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Synthesis and reactivity of heteroleptic zinc(I) complexes toward heteroallenes†

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Heteroleptic zinc(I) complexes $L^1Zn-ZnCp^*$ ($L^1 = HC[C(CF_3)NC_6F_5]_2$ **1**; $L^2 = HC[C(Me)NDipp]_2$; Dipp = 2,6-*i*-Pr₂C₆H₃ **2**) are synthesized by reactions of $Cp^*_2Zn_2$ with L^1H and L^2ZnH . **2** reacts with *t*-BuNCO to give unprecedented carbamate complex (**4**), while reactions with RN_3 gave bis-hexazene, triazenide, and trimeric azide complexes (**5–7**).

Since the discovery of $Cp^*_2Zn_2$ ($Cp^* = C_5Me_5$) by Carmona *et al.*,¹ Zn(I) complexes have received increasing interest.² In contrast to $Cp^*_2Zn_2$, which is accessible by reactions of Cp^*_2Zn with $(C_2H_5)_2Zn$ and by reduction of Cp^*_2Zn and $ZnCl_2$ with KH ,³ the majority of Zn(I) complexes are synthesized by Wurtz-type coupling of organozinc halides $RZnX$.⁴ Such reactions also yield homotrimeric Zn_3 ⁵ and heterotetranuclear Re_2Zn_2 complexes,⁶ but this pathway typically suffers from low yields. In contrast, ligand exchange reactions of $Cp^*_2Zn_2$ with H-acidic ligands or potassium salts are more efficient routes for the synthesis of heteroleptic Zn(I) complexes.^{7–9} Apart from their bonding nature, Zn(I) complexes are of interest due to their widespread reactivity, *i.e.* disproportionation,¹ acid–base,¹⁰ protonation,¹¹ redox,¹² and cluster formation reactions,¹³ respectively. Recently, we reported an isocyanate insertion reaction into one Zn–Cp* bond of $Cp^*_2Zn_2$,¹⁴ revealing a new reaction pattern for Zn(I) complexes. Encouraged by this finding, we became interested in reactions of heteroleptic Zn(I) complexes Cp^*ZnZnL with heteroallenes, and report herein on the synthesis of $L^1ZnZnCp^*$ **1** and $L^2ZnZnCp^*$ **2**, and reactions of **2** with *t*-BuNCO and three organoazides RN_3 .

The reaction of L^3H ($L^3 = HC[C(Me)NMe]_2$, Mes = 2,4,6-Me₃C₆H₂) with $Cp^*_2Zn_2$ in 1 : 1 and 1 : 2 molar ratio yielded the

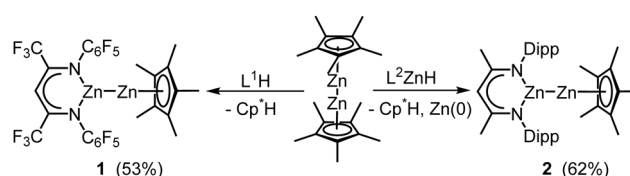
homoleptic Zn(I) complex $L^3_2Zn_2$.⁷ In contrast, the reaction of $Cp^*_2Zn_2$ with one or two equiv. of L^1H ($L^1 = HC[C(CF_3)NC_6F_5]_2$) in toluene at 6 °C gave the heteroleptic complex $L^1ZnZnCp^*$ **1** (Scheme 1), whereas L^2H ($L^2 = HC[C(Me)NDipp]_2$, Dipp = 2,6-*i*-Pr₂C₆H₃) failed to react. Inspired by a Pd(II)-induced homo-coupling reaction of $RZnH$,¹⁵ L^2ZnH was reacted with Cp^*_2Zn at 4 °C for 3 days, yielding $L^2Zn-ZnCp^*$ (**2**) and other by-products (Fig. S37, ESI†). **2** also formed in the equimolar reaction of L^2ZnH with $Cp^*_2Zn_2$ (Scheme 1), whereas substitution of the second Cp* group by reacting **2** or $Cp^*_2Zn_2$ with L^2ZnH in 1 : 1 or 1 : 2 molar ratio failed, although the desired homoleptic Zn(I) complex $L^2_2Zn_2$ is known.⁴ In contrast, $Cp^*_2Zn_2$ reacted with the stronger reductant L^2MgH to give zinc metal and L^2MgCp^* (**3**, ESI†).

The ¹H and ¹³C NMR spectra of **1** and **2** show characteristic resonances of the Cp* group and L^1 (**1**) and L^2 (**2**). The ¹⁹F NMR spectrum of **1** shows a resonance at –66.40 ppm (CF₃) and three resonances of the C₆F₅ groups in a 2 : 1 : 2 intensity ratio.

Single crystals were grown from toluene solutions at –30 °C (**1**, Fig. S42, ESI†) and 4 °C (**2**, Fig. S43, ESI†). The complexes crystallize in the triclinic space group $P\bar{1}$ (**1**) and the monoclinic space group $P2_1$ (**2**). The Zn1–Zn2 bond of **1** (2.2883(5) Å) is shorter than that of **2** (2.3008(2) Å) and other Zn(I) complexes, but comparable to those in $[Zn]_8$ clusters (2.27–2.29 Å).¹⁶ The Cp* groups are η⁵-bonded with Zn2–Cp*(_{centre}) distances of 1.8858(4) Å (**1**) and 1.9215(3) Å (**2**) and Cp*(_{centre})–Zn1–Zn2 bond angles of 177.2° (**1**) and 177.5° (**2**), which are close to linearity as observed in $Zn_2Cp^*_2$ ¹ and Cp^*ZnZnL .^{8b,14} The Zn1 atoms are three-coordinated, and the Zn1–N1/2 bonds of **1** (1.9917(13),

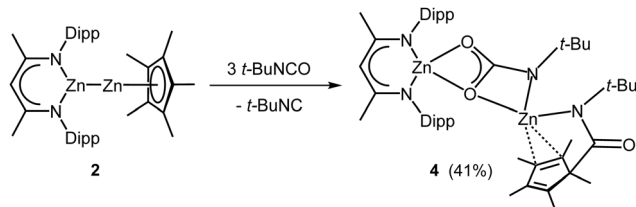
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† Electronic supplementary information (ESI) available: Experimental, analytical (NMR, IR spectra, elemental analysis) and crystallographic data of **1–7**. CCDC 2111218 (**1**), 2111219 (**2**), 2111220 (**3**), 2111221 (**4**), 2111225 (**4S**), 2111222 (**5**), 2111223 (**6**) and 2111224 (**7**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d1cc05617d



Scheme 1 Synthesis of heteroleptic Zn(I) complexes **1** and **2**.





Scheme 2 Synthesis of complex 4.

2.0140(13) Å) are longer than those of **2** (1.9580(10), 1.9598(10) Å), in accordance with the reduced electron donor capacity of the fluorinated L¹ ligand,¹⁷ but comparable to those of homoleptic complexes L₂Zn₂ and L₃Zn₂.^{4,7}

With heteroleptic complex **2** in hand, we explored its reactivity toward heteroallenes. Homoleptic Cp*₂Zn₂ reacted with RNCO (R = *t*-Bu, Dipp) at ambient temperature with insertion into one Zn–Cp* bond.¹⁴ In contrast, the reaction of heteroleptic Zn(i) complex **2** with *t*-BuNCO at 70 °C for 4 days gave complex **4** in 41% yield (Scheme 2), whereas no reaction occurred with DippNCO even at 100 °C. The formation of **4** results from insertion of *t*-BuNCO into the Zn–Zn and Zn–Cp* bonds and cleavage of a C=O bond accompanied by the formation of *t*-BuNC as was confirmed by *in situ* ¹H NMR spectroscopy (Fig. S39, ESI[†]). Any attempts to isolate reaction intermediates by varying the temperature and the molar ratio of the reagents failed. However, an excess of *t*-BuNCO promotes the reaction, as **4** was not formed in a 1 : 1 molar ratio reaction at 70 °C. The analogous reaction of L₃Zn₂⁷ with *t*-BuNCO also quantitatively gave a zinc carbamate complex **4S** (Fig. S40 and S46, ESI[†]) and *t*-BuNC.

Complex **4** is thermally stable and decomposes at 210 °C. The ¹H NMR spectrum shows two singlets of the *t*-Bu groups and five singlets of the Cp* group, indicating an asymmetric nature of the complex in solution. The ¹³C NMR spectrum also shows five singlets of the Me groups of the Cp* ligand as well as two singlets of the tertiary C atom of the *t*-Bu groups and resonances of the NCO units at 170.1 and 172.8 ppm, respectively.

Single crystals of **4**, which crystallize in the monoclinic space group *P*₂₁/*c* (Fig. 1), were grown from a saturated toluene solution at 4 °C. Both Zn atoms adopt distorted tetrahedral coordination spheres and are bridged by a carbamate unit.

The Zn1–O2/3 (2.0697(8), 2.0309(8) Å) bond lengths are comparable to those of the zinc carbamate complex L₂ZnO₂CN(*i*-Pr)₂ (2.028(2), 2.041(1) Å),¹⁸ but longer compared to those of the carboxylate complexes [L₂Zn(μ,η²-O₂CR)]₂ (R = H, Me, Ph, Oi-Pr), which range from 1.936 to 2.027 Å.¹⁹ The Zn2–N3/4 (1.9000(9), 1.9169(9) Å) bond lengths are virtually identical to that of Cp*Zn–Zn(N(*t*-Bu)C(Cp*)O) (1.9148(9) Å),¹⁴ while the Zn2–O3 distance (2.2780(8) Å) is rather long, indicating a rather weak coordinative interaction. The C–O (1.2819(12), 1.3273(12) Å) and C–N bond lengths (1.3270(13) Å) indicate a delocalized π-electron system within the carbamate unit. The Cp* ligand is η²-coordinated to Zn2, and the Zn–C bonds (2.4906(11), 2.5135(11) Å) are elongated compared to Zn–π complexes with η² interactions, *i.e.* alkyne-coordinated ZnBr₂ (2.217(5), 2.393(5) Å)²⁰

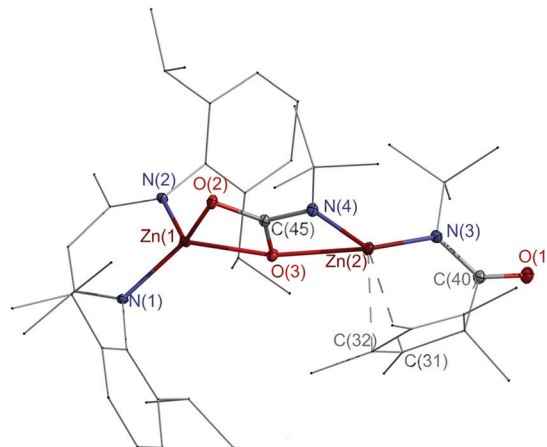
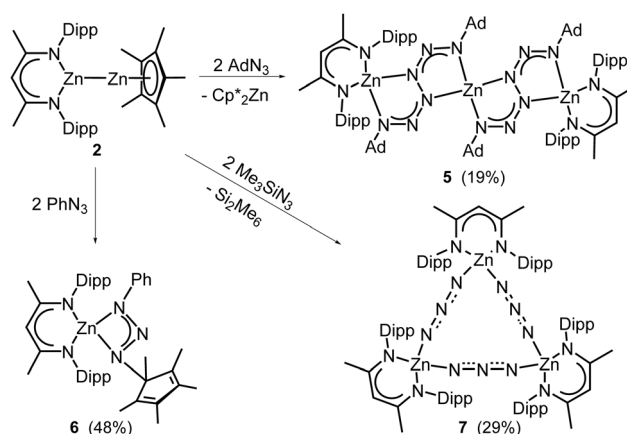


Fig. 1 Molecular structure of **4**. Thermal ellipsoids are drawn at 30% probability level. Parts of the ligands are drawn in wire/stick model, while H atoms are omitted for clarity.

and [PhC(*Nt*-Bu)₂(Cp*)Si–Zn(Cp*)Cl] (2.2519(26), 2.1224(29) Å),²¹ but shorter than those in Zn(C₆F₅)₂(tol.) (2.784(2), 2.6847(15) Å)²² and arylacetylene-substituted calix[4]arene zinc complexes (2.7695(37), 3.0667(37) Å).²³

Complex **2** was then reacted with organoazides RN₃ (R = Ph, Ad, SiMe₃). In contrast to homoleptic L₃Zn₂, which was found to react with RN₃ with formation of zinc hexazene [(L³Zn)₂(μ-η²:η²-N₆R₂)] (R = Ph, 2,6-*i*-Pr₂C₆H₃) or dimeric zinc azide complexes [(L³Zn)(μ-N₃)₂] (R = Me₃Si, Me₃Sn),^{12c} the reaction of heteroleptic complex **2** with 2 equiv. of AdN₃ at 70 °C for 2 days yielded the first bis-hexazene complex **5** (Scheme 3), which is thermally stable in solution up to 100 °C and in the solid state (decomposition temperature > 300 °C), respectively. Complex **5** is likely formed *via* the Cp*Zn(η²:η²-N₆Ad₂)ZnL² intermediate, followed by intramolecular elimination of Cp*₂Zn.

In contrast, the reaction of **2** with PhN₃ gave the zinc triazenide complex **6** in 48% yield (Scheme 3). Alkaline or alkaline earth metal triazenides are typically formed in reactions of aryl azides and organolithium and magnesium

Scheme 3 Synthesis of complexes **5**–**7**.

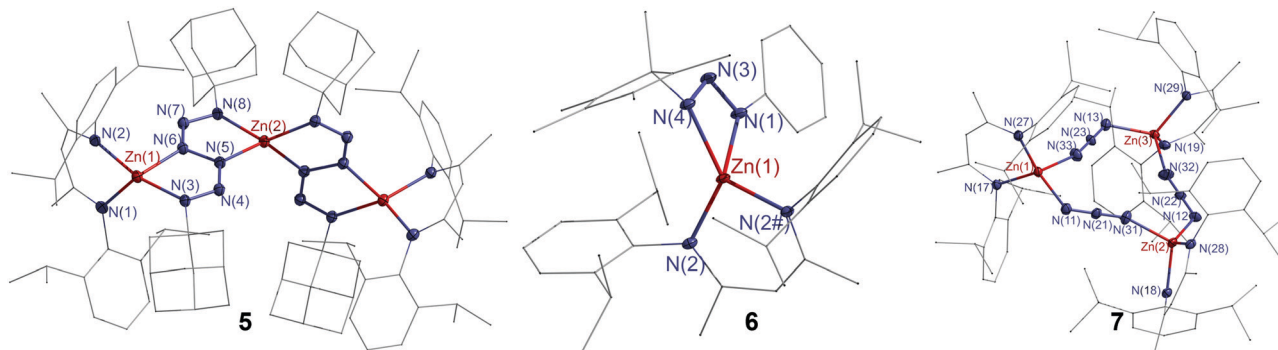


Fig. 2 Molecular structure of 5–7. Thermal ellipsoids drawn at 30% probability level, parts of the ligands are in a wire/stick model, and hydrogen atoms are omitted for clarity. 7 contains two molecules in the asymmetric unit (only the Zn(1)-containing molecule is discussed).

complexes,²⁴ hence the formation of 6 likely results from a nucleophilic attack of the Cp* ligand. Since no reaction was observed in a control experiment of L²ZnCp* with PhN₃, we assume that the first reaction step is an insertion reaction of PhN₃ into the Zn–Zn bond of 2. Low-valent metal complexes are known to react with RN₃ with formation of metal triazenides as was shown for homo- (Al, Cr) and heterobimetallic (In–Zn) complexes,²⁵ while a dinuclear iron complex was formed by the reaction of an Fe–N₂ complex with AdN₃.²⁶ The reaction of 2 with Me₃SiN₃ occurred with reductive elimination of Si₂Me₆ as was reported for the analogous reaction of L³Zn₂^{12c} and formation of complex 7 featuring a pseudo triangular Zn₃N₉ moiety (Scheme 3). 7 also formed in 78% yield in the reaction of L²ZnH and Me₃SiN₃.

¹H and ¹³C NMR spectra of 5 and 6 show resonances of L² and Ad (5) and Cp* and Ph (6), while 7 shows two sets of resonances of L² due to two conformers in solution, which form a temperature-dependent equilibrium as confirmed by VT-¹H NMR (Fig. S41, ESI[†]). IR spectra show absorption bands of the hexazene (1265, 1218 cm⁻¹, 5), triazene (1313, 1255 cm⁻¹, 6) and azide groups (2157, 2124 cm⁻¹, 7).

Single crystals of 5–7 were grown from toluene solutions. Complexes 5 and 6 crystallize in the monoclinic space groups *P2₁/n* and *P2₁/m* and complex 7 in the triclinic space group *P1̄* (Fig. 2). Complex 5 contains two bridging hexazene ligands. The Zn1–N1/2 bonds within the C₃N₂Zn ring are slightly shorter than the Zn1–N3/6 bonds (2.0024(19), 2.0378(18) Å) in the neighbouring N₄Zn ring, but comparable to Zn–N3/6 bonds (2.0079(18), 1.9817(19) Å) in the nonadjacent N₄Zn ring. The N5–N6 distance (1.400(3) Å) is typical for a single bond, while the other N–N bond lengths (1.297(3)–1.301(3) Å) of the hexazene unit indicate an allyl-like nature as was previously reported for metal hexazene complexes.^{12c,27} The Zn atom in triazene complex 6 is tetrahedrally coordinated by four N atoms of the L² ligand and the triazene group. The N–N bond lengths within the ZnN₃ metallacycle (1.297(6), 1.307(5) Å) indicate a delocalized π-electron system within the N₃ moiety. The Zn–N2 bonds (1.9592(10) Å) are shorter than the Zn–N1/3 bonds (2.0524(13), 2.0869(14) Å). The only structurally characterized zinc triazene complex [Dipp₂N₃]₂Zn, which was prepared by an ethane elimination reaction of ZnEt₂ with Dipp₂N₃H,²⁸ shows comparable structure parameters.

In contrast to dimeric [(L³Zn)(μ-N₃)₂]²⁹ complex 7 forms a pseudo-triangular Zn₃N₉ moiety with bridging N₃ units, resulting in an almost planar Zn₃N₉ metallacycle (r.m.s. deviation from the least-squares plane 0.0655 Å), and each Zn atom is further coordinated by one L² ligand. The Zn–N bonds (1.952(5)–2.027(5) Å) within the Zn₃N₉ moiety are slightly longer than those in the C₃N₂Zn rings (1.945(4)–1.959(5) Å). The N–N–N angles of 178.0(7)°, 179.1(7)° and 178.9(7)° are almost linear, and the N–N bond lengths range from 1.147(7) to 1.192(7) Å.

To summarize, heteroleptic Zn(I) complexes L^{1/2}ZnZnCp* (1, 2) were synthesized and reactions of L²ZnZnCp* 2 with heteroallenes are reported. The reaction with *t*-BuNCO proceeded with insertion into both the Zn–Zn and the Zn–Cp* bonds and formation of carbamate complex 4, whereas reactions with RN₃ yielded unprecedented bis-hexazene, triazene, and trimeric azide complexes 5–7, respectively.

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Conflicts of interest

There are no conflicts to declare.

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