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Insertion Reactions of Heterocumulenes with Zincocene Cp^*_2Zn

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Dedicated to Prof. K. Jurkschat on the Occasion of his 60th Birthday

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Zincocene Cp^*_2Zn reacts with carbodiimides $\text{C}(\text{NR})_2$ with insertion into the Zn-Cp^* bond and formation of $[(\text{Cp}^*\text{C}(\text{NR})_2)_2\text{Zn}]$ ($\text{R} = \text{Et}$, **1**, *i*-Pr **2**, Cy **3**). In addition, the reaction of Cp^*_2Zn with CS_2 under dry conditions gives $(\text{Cp}^*\text{CS}_2)_2\text{Zn}$ **4**, whereas in the presence of a small amount of water $[\text{Zn}_4(\mu_4\text{-O})(\text{S}_2\text{CCp}^*)_6]$ **5** is obtained. **1** - **4**

were characterized by NMR (^1H , ^{13}C) and IR spectroscopy as well as elemental analysis and single crystal X-ray diffraction (**2** - **4**, **5** of poor quality). The solid state structure of **5** is comparable to the carboxylate complex previously obtained from the reaction of Cp^*_2Zn with CO_2 .

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Introduction

The activation of CO_2 and its effective utilization as C_1 -feedstock in organic chemistry is still an ongoing research topic in metal organic chemistry.^[1] Unfortunately, due to its thermodynamic stability and kinetic inertness, only highly nucleophilic reagents such as organolithium and Grignard reagents readily react with CO_2 with C-C bond formation. Moreover, activation reactions of CO_2 via coordination to transition metal complexes, which lowers the activation energy for further reactions, have also been studied^[2] and carboxylation reactions of organoboronic acids, organozinc and organotin reagents using CO_2 were found to be catalyzed by late transition metal complexes.^[3]

Compared to CO_2 , heterocumulenes such as CS_2 and COS show an enhanced reactivity. Even though both compounds are neither naturally abundant nor a chemical waste product, their increased reactivity was expected to be helpful for the development of a deeper understanding of the mechanism of C-C bond formation reactions. Consequently, reactions of main group metal, transition metal and lanthanide and actinide metal complexes have been reported.^[4]

We recently became interested in activation reactions of heterocumulenes with organozinc reagents R_2Zn , which have been established in the past as soft nucleophiles in organic reactions. While zinc hydrides, zinc alkoxides and zinc amides are known to react with CO_2 with insertion into the Zn-H , Zn-O and Zn-N bond^[5] and therefore serve as *living single-site catalysts* for the ring-opening

polymerization (ROMP) of lactide,^[6] the epoxide/ CO_2 copolymerization^[7] and the terpolymerization of epoxide, cyclic anhydrides and CO_2 ,^[8] zinc dialkyls almost completely failed to react with CO_2 with insertion into the Zn-C bond. However, we succeeded in the direct carboxylation reaction of zincocene Cp^*_2Zn with CO_2 in the absence of any transmetalation reagent.^[9] The resulting zinc oxocarboxylate $[\text{Zn}_4(\mu_4\text{-O})(\text{O}_2\text{CCp}^*)_6]$ contains a central $[\text{Zn}_4\text{O}]^{6+}$ tetrahedron as was typically observed in basic zinc acetate,^[10] carbonates and carbamates,^[5] phosphates and phosphonates^[11] as well as in metal organic frameworks (MOFs) such as MOF-5 and IRMOF-9.^[12] Moreover, we reported on reactions of organozinc reagents with various carbodiimides, $\text{C}(\text{NR})_2$, and isocyanates RNCO ,^[13] and Carmona reported on the insertion reaction of CNXyl into the Zn-Cp^* bond of zincocene.^[14] Interestingly, bis(phosphinimino)methanide complexes of the type $[(\text{Me}_3\text{SiNPPH}_2)_2\text{CH}]\text{ZnR}$ ($\text{R} = \text{Me}$, Ph) were reported to react with carbodiimides, ketenes and isocyanates via nucleophilic addition of the methine carbon atom of the $\{\text{CH}(\text{Ph}_2\text{PNSiMe}_3)_2\}$ ligand to the heterocumulenes and C-C bond formation.^[15]

Herein we report on insertion reactions of carbodiimides as well as of CS_2 with zincocene, Cp^*_2Zn . The resulting complexes $[(\text{Cp}^*\text{C}(\text{NR})_2)_2\text{Zn}]$ ($\text{R} = \text{Et}$, **1**, *i*-Pr **2**, Cy **3**) and $(\text{Cp}^*\text{CS}_2)_2\text{Zn}$ **4** were characterized by multinuclear NMR (^1H , ^{13}C) and IR spectroscopy, elemental analyses and single crystal X-ray diffraction.

Results and Discussion

A toluene solution of Cp^*_2Zn reacts with a twofold amount of RNCNR ($\text{R} = \text{Et}$, *i*-Pr, Cy) at ambient temperature within 1 h with insertion of the carbodiimide into the Zn-Cp^* bond and subsequent formation of the corresponding homoleptic bisamidinate complexes $[(\text{Cp}^*\text{C}(\text{NR})_2)_2\text{Zn}]$ ($\text{R} = \text{Et}$, **1**, *i*-Pr **2**, Cy **3**).

The formation of **1** – **3** was monitored by *in situ* ^1H NMR spectroscopy. The progress of the reaction is shown by the continuously decreasing resonance of the Zn-bonded Cp* groups (1.88 ppm in toluene- d_8). Simultaneously, three new singlets with a relative intensity of 1:2:2 steadily increases, indicating the formation of σ -bonded Cp* groups. Moreover, the ^{13}C NMR spectra of **1** – **3** each show an additional signal at 170.6 (**1**), 167.9 (**2**) and 167.8 (**3**) ppm, respectively, due to the amidinate backbone as was previously observed by us for amidinate and amidate zinc complexes.^[16,17]

Scheme 1. Synthesis of $[\text{Cp}^*\text{C}(\text{NR})_2]_2\text{Zn}$

Single crystals of **2** and **3** were obtained from solutions in toluene upon storage at $-30\text{ }^\circ\text{C}$. **2** and **3** crystallize in the monoclinic space group $P2_1/c$ (**2**) and $P2_1/n$ (**3**), respectively, with four molecules in the unit cell.^[18]

Figure 1. Molecular structure of **2**. Non-interacting H atoms are omitted for clarity. Thermal ellipsoids at 50% probability levels. Selected bond lengths [Å] and angles [°]: Zn1–N1 2.0087(14), Zn1–N3 2.0110(14), Zn1–N2 2.0175(14), Zn1–N4 2.0212(15) N1–C33 1.336(2), N2–C33 1.345(2), N3–C34 1.345(2), N4–C34 1.328(2); N1–Zn1–N3 131.65(6), N1–Zn1–N2 65.86(6), N3–Zn1–N2 137.07(6), N1–Zn1–N4 132.07(6), N3–Zn1–N4 65.75(6), N2–Zn1–N4 138.10(6), N1–C33–N2 109.49(15), N3–C34–N4 109.97(15), C33–N1–Zn1 92.66(10), C33–N2–Zn1 92.00(10), C34–N3–Zn1 92.06(10), C34–N4–Zn1 92.13(10). $\text{CH}\cdots\pi$ interactions C21–H21 $\cdots$ R(C1 C2 C3 C4 C5) $d(\text{H}\cdots\text{M})$ 2.24 Å, $d(\text{H}\cdots\text{R})$ 2.2315(19) Å, $\angle(\text{CHM})$ 135.0°, $\angle(\text{HMR})$ 85.0°; C30–H30 $\cdots$ R(C11 C12 C13 C14 C15) $d(\text{H}\cdots\text{M})$ 2.27 Å, $d(\text{H}\cdots\text{R})$ 2.2622(19) Å, $\angle(\text{CHM})$ 133.8°, $\angle(\text{HMR})$ 85.2°.^[19]

The Zn atoms are tetrahedrally coordinated by two chelating amidinate groups. The Zn–N distances (2.0087(14) – 2.0212(15) **2**; 1.9925(11) – 2.0106(11) Å **3**) are almost identical to those previously observed for bisamidinate complexes.^[16] The C–N bond length in the amidinate group are in between the typical values for double (1.29 Å) and single bonds (1.47 Å), clearly indicating a delocalized π -electron system as was expected. The average endocyclic N–Zn–N bond angles (65.81° **2**; 65.84° **3**) are smaller than the exocyclic ones (134.72° **2**; 134.8° **3**) and the average N–C–N bond angles (109.73° **2**; 109.43° **3**) are within the typical range previously reported for zinc bisamidinate

complexes.^[16] The difference in the endo- and exocyclic N–Zn–N angles lead to an elongation of the coordination tetrahedron along an -4 -axis. The similar values of the geometrical parameters of the central molecule cores prove the steric influence of the organic substituents to be rather limited. **2** and **3** show axial chirality due to the presence of intramolecular $\text{CH}\cdots\pi$ interactions. Since the space groups of both compounds are centro-symmetric they are racemic. The asymmetric units were chosen to contain the R enantiomer. The stability of the conformation in solution was not investigated. As potential acceptor atoms are well shielded in the centre of the molecule no intermolecular interactions can be found (shortest intermolecular H $\cdots$ N distance: 3.53 Å in **2** > 4 Å in **3**) and the packing is constituted by most dense packing alone.

Figure 2. Molecular structure of **3**. Non-interacting H atoms are omitted for clarity. Thermal ellipsoids at 50% probability levels. Selected bond lengths [Å] and angles [°]: Zn1–N1 2.0027(11), Zn1–N2 2.0056(11), Zn1–N3 1.9925(11), Zn1–N4 2.0106(11), N1–C45 1.3275(16), N2–C45 1.3410(16), N3–C46 1.3296(16), N4–C46 1.3354(16); N3–Zn1–N1 135.91(5), N3–Zn1–N2 131.50(5), N1–Zn1–N2 65.91(4), N3–Zn1–N4 65.76(4), N1–Zn1–N4 135.41(5), N2–Zn1–N4 136.37(5), N1–C45–N2 109.57(11), N3–C46–N4 109.28(11), C45–N1–Zn1 92.52(8), C45–N2–Zn1 91.98(8), C46–N3–Zn1 92.96(8), C33–N(3)–Zn(1) 135.88(8), C(46)–N(4)–C(39) 134.70(11), C46–N4–Zn1 91.99(8). $\text{CH}\cdots\pi$ interactions C21–H21 $\cdots$ R(C1 C2 C3 C4 C5) $d(\text{H}\cdots\text{M})$ 2.32 Å, $d(\text{H}\cdots\text{R})$ 2.3014(13) Å, $\angle(\text{CHM})$ 128.8°, $\angle(\text{HMR})$ 82.7°, C33–H33 $\cdots$ R(C11 C12 C13 C14 C15) $d(\text{H}\cdots\text{M})$ 2.28 Å, $d(\text{H}\cdots\text{R})$ 2.2693(14) Å, $\angle(\text{CHM})$ 131.4°, $\angle(\text{HMR})$ 84.4°.

Since Cp^*_2Zn was found to readily react with CO_2 ,^[9] isocyanates CNXyl ,^[14] RNCO ^[17] and RNCNR with insertion into the Zn–Cp* bond, we became interested in the reaction of zincocene with CS_2 . Compared to CO_2 , CS_2 was reported to show an enhanced chemical reactivity. Therefore it came not as a surprise, that Cp^*_2Zn was found to readily react with CS_2 at ambient temperature in almost quantitative yield with formation of $(\text{Cp}^*\text{CS}_2)_2\text{Zn}$ **4**. Moreover, the presence of a small amount of water yielded $[\text{Zn}_4(\mu_4\text{-O})(\text{S}_2\text{CCp}^*)_6]$ **5** including a central Zn_4O core as was previously observed for the reaction of Cp^*_2Zn with CO_2 .^[9]

Scheme 2. Synthesis of $(\text{Cp}^*\text{CS}_2)_2\text{Zn}$ **4** and $[\text{Zn}_4(\mu_4\text{-O})(\text{S}_2\text{CCp}^*)_6]$ **5**

The ^1H NMR spectrum of **4** shows three resonances at 1.48, 1.63 and 1.84 ppm, respectively, due to the presence of σ -bound Cp* groups. Moreover, the characteristic S=C=S absorption band in the IR spectrum of CS₂ at 1482 cm⁻¹ is shifted to 1445 (ν_{asym}) and 1177 cm⁻¹ (ν_{sym}) in **4** as was previously reported for Me₂Al(μ -Ni-Pr₂)₂Mg(S₂CMe) (1142, 1017 cm⁻¹)^[20] and Cp*W(NO)(η^2 -S₂CNH*t*-Bu)(O*t*-Bu) (1142, 1017 cm⁻¹).^[21] Unfortunately, the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **4** and **5** did not exhibit resonances for the CS₂ carbon atoms, which were expected to be shifted to lower field compared to that of free CS₂ (192.6 ppm). Comparable findings were recently reported.^[22] Typically, values far above 200 ppm were reported,^[22,23] even though Limberg *et al.* very recently observed a resonance at 172.5 ppm for a dinuclear Cu-CS₂ complex.^[24]

Single crystals of **4** were obtained from thf solution upon storage at -30 °C.^[18] **4**, which was obtained as thf-adduct, crystallizes in the P-1. In contrast, **5** was obtained from a solution in toluene. Unfortunately, the quality of the crystals was rather low. As a consequence, the structural parameters of **5** cannot be discussed in detail, even though the connectivity and composition of the compound was proven.

Figure 3. Molecular structure of **4xTHF**. H atoms are omitted for clarity. Thermal ellipsoids at 50% probability levels. Selected bond lengths [Å] and angles [°]: Zn1-O1 2.0335(16), Zn1-S1 2.5785(7), Zn1-S2 2.3197(6), Zn1-S3 2.3008(6), Zn1-S4 2.6965(7), S1-C1 1.664(2), S2-C1 1.697(2), S3-C2 1.7045(19), S4-C2 1.668(2); O1-Zn1-S3 107.98(5), O1-Zn1-S2 108.70(5), S3-Zn1-S2 142.72(2), O1-Zn1-S1 96.45(6), S3-Zn1-S1 109.76(2), S2-Zn1-S1 72.41(2), O1-Zn1-S4 92.83(6), S3-Zn1-S4 71.38(2), S2-Zn1-S4 100.29(2), S1-Zn1-S4 169.66(2), C1-S1-Zn1 80.35(7), C1-S2-Zn1 87.94(7), C2-S3-Zn1 89.81(7), C2-S4-Zn1 77.93(7), S1-C1-S2 119.30(11), S4-C2-S3 120.88(11).

The central Zn atom in **4** is coordinated by two chelating thiothiophene groups and a single thf molecule, hence resulting in a distorted trigonal-bipyramidal coordination mode. The thiothiophene groups each show one short Zn-S bond toward the equatorial sulfur atoms (Zn1-S2 2.3197(6); Zn1-S3 2.3008(6) Å) and one long Zn-S bond toward the axial sulfur atoms (Zn1-S1 2.5785(7); Zn1-S4 2.6965(7) Å), most likely resulting from the coordination of the thf molecule. The Zn1-O1 bond length of 2.0335(16) Å is in the typical range for coordinated thf molecules to tetrahedrally coordinated Zn(II) centers. The axial S1-Zn1-S4 unit deviates slightly from linearity (169.66(2)°), while S2, S3, O1 and Zn1 are located on a plane (r.m.s. deviation from best plane 0.0413 Å). However within the plane the trigonal coordination of Zn1 is distorted towards T-shaped geometry (S-Zn-O ~108°, S-Zn-S 142.72(2)°) and the S1...S4 vector

is not perpendicular to this plane (72.5°) as in a regular trigonal-bipyramid. This coordination environment is comparable to those of other Zn complexes bearing two ligands with a chelating CS₂⁻ unit and a total coordination number of 5. A search in the CSD database^[25] gave 97 structures matching this fragment, of which 79 adopt a planar arrangement of the equatorial positions (Zn atoms deviating less than 0.07 Å from the S/S/X plane). The mean angle between this plane and the vector between the axial positions is 2° larger than the one observed in **4** (74.4°).

Figure 4. Molecular structure of **5**. Due to the poor scattering power of the crystals only the connectivity could be determined reliably. The oxygen atom is placed on an inversion centre and thus the positions of the zinc atoms (and probably sulfur atoms) are disordered over two positions (only one component displayed).

In contrast to **2** and **3**, the coordinating atoms in **4** do not bear any residual groups, hence allowing the establishment of intermolecular interactions. Two neighbouring molecules (-x+1, -y+1, -z+1) show short S...S contacts, whose lengths either equal approximately the sum of the van-der-Waals radii or are about 0.3 Å shorter, respectively (3.3261(12) Å, 3.6556(9) Å). A CH...S hydrogen bond (C20-H20A...S3[-x, -y+1, -z+1], d(H...A) 2.98 Å, <(DHA) 141.8°) connects these dimers to form chains parallel to *a*.

Figure 5. Intermolecular interactions in the packing of **4**.

Conclusions

In conclusion, we have demonstrated that zincocene readily reacts with heterocumulenes such as carbodiimides and carbon disulfide with insertion into the Zn-Cp* bond and subsequent formation of homoleptic bisamidinate and bis(thio)carboxylate complexes. The potential capability of **4** to serve as *single source precursor* for the solution-based and gas-phase based (MOCVD) formation of ZnS is currently investigated.

Experimental Section

All manipulations were performed under an Ar atmosphere.

Cp*₂Zn was prepared according to literature methods.^[26] ¹H, ¹³C{¹H} NMR spectra were recorded on a Bruker DMX 300 spectrometer and are referenced to internal C₆D₅H (¹H: δ = 7.154; ¹³C: δ = 128.0). IR spectra were recorded on an ALPHA-T FT-IR spectrometer equipped 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 Essen.

[Cp*₂C(NR)₂]₂Zn. Solutions of 0.34 g Cp*₂Zn (1 mmol) and two equivalents of carbodiimide RNCNR were dissolved in 10 ml of toluene and stirred for 1 h at ambient temperature. Colorless crystals of [Cp*₂C(NR)₂]₂Zn (R = Et **1**, *i*-Pr **2**, Cy **3**) were formed within 12 h after storage at -30 °C.

1: Yield: 0.49 g (94 %). Melting point: > 220 °C. Anal. Found (calcd) for C₃₀H₅₀N₄Zn (540.19 g/mol): H 10.8 (10.8), C 66.6 (66.7), N 10.3 (10.4). ¹H NMR (300 MHz, C₆D₆, 25 °C): δ = 1.11 (t, ³J_{HH} = 7.1 Hz, 6H, CH₂CH₃), 1.31 (t, ³J_{HH} = 7.1 Hz, 6H, CH₂CH₃), 1.40 (s, 6H, C₅Me₅), 1.65 (s, 12H, C₅Me₅), 1.88 (s, 12H, C₅Me₅), 2.80 (q, ³J_{HH} = 7.1 Hz, 4H, CH₂CH₃), 3.64 (q, ³J_{HH} = 7.0 Hz, 4H, CH₂CH₃). ¹³C{¹H} NMR (75 MHz, C₆D₆, 25 °C): δ = 10.9 (C₅Me₅), 11.0 (C₅Me₅), 19.4 (C₅Me₅), 20.5 (NCH₂CH₃), 23.9 (NCH₂CH₃), 38.0 (NCH₂CH₃), 42.2 (NCH₂CH₃), 65.2 (C₅Me₅), 134.5 (C₅Me₅), 141.5 (C₅Me₅), 170.6 (CN₂). IR: ν 2961, 2919, 2849, 1657, 1457, 1480, 1427, 1369, 1341, 1320, 1283, 1260, 1238, 1210, 1134, 1096, 1063, 1034, 965, 890, 803, 759, 700, 674, 596, 510.

2: Yield: 0.57 g (97 %). Melting point: > 220 °C. Anal. Found (calcd) for C₃₄H₅₈N₄Zn (588.21 g/mol): H 9.9 (9.9), C 69.4 (69.4), N 9.5 (9.5). ¹H NMR (300 MHz, C₆D₆, 25 °C): δ = 1.00 (d, ³J_{HH} = 5.9 Hz, 6H, CH(CH₃)₂), 1.03 (d, ³J_{HH} = 6.0 Hz, 6H, CH(CH₃)₂), 1.31 (d, ³J_{HH} = 5.9 Hz, 6H, CH(CH₃)₂), 1.33 (d, ³J_{HH} = 5.9 Hz, 6H, CH(CH₃)₂), 1.45 (s, 6H, C₅Me₅), 1.67 (s, 12H, C₅Me₅), 1.95 (s, 12H, C₅Me₅), 3.38 (sept, 2H, CH(CH₃)₂), 4.44 (sept, 2H, CH(CH₃)₂). ¹³C{¹H} NMR (75 MHz, C₆D₆, 25 °C): δ = 11.0 (C₅Me₅), 11.4 (C₅Me₅), 24.6 (C₅Me₅), 28.6 (NCH(CH₃)₂), 28.7 (NCH(CH₃)₂), 43.7 (NCH(CH₃)₂), 45.4 (NCH(CH₃)₂), 65.7 (C₅Me₅), 134.0 (C₅Me₅), 135.0 (C₅Me₅), 167.9 (CN₂). IR: ν 2961, 2921, 2847, 1645, 1480, 1426, 1368, 1318, 1281, 1261, 1239, 1211, 1134, 1096, 1061, 969, 888, 803, 700, 675, 508.

3: Yield: 0.70 g (93 %). Melting point: > 220 °C. Anal. Found (calcd) for C₄₆H₇₄N₄Zn (748.46 g/mol): H 11.0 (10.9), C 74.0 (73.8), N 7.5 (7.5). ¹H NMR (300 MHz, C₆D₆, 25 °C): δ = 1.14 – 1.44 (m, 12H, CH₂), 1.40 (s, 6H, C₅Me₅), 1.56 – 1.68 (m, 4H, CH₂), 1.71 (s, 12H, C₅Me₅), 1.76 – 1.88 (m, 2H, CH₂), 1.98 (s, 12H, C₅Me₅), 2.19 (m, 2H, CH₂), 2.94 (m, 1H, CH_{ax}), 4.04 (m, 1H, CH_{ax}). ¹³C{¹H} NMR (75 MHz, C₆D₆, 25 °C): δ = 11.1 (C₅Me₅), 11.2 (C₅Me₅), 11.3 (C₅Me₅), 24.4 (CH₂), 26.6 (CH₂), 26.7 (CH₂), 38.4 (CH₂), 38.5 (CH₂), 39.7 (CH₂), 39.8 (CH₂), 52.0 (NCH), 52.4 (NCH), 65.7 (C₅Me₅), 134.1 (C₅Me₅), 143.5 (C₅Me₅), 143.6

(C₅Me₅), 167.8 (CN₂). IR: ν 2916, 2847, 1421, 1353, 1340, 1294, 1257, 1237, 1202, 1081, 1062, 1027, 990, 898, 887, 803, 663, 569, 541, 504.

(Cp*₂CS₂)₂Zn **4**. CS₂ (0.08 g, 1 mmol) was added dropwise to a solution of 0.17 g Cp*₂Zn (0.5 mmol) in 15 ml toluene and stirred for 2 h at ambient temperature. The solvent was removed in vacuo and the solid residue was dissolved in 5 mL of thf.

Yield: 0.23 g (83 %). Melting point: > 220 °C. Anal. Found (calcd) for C₂₂H₃₀S₄Zn*₂C₄H₈O (560.17 g/mol): H 6.9 (6.8), C 55.9 (55.7). ¹H NMR (300 MHz, C₆D₆, 25 °C): δ = 1.48 (s, 3H, C₅Me₅), 1.63 (s, 6H, C₅Me₅), 1.84 (s, 6H, C₅Me₅). ¹³C{¹H} NMR (75 MHz, C₆D₆, 25 °C): δ = 11.0 (C₅Me₅), 11.4 (C₅Me₅), 21.3 (C₅Me₅), 77.9 (C₅Me₅), 125.7 (C₅Me₅), 137.8 (C₅Me₅). IR: ν 2929, 2906, 2825, 1445, 1261, 1157, 1096, 1013, 813, 799, 671, 544.

Orange crystals of **4 x thf** were isolated after storage of a solution of **4** in thf for 12 h at -30 °C.

[Zn₄(μ₄-O)(S₂CCp*)₆] **5**. CS₂ (0.31 g, 4 mmol) was added dropwise to 0.34 g Cp*₂Zn (1.0 mmol) dissolved in 15 ml of toluene and stirred for 10 min at ambient temperature. Then, water (4.5 μl, 0.25 mmol) was added and the resulting solution stirred for additional 2 h. Colorless crystals of **5**, which were not suitable for a full crystallographic analysis,^[18] were formed within 24 h upon storage at -30 °C.

Yield: 0.11 g (28 %). Melting point: > 220 °C. Anal. Found (calcd) for C₆₆H₉₀OS₁₂Zn₄ (1545.69 g/mol): H 6.1 (5.9), C 52.6 (51.3). ¹H NMR (300 MHz, C₆D₆, 25 °C): δ = 1.49 (s, 3H, C₅Me₅), 1.62 (s, 6H, C₅Me₅), 1.85 (s, 6H, C₅Me₅). ¹³C{¹H} NMR (75 MHz, C₆D₆, 25 °C): δ = 10.6 (C₅Me₅), 10.9 (C₅Me₅), 11.7 (C₅Me₅), 79.8 (C₅Me₅), 138.0 (C₅Me₅), 143.7 (C₅Me₅). IR: ν 2966, 2913, 2852, 1656, 1600, 1495, 1437, 1379, 1363, 1260, 1227, 1145, 1072, 999, 955, 868, 789, 729, 709, 660, 646, 616, 600, 531, 465.

Supporting Information X-ray crystallographic data of **1** are given in the electronic supplement. The crystallographic data (without structure factors) were also deposited as „supplementary publication no. CCDC-865384 (**2**), CCDC-865383 (**3**) and CCDC-865385 (**4**) at the Cambridge Crystallographic Data Centre. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre: CCDC, 12 Union Road, Cambridge, CB21EZ (Fax: (+44)1223/336033; E-mail: deposit@ccdc.cam.ac.uk).

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- [19] **M**: centroid of the aromatic ring, **R**: mean plane of the aromatic ring, <(HMR) describes the orientation of the hydrogen atom above the pi-system. In case of <(HMR) = 90° the hydrogen is located exactly over the centre of the ring.
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Insertion Reactions of Heterocumulenes with Zincocene Cp^*_2Zn

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