnight and filtered to give an orange solution. Removal of solvent in vacuo gave the crude product as orange solid. Recrystallization from a concentrated pentane solution at room temperature yielded crystalline orange blocks. Yield: 380 mg (0.640 mmol; 71%). M.p.: 281 °C -283 °C (dec.). ¹H NMR (600 MHz, C₆D₆, 25 °C): δ = 6.80 (s, 2 H, Mes-aryl-CH), 6.70 (d, J = 4.1 Hz, 2 H, pyrrole-CH), 6.38 (d, J = 4.1 Hz, 2 H, pyrrole-CH), 5.73 (s, 1 H, ZnH), 2.28 (s, 12 H, Ad-α-CH₂), 2.22 [s, 3 H, C₆H₂(CH₃)₃], 2.18 [s, 6 H, C₆H₂(CH₃)₃], 1.99 (br., 6 H, Ad-CH), 1.83-1.81 (m, 6 H, Ad-CH), 1.65-1.63 (m, 6 H, Ad-*CH*) ppm. ¹³C{¹H} NMR (151 MHz, C₆D₆, 25 °C): δ = 173.2 (C_{arom}), 144.0 (C_{arom}), 138.5 (C_{arom}), 136.1 (C_{arom}), 135.9 (C_{arom}), 135.4 (Carom), 131.5 (Carom), 126.9 (Carom), 114.5 (Carom), 41.7 (Caliph), 35.9 (Caliph), 35.6 (Caliph), 28.1 (Caliph), 20.0 (Caliph), 19.0 (Caliph) ppm. $C_{38}H_{46}N_2Zn$ (594.30 g·mol⁻¹): calcd. C 76.56, H 7.78, N 4.70; found: C 76.04, H 8.01, N 4.55%.

Synthesis of (MesDPM)ZnEt (2-Mes): In a 50 mL Schlenk flask MesDPM-H (1.98 g, 3.97 mmol) was suspended in benzene (25 mL). Neat Et₂Zn (488 µL, 4.76 mmol, 1.2 equiv.) was added to the stirred vellow ochre suspension resulting in a bright orange solution. The reaction mixture was heated to 60 °C overnight and the solvent was removed in vacuo yielding an orange powder in quantitative yield. Recrystallization from benzene at room temperature yielded orange crystalline blocks. Yield: 2.28 g (3.86 mmol; 97%). ¹H NMR (600 MHz, C_6D_6 , 25 °C): δ = 6.86 (s, 2 H, Mes-aryl-CH), 6.79 (s, 4 H, Mes-aryl-CH), 6.76 (d, J = 4.0 Hz, 2 H, pyrrole-CH), 6.20 (d, J = 4.0 Hz, 2 H, pyrrole-CH), 2.29 [s, 6 H, C₆H₂(CH₃)₃], 2.24 [s, 3 H, C₆H₂(CH₃)₃], 2.19 [s, 12 H, C₆H₂(CH₃)₃], 2.10 [s, 6 H, C₆H₂(CH₃)₃], 0.64 (t, J = 8.1 Hz, 3 H, ZnCH₂CH₃), -0.20 (q, J = 8.1 Hz, 2 H, ZnCH₂CH₃) ppm. ¹³C{¹H} NMR (151 MHz, C₆D₆, 25 °C): δ = 162.5 (Carom), 146.1 (Carom), 140.0 (Carom), 138.0 (Carom), 137.5 (Carom), 137.0 (C_{arom}), 136.9 (C_{arom}), 135.9 (C_{arom}), 133.4 (C_{arom}), 132.2 (Carom), 128.7 (Carom), 128.2 (Carom), 119.6 (Carom), 21.2 (Caliph), 21.2 (Caliph), 20.8 (Caliph), 20.2 (Caliph), 11.28 (Caliph), -0.3 (Caliph) ppm. C₃₈H₄₂N₂Zn (590.26 g·mol⁻¹): calcd. C 77.08, H 7.15, N 4.73; found: C 76.75, H 7.13, N 4.64%.

Synthesis of (^{Mes}DPM)ZnI (3-Mes): In a 50 mL Schlenk flask (^{Mes}DPM)ZnEt (400 mg, 0.677 mmol) was dissolved in benzene (12 mL). A solution of elemental iodine (189 mg, 0.745 mmol, 1.1 equiv.) in *n*-heptane (10 mL) was added at room temperature. The reaction mixture was stirred at room temperature overnight and the solvent and excess of iodine were removed in vacuo yielding an orange powder in quantitative yield. Trituration with *n*-hexane (3 × 3 mL) and recrystallization in a toluene/*n*-hexane mixture at -20 °C yielded crystalline orange blocks. Yield: 409 mg (0.595 mmol; 88%). ¹H NMR (400 MHz, C₆D₆, 25 °C): δ = 6.83 (s, 2 H, Mes-aryl-CH), 6.82 (s, 4 H, Mes-aryl-CH), 6.76 (d, *J* = 4.0 Hz, 2 H, pyrrole-CH), 6.12 (d, *J* =

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4.1 Hz, 2 H, pyrrole-*CH*), 2.24 [s, 3 H, $C_6H_2(CH_3)_3$], 2.21 [s, 6 H, $C_6H_2(CH_3)_3$], 2.16 [s, 12 H, $C_6H_2(CH_3)_3$], 2.11 [s, 6 H, $C_6H_2(CH_3)_3$] ppm. ¹³C{¹H} NMR (101 MHz, C_6D_6 , 25 °C): $\delta = 163.4$ (C_{arom}), 146.0 (C_{arom}), 140.0 (C_{arom}), 138.7 (C_{arom}), 137.8 (C_{arom}), 136.9 (C_{arom}), 135.3 (C_{arom}), 137.8 (C_{arom}), 131.7 (C_{arom}), 129.0 (C_{arom}), 127.9 (C_{arom}), 120.4 (C_{arom}), 21.3 (C_{aliph}), 21.2 (C_{aliph}), 20.9 (C_{aliph}), 20.0 (C_{aliph}) ppm. $C_{36}H_{37}N_2ZnI$ (688.13 g·mol⁻¹): calcd. C 62.67, H 5.41, N 4.06; found: C 63.02, H 5.37, N 3.97%.

Synthesis of (MesDPM)ZnH (4-Mes): In a 25 mL Schlenk flask (MesDPM)ZnI (256 mg, 0.372 mmol) was dissolved in benzene (15 mL) and K[(iPr)NHBH₃] (62.1 mg, 0.559 mmol, 1.5 equiv.) was added. The milky orange suspension was stirred at room temperature overnight and filtered through a syringe filter to give an orange solution. Removal of solvent in vacuo gave the crude product as orange solid. Recrystallization from a concentrated toluene solution at -20 °C yielded a first crop of crystalline orange blocks. Yield: 120 mg (0.213 mmol; 57%). M.p.: 243 °C - 245 °C (dec.). ¹H NMR (600 MHz, C_6D_6 , 25 °C): δ = 6.86 (s, 2 H, Mes-aryl-CH), 6.77 (s, 4 H, Mes-aryl-CH), 6.74 (d, J = 4.0 Hz, 2 H, pyrrole-CH), 6.21 (d, J = 4.0 Hz, 2 H, pyrrole-CH), 3.96 (s, 1 H, ZnH), 2.28 [s, 6 H, C₆H₂(CH₃)₃], 2.25 [s, 3 H, C₆H₂(CH₃)₃], 2.16 [s, 12 H, C₆H₂(CH₃)₃], 2.11 [s, 6 H, C₆H₂(CH₃)₃] ppm. ¹³C{¹H} NMR (151 MHz, C₆D₆, 25 °C): δ = 162.6 (C_{arom}), 146.1 (C_{arom}), 139.9 (C_{arom}), 138.0 (C_{arom}), 137.6 (C_{arom}), 136.9 (C_{arom}), 136.9 (C_{arom}), 135.7 (C_{arom}), 132.9 (Carom), 132.3 (Carom), 128.6 (Carom), 128.4 (Carom), 119.8 (Carom), 21.2 (Caliph), 21.2 (Caliph), 20.9 (Caliph), 20.1 (Caliph) ppm. C36H38N2Zn (562.23 g·mol⁻¹): calcd. C 76.65, H 6.79, N 4.97; found: C 75.98, H 6.68, N 4.59%.

Synthesis of (Mes*DPM)ZnEt (2-Mes*): In a 50 mL Schlenk flask Mes*DPM-H (422 mg, 0.485 mmol) was suspended in benzene (15 mL). Neat Et₂Zn (69.5 µL, 0.678 mmol, 1.4 equiv.) was added to the stirred red suspension resulting in a pink solution. The reaction mixture was heated to 60 °C overnight and the solvent was removed in vacuo yielding a pink powder in quantitative yield. Recrystallization from toluene/n-hexane at -20 °C yielded red crystalline blocks. Yield: 397 mg (0.412 mmol; 85%). ¹**H NMR** (600 MHz, C₆D₆, 25 °C): δ = 7.70 (s, 4 H, Mes-aryl-CH), 7.43 (d, J = 7.1 Hz, 4 H, phenyl-CH), 7.31 (d, J = 6.9 Hz, 8 H, phenyl-CH), 7.24–7.14 (m, 18 H, phenyl-CH), 6.77 (s, 2 H, Mes-aryl-CH), 6.19 (d, J = 4.0 Hz, 2 H, pyrrole-CH), 5.87 (d, J = 4.0 Hz, 2 H, pyrrole-CH), 2.20 [s, 3 H, C₆H₂(CH₃)₃], 2.03 [s, 6 H, $C_6H_2(CH_3)_3$], 0.86 (t, J = 8.1 Hz, 3 H, ZnCH₂CH₃), 0.16 (q, J = 8.1 Hz, 2 H, ZnCH₂CH₃) ppm. ¹³C{¹H} NMR (151 MHz, C_6D_6 , 25 °C): δ = 160.7 (C_{arom}), 145.2 (C_{arom}), 143.5 (C_{arom}), 142.4 (C_{arom}), 142.2 (C_{arom}), 141.0 (C_{arom}), 139.5 (C_{arom}), 137.1 (C_{arom}), 136.6 ($C_{\rm arom}$), 135.9 ($C_{\rm arom}$), 133.0 ($C_{\rm arom}$), 130.1 ($C_{\rm arom}$), 129.9 ($C_{\rm arom}$) rom), 129.1 (Carom), 128.6 (Carom), 128.1 (Carom), 128.0 (Carom), 127.8 (Carom), 127.7 (Carom), 126.8 (Carom), 122.1 (Carom), 21.2 (Caliph), 19.9 (C_{aliph}), 11.1 (C_{aliph}), 2.4 (C_{aliph}) ppm. C₆₈H₅₄N₂Zn (964.57 g·mol⁻¹): calcd. C 84.67, H 5.64, N 2.90; found: C 84.46, H 5.61, N 2.88 %.

Synthesis of (Mes*DPM)ZnI (3-Mes*): In a 50 mL Schlenk flask (Mes*DPM)ZnEt (399 mg, 0.414 mmol) was suspended in benzene (20 mL). A solution of elemental iodine (110 mg, 0.433 mmol, 1.05 equiv.) in *n*-heptane (15 mL) was added at room temperature. The reaction mixture was heated at 60 °C overnight and the solvent and excess of iodine were removed in vacuo yielding a dark purple powder. Trituration with *n*-hexane (2×15 mL) yielded a purple solid. Yield: 370 mg (0.348 mmol; 84%). Single crystals (red blocks) suitable for X-ray analysis were obtained upon heating a suspension of the crude product in boiling toluene. ¹H NMR (600 MHz, C₆D₆, 25 °C): δ = 7.70 (s, 4 H, Mes-aryl-CH), 7.16–7.14 (m, 12 H, phenyl-CH), 6.73 (s,

2 H, Mes-aryl-CH), 6.12 (d, J = 4.1 Hz, 2 H, pyrrole-CH), 5.88 (d, J = 4.1 Hz, 2 H, pyrrole-CH), 2.18 (s, 3 H, $C_6H_2(CH_3)_3$), 1.92 (s, 6 H, $C_6H_2(CH_3)_3$ ppm. ¹³C{¹H} NMR (151 MHz, C_6D_6 , 25 °C): $\delta = 161.5$ (C_{arom}), 145.2 (C_{arom}), 143.3 (C_{arom}), 142.8 (C_{arom}), 142.0 (C_{arom}), 141.1 (Carom), 139.6 (Carom), 137.5 (Carom), 136.6 (Carom), 135.1 (Carom), 131.6 (Carom), 131.4 (Carom), 130.4 (Carom), 129.1 (Carom), 128.7 (Carom), 128.1 (Carom), 128.0 (Carom), 127.8 (Carom), 127.7 (Carom), 126.9 (Carom), 122.9 (Carom), 21.4 (Caliph), 19.8 (Caliph) ppm. Several attempts to obtain satisfactory elemental analytical data were without success. Although the C and N values are outside the range viewed as establishing analytical purity, they are provided to illustrate the best values obtained to date. $C_{66}H_{49}N_2IZn$ (1062.42 g·mol⁻¹): calcd. C 74.62, H 4.65, N 2.64; found: C 76.55, H 5.01, N 2.19%. Due to the poor solubility of (Mes*DPM)ZnI, attempted synthesis of (Mes*DPM)ZnI via salt metathesis with K[(iPr)NHBH3] was not satisfactory and an alternative pathway over intermediate (Mes*DPM)ZnO-SiPh₃ (5-Mes*) was chosen.

Synthesis of (Mes*DPM)ZnOSiPh3 (5-Mes*): In a 25 mL Schlenk flask (Mes*DPM)ZnEt (213 mg, 0.221 mmol) was suspended in benzene (10 mL). Neat Ph₃SiOH (61 mg, 0.221 mmol, 1.0 equiv.) was added at room temperature in one portion. The reaction mixture was heated at 60 °C overnight. Residual solvent was removed in vacuo and the crude product was triturated with *n*-hexane $(3 \times 10 \text{ mL})$ to give a purple solid. Yield: 169 mg (0.131 mmol; 60%). Single crystals (red blocks) suitable for X-ray analysis were obtained from a toluene/THF mixture at -20 °C. The complex crystallized as its THF adduct: (^{Mes*}DPM)ZnOSiPh₃·(THF). ¹H NMR (600 MHz, C₆D₆, 25 °C): δ = 7.49 (d, J = 6.8 Hz, 6 H, phenyl-CH), 7.38 (s, 4 H, Mes-aryl-CH), 7.34-7.24 (m, 12 H, phenyl-CH), 7.21-7.17 (m, 4 H, phenyl-CH), 7.14–7.09 (m, 15 H, phenyl-CH), 6.96 (t, J = 7.4 Hz, 3 H, phenyl-CH), 6.89 (t, J = 7.4 Hz, 6 H, phenyl-CH), 6.74 (s, 2 H, Mes-aryl-CH), 6.14 (d, J = 4.0 Hz, 2 H, pyrrole-CH), 5.8 (d, J = 4.1 Hz, 2 H, pyrrole-CH), 2.19 [s, 3 H, C₆H₂(CH₃)₃], 1.99 [s, 6 H, C₆H₂(CH₃)₃] ppm. ¹³C{¹H} NMR (151 MHz, C₆D₆, 25 °C): δ = 161.3 (C_{arom}), 142.8 (Carom), 142.2 (Carom), 141.8 (Carom), 141.5 (Carom), 140.7 (Carom), 140.6 (Carom), 140.6 (Carom), 136.6 (Carom), 135.9 (Carom), 131.9 (Carom), 131.8 (Carom), 130.0 (Carom), 129.0 (Carom), 128.8 (Carom), 128.6 (Carom), 128.5 (Carom), 128.1 (Carom), 128.0 (Carom), 127.8 (Carom), 127.6 (Carom), 127.5 (Carom), 127.0 (Carom), 123.2 (Carom), 21.2 (Caliph), 20.0 (Caliph) ppm. Several attempts to obtain satisfactory elemental analytical data were without success. Although the C value is outside the range viewed as establishing analytical purity, it is provided to illustrate the best values obtained to date. C88H72O2N2SiZn (1283.02 g·mol⁻¹): calcd. C 82.38, H 5.66, N 2.18; found: C 80.40, H 5.95, N 1.70%.

Synthesis of (Mes*DPM)ZnH (4-Mes*): In a 25 mL Schlenk flask (Mes*DPM)ZnOSiPh₃ (169 mg, 0.132 mmol) was suspended in benzene (15 mL) and PhSiH₃ (17.0 µL, 0.138 mmol, 1.05 equiv.) was added in one portion. The pink reaction mixture was stirred at room temperature overnight. Removal of solvent in vacuo and trituration with *n*-hexane $(2 \times 5 \text{ mL})$ yielded the crude product as pink solid. Recrystallization from a concentrated toluene solution at -20 °C yielded crystalline red blocks. Yield: 48 mg (0.051 mmol; 39%). M.p.: 185 °C – 190 °C (dec.). ¹H NMR (600 MHz, C₆D₆, 25 °C): δ = 7.72 (s, 4 H, Mes-aryl-CH), 7.44-7.40 (m, 4 H, phenyl-CH), 7.33-7.29 (m, 8 H, phenyl-CH), 7.20-7.16 (m, 12 H, phenyl-CH), 7.16-7.12 (m, 6 H, phenyl-CH), 6.78 (s, 2 H, Mes-aryl-CH), 6.18 (d, J = 4.0 Hz, 2 H, pyrrole-CH), 5.87 (d, J = 4.0 Hz, 2 H, pyrrole-CH), 4.03 (s, 1 H, ZnH), 2.20 [s, 3 H, C₆H₂(CH₃)₃], 2.04 [s, 6 H, C₆H₂(CH₃)₃] ppm. ¹³C{¹H} **NMR** (151 MHz, C₆D₆, 25 °C): δ = 160.5 (C_{arom}), 144.9 (C_{arom}), 143.6 (Carom), 142.3 (Carom), 142.3 (Carom), 140.8 (Carom), 139.4 (Carom), Zeitschrift für anorganische und allgemeine Chemie

137.2 (C_{arom}), 136.6 (C_{arom}), 135.6 (C_{arom}), 132.4 (C_{arom}), 131.0 (C_{arom}), 130.3 (C_{arom}), 129.0 (C_{arom}), 128.3 (C_{arom}), 128.1 (C_{arom}), 128.0 (C_{arom}), 127.8 (C_{arom}), 127.7 (C_{arom}), 126.8 (C_{arom}), 121.9 (C_{arom}), 21.2 (C_{aliph}), 19.7 (C_{aliph}) ppm. $C_{66}H_{50}N_2Zn$ (936.52 g·mol⁻¹): calcd. C 84.65, H 5.38, N 2.99; found: C 85.11, H 5.68, N 3.33%.

Synthesis of (AnthDPM)ZnEt (2-Anth): In a 50 mL Schlenk flask AnthDPM-H (503 mg, 0.818 mmol) was suspended in benzene (15 mL). Neat Et₂Zn (100 µL, 0.982 mmol, 1.2 equiv.) was added to the stirred red suspension resulting in a pink solution. The reaction mixture was heated to 60 °C overnight and the solvent was removed in vacuo yielding a purple powder in quantitative yield. Recrystallization from toluene at -20 °C yielded red crystalline blocks. Yield: 521 mg (0.736 mmol; 90%). ¹**H NMR** (600 MHz, C₆D₆, 25 °C): δ = 8.11 (d, J = 8.7 Hz, 4 H, Anth-aryl-CH), 8.07 (s, 2 H, Anth-aryl-CH), 7.69– 7.64 (m, 4 H, Anth-aryl-CH), 7.14-7.05 (m, 8 H, Anth-aryl-CH), 6.96 (d, J = 4.1 Hz, 2 H, pyrrole-CH), 6.96 (s, 2 H, Mes-aryl-CH), 6.56 (d, J = 4.0 Hz, 2 H, pyrrole-CH), 5.88 [d, J = 4.1 Hz, 2 H, pyrrole-CH], 2.50 [s, 6 H, $C_6H_2(CH_3)_3$], 2.31 [s, 3 H, $C_6H_2(CH_3)_3$], -1.01 (t, J = 8.1 Hz, 3 H, $ZnCH_2CH_3$), -1.95 (q, J = 8.1 Hz, 2 H, $ZnCH_2CH_3$) ppm. ¹³C{¹H} NMR (151 MHz, C₆D₆, 25 °C): δ = 160.5 (C_{arom}), 147.0 (Carom), 141.0 (Carom), 137.8 (Carom), 137.1 (Carom), 135.8 (Carom), 132.4 (Carom), 131.8 (Carom), 131.8 (Carom), 130.6 (Carom), 128.8 $(C_{\rm arom})$, 128.6 $(C_{\rm arom})$, 128.0 $(C_{\rm arom})$, 126.5 $(C_{\rm arom})$, 126.4 $(C_{\rm arom})$, 125.3 (Carom), 122.4 (Carom), 21.3 (Caliph), 20.6 (Caliph), 9.8 (Caliph), -0.9 (C_{aliph}) ppm. $C_{48}H_{38}N_2Zn$ (708.23 g·mol⁻¹): calcd. C 81.40, H 5.41, N 3.96; found: C 80.98, H 5.38, N 3.85%.

Synthesis of (AnthDPM)ZnOSiPh3 (5-Anth): In a 50 mL Schlenk flask (AnthDPM)ZnEt (448 mg, 0.633 mmol) was dissolved in benzene (20 mL). Neat Ph₃SiOH (174 mg, 0.630 mmol, 1.0 equiv.) was added at room temperature in one portion. The reaction mixture was heated at 60 °C overnight. Residual solvent was removed in vacuo and the crude product was triturated with *n*-hexane $(2 \times 15 \text{ mL})$ to give a dark purple solid. Yield: 479 mg (0.502 mmol; 79%). ¹H NMR (600 MHz, C_6D_6 , 25 °C): $\delta = 8.37$ (d, J = 8.8 Hz, 4 H, Anth-aryl-CH), 7.86 (s, 2 H, Anth-aryl-CH), 7.57 (d, J = 8.4 Hz, 4 H, Anth-aryl-CH), 7.27–7.20 (m, 4 H, Anth-aryl-CH), 7.16–7.12 (m, 6 H, phenyl-CH), 6.98 (t, J =7.3 Hz, 3 H, phenyl-CH), 6.90 (s, 2 H, Mes-aryl-CH), 6.87 (d, J = 3.9 Hz, 2 H, pyrrole-CH), 6.68 (t, J = 7.4 Hz, 6 H, phenyl-CH), 6.57 (d, J = 4.0 Hz, 2 H, pyrrole-CH), 6.35 (d, J = 7.0 Hz, 6 H, Anth-aryl-CH), 2.36 (s, 6 H, C₆H₂(CH₃)₃), 2.28 [s, 3 H, C₆H₂(CH₃)₃] ppm. ¹³C{¹H} NMR (101 MHz, C₆D₆, 25 °C): δ = 160.0 (C_{aron}), 146.2 (Carom), 141.9 (Carom), 140.3 (Carom), 137.9 (Carom), 137.1 (Carom), 135.6 (Carom), 134.6 (Carom), 133.0 (Carom), 131.8 (Carom), 131.4 (C_{arom}), 129.7 (C_{arom}), 128.8 (C_{arom}), 128.0 (C_{arom}), 127.8 (C_{arom}), 127.2 (C_{arom}), 126.9 (C_{arom}), 125.7 (C_{arom}), 125.2 (C_{arom}), 123.9 (C_{arom}), 21.3 (C_{aliph}), 20.5 (C_{aliph}) ppm. Several attempts to obtain satisfactory elemental analytical data were without success. Although the C, N and H values are outside the range viewed as establishing analytical purity, they are provided to illustrate the best values obtained to date. C64H48N2OSiZn (954.27 g·mol-1): calcd. C 80.53, H 5.07, N 2.93; found: C 82.02, H 5.57, N 2.44 %.

Synthesis of (^{Anth}DPM)ZnH·(THF) (4-Anth·(THF)): In a 50 mL Schlenk flask (^{Anth}DPM)ZnOSiPh₃ (628 mg, 0.658 mmol) was suspended in a mixture of benzene (15 mL) and THF (15 mL). PhSiH₃ (90.0 μ L, 0.724 mmol, 1.1 equiv.) was added in one portion. The purple reaction mixture was heated at 60 °C overnight. Removal of solvent in vacuo and trituration with *n*-hexane (4 × 10 mL) yielded the crude product as dark purple solid. Recrystallization from a concentrated toluene/THF solution at -20 °C yielded crystalline red blocks. Yield: 332 mg (0.441 mmol; 67%). M.p.: 268 °C - 274 °C (dec.). ¹H NMR (600 MHz, C₆D₆, 25 °C): δ = 8.07 (d, *J* = 7.9 Hz, 6 H, Anth-

aryl-CH), 7.66 (d, J = 8.3 Hz, 4 H, Anth-aryl-CH), 7.15–7.08 (m, 8 H, Anth-aryl-CH), 6.97–6.95 (m, 4 H, pyrrole-CH and Mes-aryl-CH), 6.56 (d, J = 4.0 Hz, 2 H, pyrrole-CH), 3.23–3.21 (m, 4 H, THF-CH₂), 2.57 (s, 1 H, ZnH), 2.50 [s, 6 H, C₆H₂(CH₃)₃], 2.32 [s, 3 H, C₆H₂(CH₃)₃], 1.16–1.14 (m, 4 H, THF-CH₂) ppm. ¹³C{¹H} NMR (151 MHz, C₆D₆, 25 °C): $\delta = 160.2$ (C_{arom}), 147.0 (C_{arom}), 140.9 (C_{arom}), 137.7 (C_{arom}), 130.7 (C_{arom}), 128.1 (C_{arom}), 128.1 (C_{arom}), 127.0 (C_{arom}), 126.1 (C_{arom}), 125.2 (C_{arom}), 122.3 (C_{arom}), 67.9 (C_{THF}), 25.5 (C_{THF}), 21.4 (C_{aliph}), 20.5 (C_{aliph}) ppm. C₅₀H₄₂N₂OZn (752.28 g·mol⁻¹): C 79.83, H 5.63, N 3.72%; found: C 79.84, H 5.75, N 3.39%.

Supporting Information (see footnote on the first page of this article): Crystal structure data including ORTEP representations, selected 1D, 2D and DOSY NMR spectra.

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Keywords: Hydride; Zinc; Dipyrromethene; B(C₆F₅)₃

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Low-Coordinate Monomeric Zinc Hydride Complexes	with						
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$B(C_{6}F_{5})_{3}$							

