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

Bin Li, Kevin Huse, Christoph Wölper and Stephan Schulz*

Heteroleptic zinc(i) complexes $L^1L^2Zn-ZnCp^*$ ($L^1 = HC[C(CF_3)_2NC_6F_5]_2$ 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).

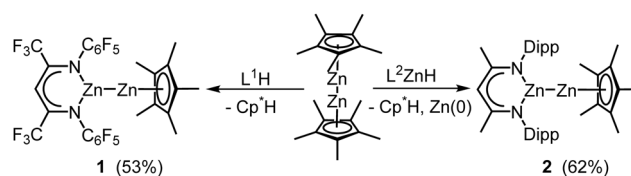
Since the discovery of $Cp^*_2Zn_2$ ($Cp^* = C_5Me_5$) by Carmona *et al.*,¹ Zn(i) complexes have received increasing interest.² In contrast to $Cp^*_2Zn_2$, which is accessible by reactions of Cp^*_2Zn with $(C_2H_5)_2Zn$ and by reduction of Cp^*_2Zn and $ZnCl_2$ with KH,³ the majority of Zn(i) complexes 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 ($L^1 = HC[C(CF_3)_2NC_6F_5]_2$) 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),

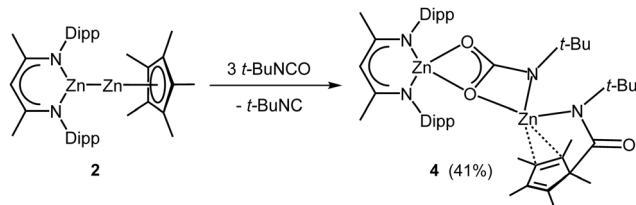


Scheme 1 Synthesis of heteroleptic Zn(i) complexes 1 and 2.

Institute of Inorganic Chemistry and Center for Nanointegration Duisburg-Essen (CENIDE), University of Duisburg-Essen, 45117 Essen, Germany.
E-mail: stephan.schulz@uni-due.de

† 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 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 L²₂Zn₂ and L³₂Zn₂.^{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 L³₂Zn₂⁷ 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

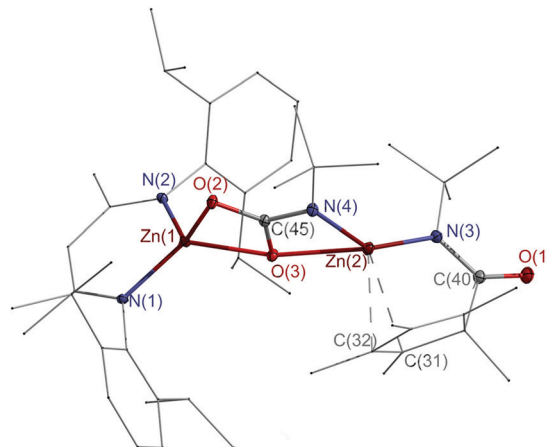
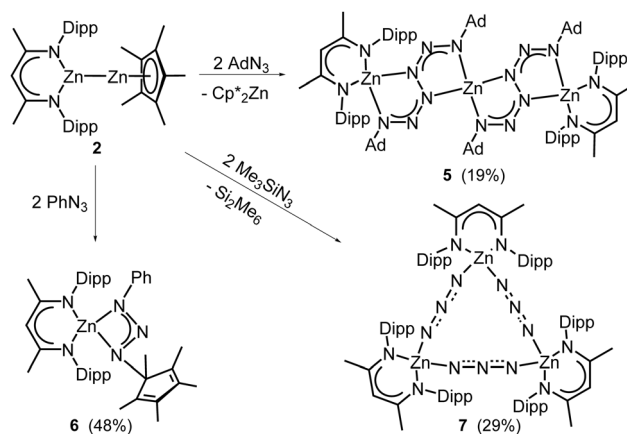


Fig. 1 Molecular structure of **4**. Thermal ellipsoids are drawn at 30% probability level. Parts of the ligands are drawn in wire/stick model, while H atoms are omitted for clarity.

and [PhC(N*t*-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 L³₂Zn₂, 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(μ-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**.

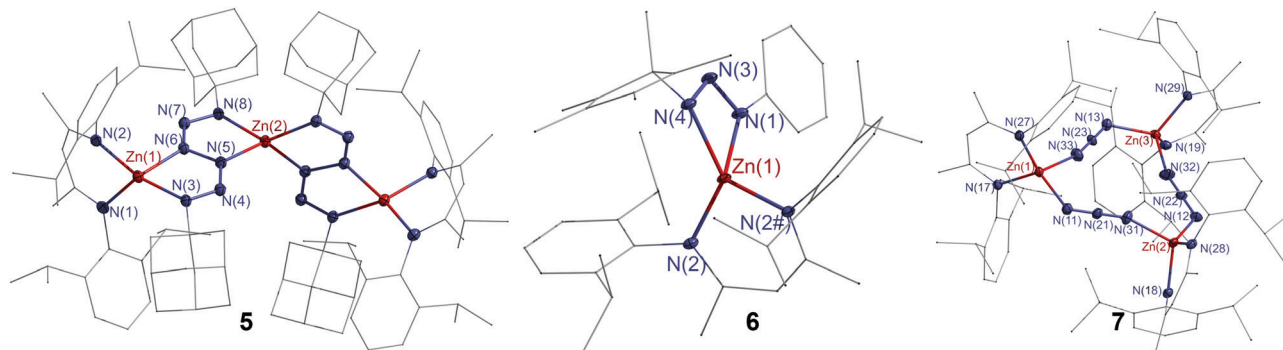


Fig. 2 Molecular structure of **5–7**. Thermal ellipsoids drawn at 30% probability level, parts of the ligands are in a wire/stick model, and hydrogen atoms are omitted for clarity. **7** contains two molecules in the asymmetric unit (only the Zn(1)-containing molecule is discussed).

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 L^2ZnCp^* with PhN_3 , we assume that the first reaction step is an insertion reaction of PhN_3 into the Zn–Zn bond of **2**. Low-valent metal complexes are known to react with RN_3 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– N_2 complex with AdN_3 .²⁶ The reaction of **2** with Me_3SiN_3 occurred with reductive elimination of Si_2Me_6 as was reported for the analogous reaction of $L^3Zn_2^{12c}$ and formation of complex **7** featuring a pseudo triangular Zn_3N_9 moiety (Scheme 3). **7** also formed in 78% yield in the reaction of L^2ZnH and Me_3SiN_3 .

1H and ^{13}C NMR spectra of **5** and **6** show resonances of L^2 and Ad (**5**) and Cp* and Ph (**6**), while **7** shows two sets of resonances of L^2 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**), triazenide (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 $P2_1/n$ and $P2_1/m$ and complex **7** in the triclinic space group $P\bar{1}$ (Fig. 2). Complex **5** contains two bridging hexazene ligands. The Zn1–N1/2 bonds within the C_3N_2Zn ring are slightly shorter than the Zn1–N3/6 bonds (2.0024(19), 2.0378(18) Å) in the neighbouring N_4Zn ring, but comparable to Zn–N3/6 bonds (2.0079(18), 1.9817(19) Å) in the nonadjacent N_4Zn 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 L^2 ligand and the triazene group. The N–N bond lengths within the ZnN_3 metallacycle (1.297(6), 1.307(5) Å) indicate a delocalized π -electron system within the N_3 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 triazenide complex $[Dipp_2N_3]_2Zn$, which was prepared by an ethane elimination reaction of $ZnEt_2$ with $Dipp_2N_3H$,²⁸ shows comparable structure parameters.

In contrast to dimeric $[(L^3Zn)(\mu-N_3)]_2$,²⁹ complex **7** forms a pseudo-triangular Zn_3N_9 moiety with bridging N_3 units, resulting in an almost planar Zn_3N_9 metallacycle (r.m.s. deviation from the least-squares plane 0.0655 Å), and each Zn atom is further coordinated by one L^2 ligand. The Zn–N bonds (1.952(5)–2.027(5) Å) within the Zn_3N_9 moiety are slightly longer than those in the C_3N_2Zn 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 $L^2ZnZnCp^*$ **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 RN_3 yielded unprecedented bis-hexazenide, triazenide, and trimeric azide complexes **5–7**, respectively.

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Conflicts of interest

There are no conflicts to declare.

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