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Insertion Reactions of Heterocumulenes with Zincocene Cp^*_2Zn

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Dedicated to Professor Klaus Jurkschat on the Occasion of His 60th Birthday

Keywords: Heterocumulene; Insertion reaction; Zinc; C–C bond formation; X-ray diffraction

Abstract. Zincocene Cp^*_2Zn reacts with carbodiimides $C(NR)_2$ with insertion into the Zn–Cp* bond and formation of $[(Cp^*C(NR)_2]_2Zn$ [*R* = Et (**1**), *i*Pr (**2**), Cy (**3**)]. In addition, the reaction of Cp^*_2Zn with CS_2 under dry conditions gives $(Cp^*CS_2)_2Zn$ (**4**), whereas in the presence of a small amount of water $[Zn_4(\mu_4\text{-}O)(S_2CCp^*)_6]$ (**5**) is obtained. Compounds **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.

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 by coordination to transition metal complexes, which lowers the activation energy for further reactions, were also 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 were 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 chemistry. 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 (ROP) 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 $[Zn_4(\mu_4\text{-}O)(O_2CCp^*)_6]$ contains a central $[Zn_4O]^{6+}$ 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, $C(NR)_2$, and isocyanates *R*NCO,[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 $[\{(Me_3SiNPPh_2)_2CH\}ZnR]$ (*R* = Me, Ph) were reported to react with carbodiimides, ketenes, and isocyanates via nucleophilic addition of the methine carbon atom of the $\{CH(Ph_2PNSiMe_3)_2\}$ 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 $[(Cp^*C(NR)_2]_2Zn$ [*R* = Et (**1**), *i*Pr (**2**), Cy (**3**)] and $(Cp^*CS_2)_2Zn$ (**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 *R*NCN*R* (*R* = 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 $[Cp^*C(NR)_2]_2Zn$ [*R* = Et (**1**), *i*Pr (**2**), Cy (**3**)].

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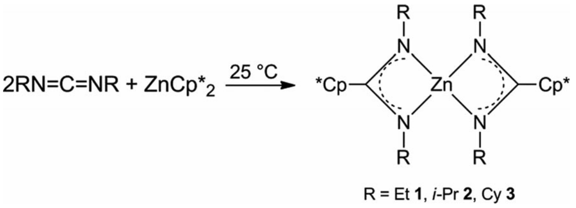
The formation of **1**–**3** was monitored by in situ ^{1}H NMR spectroscopy. The progress of the reaction is shown by the continuously decreasing resonance of the Zn-bonded Cp* groups (δ =1.88 ppm in [D$_8$]toluene). Simultaneously, three new singlet signals with a relative intensity of 1:2:2 steadily 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).



Scheme 1. Synthesis of [Cp*C(N*R*)$_2$]$_2$Zn.

Single crystals of **2** and **3** were obtained from solutions in toluene upon storage at –30 °C. Complexes **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).

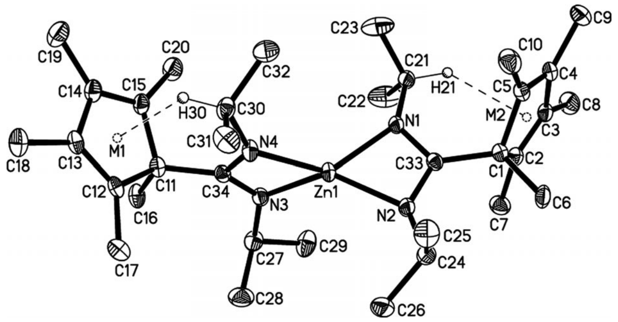


Figure 1. Molecular structure of **2**. Non-interacting hydrogen atoms are omitted for clarity. Thermal ellipsoids at 50 % probability levels. Selected bond lengths /Å and angles /°: Zn1–N1 2.0087(14), Zn1–N3 2.0110(14), Zn1–N2 2.0175(14), Zn1–N4 2.0212(15) N1–C33 1.336(2), N2–C33 1.345(2), N3–C34 1.345(2), 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). CH···π interactions C21–H21···R (C1 C2 C3 C4 C5) *d*(H···M) 2.24 Å, *d*(H···R) 2.2315(19) Å, <(CHM) 135.0°, <(HMR) 85.0°; C30–H30···R (C11 C12 C13 C14 C15) *d*(H···M) 2.27 Å, *d*(H···R) 2.2622(19) Å, <(CHM) 133.8°, <(HMR) 85.2°.[19]

The zinc atoms are tetrahedrally coordinated by two chelating amidinate groups. The Zn–N distances [**2**: 2.0087(14)–2.0212(15) Å; **3**: 1.9925(11)–2.0106(11) Å] 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 (**2**: 65.81°; **3**: 65.84°) are smaller than the exocyclic ones (**2**: 134.72°; **3**: 134.8°) and the average N–C–N bond angles (**2**: 109.73°; **3**: 109.43°) 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 $\bar{4}$ 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 CH···π 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 center of the molecule no intermolecular interactions can be found (shortest intermolecular H···N distance: 3.53 Å in **2** and >4 Å in **3**) and the packing is constituted by most dense packing alone (Figure 2).

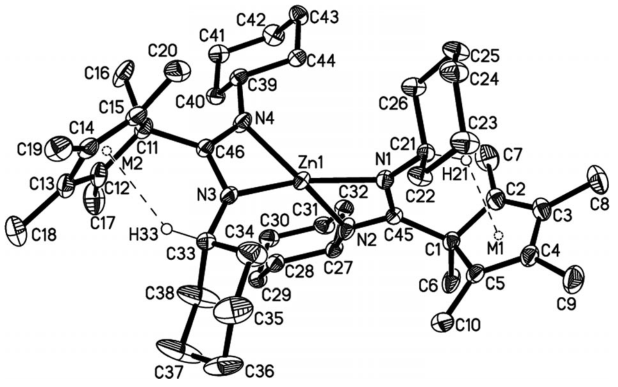
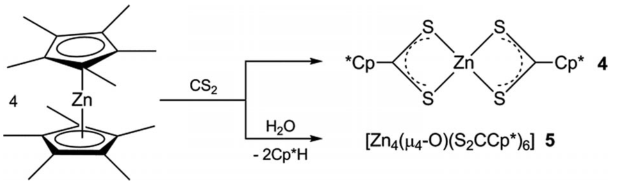


Figure 2. Molecular structure of **3**. Non-interacting hydrogen atoms are omitted for clarity. Thermal ellipsoids at 50 % probability levels. Selected bond lengths /Å and angles /°: Zn1–N1 2.0027(11), Zn1–N2 2.0056(11), Zn1–N3 1.9925(11), Zn1–N4 2.0106(11), N1–C45 1.3275(16), N2–C45 1.3410(16), N3–C46 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), C(33)–N(3)–Zn(1) 135.88(8), C(46)–N(4)–C(39) 134.70(11), C46–N4–Zn1 91.99(8). CH···π interactions C21–H21···R (C1 C2 C3 C4 C5) *d*(H···M) 2.32 Å, *d*(H···R) 2.3014(13) Å, <(CHM) 128.8°, <(HMR) 82.7°, C33–H33···R (C11 C12 C13 C14 C15) *d*(H···M) 2.28 Å, *d*(H···R) 2.2693(14), <(CHM) 131.4°, <(HMR) 84.4°.

Since Cp*$_2$Zn was found to react readily with CO$_2$,[9] isocyanates CNXyl,[14] *R*NCO,[17] and *R*NCN*R* 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*$_2$Zn was found to react readily with CS$_2$ at ambient temperature in almost quantitative yield with formation of (Cp*CS$_2$)$_2$Zn (**4**). Moreover, the presence of a small amount of water yielded [Zn$_4$(μ$_4$-O)(S$_2$CCp*)$_6$] (**5**) including a central Zn$_4$O core as was previously observed for the reaction of Cp*$_2$Zn with CO$_2$[9] (Scheme 2).

The ^{1}H NMR spectrum of **4** shows three resonances at δ = 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 CS$_2$ at 1482 cm^{-1} is shifted



Scheme 2. Synthesis of (Cp*CS$_2$)$_2$Zn (**4**) and [Zn$_4$(μ$_4$-O)(S$_2$CCp*)$_6$] (**5**).

to 1445 (ν_{asym}) and 1177 cm^{-1} (ν_{sym}) in **4** as was previously reported for Me$_2$Al(μ-N*i*Pr$_2$)$_2$Mg(S$_2$CMe) (1142, 1017 cm^{-1}) [20] and Cp*W(NO)(η^2-S$_2$CNH*t*Bu)(O*t*Bu) (1142, 1017 cm^{-1}).[21] Unfortunately, the ^{13}C{^{1}H} NMR spectra of **4** and **5** did not exhibit resonances for the *C*S$_2$ carbon atoms, which were expected to be shifted to lower field compared to that of free CS$_2$ (δ =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 δ = 172.5 ppm for a dinuclear Cu-CS$_2$ complex.[24]

Single crystals of **4** were obtained from thf solution upon storage at –30 °C.[18] Compound **4**, which was obtained as thf adduct, crystallizes in the $P\bar{1}$ space group (Figure 3). 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 4).

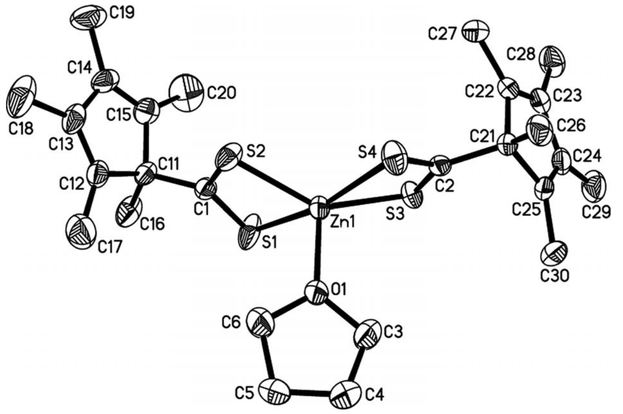


Figure 3. Molecular structure of **4**·thf. Hydrogen atoms are omitted for clarity. Thermal ellipsoids at 50 % probability levels. Selected bond lengths /Å and angles /°: Zn1–O1 2.0335(16), Zn1–S1 2.5785(7), Zn1–S2 2.3197(6), Zn1–S3 2.3008(6), Zn1–S4 2.6965(7), S1–C1 1.664(2), S2–C1 1.697(2), S3–C2 1.7045(19), 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 zinc atom in **4** is coordinated by two chelating thiocarboxylate groups and a single thf molecule, hence resulting in a distorted trigonal-bipyramidal coordination mode. The thiocarboxylate 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 central Zn^{II} atoms. The axial S1–Zn1–S4 unit deviates slightly from linearity [169.66(2)°], whereas 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 arrangement [S–Zn–O ca. 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 zinc complexes bearing two ligands with a chelating CS$_2^-$ 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 (zinc 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°).

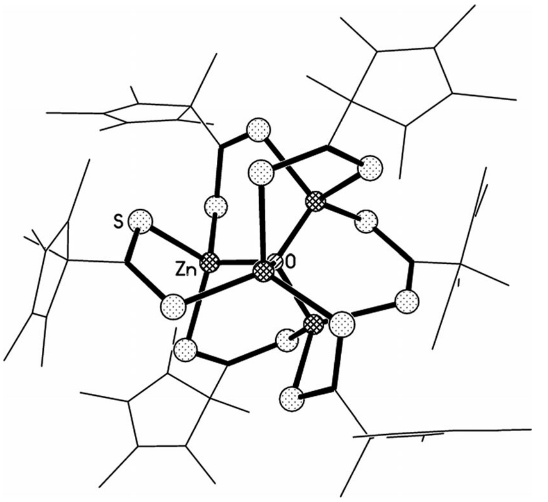


Figure 4. Molecular structure of **5**. Due to the poor scattering power of the crystals only the connectivity could be determined reliably. The oxygen atom is placed on an inversion center and thus the positions of the zinc atoms (and probably sulfur atoms) are disordered over two positions (only one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

Conclusions

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

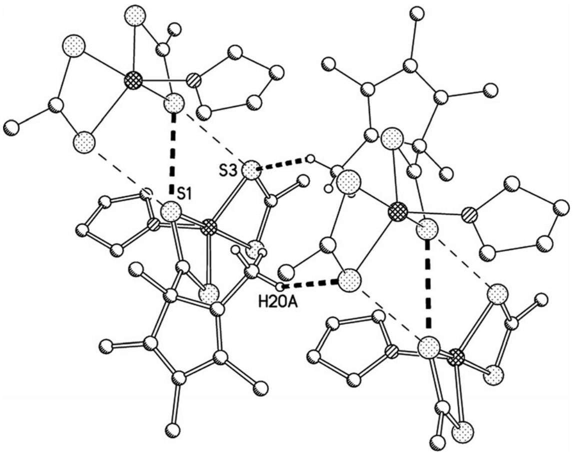


Figure 5. Intermolecular interactions in the packing of **4**.

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

General: All manipulations were performed in an argon atmosphere. Cp^*_2Zn was prepared according to literature methods.[26] ^1H, $^{13}C\{^1H\}$ NMR spectra were recorded with a Bruker DMX 300 spectrometer and are referenced to internal C_6D_5H (^1H: δ = 7.154; ^{13}C: δ = 128.0 ppm). IR spectra were recorded with 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 elemental analysis laboratory of the University of Essen.

[Cp*C(N*R*)$_2$]$_2$Zn (1–3): Solutions of Cp^*_2Zn (0.34 g, 1 mmol) and two equivalents of carbodiimide *R*NCN*R* were dissolved in toluene (10 mL) and stirred for 1 h at ambient temperature. Colorless crystals of [Cp*C(N*R*)$_2$]$_2$Zn [*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 $C_{30}H_{50}N_4Zn$ (540.19): H 10.8 (10.8), C 66.6 (66.7), N 10.3 (10.4) %. **^{1}H NMR** (300 MHz, C_6D_6, 25 °C): δ = 1.11 (t, $^3J_{HH}$ = 7.1 Hz, 6 H, CH_2CH_3), 1.31 (t, $^3J_{HH}$ = 7.1 Hz, 6 H, CH_2CH_3), 1.40 (s, 6 H, C_5Me_5), 1.65 (s, 12 H, C_5Me_5), 1.88 (s, 12 H, C_5Me_5), 2.80 (q, $^3J_{HH}$ = 7.1 Hz, 4 H, CH_2CH_3), 3.64 (q, $^3J_{HH}$ = 7.0 Hz, 4 H, CH_2CH_3). **^{13}C{^{1}H} NMR** (75 MHz, C_6D_6, 25 °C): δ = 10.9 (C_5Me_5), 11.0 (C_5Me_5), 19.4 (C_5Me_5), 20.5 (NCH_2CH_3), 23.9 (NCH_2CH_3), 38.0 (NCH_2CH_3), 42.2 (NCH_2CH_3), 65.2 (C_5Me_5), 134.5 (C_5Me_5), 141.5 (C_5Me_5), 170.6 (CN_2). **IR**: $\tilde{\nu}$ = 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 cm^{-1}.

2: Yield 0.57 g (97 %). Melting point: >220 °C. Anal. Found (calcd) for $C_{34}H_{58}N_4Zn$ (588.21): H 9.9 (9.9), C 69.4 (69.4), N 9.5 (9.5) %. **^{1}H NMR** (300 MHz, C_6D_6, 25 °C): δ = 1.00 [d, $^3J_{HH}$ = 5.9 Hz, 6 H, $CH(CH_3)_2$], 1.03 [d, $^3J_{HH}$ = 6.0 Hz, 6 H, $CH(CH_3)_2$], 1.31 [d, $^3J_{HH}$ = 5.9 Hz, 6 H, $CH(CH_3)_2$], 1.33 [d, $^3J_{HH}$ = 5.9 Hz, 6 H, $CH(CH_3)_2$], 1.45 (s, 6 H, C_5Me_5), 1.67 (s, 12 H, C_5Me_5), 1.95 (s, 12 H, C_5Me_5), 3.38 [sept, 2 H, $CH(CH_3)_2$], 4.44 [sept, 2 H, $CH(CH_3)_2$]. **^{13}C{^{1}H} NMR** (75 MHz, C_6D_6, 25 °C): δ = 11.0 (C_5Me_5), 11.4 (C_5Me_5), 24.6 (C_5Me_5), 28.6 [$NCH(CH_3)_2$], 28.7 [$NCH(CH_3)_2$], 43.7 [$NCH(CH_3)_2$], 45.4 [$NCH(CH_3)_2$], 65.7 (C_5Me_5), 134.0 (C_5Me_5), 135.0 (C_5Me_5), 167.9 (CN_2). **IR**: $\tilde{\nu}$ = 2961, 2921, 2847, 1645, 1480, 1426, 1368, 1318, 1281, 1261, 1239, 1211, 1134, 1096, 1061, 969, 888, 803, 700, 675, 508 cm^{-1}.

3: Yield 0.70 g (93 %). Melting point: >220 °C. Anal. Found (calcd) for $C_{46}H_{74}N_4Zn$ (748.46): H 11.0 (10.9), C 74.0 (73.8), N 7.5 (7.5) %. **^{1}H NMR** (300 MHz, C_6D_6, 25 °C): δ = 1.14–1.44 (m, 12 H, CH_2), 1.40 (s, 6 H, C_5Me_5), 1.56–1.68 (m, 4 H, CH_2), 1.71 (s, 12 H, C_5Me_5), 1.76–1.88 (m, 2 H, CH_2), 1.98 (s, 12 H, C_5Me_5), 2.19 (m, 2 H, CH_2), 2.94 (m, 1 H, CH_{ax}), 4.04 (m, 1 H, CH_{ax}). **^{13}C{^{1}H} NMR** (75 MHz, C_6D_6, 25 °C): δ = 11.1 (C_5Me_5), 11.2 (C_5Me_5), 11.3 (C_5Me_5), 24.4 (CH_2), 26.6 (CH_2), 26.7 (CH_2), 38.4 (CH_2), 38.5 (CH_2), 39.7 (CH_2), 39.8 (CH_2), 52.0 (NCH), 52.4 (NCH), 65.7 (C_5Me_5), 134.1 (C_5Me_5), 143.5 (C_5Me_5), 143.6 (C_5Me_5), 167.8 (CN_2). **IR**: $\tilde{\nu}$ = 2916, 2847, 1421, 1353, 1340, 1294, 1257, 1237, 1202, 1081, 1062, 1027, 990, 898, 887, 803, 663, 569, 541, 504 cm^{-1}.

(Cp*CS$_2$)$_2$Zn (4): CS_2 (0.08 g, 1 mmol) was added dropwise to a solution of Cp^*_2Zn (0.17 g, 0.5 mmol) in toluene (15 mL) 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 $C_{22}H_{30}S_4Zn{*}C_4H_8O$ (560.17): H 6.9 (6.8), C 55.9 (55.7) %. **^{1}H NMR** (300 MHz, C_6D_6, 25 °C): δ = 1.48 (s, 3 H, C_5Me_5), 1.63 (s, 6 H, C_5Me_5), 1.84 (s, 6 H, C_5Me_5). **^{13}C{^{1}H} NMR** (75 MHz, C_6D_6, 25 °C): δ = 11.0 (C_5Me_5), 11.4 (C_5Me_5), 21.3 (C_5Me_5), 77.9 (C_5Me_5), 125.7 (C_5Me_5), 137.8 (C_5Me_5). **IR**: $\tilde{\nu}$ = 2929, 2906, 2825, 1445, 1261, 1157, 1096, 1013, 813, 799, 671, 544 cm^{-1}.

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

[Zn$_4$(μ$_4$-O)(S$_2$CCp*)$_6$] (5): CS_2 (0.31 g, 4 mmol) was added dropwise to Cp^*_2Zn (0.34 g, 1.0 mmol) dissolved in toluene (15 mL) and stirred for 10 min at ambient temperature. Afterwards, 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 $C_{66}H_{90}OS_{12}Zn_4$ (1545.69): H 6.1 (5.9), C 52.6 (51.3) %. **^{1}H NMR** (300 MHz, C_6D_6, 25 °C): δ = 1.49 (s, 3 H, C_5Me_5), 1.62 (s, 6 H, C_5Me_5), 1.85 (s, 6 H, C_5Me_5). **^{13}C{^{1}H} NMR** (75 MHz, C_6D_6, 25 °C): δ = 10.6 (C_5Me_5), 10.9 (C_5Me_5), 11.7 (C_5Me_5), 79.8 (C_5Me_5), 138.0 (C_5Me_5), 143.7 (C_5Me_5). **IR**: $\tilde{\nu}$ = 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 cm^{-1}.

X-ray crystallographic data of **1** are given in the Supporting Information. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-865384 (**2**), CCDC-865383 (**3**), and CCDC-865385 (**4**) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

Supporting Information (see footnote on the first page of this article): X-ray crystallographic data of **2**, **3**, and **4** are given in the Supporting Information.

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[18] Bruker AXS D8 Kappa diffractometer with APEX2 detector [Mo-K_α radiation, λ = 0.71073 Å; T = 100(1) K]. The structures were solved by Direct Methods (SHELXS-97, G. M. Sheldrick, *Acta Crystallogr. Sect. A* **1990**, *46*, 467) and refined by full-matrix least-squares on F^2. Semi-empirical absorption correction from equivalent reflections on basis of multi-scans (Bruker AXS APEX2) was applied. All non-hydrogen atoms were refined anisotropically and hydrogen atoms by a riding model. (G. M. Sheldrick, *SHELXL-97*, Program for Crystal Structure Refinement, Universität Göttingen, **1997**; see also: G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2008**, *64*, 112; and ShelXle, *A Qt GUI for SHELXL*: C. B. Hübschle, G. M. Sheldrick, B. Dittrich, *J. Appl. Crystallogr.* **2011**, *44*, 1281–1284). **2**: $C_{34}H_{58}N_4Zn$, M = 588.21, colorless crystal (0.24 × 0.17 × 0.13 mm); monoclinic, space group $P2_1/c$; a = 17.6478(4), b = 13.5140(4), c = 15.6798(4) Å; β = 111.7080(10)°, V = 3474.31(16) Å^3; Z = 4; μ = 0.733 mm^{-1}; $\rho_{calcd.}$ = 1.125 g·cm^{-3}; 48455 reflexes ($2\theta_{max}$ = 55°), 7688 unique (R_{int} = 0.0306); 353 parameters; largest max./min. in the final difference Fourier synthesis 1.516 e·Å^{-3} [0.87 Å from Zn(1)]/–0.282 e·Å^{-3}; max./min. transmission 0.75/0.64; R_1 = 0.0354 [$I > 2\sigma(I)$], wR_2 (all data) = 0.0972. **3**: $C_{46}H_{74}N_4Zn$, M = 748.46, colorless crystal (0.28 × 0.25 × 0.17 mm); monoclinic space group $P2_1/n$; a = 9.4418(2), b = 24.2941(6), c = 19.4946(5) Å; β = 102.120 (1)°, V = 4372.00(18) Å^3; Z = 4; μ = 0.596 mm^{-1}; $\rho_{calcd.}$ = 1.137 g·cm^{-3}; 42536 reflexes ($2\theta_{max}$ = 56°), 10623 unique (R_{int} = 0.0189); 460 parameters; largest max./min. in the final difference Fourier synthesis 0.403 e·Å^{-3}/–0.266 e·Å^{-3}; max./min. transmission 0.75/0.67; R_1 = 0.02327[$I > 2\sigma(I)$], wR_2 (all data) = 0.0878. The ADP of C37 and C38 indicates severe disorder which could not be resolved. **4**: $C_{26}H_{38}OS_4Zn$, M = 560.17, orange crystal (0.37 × 0.25 × 0.07 mm); triclinic, space group $P\bar{1}$; a = 8.7117(13), b = 11.1680(17), c = 15.319(2) Å; α = 75.571(7)°, β = 83.278(7)°, γ = 87.783(7)°, V = 1433.4(4) Å^3; Z = 2; μ = 1.164 mm^{-1}; $\rho_{calcd.}$ = 1.298 g·cm^{-3}; 30201 reflexes ($2\theta_{max}$ = 54°), 6082 unique (R_{int} = 0.0257); 289 parameters; largest max./min. in the final difference Fourier synthesis 0.733 e·Å^{-3}/–0.484 e·Å^{-3}; max./min. transmission 0.75/0.60; R_1 = 0.0324 [$I > 2\sigma(I)$], wR_2 (all data) = 0.0873. **5**: $C_{66}H_{90}OS_{12}Zn_4 \cdot xC_7H_8$, M = 1545.58, orange block (0.15 × 0.13 × 0.08 mm); triclinic, space group $P\bar{1}$; a = 11.9105(7) Å, b = 12.5796(7) Å, c = 15.3242(9) Å; α = 103.415(3)°, β = 90.586(3)°, γ = 108.541(3)°, V = 2108.6(2) Å^3; Z = 1. The scattering power of the crystals was poor ($2\theta_{max}$< 48°) likely because of the disorder of the zinc/sulfur core of the molecule. In addition high electron density remained in the final difference Fourier synthesis, which could be partly identified as disordered toluene but not refined properly. SQUEEZE mildly improved the refinement but could not fix the poor data quality.

However the data were sufficient to establish the connectivity of the molecule.
[19] M: centroid of the aromatic ring, R: mean plane of the aromatic ring, <(HMR) describes the orientation of the hydrogen atom above the π-system. In case of <(HMR) = 90° the hydrogen is located exactly over the center of the ring.
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