

## (MeZn)<sub>2</sub>(μ-η<sup>2</sup>:η<sup>2</sup>-N<sub>6</sub>Ph<sub>2</sub>) - A Powerful Starting Reagent for the Synthesis of Metal Hexazene Complexes

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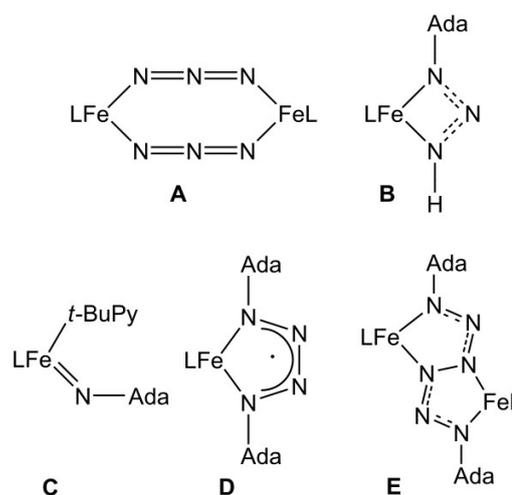
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**ABSTRACT:** [(MeL<sup>Dipp</sup>Zn)<sub>2</sub>(μ-η<sup>2</sup>:η<sup>2</sup>-PhN<sub>6</sub>Ph)] (**3**), which was synthesized by reaction of MeL<sup>Dipp</sup><sub>2</sub>Zn<sub>2</sub> with PhN<sub>3</sub>, reacts with two equivalents of Me<sub>2</sub>Zn to [(MeZn)<sub>2</sub>(μ-η<sup>2</sup>:η<sup>2</sup>-PhN<sub>6</sub>Ph)] (**2**). The reaction of **2** with pyridine gave [(MeZn)<sub>2</sub>(μ-η<sup>2</sup>:η<sup>2</sup>-PhN<sub>6</sub>Ph)(Py)<sub>2</sub>] (**4**), while reactions with H-acidic ligands (MeL<sup>Mes</sup>H, MeL<sup>Ph</sup>H) occurred with elimination of methane and formation of [(MeL<sup>Mes</sup>Zn)<sub>2</sub>(μ-η<sup>2</sup>:η<sup>2</sup>-PhN<sub>6</sub>Ph)] (**1**) and [(MeL<sup>Ph</sup>Zn)<sub>2</sub>(μ-η<sup>2</sup>:η<sup>2</sup>-PhN<sub>6</sub>Ph)] (**5**). The reaction of **1** with two equivalents of MeLi yielded the heterobimetallic hexazene complex [(MeZn)(μ-η<sup>2</sup>:η<sup>2</sup>-PhN<sub>6</sub>Ph)(Li)], which was found to undergo stepwise reaction with Me<sub>2</sub>AlCl to [MeZn(μ-η<sup>2</sup>:η<sup>2</sup>-PhN<sub>6</sub>Ph)AlMe<sub>2</sub>] and finally [(Me<sub>2</sub>Al)<sub>2</sub>(μ-η<sup>2</sup>:η<sup>2</sup>-PhN<sub>6</sub>Ph)(thf)<sub>2</sub>] (**6**). **3** - **6** were characterized by elemental analysis, NMR spectroscopy and single crystal X-ray diffraction. Quantum chemical calculations were performed in order to investigate the electronic structure of **4'** and **6'** in more detail and to identify the absorption bands of the hexazene unit.

### INTRODUCTION

Reactions of low-valent metal organic complexes with azides RN<sub>3</sub> have been widely studied.<sup>[1]</sup> Two-electron reductants such as monovalent [Cp\*Al]<sub>4</sub> (Cp\* = C<sub>5</sub>Me<sub>5</sub>) typically react with elimination of N<sub>2</sub> and formation of iminoalanes [Cp\*AlNR']<sub>x</sub>.<sup>[2]</sup> In contrast, one-electron reductants such as Al<sub>2</sub>(CH(TMS)<sub>2</sub>)<sub>4</sub> were found to react with insertion of the RN<sub>3</sub> unit into the Al-Al bond or with reductive cleavage of the R-N<sub>3</sub> bond and subsequent elimination of R-R and formation of azido-bridged complexes.<sup>[3]</sup> Comparable mechanism were observed for reactions of the Fe(II) hydride [tBuL<sup>Dipp</sup>FeH]<sub>2</sub> (tBuL<sup>Dipp</sup> = HC[C(t-Bu)N(2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>]) and for the Fe(I) complex [tBuL<sup>Dipp</sup>Fe]<sub>2</sub>N<sub>2</sub> with Me<sub>3</sub>SiN<sub>3</sub>, yielding [tBuL<sup>Dipp</sup>FeN<sub>3</sub>]<sub>2</sub> (**A**) with bridging azido groups as well as Si<sub>2</sub>Me<sub>6</sub>.<sup>[4]</sup> In contrast, [tBuL<sup>Dipp</sup>FeH]<sub>2</sub> reacts with AdN<sub>3</sub> with insertion into the Fe-H bond and formation of the triazenido complex [tBuL<sup>Dipp</sup>Fe(N(H)NNAd)]<sub>2</sub> (**B**).<sup>[4]</sup> The analogous reaction of [MeL<sup>Dipp</sup>Fe]<sub>2</sub>N<sub>2</sub> (MeL<sup>Dipp</sup> = HC[C(Me)N(2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>]), a convenient Fe(I) source,<sup>[5]</sup> with AdN<sub>3</sub> in the presence of coordinating *tert*-butyl pyridine yielded the metastable imidoiron(III) complex MeL<sup>Dipp</sup>Fe(NAd)(*t*-BuPy) (**C**),<sup>[6]</sup> which was found to consequently react with another equivalent of AdN<sub>3</sub> in a dipolar 1,3-cycloaddition reaction with formation of MeL<sup>Dipp</sup>Fe(AdNNNAd) (**D**) containing a monoanionic (radical) tetrazene ligand.<sup>[7]</sup> Key step is the displacement of N<sub>2</sub> in [MeL<sup>Dipp</sup>Fe]<sub>2</sub>N<sub>2</sub> by the strongly coordinating solvent. The resulting monometallic, solvated complex MeL<sup>Dipp</sup>Fe(solv.) reacts with AdN<sub>3</sub> with formation of non-isolable MeL<sup>Dipp</sup>Fe<sup>II</sup>(N<sub>3</sub>Ad<sup>-</sup>) containing a radical monoanion, which eliminates N<sub>2</sub> with subsequent formation of MeL<sup>Dipp</sup>Fe=NAd. This Fe(III) imido complex finally reacts to the tetrazene

complex.<sup>[7]</sup> Tetrazene complexes were also obtained from reactions of Al(I),<sup>[8,9,10]</sup> Ga(I)<sup>[11]</sup> and Fe(I)<sup>[12]</sup> complexes with two equivalents of AdN<sub>3</sub>. In contrast, in the absence of any coordination solvents, the first hexazene complex [MeL<sup>Dipp</sup><sub>2</sub>Fe]<sub>2</sub>(μ-η<sup>2</sup>:η<sup>2</sup>-PhN<sub>6</sub>Ph) (**E**) containing a dianionic Ad<sub>2</sub>N<sub>6</sub> unit was obtained (scheme 1).<sup>[13]</sup> According to QM/MM computations,<sup>[14]</sup> the diiron organoazide intermediate (MeL<sup>Dipp</sup>Fe)<sub>2</sub>(μ-N<sub>3</sub>Ad) is formed first, which yields the hexazene complex upon addition of a second AdN<sub>3</sub> molecule.



**Scheme 1:** Representative Fe-N compounds as obtained from reactions of  $\beta$ -diketiminato iron complexes with RN<sub>3</sub>.

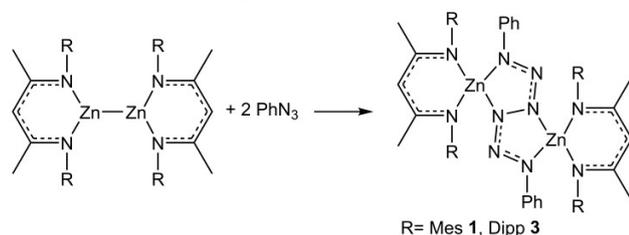
Metal hexazene complexes, which in remarkable contrast to neutral hexaazadienes are thermally very stable,<sup>[15-19]</sup> have received growing interest since their initial discovery by Holland.<sup>[13]</sup> They are typically synthesized by reactions of strong one-electron reductants with organic azide RN<sub>3</sub>. In particular the sterically demanding 1-azidoadamantane (AdN<sub>3</sub>) was investigated in reactions with iron(I)<sup>[13,20]</sup> and magnesium(I) complexes<sup>[21,22]</sup> containing N,N'-chelating  $\beta$ -diketiminato ligands. In addition, an iron(III) hexazene complex was prepared by reaction of AdN<sub>3</sub> with a less reducing bis(alkoxide) iron(II) complex.<sup>[23]</sup> According to density functional theory (DFT) studies, the latter reaction proceeds via initial formation of a dimeric complex containing two Fe(III) ions antiferromagnetically coupled to the monoreduced, bridging azide radicals, which then reacts to the hexazene complex.<sup>[23]</sup>

We recently reported on reactions of the one-electron reducing Zn(I) complex  $(\text{MeL}^{\text{Mes}})_2\text{Zn}_2$  ( $\text{MeL}^{\text{Mes}} = \text{HC}[\text{C}(\text{Me})\text{N}(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)]_2$ ) with organic azides including the sterically less demanding PhN<sub>3</sub>, yielding the first Zn(II) hexazene complex  $[(\text{MeL}^{\text{Mes}}\text{Zn})_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-PhN}_6\text{Ph})]$  (**1**).<sup>[24]</sup> Reactivity studies proved that **1** is a suitable hexazene transfer reagent. Reactions with main group metal and transition metal alkyl complexes such as ZnMe<sub>2</sub>, AlMe<sub>3</sub> and MeLi in different molar ratios occurred with elimination of  $\text{MeL}^{\text{Mes}}\text{ZnMe}$  and subsequent formation of homo- and heterobimetallic hexazene complexes such as  $[(\text{MeZn})_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-PhN}_6\text{Ph})]$  (**2**),  $[(\text{Me}_2\text{Al})_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-PhN}_6\text{Ph})]$ ,  $[\text{MeZn}(\mu\text{-}\eta^2\text{:}\eta^2\text{-PhN}_6\text{Ph})\text{AlMe}_2]$  and  $[(\text{MeZn})(\mu\text{-}\eta^2\text{:}\eta^2\text{-PhN}_6\text{Ph})(\text{Li})]$ , respectively.<sup>[25]</sup> Unfortunately, only **2** was structurally characterized by single crystal X-ray diffraction.

Herein we report on the synthesis of two hexazene complexes and their reactions with a Lewis base (pyridine), H-acidic ligands ( $\text{MeL}^{\text{MesH}}$ ,  $\text{MeL}^{\text{PhH}} = \text{HC}[\text{C}(\text{Me})\text{N}(\text{Ph})]_2$ ) as well as metal alkyls (ZnMe<sub>2</sub>, MeLi) and a metal halides (Me<sub>2</sub>AlCl).

## Results and Discussion

The reaction of  $\text{MeL}^{\text{Dipp}}_2\text{Zn}_2$  with 2 eq PhN<sub>3</sub> yielded an orange crystalline solid (scheme 2), whose <sup>1</sup>H and <sup>13</sup>C NMR spectra showed resonances of the  $\beta$ -diketiminato ligand and the Ph groups in the expected 1:1 molar ratio. The formation of the hexazene complex  $[(\text{MeL}^{\text{Dipp}}\text{Zn})_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-PhN}_6\text{Ph})]$  (**3**) is further supported by its IR spectrum, which shows absorption bands at 946, 1210, 1257 and 1346 cm<sup>-1</sup>, which agree well to those observed for **1** (947, 1198, 1259, 1349 cm<sup>-1</sup>).<sup>[24]</sup>



### Scheme 2: Reactions of one-electron reducing Zn(I) compounds with PhN<sub>3</sub>.

Orange crystals of **3** were obtained upon storage of a solution of **3** in fluorobenzene at 4 °C (fig. 1). A single crystal X-ray diffraction study revealed the formation of the hexa-

zene complex  $[(\text{MeL}^{\text{Dipp}}\text{Zn})_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-PhN}_6\text{Ph})]$  (**3**), which crystallizes in the triclinic space group P-1 with one molecule in the unit cell. **3** contains a crystallographic inversion center between N5 and N5A, that renders the two halves of the molecule equivalent. The Zn atoms in **3** are slightly out of the plane (deviation from least-squares plane of N1, N2, C1, C2 and C3: 0.564(3) Å) of the six-membered C<sub>3</sub>N<sub>2</sub>Zn rings as was observed in the starting Zn(I) complex  $\text{MeL}^{\text{Dipp}}_2\text{Zn}_2$ .<sup>[26]</sup> The C-C, C-N and Zn-N bond lengths as well as the endocyclic and exocyclic bond angles of the six-membered ring of **3** are nearly identical to those observed in  $\text{MeL}^{\text{Dipp}}_2\text{Zn}_2$ .<sup>[26]</sup> The ZnN<sub>4</sub> moiety forms an almost perfect planar metallacycle (r.m.s deviation from least-squares plane 0.0037 Å) as was observed for **1**. The central structural motif of **3** is the dianionic hexazenediide PhN<sub>6</sub>Ph, which adopts a bridging position and is connected to two four-coordinate Zn atoms. The central N5–N5A bond (1.398(5) Å) is significantly elongated compared to the almost identical N3–N4 (1.313(3) Å) and N4–N5 bonds (1.302(3) Å) as is typical for metal hexazene complexes. The N3–N4–N5 bond angle of 117.0° is also comparable to those previously reported for hexazene complexes.<sup>[13,20-25]</sup>

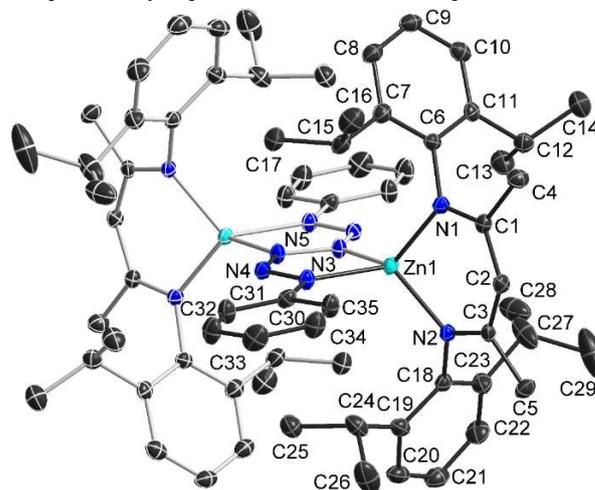
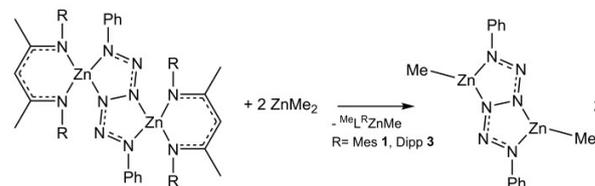


Figure 1: Molecular structure of **3**; H atoms and disordered solvent molecule are omitted for clarity.

As was observed for **1**, **3** reacts with 2 equivalents of ZnMe<sub>2</sub> with elimination of  $\text{MeL}^{\text{Dipp}}\text{ZnMe}$  (scheme 3), which was identified by <sup>1</sup>H NMR spectroscopy, and subsequent formation of the known hexazene complex  $[(\text{MeZn})_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-PhN}_6\text{Ph})]$  (**2**), which was obtained as dark red solid.<sup>[25]</sup>



### Scheme 3: Synthesis of $[(\text{MeZn})_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-PhN}_6\text{Ph})]$ **2**.

**2** is insoluble in non-coordinating solvents such as pentane, cyclohexane or toluene, most likely resulting from the intermolecular Zn...N interactions (2.275(2) Å) between adjacent hexazene complexes in **2** due to the electron defi-

ciency of the threefold-coordinated Zn atom, which lead to a ladder-like one-dimensional polymeric structure of **2**. However, the intermolecular Zn $\cdots$ N interactions can be disrupted in reactions with strong Lewis bases such as acetonitrile<sup>[25]</sup> and pyridine (scheme 4), resulting in the formation of the Lewis base-coordinated hexazene complex (MeZn)<sub>2</sub>( $\mu$ - $\eta^2$ : $\eta^2$ -PhN<sub>6</sub>Ph)(Py)<sub>2</sub> (**4**).

Crystals of **2** were suspended in C<sub>6</sub>D<sub>6</sub>, yielding a deep red suspension, which immediately turned to a yellow solution upon addition of pyridine. **4** shows the expected resonances of the Zn-Me substituent, the Ph groups of the hexazene moiety and the coordinating pyridine in a relative intensity of 1:1:1. The <sup>1</sup>H NMR resonances of the pyridine molecule (7.17, 7.88 and 8.16 ppm) are significantly shifted compared to free pyridine (6.66, 6.86 and 8.53 ppm).<sup>[27]</sup>

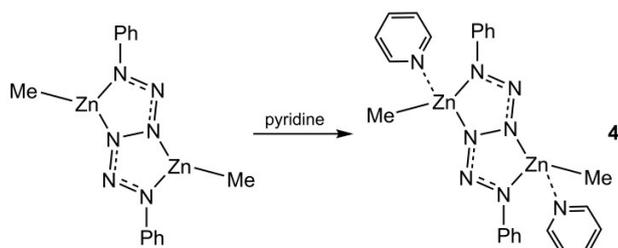
**Table 1: Bond lengths[Å] and angles[°] of the hexazene unit in structurally characterized zinc hexazene complexes.**

	N1-N2	N2-N3	N3-N3'	N1-N2-N3
$[(\text{MeL}^{\text{Mes}}\text{Zn})_2(\mu\text{-}\eta^2\text{-}\eta^2\text{-PhN}_6\text{Ph})]$ <b>1</b> <sup>[24]</sup>	1.304	1.302	1.403	117.350
$[(\text{MeZn})_2(\mu\text{-}\eta^2\text{-}\eta^2\text{-PhN}_6\text{Ph})]$ <b>2</b> <sup>[25]</sup>	1.305	1.299	1.377	118.374
$[(\text{Me}(\text{Do})\text{Zn})_2(\mu\text{-}\eta^2\text{-}\eta^2\text{-PhN}_6\text{Ph})]$ <sup>[25]</sup>	1.310	1.297	1.402	117.352
$[(\text{MeL}^{\text{Dipp}}\text{Zn})_2(\mu\text{-}\eta^2\text{-}\eta^2\text{-PhN}_6\text{Ph})]$ <b>3</b> <sup>[a]</sup>	1.313(3)	1.302(3)	1.398(5)	117.0
$[(\text{MeZn})_2(\mu\text{-}\eta^2\text{-}\eta^2\text{-PhN}_6\text{Ph})(\text{Py})_2]$ <b>4</b> <sup>[a]</sup>	1.308(13)	1.298(13)	1.395(19)	117.21(9)
$[(\text{MeL}^{\text{Ph}}\text{Zn})_2(\mu\text{-}\eta^2\text{-}\eta^2\text{-PhN}_6\text{Ph})]$ <b>5</b> <sup>[a]</sup>	1.311(11)	1.297(14)	1.405(2)	117.21(11)

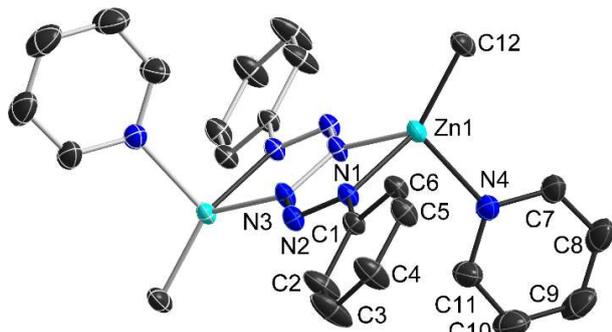
Do: CH<sub>3</sub>CN; <sup>[a]</sup> this work**Table 2: CH...π interactions in 4.**

D-H...Cnt	Symmetry operator	H...Cnt	D-H...Cnt	H...R	R/Cnt...H
C9-H9...Cnt1	-x+1/2, -y+1/2, -z+1	2.78	151.2	2.691	83.9
C10-H10...Cnt1	-x, -y+1, -z+1	3.85	126.5	2.726	50.1
C11-H11...Cnt1	-x, -y+1, -z+1	3.67	136.4	3.292	70.9

Cnt1: centroid of the phenyl ring

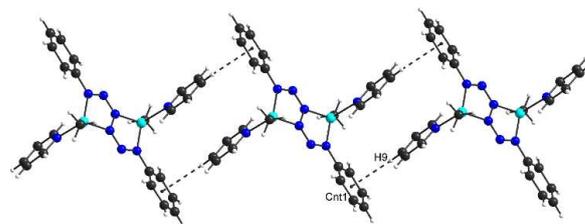
**Scheme 4: Synthesis of  $[(\text{MeZn})_2(\mu\text{-}\eta^2\text{-}\eta^2\text{-PhN}_6\text{Ph})(\text{Py})_2]$  **4**.**

Single crystals of **4** were obtained from a concentrated solution in C<sub>6</sub>D<sub>6</sub> after storage at ambient temperature for 12 hours (fig. 2).

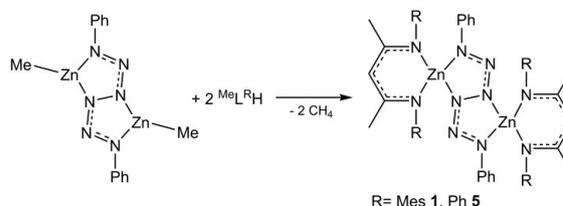
Figure 2: Molecular structure of **4**; H atoms omitted for clarity.

**4** crystallizes in the monoclinic space group *C2/c* with the molecule placed on a center of inversion. The zinc atoms are slightly out of the plane of the N<sub>4</sub>Zn rings (r.m.s. deviation from the least squares plane 0.0014 Å). The N–N bond lengths and N1–N2–N3 bond angle within the hexazene unit are comparable to those observed in **2** and **3** (table 1). The packing is dominated by two sets of chains parallel to [110] and [1-10], which are formed via the *C*-centering

vector. The two sets are related by 2<sub>1</sub> screw or *c*-glide-plane symmetry depending on which part of the centrosymmetric molecule is considered.

Figure 3: Intermolecular interactions in **4** leading to chains in the solid state.

The CH...π interaction between H9 and the π-system of the phenyl ring connects the individual molecules within the chains (table 2).<sup>[28]</sup> H10 and H11 form an edge-to-face CH...π interaction from the opposite side of the ring, which facilitates the connection between the sets of chains (fig. 3). This arrangement leads to a π-stacking along [001], but considering the inter-centroid distance of more than 4 Å, any π/π interactions will be very weak - if present at all. Consequently, the former interactions dominate the formation of this particular packing.

**Scheme 5: Reactions of 2 with H-acidic ligands.**

In addition to the tendency of **2** to undergo Lewis acid-base reactions, **2** may also serve as suitable starting reagent for further ligand exchange reactions with H-acidic

ligands. For instance, reactions of **2** with  $\text{MeL}^{\text{Mes}}\text{H}$  or  $\text{MeL}^{\text{Ph}}\text{H}$  occurred with elimination of methane (scheme 5), which was identified by *in situ*  $^1\text{H}$  NMR spectroscopy due to its

**Table 3: Intermolecular interactions in 6.**

D-H...A	Symmetry operator	H...A	D...A	D-H...A	
C3-H3...O1	-x+1, -y+1, -z+1	2.64	3.553	162.4	
D-H...Cnt	Symmetry operator	H...Cnt	D-H...Cnt	H...R	R/Cnt...H
C7-H7A...Cnt1	x, y+1, z	3.28	142.0	3.045	75.8
C12-H12B...Cnt1	x-1, y, z	3.32	111.9	3.211	83.6
C10-H10A...Cnt1	x-1, y, z	3.47	130.4	2.762	58.6
C9-H9A...Cnt2	-x, -y+1, -z	3.58	142.2	3.003	63.4

Cnt1: centroid of the phenyl ring, Cnt2: centroid of N1, N2, N3, N3'

**5** crystallizes in the triclinic space group P-1 with one molecule in the unit cell (fig. 4).

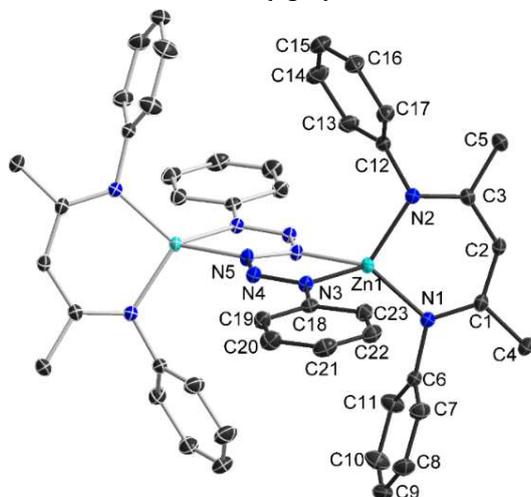
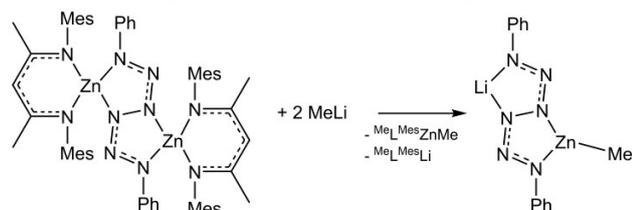


Figure 4: Molecular structure of **5**; H atoms are omitted for clarity.

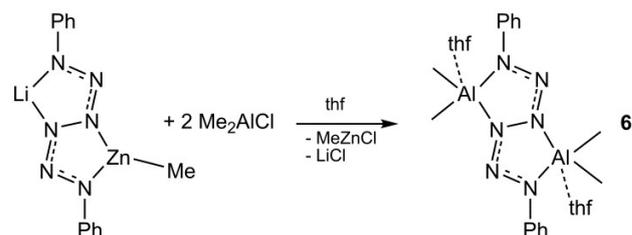
The Zn atoms in **5** are slightly out of the plane (deviation from least-squares plane of N1, N2, C1, C2 and C3: 0.0819(14) Å) of the six-membered  $\text{C}_3\text{N}_2\text{Zn}$  rings, whereas the  $\text{N}_4\text{Zn}$  metallacycle is almost perfectly planar (r.m.s deviation from least-squares plane 0.0069 Å). The central N5–N5' bond (1.395(19) Å) again is significantly elongated compared to the almost identical N3–N4 (1.308(13) Å) and N4–N5 bonds (1.298(13) Å) as was observed for **1** - **3**. The N3–N4–N5 bond angle of 117.21(9)° and the N–N bond lengths within the hexazenediide unit are comparable to those previously observed in hexazene complexes.<sup>[13,20–25]</sup>



**Scheme 6: Synthesis of  $(\text{MeZn})(\mu\text{-}\eta^2\text{:}\eta^2\text{-PhN}_6\text{Ph})(\text{Li})$ .**

resonance at 0.16 ppm,<sup>[27]</sup> and subsequent formation of the hexazene complexes **1** and  $[(\text{MeL}^{\text{Ph}}\text{Zn})_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-PhN}_6\text{Ph})]$  (**5**), whereas no reaction was observed for **2** with  $\text{MeL}^{\text{Dipp}}\text{H}$ .

We reported recently on reactions of **1** with MeLi. The reaction with one equivalent occurred with elimination of  $\text{MeL}^{\text{Mes}}\text{ZnMe}$  and formation of the heterobimetallic hexazene complex  $(\text{MeL}^{\text{Mes}}\text{Zn})(\mu\text{-}\eta^2\text{:}\eta^2\text{-PhN}_6\text{Ph})(\text{Li})$ , while the reaction with two equivalents occurred with stepwise elimination of  $\text{MeL}^{\text{Mes}}\text{ZnMe}$  and  $\text{MeL}^{\text{Mes}}\text{Li}$  and formation of  $(\text{MeZn})(\mu\text{-}\eta^2\text{:}\eta^2\text{-PhN}_6\text{Ph})(\text{Li})$  (scheme 6).<sup>[25]</sup> Unfortunately, several attempts to grow single crystals of these heterobimetallic hexazene complexes failed, to date. We became therefore interested in further transmetallation reactions of  $(\text{MeZn})(\mu\text{-}\eta^2\text{:}\eta^2\text{-PhN}_6\text{Ph})(\text{Li})$  and investigated its reaction with different amounts of  $\text{Me}_2\text{AlCl}$  in thf solution.



**Scheme 7: Synthesis of  $[(\text{Me}_2\text{Al})_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-PhN}_6\text{Ph})(\text{thf})_2]$  **6**.**

The reaction of  $(\text{MeZn})(\mu\text{-}\eta^2\text{:}\eta^2\text{-PhN}_6\text{Ph})(\text{Li})$  with one equivalent of  $\text{Me}_2\text{AlCl}$  in thf solution proceeded only with elimination of LiCl, which was identified by *in situ*  $^7\text{Li}$  NMR spectroscopy at 0.59 ppm (fig. S12), and formation of insoluble  $(\text{MeZn})(\mu\text{-}\eta^2\text{:}\eta^2\text{-PhN}_6\text{Ph})(\text{AlMe}_2)$ . Addition of the second equivalent of  $\text{Me}_2\text{AlCl}$  either to an *in situ* prepared sample of  $(\text{MeZn})(\mu\text{-}\eta^2\text{:}\eta^2\text{-PhN}_6\text{Ph})(\text{AlMe}_2)$  or to an isolated sample of  $(\text{MeZn})(\mu\text{-}\eta^2\text{:}\eta^2\text{-PhN}_6\text{Ph})(\text{AlMe}_2)$  finally yielded the homobimetallic aluminum hexazene complex  $[(\text{Me}_2\text{Al})_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-PhN}_6\text{Ph})(\text{thf})_2]$  (**6**) (scheme 7).

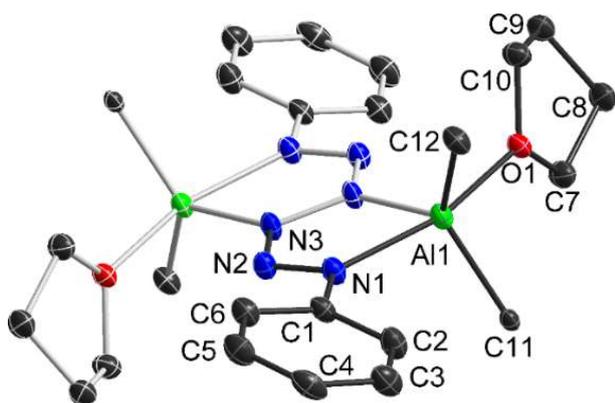


Figure 5: Molecular structure of **6** (displacement parameters are drawn at 50 % probability level, H atoms omitted) showing the atom-numbering scheme; selected bond lengths (Å) and angles (°): Al1-C11 2.0116(16), Al1-C12 1.9857(17), Al1-N1 2.0745(14), Al1-N3' 1.9693(15), N1-N2 1.303(2), N2-N3 1.3084(19), N3-N3' 1.414(2); C11-Al1-C12 124.93(7), C142-Al1-N1 94.16(6), C11-Al1-N3' 114.93(7), C11-Al1-N1 99.32(6), C142-Al1-N3' 120.12(7), N1-Al1-N3' 73.85(6), N1-N2-N3 115.24(13), N2-N3-N3' 113.50(16), Al1-N1-N2 127.72(10).

Table 4: Calculated and experimental IR data of all known hexazene compounds.

Compound	N1-N2-N3	N1-N2 (incl. Ph ring deformations for <b>6'</b> )	N1-C <sub>Ph</sub>	N2-N3 (incl. Ph ring deformations)
calc. <b>1'</b>	949	1209	1278	1302 / 1333 / 1356
calc. <b>2'</b> <sup>[25]</sup>	947	1204	1264	1294 / 1324 / 1347
calc. <b>4'</b> <sup>[a]</sup>	941	1200	1266	1299 / 1328 / 1353
calc. <b>6'</b> <sup>[a]</sup>	951	1228 / 1308	1276	1328 / 1352
calc. [MeZn] <sub>2</sub> N <sub>6</sub> Ph <sub>2</sub> [CH <sub>3</sub> CN] <sub>2</sub> <sup>[25]</sup>	943	1201	1269	1299 / 1330 / 1352
[MeL <sup>Dipp</sup> Fe] <sub>2</sub> N <sub>6</sub> Ad <sub>2</sub> <sup>[13]</sup>	933	1211	1261	1315
[ <sup>t</sup> BuL <sup>Dipp</sup> Fe] <sub>2</sub> N <sub>6</sub> Ad <sub>2</sub> <sup>[13]</sup>		1215	1257	1315
[{R'C(NDipp) <sub>2</sub> }Fe] <sub>2</sub> N <sub>6</sub> Ad <sub>2</sub> <sup>[20]</sup>	933	1191	1257	1339
[( <i>t</i> -Bu <sub>2</sub> PhCO) <sub>2</sub> Fe] <sub>2</sub> N <sub>6</sub> Ad <sub>2</sub> <sup>[23]</sup>	980	1179	1271	≈1337
[MeL <sup>Dipp</sup> Mg] <sub>2</sub> N <sub>6</sub> Ad <sub>2</sub> <sup>[21]</sup>	933	1173	1263	1378
[ <sup>t</sup> BuL <sup>Dipp</sup> Mg] <sub>2</sub> N <sub>6</sub> Ad <sub>2</sub> <sup>[22]</sup>	935	1173	1260	1365
[MeL <sup>Mes</sup> Mg] <sub>2</sub> N <sub>6</sub> Ad <sub>2</sub> <sup>[22]</sup>	-	1199	1269	-
[MeL <sup>Mes</sup> Zn] <sub>2</sub> N <sub>6</sub> Ph <sub>2</sub> <b>1</b> <sup>[24]</sup>	947	1198	1259	1300 / 1323 / 1349
[MeL <sup>Dipp</sup> Zn] <sub>2</sub> N <sub>6</sub> Ph <sub>2</sub> <b>3</b> <sup>[a]</sup>	946	1210	1257	1303 / 1320 / 1346
[MeL <sup>Ph</sup> Zn] <sub>2</sub> N <sub>6</sub> Ph <sub>2</sub> <b>5</b> <sup>[a]</sup>	949	1199	1258	1302 / 1324 / 1355
[MeZn] <sub>2</sub> N <sub>6</sub> Ph <sub>2</sub> <b>2</b> <sup>[25]</sup>	954	1197	1257	1300 / 1323 / 1343
[MeZn] <sub>2</sub> N <sub>6</sub> Ph <sub>2</sub> [CH <sub>3</sub> CN] <sub>2</sub> <sup>[25]</sup>	943	1203	1262	1301 / 1324 / 1340
[MeZn] <sub>2</sub> N <sub>6</sub> Ph <sub>2</sub> [Py] <sub>2</sub> <b>4</b> <sup>[a]</sup>	942	1187	1256	1303 / 1324 / 1346
[MeL <sup>Mes</sup> Zn]N <sub>6</sub> Ph <sub>2</sub> [Li] <sup>[25][b]</sup>	962	1207	1257	1302 / 1325 / 1337
[MeZn]N <sub>6</sub> Ph <sub>2</sub> [Li] <sup>[25][b]</sup>	963	1204	1257	1301 / 1324 / 1335
[Me <sub>2</sub> Al] <sub>2</sub> N <sub>6</sub> Ph <sub>2</sub> [thf] <sub>2</sub> <b>6</b> <sup>[a]</sup>	954	1232 / 1306	1279	1326 / 1341

R' = 2,6-dimethylpiperidine; <sup>[a]</sup> this work; <sup>[b]</sup> Careful reinvestigation gave slightly different values than the originally reported ones.

The by-product MeZnCl was identified by *in situ* <sup>1</sup>H NMR spectroscopy due to its resonance at -0.89 ppm (fig. S13). **6** precipitated as a crystalline solid which is only barely

soluble in thf. Therefore, NMR data of **6** could not be obtained in thf. **6** can also be prepared by reaction of **2** with two equivalents of Me<sub>2</sub>AlCl in thf solution, which proceeds

with elimination of MeZnCl as was shown by *in situ*  $^1\text{H}$  NMR spectroscopy, as well as by reaction of **1** with AlMe<sub>3</sub> as was described previously.<sup>[25]</sup>

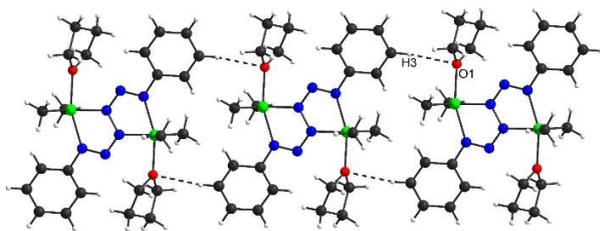


Figure 6: O...H interactions in **6**.

Single crystals of **6** were obtained from a suspension of (MeZn)( $\mu$ - $\eta^2$ : $\eta^2$ -PhN<sub>6</sub>Ph)(Li) in thf, which was carefully overlaid with a solution of Me<sub>2</sub>AlCl in thf, upon standing (without stirring) at ambient temperature for 12 hours. **6** crystallizes in the triclinic space group P-1 with one molecule in the unit cell (figure 5). The central N3-N3A bond (1.414(2) Å) is significantly elongated compared to the almost identical N1-N2 (1.303(2) Å) and N2-N3 bonds (1.308(19) Å). The N1-N2-N3 bond angle of 115.25(13)° and the N-N bond lengths within the hexazenediide unit are comparable to those previously observed in metal hexazene complexes.<sup>[13,20-25]</sup>

The molecules form strings in the crystal packing which are stabilized by non-classical hydrogen bonds (C3-H3...O1: H...A 2.64 Å DHA 162.4°) as shown in figure 6. In addition, these strings are further connected by CH... $\pi$  interactions (table 3).<sup>[28]</sup>

### Calculations and IR discussion

Quantum chemical calculations of the gas phase structures and vibrational spectra of several Zn-hexazene complexes were previously performed<sup>[24,25]</sup> using density functional theory with the BP86 functional<sup>[29]</sup> and a third generation dispersion correction (DFT+D3).<sup>[30,31]</sup> Herein we use the same method in conjunction with a triple-zeta basis set<sup>[32]</sup> for the determination of the molecular structures and IR spectra of isolated molecules **4'** and **6'**, respectively.<sup>[31,33]</sup> Geometry optimization lead to *C<sub>i</sub>* symmetrical structures for **4'** (Zn-N1 2.070, Zn-N3 2.052, N1-N2 1.312, N2-N3 1.302, N3-N3' 1.401 Å, N1-N2-N3 117.16°) and **6'** (Al-N1 2.082, Al-N3 1.996, N1-N2 1.303, N2-N3 1.304, N3-N3' 1.399 Å, N1-N2-N3 115.65°). The N-N bond lengths typically agree within 0.005 Å with the crystallographic data and the N1-N2-N3 bond angles within 0.4°. The bond lengths between N1 and N3 and the metal atoms agree somewhat less well, but still within about 0.03 Å. According to NPA calculations, an Al atom in **6'** is more positively charged (1.72 e) than a Zn atom in **4'** (1.46 e), most likely resulting from the coordinative bond to a more electronegative atom (O instead of N) and the presence of an additional polar metal-carbon bond. On the other hand, the N<sub>6</sub> unit in Al-hexazene with -1.44 e is less charged than in Zn-hexazene (-1.79 e). Of these total charges on the hexazenediide unit -0.39 e are found on N1 and -0.31 e on N3 in **6'**, while the corresponding values are -0.50 e and -0.36 e for **4'**.

An important IR spectroscopic signature for the presence of a hexazenediide unit is the antisymmetric linear combination of the N1-N2-N3 / N1'-N2'-N3' bending vibrations, simply denoted as N1-N2-N3 in table 4. It is relatively

intense and in general lies in a fairly empty region of the spectrum, i.e. at 942 and 954 cm<sup>-1</sup> for **4** and **6**, respectively. Our calculated line positions for the gas phase structures **4'** and **6'** agree within 3 cm<sup>-1</sup> (cf. table 4). In the Zn-hexazene **4'** the antisymmetric linear combination of the N1-N2 / N1'-N2' stretch vibration at 1200 cm<sup>-1</sup> can clearly be distinguished from the antisymmetric linear combination of the N1-C<sub>Ph</sub> / N1'-C<sub>Ph</sub>' stretch vibration at 1266 cm<sup>-1</sup>, which deviate by up to 13 cm<sup>-1</sup> (cf. table 4) from the experimental line positions. The remaining antisymmetric linear combination of the hexazenediide unit stretch vibrations (N2-N3 / N2'-N3') couples strongly with in plane phenyl ring deformations. This coupling leads to a splitting into three lines at 1299, 1328 and 1353 cm<sup>-1</sup> in **4'**, which agree quite well with the bands observed in the experimental spectrum of **4** (1303, 1324, 1346 cm<sup>-1</sup>). While the occurrence of hexazenediide / phenyl couplings was previously mentioned,<sup>[25]</sup> the details were not yet discussed and therefore corresponding data for some of the compounds discussed in Ref. [24,25] appended to table 4. The theoretical IR spectra of the symmetrical Zn-hexazene compounds unexceptional show the triplet of lines at about 1300 / 1330 / 1350 cm<sup>-1</sup>, which are characteristic for coupled N2-N3-stretch and phenyl-ring deformations. The degree of mixing of these coupled bands depends on the specific case (though the N2-N3-stretch seems to dominate the band at about 1350 cm<sup>-1</sup> in most cases). This band triplet was also detected in a reexamination of the previous experimental IR-spectra (cf. table 4). Note that for **5** the band at 1355 cm<sup>-1</sup> is only a shoulder of an intense line. While in Ref. [24] we assigned the higher frequency component (953 cm<sup>-1</sup>) of the experimentally observed band doublet to the N1-N2-N3 bend vibration we now assign this to the lower frequency component (947 cm<sup>-1</sup>). Note that for **5** this vibration (949 cm<sup>-1</sup>) is seen as a shoulder of another intense line only.

The phenyl-ring deformations of the Al-hexazene compound **6'** couple with both N1-N2 (N1'-N2') and N2-N3 (N2'-N3') stretch vibrations, leading to a somewhat different assignment of the bands (cf. table 4). Furthermore, the N1-N2 (N1'-N2') and N1-C<sub>Ph</sub> (N1'-C<sub>Ph</sub>') stretch vibrations couple more strongly than in the Zn-hexazene compounds. The agreement between the calculated gas phase spectrum of **6'** and the experimental solid state spectrum of **6** is very satisfactory. Please note that in the original paper, we assigned the N1-N2-N3 bend vibration of [MeZn]N<sub>6</sub>Ph<sub>2</sub>[Li] at 921 cm<sup>-1</sup>,<sup>[25]</sup> but 963 cm<sup>-1</sup> (small shoulder) seems to be more realistic according to our current studies.

### Conclusion

We demonstrated the promising potential of [(MeZn)<sub>2</sub>( $\mu$ - $\eta^2$ : $\eta^2$ -PhN<sub>6</sub>Ph)] **2** to serve as building block for the synthesis of new zinc hexazene complexes via ligand substitution reactions with H-acidic ligands. In addition, the promising potential of **2** for the synthesis of new metal hexazene complexes was proven in its reaction with Me<sub>2</sub>AlCl, yielding the first aluminum hexazene complex **6**. Moreover, this reaction further proved the existence of the postulated hexazene complex (MeZn)( $\mu$ - $\eta^2$ : $\eta^2$ -PhN<sub>6</sub>Ph)(Li), which may further serve as hexazenediide transfer reagent in salt elimination reactions with metal chlorides. This reaction pathway, which does not require low-valent one-

electron reductants such as Fe(I), Mg(I) and Zn(I) complexes as starting reagents, may offer a general access to metal hexazene complexes. Quantum chemical calculations revealed the structures of **4** and **6** and provided valuable information on the most characteristic IR absorption bands of the dianionic hexazenediide unit, which will help in the future to identify the formation of these interesting complexes.

## EXPERIMENTAL SECTION

Manipulations were performed in a glove box under an Ar-atmosphere or with standard Schlenk techniques. Dry solvents were obtained from a solvent purification system (MBraun) and degassed prior to use.  $\text{Me}_2\text{LiDipp}_2\text{Zn}_2$ ,<sup>[26]</sup>  $\text{PhN}_3$ ,<sup>[34]</sup> and  $(\text{MeZn})_2\text{Ph}_2\text{N}_6$ <sup>[25]</sup> were prepared according to literature methods. A Bruker Avance 300 spectrometer was used for NMR spectroscopy.  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were referenced to internal  $\text{C}_6\text{D}_5\text{H}$  ( $^1\text{H}$ :  $\delta = 7.154$ ;  $^{13}\text{C}$ :  $\delta = 128.0$ ). IR spectra were recorded on an Alpha-T FT-IR spectrometer with a single reflection ATR sampling module. Melting points were measured in sealed capillaries and were not corrected. Elemental analyses were performed at the *Elementaranalyse Labor* of the University of Duisburg-Essen.

The sensitivity of all metal hexazene complexes toward heat and shock was investigated, but we never observed any sign of (explosive) decomposition! Heating the complexes at temperatures higher than their melting points typically resulted in controlled decomposition with elimination of  $\text{N}_2$ . However, safety precautions should be taken when working with this type of complex.

**(MeLiDippZn)<sub>2</sub>( $\mu$ - $\eta^2$ : $\eta^2$ -PhN<sub>6</sub>Ph) 3.**  $\text{Me}_2\text{LiDipp}_2\text{Zn}_2$  (96 mg, 100  $\mu\text{mol}$ ) was dissolved in fluorobenzene and  $\text{PhN}_3$  (30 mg, 200  $\mu\text{mol}$ ) was added. The resulting red solution was stirred over night at room temperature. An orange solid was isolated by filtration, which was dried in vacuum. The solid was dissolved in fluorobenzene. **3** was isolated by crystallization at 4 °C as orange crystals. The crystals were suitable for a single crystal X-ray diffraction study.

Yield: 98 mg (82 %). m.p.: 307 °C. –  $\text{C}_{70}\text{H}_{92}\text{N}_{10}\text{Zn}_2$  (1204.34): calcd. C 69.31, H 7.70, N 11.63; found C 69.21, H 7.72, N 11.65. – IR:  $\nu = 3059, 2962, 2926, 2866, 1593, 1551, 1518, 1461, 1439, 1400, 1345, 1320, 1302, 1257, 1210, 1088, 1015, 946, 860, 794, 756, 724, 691, 631, 527, 464, 397 \text{ cm}^{-1}$ . –  $^1\text{H-NMR}$ : (300 MHz,  $\text{C}_6\text{D}_6$ , 25 °C):  $\delta = 0.12$  (d, 12 H,  $\text{CH}(\text{CH}_3)_2$ ), 0.89 (d, 12 H,  $\text{CH}(\text{CH}_3)_2$ ), 1.29 (d, 12 H,  $\text{CH}(\text{CH}_3)_2$ ), 1.49 (d, 12 H,  $\text{CH}(\text{CH}_3)_2$ ), 1.62 (s, 12 H,  $\text{CHCH}_3$ ), 2.95 (m, 4 H,  $\text{CH}(\text{CH}_3)_2$ ), 3.39 (m, 4 H,  $\text{CH}(\text{CH}_3)_2$ ), 4.92 (s, 2 H, *CH*), 6.67 (dd, 4 H, *Ph-m-H*), 6.95 (t, 2 H, *Ph-p-H*), 7.04 (m, 12 H, *Ar-H*), 7.32 (m, 4 H, *Ph-o-H*). –  $^{13}\text{C-NMR}$ : (151 MHz,  $\text{C}_6\text{D}_6$ , 25 °C):  $\delta = 24.4$  ( $\text{C}(\text{CH}_3)_2$ ), 26.1 ( $\text{CCH}_3$ ), 27.6 ( $\text{C}(\text{CH}_3)_2$ ), 28.9 (*CH*), 94.2 ( $\gamma$ -C), 123.8 (*p-Ph*), 124.56 (*p-Ar*), 126.1 (*m-Ph*), 129.2 (*m-Ar*), 142.4 (*o-Ph*), 143.5 (*o-Ar*), 144.1 (*i-Ar*), 147.9 (*i-Ph*), 169.5 ( $\beta$ -C).

**(MeZn)<sub>2</sub>( $\mu$ - $\eta^2$ : $\eta^2$ -PhN<sub>6</sub>Ph)(Py)<sub>2</sub> 4. 2** (16 mg, 40  $\mu\text{mol}$ ) was suspended in 2 mL  $\text{C}_6\text{D}_6$  and  $\text{C}_5\text{H}_5\text{N}$  (6.4  $\mu\text{L}$ , 80  $\mu\text{L}$ ) was added. The reaction mixture was stirred for 1 h. The orange solution was stored over night at room temperature, yielding an orange solid. The solution was separated from the solid by filtration. **4** was isolated by crystallization at 4 °C as orange crystals. The crystals were suitable for a single crystal X-ray diffraction study.

Yield: 19 mg (87 %). M.P.: 206 °C (dec.). –  $\text{C}_{24}\text{H}_{26}\text{N}_6\text{Zn}_2$  (557.29): calcd. C 51.73, H 4.70, N 20.11; found C 51.77, H 4.72, N 20.14. – IR:  $\nu = 3065, 3038, 3022, 2961, 2934, 2900, 2831, 1599, 1552, 1520, 1483, 1454, 1396, 1345, 1324, 1302, 1255, 1210, 1186, 1149, 1096, 1063, 1037, 1010, 941, 897, 861, 798, 760, 752, 719, 691, 654, 625, 529, 498, 452, 431, 413, 403 \text{ cm}^{-1}$ . –  $^1\text{H-NMR}$ : (300 MHz,  $\text{C}_6\text{D}_6$ , 25 °C):  $\delta = -0.22$  ( $\text{ZnCH}_3$ ), 6.63 (m, 2 H, *Ph-p-H*), 6.85 (m, 4 H, *Ph-m-H*), 7.11 (m, 4 H, *Ph-o-H*), 7.17 (m, 2 H, *py-p-H*), 7.87 (m, 4 H, *py-m-H*), 8.14 (m, 4 H, *py-o-H*). –  $^{13}\text{C-NMR}$ : (75 MHz,  $\text{C}_6\text{D}_6$ , 25 °C):  $\delta = -16.1$  ( $\text{CH}_3$ ), 119.3 (*Ph*), 124.1 (*py*), 124.9 (*Ph*), 129.9 (*Ph*), 137.9 (*p-py*), 148.6 (*i-Ph*), 150.3 (*o-py*).

**(MeL<sup>Ph</sup>Zn)<sub>2</sub>( $\mu$ - $\eta^2$ : $\eta^2$ -PhN<sub>6</sub>Ph) 5. 2** (8 mg, 20  $\mu\text{mol}$ ) and  $\text{MeL}^{\text{Ph}}\text{H}$  (10 mg, 40  $\mu\text{mol}$ ) were dissolved in toluene and stirred for 5 h at

room temperature. The orange solution was stored over night at 4 °C. An orange solid was isolated by filtration, which was dried in vacuum. The solid was dissolved in fluorobenzene. **5** was isolated by crystallization at 18 °C as orange crystals. The crystals were suitable for a single crystal X-ray diffraction study.

Yield: 14 mg (83 %). m.p.: 237 °C. –  $\text{C}_{46}\text{H}_{44}\text{N}_{10}\text{Zn}_2$  (867.69): calcd. C 63.68, H 5.11, N 16.14; found C 63.68, H 5.16, N 16.18. – IR:  $\nu = 3056, 3022, 2962, 2923, 1628, 1595, 1551, 1527, 1484, 1451, 1397, 1355, 1325, 1258, 1199, 1186, 1167, 1070, 1007, 957, 899, 864, 785, 751, 724, 697, 662, 636, 615, 598, 561, 519, 497, 452, 391 \text{ cm}^{-1}$ . –  $^1\text{H-NMR}$ : 1.77 (s, 12 H,  $\text{C}(\text{CH}_3)_2$ ), 4.78 (s, 2 H, *CH*), 6.78 – 7.60 (m, 30 H, *Ph-H*). –  $^{13}\text{C-NMR}$ : (75 MHz,  $\text{C}_6\text{D}_6$ , 25 °C):  $\delta = 23.6$  ( $\text{CCH}_3$ ), 96.4 ( $\gamma$ -C), 124.5 (*p-Ph*), 124.8 (*p-Ph*), 128.0 (*m-Ph*), 128.3 (*m-Ph*), 129.4 (*o-Ph*), 129.7 (*o-Ph*), 149.6 (*i-Ph*), 149.8 (*i-Ph*), 167.7 ( $\text{CCH}_3$ ).

**(Me<sub>2</sub>Al)<sub>2</sub>( $\mu$ - $\eta^2$ : $\eta^2$ -PhN<sub>6</sub>Ph)(thf)<sub>2</sub> 6. 2** (12 mg, 30  $\mu\text{mol}$ ) was dissolved in THF and  $\text{Me}_2\text{AlCl}$  (5.5  $\mu\text{L}$ , 60  $\mu\text{mol}$ ) was added. The solution was stirred for 1 h at room temperature. **6** was isolated by crystallization at 18 °C as orange crystals. The crystals were suitable for a single crystal X-ray diffraction study.

Yield: 13 mg (89 %). m.p.: 204 °C (dec.). –  $\text{C}_{24}\text{H}_{38}\text{Al}_2\text{N}_6\text{O}_2$  (496.57): calcd. C 58.05, H 7.71, N 16.92, O 6.44; found C 58.01, H 7.63, N 16.89, O 6.43. – IR:  $\nu = 2980, 2933, 2902, 2834, 1593, 1488, 1456, 1340, 1325, 1306, 1278, 1232, 1195, 1098, 1077, 1040, 1019, 953, 918, 903, 859, 791, 759, 736, 690, 665, 631, 552, 524, 489, 475, 449, 419 \text{ cm}^{-1}$ .

**Single crystal X-ray diffraction.** Crystallographic data of **3 - 6**, which were collected on a Bruker D8 Kappa APEX2 diffractometer (MoK $\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$ ) at 100(1) K, are summarized in Table S1 (SI). The structures were solved by Direct Methods (SHELXS-97)<sup>[35]</sup> and refined anisotropically by full-matrix least-squares on F<sup>2</sup> (SHELXL-2014)<sup>[36,37]</sup>. Absorption corrections were performed semi-empirically from equivalent reflections on basis of multi-scans (Bruker AXS APEX2, TWINABS). Hydrogen atoms were refined using a riding model or rigid methyl groups. **3** contains a fluorobenzene molecule whose F atom is disordered over four sites. **4** was non-merohedrally twinned and refined against HKLF4 data. **5** was non-merohedrally twinned and refined against HKLF5 data.

The crystallographic data of **3 - 6** (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-1443045 (**3**), CCDC-1443042 (**4**), CCDC-1443043 (**5**) and CCDC-1443044 (**6**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB21EZ (fax: (+44) 1223/336033; e-mail: deposit@ccdc.cam.ac.uk).

## ASSOCIATED CONTENT

### Supporting Information

Electronic Supplementary Information (ESI) available: Cif files of **3 - 6**. In addition, NMR and IR spectra of **3 - 6** and in situ  $^1\text{H}$  NMR spectra of the reaction of  $(\text{MeZn})(\mu\text{-}\eta^2\text{-}\eta^2\text{-PhN}_6\text{Ph})(\text{Li})$  with one and two equivalents of  $\text{Me}_2\text{AlCl}$  are given in the SI. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interests.

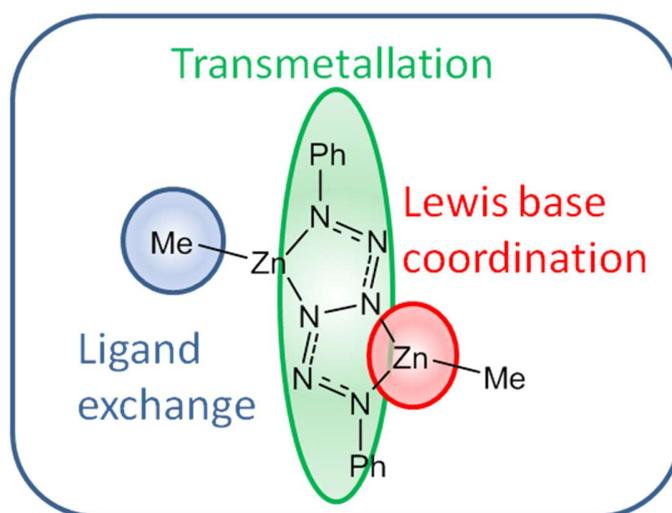
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## REFERENCES

- [1] Review on reactions of transition metal complexes with organic azides: Cenini, S.; Gallo, E.; Caselli, A.; Ragaini, F.; Fantauzzi, S.; Piangiolino, C. *Coord. Chem. Rev.* **2006**, *250*, 1234-1253.
- [2] a) Schulz, S.; Thomas, F.; Priesmann, W.; Nieger, M. *Organometallics* **2006**, *25*, 1392-1398; b) Schulz, S.; Voigt, A.; Roesky, H. W.; Häming, L.; Herbst-Irmer, R. *Organometallics* **1996**, *15*, 5252-5253; c) Schulz, S.; Häming, L.; Herbst-Irmer, R.; Roesky, H. W.; Sheldrick, G. M. *Angew. Chem.* **1994**, *106*, 1052-1054; *Angew. Chem., Int. Ed.* **1994**, *33*, 969-970.
- [3] Uhl, W.; Gerding, R.; Pohl, S.; Saak, W. *Chem. Ber.* **1995**, *128*, 81-85.
- [4] Yu, Y.; Sadique, A. R.; Smith, J. M.; Dugan, T. R.; Cowley, R. E.; Brennessel, W. W.; Flaschenriem, C. J.; Bill, E.; Cundari, T. R.; Holland, P. L. *J. Am. Chem. Soc.* **2008**, *130*, 6624-6638.
- [5] Smith, J. M.; Sadique, A. R.; Cundari, T. R.; Rodgers, K. R.; Lukat-Rodgers, G.; Lachicotte, R. J.; Flaschenriem, C. J.; Vela, J.; Holland, P. L. *J. Am. Chem. Soc.* **2006**, *128*, 756-769.
- [6] Eckert, N. A.; Vaddadi, S.; Stoian, S.; Lachicotte, R. J.; Cundari, T. R.; Holland, P. L. *Angew. Chem., Int. Ed.* **2006**, *45*, 6868-6871; *Angew. Chem.* **2006**, *118*, 7022-7025.
- [7] Cowley, R. E.; Bill, E.; Neese, F.; Brennessel, W. W.; Holland, P. L. *Inorg. Chem.* **2009**, *48*, 4828-4836.
- [8] Cui, C.; Roesky, H. W.; Schmidt, H.-G.; Noltemeyer, M. *Angew. Chem.* **2000**, *112*, 4705-4707; *Angew. Chem., Int. Ed.* **2000**, *39*, 4531-4533.
- [9] Zhu, H.; Yang, Z.; Magull, J.; Roesky, H. W.; Schmidt, H.-G.; Noltemeyer, M. *Organometallics* **2005**, *24*, 6420-6425.
- [10] Nagendran, S.; Roesky, H. W. *Organometallics* **2008**, *27*, 457-492.
- [11] Hardman, N. J.; Power, P. P. *Chem. Commun.* **2001**, 1184-1185.
- [12] Mock, M. T.; Popescu, C. V.; Yap, G. P. A.; Dougherty, W. G.; Riordan, C. G. *Inorg. Chem.* **2008**, *47*, 1889-1891.
- [13] Cowley, R. E.; Elhaik, J.; Eckert, N. A.; Brennessel, W. W.; Bill, E.; Holland, P. L. *J. Am. Chem. Soc.* **2008**, *130*, 6074-6075.
- [14] Cowley, R. E.; DeYonker, N. J.; Eckert, N. A.; Cundari, T. R.; DeBeer, S.; Bill, E.; Ottenwaelder, X.; Flaschenriem, C.; Holland, P. L. *Inorg. Chem.* **2010**, *49*, 6172-6187.
- [15] Berson, F. R. *The High Nitrogen Compounds*, Wiley, New York, 1984.
- [16] Nuyken, O.; Scherer, C.; Baidl, A.; Brenner, A. R.; Dahn, U.; Gärtner, R.; Kaiser-Röhrich, S.; Kollefrath, R.; Matusche, P.; Voit, B. *Prog. Polym. Sci.* **1997**, *22*, 93-183.
- [17] Hofmann, K. A.; Hock, H. *Chem. Ber.* **1911**, *44*, 2946-2956.
- [18] Mackay, D.; McIntyre D. D.; Taylor, N. J. *J. Org. Chem.* **1982**, *47*, 532-535.
- [19] Fitchett C. M.; Richardson, C.; Steel, P. J. *Org. Biomol. Chem.* **2005**, *3*, 498-502.
- [20] Fohlmeister, L.; Jones, C. *Aust. J. Chem.* **2014**, *67*, 1011-1016.
- [21] Bonyhady, S. J.; Green, S. P.; Jones, C.; Nembenna, S.; Stasch, A. *Angew. Chem.* **2009**, *121*, 3017-3021; *Angew. Chem. Int. Ed.* **2009**, *48*, 2973-2977.
- [22] Bonyhady, S. J.; Jones, C.; Nembenna, S.; Stasch, A.; Edwards, A. J. McIntyre, G. J. *Chem. – Eur. J.* **2010**, *16*, 938-955.
- [23] Bellow, J. A.; Martin, P. D.; Lord, R. L.; Groysman, S. *Inorg. Chem.* **2013**, *52*, 12335-12337.
- [24] Gondzik, S.; Schulz, S.; Bläser, D.; Wölper, C.; Haack, R.; Jansen, G. *Chem. Comm.* **2014**, *52*, 927-929.
- [25] Gondzik, S.; Wölper, C.; Haack, R.; Jansen, G.; Schulz, S. *Dalton Trans.* **2015**, *44*, 15703-15711.
- [26] Wang, Y. Z.; Quillian, B.; Wei, P. R.; Wang, H. Y.; Yang, X. J.; Xie, Y. M.; King, R. B.; Schleyer, P. v. R.; Schaefer III, H. F.; Robinson, G. H. *J. Am. Chem. Soc.* **2005**, *127*, 11944-11945.
- [27] Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. *Organometallics* **2010**, *29*, 2176-2179.
- [28] a) Steiner, T. *Angew. Chem.* **2002**, *114*, 50-78; *Angew. Chem. Int. Ed.* **2002**, *41*, 48-76; b) Desiraju, G. R.; Steiner, T. in "The Weak Hydrogen Bond in Structural Chemistry and Biology.", IUCr Monographs on Crystallography, Vol. 9. New York: Oxford University Press, **1999**.
- [29] a) A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098-3100; b) J. P. Perdew, *Phys. Rev. B* **1986**, *33*, 8822-8824.
- [30] S. Grimme, *WIREs Comput. Mol. Sci.* **2011**, *1*, 211-228.
- [31] F. Furche, R. Ahlrichs, C. Hättig, W. Klopper, M. Sierka, F. Weigend, *WIREs Comput. Mol. Sci.* **2014**, *4*, 91-100.
- [32] a) F. Weigend, F. Furche, R. Ahlrichs, *J. Chem. Phys.* **2003**, *119*, 12753-12762; b) F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297-3305.
- [33] a) TURBOMOLE V6.3 2011, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989-2007, TURBOMOLE GmbH, since 2007; available from <http://www.turbomole.com>; b) R. Ahlrichs, M. Bär, M. Häser, H. Horn, C. Kölmel, *Chem. Phys. Letters* **1989**, *162*, 165-169; c) M. Häser, R. Ahlrichs, *J. Comput. Chem.* **1989**, *10*, 104-111; d) O. Treutler, R. Ahlrichs, *J. Chem. Phys.* **1995**, *102*, 346-354; e) M. v. Arnim, R. Ahlrichs, *J. Chem. Phys.* **1999**, *111*, 9183-9190.
- [34] Barral, K.; Moorhouse, A. D.; Moses, J. E. *Org. Lett.* **2007**, *9*, 1809-1811.
- [35] Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467-473.
- [36] Sheldrick, G. M. SHELXL-2014, Program for the Refinement of Crystal Structures University of Göttingen, Göttingen (Germany) **2014**. (see also: Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112-122)
- [37] shelXle, A Qt GUI for SHELXL, Hübschle, C. B.; Sheldrick, G. M.; Dittrich, B. *J. Appl. Cryst.* **2011**, *44*, 1281-1284.

$[(\text{MeZn})_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-PhN}_6\text{Ph})]$  (**2**), which was synthesized by reaction of  $[(^{\text{Me}}\text{L}^{\text{Dipp}}\text{Zn})_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-PhN}_6\text{Ph})]$  (**3**) with  $\text{ZnMe}_2$ , reacts with H-acidic ligands LH with ligand exchange ( $\text{L} = ^{\text{Me}}\text{L}^{\text{Ph}}$  **5**) and with pyridine with formation of the Lewis acid-base adduct  $[(\text{MeZn})_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-PhN}_6\text{Ph})(\text{Py})_2]$  (**4**). In addition, transmetalation reaction of **2** with MeLi yielded the heterobimetallic hexazene complex  $[(\text{MeZn})(\mu\text{-}\eta^2\text{:}\eta^2\text{-PhN}_6\text{Ph})(\text{Li})]$ , which further reacts with one equivalent of  $\text{Me}_2\text{AlCl}$  to  $[\text{MeZn}(\mu\text{-}\eta^2\text{:}\eta^2\text{-PhN}_6\text{Ph})\text{AlMe}_2]$  and with two equivalents to the homobimetallic aluminum hexazene complex  $[(\text{Me}_2\text{Al})_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-PhN}_6\text{Ph})(\text{thf})_2]$  (**6**). **3** - **6** were characterized by single crystal X-ray diffraction, while quantum chemical calculations of **4'** and **6'** gave insights into the electronic structure and allowed identification of the absorption bands of the hexazene unit.



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