Synthesis and X-ray crystal structure of diimidosulfinate transition metal complexes

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Supporting Information Placeholder

ABSTRACT: Bis(trimethylsilyl)sulfurdiimide $S(NSiMe_3)_2$ reacts with equimolar amounts of Me_2Zn and Cp^*Zn either with insertion into the metal-carbon bond and formation of the expected S-methyl diimidosulfinate complex $[MeZn(NSiMe_3)S(Me)NSiMe_3]_2$ **1** or the unexpected complex $[Me_3SiNS(N(SiMe_3)SNSiMe_3)N(SiMe_3)Zn]_2$ **2**. Insertion reactions were also observed with Cp^*MMe_3 ($M = Ti, Zr, Hf$), yielding $Cp^*(Me)_2M[Me_3SiNS(Me)NSiMe_3]$ ($M = Ti$ **3**, Zr **4**, Hf **5**), whereas the corresponding Cl-substituted derivatives $Cp^*(Cl)_2M[Me_3SiNS(Me)NSiMe_3]$ ($M = Ti$ **6**, Zr **7**, Hf **8**) were obtained from salt elimination reactions of Li S-methyl diimidosulfinate $(Me_3SiN)_2S(Me)Li(thf)_2$ **9** with Cp^*MCl_3 . **1** – **8** were characterized by heteronuclear NMR (^1H , ^{13}C) and IR spectroscopy and the solid state structures of **1** – **5** and **9** were determined by single crystal X-ray diffraction.

S-alkyl diimidosulfinate complexes are typically prepared by reaction of the corresponding sulfurdiimide $S(NR)_2$ with different organometallic compounds RM .^[4] Alkali metal organyls are of particular interest since the resulting complexes are valuable diimidosulfinate-transfer reagents due to their high solubility in organic solvents. Lithium diimidosulfinate complexes are easily accessible by reaction of sulfurdiimides with lithium organyls, in which the nucleophilic carbanion attacks the electrophilic sulfur atom. As a consequence, a large number of lithium diimidosulfinate compounds containing different S-organo substituents have been synthesized and their structure have been investigated by X-ray diffraction and solid state NMR spectroscopy.^[5] They typically form solvent stabilized monomers or dimeric molecules in the solid state, whereas the corresponding Grignard reagents are predominantly monomeric.^[1b] Moreover, Stalke et al. successfully applied this particular synthetic approach also for the synthesis of Janus-type multidentate ligands as well as spacer-bridged bis(diimidosulfinate)s.^[6,7] In addition to the well known alkali metal and alkaline earth metal diimidosulfinate complexes $[RS(NR')_2][M(soln)]$ [$M = Li, Na, K, Rb, Cs; MgX$], which are accessible either by treating sulfurdiimides with different Grignard reagents or by reaction of *N,N'*-bis(trimethylsilyl)-aminoiminophenylsulphine $PhS(NSiMe_3)N(H)SiMe_3$ with bis(trimethylsilyl)amides $[M\{N(SiMe_3)_2\}]$ ($M = Ca, Sr, Ba$),^[8,9] several experimental studies on the synthesis of other main group and transition metal diimidosulfinate complexes have been reported. They are almost exclusively synthesized by reaction of the alkali metal diimidosulfinate with the corresponding metal halides or amides.^[7,10] Moreover, simple Lewis acid-base adducts of sulfurdiimide with several metal halides such as $TiCl_4$, $GaCl_3$ and $SnCl_4$, respectively, have been synthesized,^[11] while Weidlein et al. reported on insertion reactions of bis(trimethylsilyl)sulfurdiimide with trimethylalane, -gallane and -indane MMe_3 ($M = Al, Ga, In$).^[11c] In contrast, reactions of $S(NSiMe_3)_2$ with either a zirconium imide or the titanocene alkyne complex $[Cp_2Ti(\eta^2-$

Introduction

Monoanionic S-alkyl diimidosulfinate complexes $[RS(NR')_2]^-$ belong to the well known group of monoanionic heteroallyl ligands, which have been found widespread applications in coordination chemistry (Scheme 1).^[1]

Scheme 1. Monoanionic heteroallyl ligands.

These ligands show different binding modes to metals and can serve as monodentate (η^1), chelating (η^2) or bridging monodentate ($\mu-\eta^1-\eta^1$) four-electron donor ligands. They have also been referred as "steric cyclopentadienyl equivalents" since their cone angles are comparable to those of $C_5H_5^-$ and $C_5Me_5^-$ respectively,^[2] and as a consequence, they have been found technical applications in catalysis such as olefin polymerization.^[3]

$\text{Me}_3\text{SiC}_2\text{SiMe}_3$] yielded titanium trisimidodisulfite complexes in a rather complex reaction mechanism,^[12, 13] while the analogous reaction with $[\text{Cp}_2\text{Ti}(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)]$ gave an unusual four-membered metal-lacycle.^[14]

Surprisingly, reactions of sulfur diimides with homoleptic group 12 (Zn) metal complexes MR_2 as well as heteroleptic group 4 complexes Cp^*MMe_3 (M = Ti, Zr, Hf), in which the organic groups also exhibit a high carbanionic character, have not been reported to the best of our knowledge. In contrast, sulfur triimides $\text{S}(\text{NR})_3$ were shown to react with ZnMe_2 with insertion into the metal-carbon bond and formation of the zinc-S-methyltri(tert-butylimido)sulfonate $\text{Me}_x\text{M}[(\text{RN})_3\text{SMe}]$ (M = Zn, x = 1; M = Al, x = 2).^[15] Due to our general interest in the synthesis, structure and catalytic activity of transition metal complexes containing chelating N,N'-, N,O- and O,O-ligands,^[16] we became interested in reactions of bis(trimethylsilyl)-sulfur diimide with group 4 and group 12 metal complexes containing metal-Me bonds and report herein on reactions of $\text{S}(\text{NSiMe}_3)_2$ with Me_2Zn , Cp^*_2Zn and group 4 metal complexes of the general type Cp^*MMe_3 (M = Ti, Zr, Hf). In addition, salt elimination reactions between Cp^*MCl_3 (M = Ti, Zr, Hf) and S-methyl diimidodisulfinate $[\text{Li}(\text{thf})[\text{Me}_3\text{SiNS}(\text{Me})\text{NSiMe}_3]]_2$, which was obtained from the reaction of $\text{S}(\text{NSiMe}_3)_2$ with MeLi in thf, yielded the corresponding S-alkyl diimidodisulfates.

Experimental Section

General Procedures. All manipulations were performed in a Glovebox (MBraun) under an Ar atmosphere or with standard Schlenk techniques. Solvents were carefully dried over Na/K and degassed prior to use. A 2 M solution of ZnMe_2 in toluene was obtained from Sigma Aldrich and used as received, while $\text{S}(\text{NSiMe}_3)_2$,^[17] ZnCp^*_2 ,^[18] Cp^*MMe_3 ,^[19] and Cp^*MCl_3 ,^[20] were prepared according to literature methods. Due to the high vapor pressure of ZnMe_2 and its high reactivity toward water and oxygen, all manipulations must be performed under inert gas conditions. NMR spectra were recorded on a Bruker Avance 300 spectrometer at 25 °C at 300.1 MHz (^1H) and 75.5 MHz (^{13}C), respectively, and referenced to internal $\text{C}_6\text{D}_6\text{H}$ (^1H : δ = 7.154; ^{13}C : δ = 128.0) and internal THF-d_8 (^1H : δ = 3.580, 1.730; ^{13}C : δ = 25.2, 67.4). IR spectra were recorded on a Bruker 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 Duisburg-Essen.

$[\text{MeZnN}(\text{SiMe}_3)\text{S}(\text{Me})\text{NSiMe}_3]_2$ 1. $\text{S}(\text{NSiMe}_3)_2$ (0.50 g, 2.42 mmol) was dissolved in 3 ml of toluene and 2.02 ml ZnMe_2 (2.42 mmol; 1.2 M in toluene) was added to the yellow solution at ambient temperature. After 15 min of stirring a colorless solution was obtained.

The solvent was reduced and colorless crystals were obtained after storage at -30 °C for 12 hours.

Yield: 1.43 g (98 %). Mp. 49 °C. Anal. Found (calcd) for $\text{C}_{16}\text{H}_{48}\text{N}_4\text{S}_2\text{Si}_4\text{Zn}_2$ (603.80 g/mol): C, 32.15 (31.83); H, 8.08 (8.01); N, 9.53 (9.27); S, 10.50 (10.62) %. ^1H NMR (300 MHz, C_6D_6 , 25 °C): δ = -0.30 (s, 6 H, ZnMe), 0.23 (s, 36 H, SiMe_3), 2.83 (s, 6 H, SMe). ^{13}C NMR (75 MHz, C_6D_6 , 25 °C): δ = -5.27 (ZnMe), 1.99 (SiMe_3), 48.09 (SMe). ATR-IR: ν = 2949, 2901, 2830, 1414, 1294, 1245, 1161, 1051, 978, 967, 909, 826, 773, 748, 706, 677, 623, 516, 439, 382 cm^{-1} .

$[\text{Me}_3\text{SiNS}(\text{N}(\text{SiMe}_3)\text{SNSiMe}_3)\text{N}(\text{SiMe}_3)\text{Zn}]_2$ 2. ZnCp^*_2 (0.30 g, 0.97 mmol) was dissolved in 5 ml of toluene and $\text{S}(\text{NSiMe}_3)_2$ (0.30 g, 1.45 mmol) was added to the solution at ambient temperature. The yellow solution turned orange within 2 hours. The solvent was reduced and colorless crystals were obtained after storage at -30 °C for 12 hours.

Yield: 0.27 g (30 %). Mp. 146 °C (dec.). Anal. Found (calcd) for $\text{C}_{24}\text{H}_{72}\text{N}_8\text{S}_4\text{Si}_8\text{Zn}_2$ (956.59 g/mol): C, 30.25 (30.13); H, 7.46 (7.59); N, 11.35 (11.71); S, 13.0 (13.41) %. ^1H NMR (300 MHz, C_6D_6 , 25 °C): δ = 0.21 (s, 9 H, SiMe_3), 0.42 (s, 9 H, SiMe_3), 0.44 (s, 9 H, SiMe_3), 0.57 (s, 9 H, SiMe_3). ^{13}C NMR (75 MHz, C_6D_6 , 25 °C): δ = 0.89 (SiMe_3), 2.10 (SiMe_3), 2.34 (SiMe_3), 3.01 (SiMe_3). ATR-IR: ν = 2949, 2896, 1442, 1402, 1244, 987, 900, 875, 825, 769, 713, 676, 663, 617, 486, 427, 409 cm^{-1} .

General synthesis of 3 – 5. 0.48 mmol Cp^*MMe_3 (M = Ti **3**, 0.09 g; Zr **4**, 0.11 g; Hf **5**, 0.15 g) was dissolved in 5 ml fluorobenzene and $\text{S}(\text{NSiMe}_3)_2$ (0.10 g, 0.48 mmol) was added via syringe. The solution was stirred at 50 °C for 15 hours and the solvent was removed in vacuum. Crystals were obtained from a solution in 1 mL of pentane at 18 °C.

$\text{Cp}^*(\text{Me})_2\text{Ti}[\text{Me}_3\text{SiNS}(\text{Me})\text{NSiMe}_3]$ 3. Yield: 0.18 g (85 %). Mp. 93 °C (dec.). Anal. Found (calcd) for $\text{C}_{19}\text{H}_{42}\text{N}_2\text{SSi}_2\text{Ti}$ (434.68 g/mol): C, 52.25 (52.50); H, 9.71 (9.74); N, 6.37 (6.44); S, 7.18 (7.38) %. ^1H NMR (300 MHz, C_6D_6 , 25 °C): δ = 0.24 (s, 18 H, SiMe_3), 0.63 (s, 6 H, TiMe_2), 1.94 (s, 15 H, C_5Me_5), 2.05 (s, 3 H, SMe). ^{13}C NMR (75 MHz, C_6D_6 , 25 °C): δ = 2.68 (SiMe_3), 13.30 (TiMe_2), 48.80 (SMe), 65.25 (C_5Me_5), 123.26 (C_5Me_5). ATR-IR: ν = 2957, 2910, 1727, 1489, 1407, 1377, 1284, 1261, 1245, 1135, 1101, 1024, 980, 921, 833, 802, 705, 677, 627, 595, 439, 406 cm^{-1} .

$\text{Cp}^*(\text{Me})_2\text{Zr}[\text{Me}_3\text{SiNS}(\text{Me})\text{NSiMe}_3]$ 4. Yield: 0.21 g (90 %). Mp. 83 °C (dec.). Anal. Found (calcd) for $\text{C}_{17}\text{H}_{36}\text{N}_2\text{SSi}_2\text{Zr}$ (478.00 g/mol): C, 47.75 (47.74); H, 8.86 (8.86); N, 5.89 (5.86); S, 6.73 (6.71) %. ^1H NMR (300 MHz, C_6D_6 , 25 °C): δ = 0.19 (s, 18 H, SiMe_3), 0.28 (s, 6 H, ZrMe_2), 2.02 (s, 15 H, C_5Me_5), 2.09 (s, 3 H, SMe). ^{13}C NMR (75 MHz, C_6D_6 , 25 °C): δ = 2.40 (SiMe_3), 12.50 (ZrMe_2), 46.14 (SMe), 50.90 (C_5Me_5), 119.85 (C_5Me_5). ATR-IR: ν = 2955, 2933, 2920, 2867, 2805, 2772, 2726, 1492, 1439, 1376, 1279, 1257, 1244, 1139, 1116, 992, 830, 793, 752, 695, 676, 658, 555, 506, 480, 459, 423 cm^{-1} .

Cp*(Me)₂Hf[Me₃SiNS(Me)NSiMe₃] 5. Yield: 0.28 g (88 %). Mp. 71 °C (dec.). Anal. Found (calcd) for C₁₉H₄₂N₂SSi₂Hf (565.39 g/mol): C, 39.9 (40.37); H, 7.31 (7.49); N, 4.91 (4.96); S, 5.42 (5.67) %. ¹H NMR (300 MHz, C₆D₆, 25 °C): δ = 0.05 (s, 6 H, HfMe₂), 0.18 (s, 18 H, SiMe₃), 2.06 (s, 18 H, C₅Me₅, SMe). ¹³C NMR (75 MHz, C₆D₆, 25 °C): δ = 2.40 (SiMe₃), 12.39 (HfMe₂), 53.28 (SMe), 67.83 (C₅Me₅), 118.83 (C₅Me₅). ATR-IR: ν = 2956, 2819, 2870, 2806, 2782, 1492, 1440, 1417, 1376, 1280, 1245, 1136, 1128, 1092, 1065, 1024, 995, 983, 830, 797, 752, 699, 676, 627, 594, 564, 543, 493, 460, 425 cm⁻¹.

[(Me₃SiN)₂S(Me)Li(thf)]₂ 9. A solution of S(NSiMe₃)₂ (0.15 g, 0.73 mmol) in 5 mL of THF was cooled to -78 °C and 0.45 ml MeLi (0.73 mmol; 1.6 M in Et₂O) was added via syringe. The solution was allowed to reach ambient temperature and stirred for 1h. **9** was isolated in quantitative yield after removal of the solvent. Re-crystallization from THF at -30 °C gave colorless crystals of **9**.

Yield: 0.43 g (98 %). Anal. Found (calcd) for C₂₂H₅₈N₄O₂S₂Si₄Li₂ (601.08 g/mol): C, 43.87 (43.96); H, 9.64 (9.73); N, 9.20 (9.32); S, 10.56 (10.67) %. ¹H NMR (300 MHz, C₆D₆, 25 °C): δ = 0.34 (s, 18 H, SiMe₃), 1.28 (m, 4 H, thf), 2.24 (s, 6 H, SMe), 3.48 (m, 4 H, thf). ¹³C NMR (75 MHz, C₆D₆, 25 °C): δ = 2.64 (SiMe₃), 25.41 (thf), 53.49 (SMe), 68.30 (thf).

General synthesis of 6 – 8. 0.45 ml MeLi (0.73 mmol; 1.6 M in Et₂O) was added at -78 °C to a solution of S(NSiMe₃)₂ (0.15 g, 0.73 mmol) in 5 mL of THF. The resulting solution was warmed to ambient temperature, stirred for 1 h and then cooled to -78 °C. A solution of Cp*MC₃ (M = Ti **6**, 0.18 g; Zr **7**, 0.21 g; Hf **8**, 0.27 g; 0.73 mmol) in 5 ml of THF was slowly added and the resulting solution was warmed to ambient temperature. After stirring for 10 hours, the solvent was removed in vacuum and the residue was suspended in pentane, filtered and the solvent reduced in vacuum to 3 mL. Crystals of **6 – 8** were obtained after 12 hours at 18 °C.

Cp*(Cl)₂Ti[Me₃SiNS(Me)NSiMe₃] 6. Yield: 0.10 g (30 %). Mp. 142 °C (dec.). Anal. Found (calcd) for C₁₇H₃₆Cl₂N₂SSi₂Ti (475.49 g/mol): C, 42.47 (42.94); H, 7.54 (7.63); N, 5.50 (5.89); S, 6.42 (6.74) %. ¹H NMR (300 MHz, THF-*d*₈, 25 °C): δ = 0.25 (s, 18 H, SiMe₃), 2.08 (s, 15 H, C₅Me₅), 2.78 (s, 3 H, SMe). ¹³C NMR (75 MHz, THF-*d*₈, 25 °C): δ = 1.19 (SiMe₃), 12.68 (SMe), 44.64 (C₅Me₅), 125.38 (C₅Me₅). ATR-IR: ν = 2954, 2911, 2857, 1433, 1407, 1308, 1289, 1250, 1015, 997, 956, 887, 837, 771, 752, 727, 659, 622, 611, 563, 547, 475, 435, 416, 382 cm⁻¹.

Cp*(Cl)₂Zr[Me₃SiNS(Me)NSiMe₃] 7. Yield: 0.11 g (28 %). Mp. 205 °C (dec.). Anal. Found (calcd) for C₁₇H₃₆Cl₂N₂SSi₂Zr (516.06 g/mol): C, 39.9 (40.34); H, 7.13 (7.17); N, 5.12 (5.53); S, 5.86 (6.34) %. ¹H NMR (300 MHz, THF-*d*₈, 25 °C): δ = 0.24 (s, 18 H, SiMe₃), 2.17 (s, 15 H, C₅Me₅), 2.70 (s, 3 H, SMe). ¹³C NMR (75 MHz, THF-*d*₈, 25 °C): δ = 1.94 (SiMe₃), 13.39 (SMe),

48.31 (C₅Me₅), 125.91 (C₅Me₅). ATR-IR: ν = 2955, 2921, 2868, 2805, 2773, 2726, 1491, 1376, 1258, 1244, 1139, 1097, 1013, 992, 975, 937, 830, 795, 752, 677, 556, 481, 459, 425 cm⁻¹.

Cp*(Cl)₂Hf[Me₃SiNS(Me)NSiMe₃] 8. Yield: 0.14 g (32 %). Mp. 215 °C (dec.). Anal. Found (calcd) for C₁₇H₃₆Cl₂N₂SSi₂Hf (606.10 g/mol): C, 33.50 (33.69); H, 6.14 (6.15); N, 4.69 (4.62); S, 5.35 (5.29) %. ¹H NMR (300 MHz, THF-*d*₈, 25 °C): δ = 0.24 (s, 18 H, SiMe₃), 2.22 (s, 15 H, C₅Me₅), 2.67 (s, 3 H, SMe). ¹³C NMR (75 MHz, THF-*d*₈, 25 °C): δ = 1.97 (SiMe₃), 13.08 (SMe), 48.15 (C₅Me₅), 123.70 (C₅Me₅). ATR-IR: ν = 2957, 2908, 2811, 2124, 2040, 1495, 1437, 1374, 1258, 1244, 1088, 987, 938, 831, 791, 751, 654, 624, 569, 484, 449, 429, 393 cm⁻¹.

Crystal Structure Determination of 1 – 5 and 9.

Figures 1 to 4 show the diagram of the solid state structures of **1**, **2**, **5** and **9**. Crystallographic data of **1** to **5** and **9** are summarized in table S1, selected bond lengths and angles of **3 – 5** are given in table 2. The crystals were mounted on nylon loops in inert oil. Data were collected on a AXS D8 Kappa diffractometer with APEX2 detector (MoK_α radiation, λ = 0.71073 Å; T = 100(1) K). The structures were solved by Direct Methods (SHELXS-97)^[19] and refined by full-matrix least-squares on F².^[20] Absorption corrections were performed semi-empirically from equivalent reflections on basis of multi-scans (Bruker AXS APEX2). All non-hydrogen atoms were refined anisotropically, methyl hydrogen atoms as rigid groups and others by a riding model (SHELXL-97/SHELXL-2013).^[20]

The crystallographic data (without structure factors) were deposited as "supplementary publication no. CCDC-1400389 (**1**), CCDC-1400390 (**2**), CCDC-1400391 (**3**), CCDC-1400392 (**4**) CCDC-1400393 (**5**) and CCDC-1400394 (**9**) 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).

Results and Discussion

Me₂Zn and S(NSiMe₃)₂ react with insertion of the sulfurdiimide into the Zn-Me bond and subsequent formation of the expected S-methyl-diimidodisulfinate complex [MeZnN(SiMe₃)S(Me)NSiMe₃]₂ **1** (scheme 2). ¹H and ¹³C NMR spectra of **1** show new characteristic signals due to the S-Me group at 2.83 (¹H) and 48.1 ppm (¹³C), respectively. In contrast, the analogous reaction of S(NSiMe₃)₂ with Cp*₂Zn yielded a colorless crystalline solid **2** after workup. The ¹H and ¹³C NMR spectra of **2** showed resonances of magnetically inequivalent SiMe₃ units but lacked the expected resonances of the Cp* groups (table 1). In contrast, the ¹H NMR spectrum of the raw product (Fig. S.7) showed resonances of **2** and of decamethyl-1,1'-dihydrofulvalene. Additional peaks between 0 and 0.3 ppm prove the formation of additional, so far unknown, Me₃Si-containing side-products.

Scheme 2. Synthesis of **1** and **2** by reactions of $\text{S}(\text{NSiMe}_3)_2$ with Me_2Zn and Cp^*_2Zn .

Colorless crystals of **1** and **2** were obtained from toluene solutions upon storage at $-30\text{ }^\circ\text{C}$ for 12 hours. **1** crystallizes in the monoclinic space group $P2_1/c$, while **2** crystallizes in the orthorhombic space group $Pbca$, respectively.

Figure 1. Representation of $[\text{Me}_2\text{ZnN}(\text{SiMe}_3)\text{S}(\text{Me})\text{NSiMe}_3]_2$ **1**. Thermal ellipsoids are shown at 50% probability levels. Hydrogen atoms are omitted for clarity. Selected bond lengths [$\text{\AA}$] and angles [$^\circ$]: Zn1-N1 2.0472(11), Zn1-N3 2.0513(11), Zn1-N4 2.4729(12), Zn2-N2 2.0588(11), Zn2-N3 2.4626(12), Zn2-N4 2.0397(11), S1-N1 1.6141(12), S1-N4 1.6389(11), S2-N2 1.6134(13), S2-N3 1.6354(11), S1-C15 1.7883(15), S2-C16 1.7906(15); N1-Zn1-N3 114.08(5), N1-Zn1-N4 68.04(4), N3-Zn1-N4 93.61(4), N2-Zn2-N3 67.71(4), N2-Zn2-N4 112.71(4), N3-Zn2-N4 94.21(4), N1-S1-N4 103.42(6), N2-S2-N3 102.91(6), N1-S1-C15 105.34(7), N4-S1-C15 104.77(7).

1 forms an eight-membered $\text{N}_4\text{S}_2\text{Zn}_2$ boat-type conformation ring with threefold-coordinated S atoms, while the Zn atoms adopt tetrahedral coordination spheres due to weak transannular Zn-N interactions. The Zn-N bond lengths therefore differ significantly, with four short (av. 2.0493 $\text{\AA}$) and two longer transannular Zn-N bonds (av. 2.4677 $\text{\AA}$), which clearly exceed the sum of the covalent radii (1.98 $\text{\AA}$ ^[21]) but which are

below the sum of the van-der-Waals radii (2.94 $\text{\AA}$ ^[22]). The S-N bond lengths range from 1.6134(13) to 1.6389(11) $\text{\AA}$ (av. 1.6255 $\text{\AA}$), which agrees very well with values previously reported for S-alkyl diimidosulfinate complexes,^[23] clearly proving the presence of delocalized π -electrons within the N-S-N unit. They are considerably shorter than the S-Me single bonds (1.7883(15), 1.7906(15) $\text{\AA}$). The N-S-N (102.91(6), 103.42(6) $^\circ$) and N-S-C bond angles (105.34(7), 104.77(7), 104.75(7), 104.44(7) $^\circ$) are almost identical.

Figure 2. Representation of $\{\text{Me}_3\text{SiNS}[\text{N}(\text{SiMe}_3)\text{SNSiMe}_3]-\text{N}(\text{SiMe}_3)\text{Zn}\}_2$ **2**. Thermal ellipsoids are shown at 50% probability levels. Hydrogen atoms and second orientation of the disordered parts are omitted for clarity. The part depicted in light bonds is generated via a center of inversion. Selected bond lengths [$\text{\AA}$] and angles [$^\circ$]: Zn1-N1 2.3229(15), Zn1-N2 1.9793(19), Zn1a-N1 2.0763(16), Zn1a-N4 1.919(2), S1-N1 1.6706(16), S1-N2 1.6132(18), S1-N3 1.7006(16), S2-N3 1.7125(16), S2-N4 1.6703(18); N1-Zn1-N2 71.09(6) $^\circ$, N1-Zn1a-N4 105.01(7), N1-S1-N2 100.05(9), N1-S1-N3 104.98(8), N2-S1-N3 108.66(9), N3-S2-N4 106.49(8).

The formation of **2** is rather unexpected since the Cp^* ligand isn't transferred to the electrophilic sulfur atom as was observed in the analogous reaction of ZnMe_2 as well as in reactions of Cp^*_2Zn with heteroocumenes such as carbodiimides $\text{C}(\text{NR})_2$, CO_2 , CS_2 and several isocyanates RNCO .^[24] Instead, two Zn- Cp^* bond breakage reactions as well as a dimerization of two sulfur diimide molecules has occurred, which can also be described as transimination reaction with subsequent oxidation of S(IV) to S(VI). One sulfur diimide molecule connects through a nucleophilic N atom to the electrophilic sulfur atom of a second sulfur diimide molecule, resulting in the formation of a $(\text{Me}_3\text{SiN})_2\text{SN}(\text{SiMe}_3)\text{SN}(\text{SiMe}_3)$ unit, which asymmetrically coordinates (Zn1-N2 1.9793(19) $\text{\AA}$, Zn1a-N1 2.0763(16) $\text{\AA}$) as bridging diimidosulfinate to two zinc atoms. The additional NSN unit serves as pendant donor sidearm and coordinates to the second zinc atom (Zn1a-N4 1.919(2) $\text{\AA}$). In addition, Zn1 shows a fourth

(trans-annular) Zn1-N1 bond, which is slightly shorter (2.3229(15) Å) compared to the transannular Zn-N bond lengths observed in **1**. Slightly comparable diimidosulfinate ligands containing a pendent donor-arm have been reported by Stalke et al.,^[6b] which also reported on the reaction of a sterically hindered diazasulfite with N,N'-di-(*tert*-butyl)sulfur diimide, which occurred with addition of the negatively charged nitrogen atom to the electrophilic sulfur atom and subsequent formation of a triazasulfite (transimination).^[25] Alternatively, the structure of **2** can be described as an eight membered N₃S₂Zn₂ ring as was observed for **1**, which adopts a chair-type conformation resulting from the crystallographic centro-symmetry. In contrast to **1**, the Zn-N bond distances in **2** differ by almost 0.16 Å (1.919(2) – 2.0763(16) Å) and the S-N bond lengths also span a much wider range (S1-N2 1.6132(18) Å, S1-N1 1.6706(16) Å, S2-N4 1.6703(18) Å, S1-N3 1.7006(16) Å, S2-N3 1.7125(16) Å). The short S1-N2 bond points to rather localized π -electrons within in the S1-N2 bond, while the other S-N bonds are slightly elongated compared to those observed in **1**. The N11-Zn1-N2 (71.09(6)°) and N1-S1-N2 (100.05(9)°) bond angles of the bridging diimidosulfinate moiety in **2** are significantly smaller than the N1-Zn1a-N4 (105.01(7)°) and N3-S2-N4 (106.49(8)°) bond angles of the six-membered ring.

In order to prove if sulfurdiimides also react with early transition metal complexes with insertion into metal carbon bonds, S(NSiMe₃)₂ was treated with Cp^{*}MMe₃ (M = Ti, Zr, Hf). The reactions smoothly proceeded with formation of the expected S-methyl-diimidosulfinate complexes of the general type Cp^{*}(Me)₂M[Me₃SiNS(Me)NSiMe₃] (M = Ti **3**, Zr **4**, Hf **5**) as was proven by ¹H and ¹³C NMR spectroscopy. In addition, the corresponding dichloride complexes Cp^{*}(Cl)₂M[Me₃SiNS(Me)NSiMe₃] (M = Ti **6**, Zr **7**, Hf **8**) were obtained from reactions of either isolated or *in situ* generated lithium S-methyl-diimidosulfinate [(Me₃SiN)₂S(Me)Li(thf)]₂ **9** with equimolar amounts of Cp^{*}MCl₃ (scheme 3). However, while **3** – **5** and **9** are typically formed in excellent yields of 90 % and higher, **6** – **8** were only isolated in roughly 30 % after workup. Fig S 17 exemplarily shows a raw spectrum (¹H NMR) of the reaction product obtained from the reaction of **9** with Cp^{*}TiCl₃. Aside from the peaks that can be addressed to **6**, additional peaks are observable, which clearly prove the formation of additional side-products. **6** – **8** could be isolated from these mixtures by recrystallization from solutions in thf. Unfortunately, any attempt to isolate and identify the additional reaction products failed, to date. **3** – **5** are soluble in almost every non-coordinating (pentane, hexane, toluene) and coordinating solvent (Et₂O, THF), while **6** – **8** are only soluble in THF. ¹H NMR spectra of **3** – **8** each show a single resonances of the Cp^{*} group, indicating a η^5 -binding mode, as well

as single resonances of the M-Me (**3** – **5**), S-Me and SiMe₃ groups (table 1).

Scheme 3. Synthesis of **3** – **8**.

((Table 1 here))

Colorless crystals of **3**, **4** and **5** were obtained from concentrated solutions in toluene after storage at 18 °C for 12 hours. **3** to **5** crystallize in the monoclinic space group $P2_1/n$. Even though the unit cell lengths are almost the same, β in **3** differs by roughly 10° from β in **4** and **5**. Consequently, **4** and **5** may be considered as isostructural, but the molecular conformation of **3** – **5** is very similar. Figure 3 shows the molecular structure of **5**, while central bonding parameters are summarized in table 2.

Figure 3. Representation of Cp^{*}(Me)₂Hf[Me₃SiNS(Me)NSiMe₃] **5**. Thermal ellipsoids are shown at 50% probability levels. Hydrogen atoms are omitted for clarity.

The Ti-N and Ti-C bond lengths are shorter than the corresponding values of the higher homologues **4** and **5** (see table 2). The S-methyl-diimidosulfinate ligand coordinates to the group 4 metal center in a chelating binding mode and the Cp^{*} units are η^5 -bonded as

was expected from the NMR studies. The resulting coordination geometry around the central metal atom can be described as distorted tetragonal pyramid (Cp^* represented by its centroid). The $\text{Cp}^*_{\text{centr.}}-\text{M}$ bond lengths ((2.0871 Å **3**, 2.2332 Å **4**, 2.2160 Å **5**)) as well as the M-N bond lengths (2.1420(11) Å, 2.1586(10) Å **3**; 2.2656(16) Å, 2.2780(16) Å **4**; 2.2417(16) Å, 2.2588(15) Å **5**) of **3** are significantly shorter compared to those of **4** and **5**, which are almost identical as is typical for group 4 metal complexes. In contrast, the S-N bond lengths and N-S-N bond angles of **3** – **5** are almost identical, while the N1-Ti1-N2 bond angle (69.41(41)°) is slightly smaller than those of the heavier congeners (65.68(6)° **4**, 66.19(5)° **5**), respectively.

((Table 2 here))

Figure 4. Representation of $[(\text{Me}_3\text{SiN})_2\text{S}(\text{Me})\text{Li}(\text{thf})]_2$ **9**. Thermal ellipsoids are shown at 50% probability levels. Hydrogen atoms are omitted for clarity. The part depicted in light bonds is generated via a center of inversion.

Colorless crystals of **9** were obtained from a concentrated solution in THF after storage at -30°C for 12 hours. **9** crystallizes in the triclinic space group $P\bar{1}$ as a centrosymmetric dimer and its structure is shown in figure 4. Even though the S-methyl-diimidosulfinate ligands in **1** and **9** adopt bridging positions, both structures differ significantly. **1** adopts a *boat-type* conformation in which the S-methyl-diimidosulfinate ligand shows a symmetrical bridging mode with almost identical Zn-N bond lengths, while **9** adopts a *chair-type* conformation and the S-methyl-diimidosulfinate ligand coordinates in a rather asymmetric bridging binding mode between two Li metals with significantly different Li-N bond lengths (Li1-N2 2.0390(18) Å, Li1-N1a 2.0906(18) Å). In addition, the transannular Li-N bonds in **9** (Li1-N1 2.1800(17) Å) are significantly shorter compared to the transannular Zn-N bonds in **1** (Zn1-N4 2.4729(12) Å, Zn2-N3 2.4626(12) Å). As a consequence, the structure of **9** can alternatively be described as a ladder-type structure with three edge-shared four-membered rings. An additionally coordinated thf molecule results in the coordination number 4 for each Li

cation, which consequently adopt distorted tetrahedral coordination spheres. The N1-Li1-N2 bond angle (73.94(6)°) is significantly smaller than the N1-Li1-N1a (103.21(7)°) and N2-Li1-N1a (122.88(8)°) bond angles. The S-N bond length of the fourfold coordinated N atom is slightly elongated (S1-N1 1.6202(8) Å, S1-N2 1.6039(8) Å), but both values prove the formation of delocalized π -electrons within the S-methyl-diimidosulfinate unit. The N-S-N bond angle of 103.94(4)° in **9** is almost identical to that observed in **1**, but wider than those in **3** – **5**, respectively. Comparable ladder-type structures have been reported for Li- and K-diimidosulfates.^[5a, 6a, 6d, 25, 26]

Conclusion. $\text{S}(\text{NSiMe}_3)_2$ reacts with Me_2Zn , Cp^*MMe_3 (M = Ti, Zr, Hf) and MeLi with insertion into the metal-carbon bond and formation of dimeric S-methyl diimidosulfinate complexes $[\text{MeZnN}(\text{SiMe}_3)\text{S}(\text{Me})\text{NSiMe}_3]_2$ **1** and $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{S}(\text{Me})\text{Li}(\text{thf})]_2$ **9** with bridging diimidosulfinate ligands or monomeric complexes of the type $\text{Cp}^*(\text{Me})_2\text{M}[\text{Me}_3\text{SiNS}(\text{Me})\text{NSiMe}_3]$ (M = Ti **3**, Zr **4**, Hf **5**) with chelating diimidosulfinate ligands. In contrast, the reaction of Cp^*_2Zn unexpectedly occurred with transimination, yielding the complex $(\text{Me}_3\text{SiNS}[\text{N}(\text{SiMe}_3)\text{SNSiMe}_3]\text{N}(\text{SiMe}_3)\text{Zn})_2$ **2**. In addition, salt elimination reactions of **9** with Cp^*MCl_3 proceeded with formation of the expected complexes $\text{Cp}^*(\text{Cl})_2\text{M}[\text{Me}_3\text{SiNS}(\text{Me})\text{NSiMe}_3]$ (M = Ti **6**, Zr **7**, Hf **8**).

ASSOCIATED CONTENT

Supporting Information

CIF files giving crystallographic data for **1** – **5** and **9**, a table giving crystallographic details of **1** – **5** and **9** (Table S1) and figures of the solid state structures of **3** (Fig. S29) and **4** (Fig. S30), as well as ^1H and ^{13}C NMR and IR spectra of **1** – **9** (Fig. S1 – S28). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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REFERENCES

- (1) See the following and reference cited therein: a) Fleischer, R. Stalke, D. *Coord. Chem. Rev.* **1998**, *176*, 431–450; b) Stalke, D. *Chem. Commun.* **2012**, *48*, 9559–9573; c) Chivers, T. *Chem. Rev.* **1985**, *85*, 341–365; b) Brask, J. K.;

- Chivers, T. *Angew. Chem.* **2001**, *113*, 4082–4098, *Angew. Chem. Int. Ed.* **2001**, *40*, 3960–3976.
- (2) Lubben, T.V.; Wolczanski, P.T.; van Duyne, G.D. *Organometallics* **1984**, *3*, 977–983.
- (3) a) Lisovskii, A. Eisen, M. S. in *Living and Controlled Polymerization* (Ed. J. Jagur-Grodzinski), Ch. 10, pp 343–376; b) Smolensky E.; Eisen, M. S. *Dalton Trans.* **2007**, 5623–5650.
- (4) a) Hänssgen, D.; Steffens, R. *J. Organomet. Chem.* **1982**, *236*, 53–60; b) Hänssgen, D.; Steffens, R. *Z. Naturforsch.* **1985**, *40b*, 919–922.
- (5) a) Pauer, F.; Stalke, D. *J. Organomet. Chem.* **1991**, *418*, 127–145; b) Pauer, F.; Rocha, J.; Stalke, D. *Chem. Commun.* **1991**, 1477–1479; c) Freitag, S.; Kolodziejewski, W.; Pauer, F.; Stalke, D. *Dalton Trans.* **1993**, 3479–3488.
- (6) a) Meinholz, M. M.; Stalke, D. *Z. Anorg. Allg. Chem.* **2011**, *637*, 2233–2238; b) Meinholz, M. M.; Pandey, S. K.; Deuerlein, S. M.; Stalke, D. *Dalton Trans.* **2011**, *40*, 1662–1671; c) Meinholz, M. M.; Stalke, D. *Eur. J. Inorg. Chem.* **2011**, *29*, 4578–4584; d) Meinholz, M. M.; Klemmer, M.; Kriemen, E.; Stalke, D. *Chem. Eur. J.* **2011**, *17*, 9415–9422.
- (7) a) Schulz, T.; Stalke, D. *Z. Naturforsch.* **2010**, *65b*, 701–710; b) Schulz, T.; Dauer, D.-R.; Stalke, D. *Z. Naturforsch.* **2010**, *65b*, 711–718.
- (8) Schulz, T.; Deuerlein, S.; Stalke, D. *Eur. J. Inorg. Chem.* **2010**, 2178–2184.
- (9) Fleischer, R.; Stalke, D. *J. Organomet. Chem.* **1998**, *550*, 173–182.
- (10) See for instance: a) Knösel, F.; Noltemeyer, M.; Edelmann, F. T. *Z. Naturforsch.* **1989**, *44b*, 1171–1174; b) Roesky, H. W.; Grünhagen, A.; Edelmann, F. T.; Noltemeyer, M. *Z. Naturforsch.* **1989**, *44b*, 1365–1368; c) Meinholz, M. M.; Stalke, D. *Z. Naturforsch.* **2011**, *66b*, 981–984; d) Selinka, C.; Deuerlein, S.; Häuser, T.; Stalke, D. *Inorg. Chim. Acta* **2004**, *357*, 1873–1880.
- (11) a) Roesky, H. W.; Schmidt, H.-G.; Noltemeyer, M.; Sheldrick, G. M. *Chem. Ber.* **1983**, *116*, 1411–1414; b) Haas, A.; Wingender, N. *Z. Anorg. Allg. Chem.* **1989**, *576*, 151–159; c) Kottmair-Maieron, D.; Lechler, R.; Weidlein, J. *Z. Anorg. Allg. Chem.* **1991**, *593*, 111–123; d) Hasselbring, R.; Leichtweis, I.; Noltemeyer, M.; Roesky, H. W.; Schmidt, H. G.; Herzog, A. *Z. Anorg. Allg. Chem.* **1993**, *619*, 1543–1550; e) Hubrich, C.; Schulz, A.; Villinger, A. *Z. Anorg. Allg. Chem.* **2007**, *633*, 2362–2366.
- (12) Gehrman, T.; Kruck, M.; Wadepohl, H.; Gade, L. H. *Chem. Commun.* **2012**, *48*, 2397–2398.
- (13) Kaleta, K.; Kessler, M.; Beweries, T.; Arndt, P.; Spannenberg, A.; Rosenthal, U. *Eur. J. Inorg. Chem.* **2012**, 3388–3393.
- (14) Kaleta, K.; Ruhmann, M.; Theilmann, O.; Roy, S.; Beweries, T.; Arndt, P.; Villinger, A.; Jemmis, E. D.; Schulz, A.; Rosenthal, U. *Eur. J. Inorg. Chem.* **2012**, 611–617.
- (15) Walfort, B.; Leedham, A. P.; Russell, C. A.; Stalke, D. *Inorg. Chem.* **2001**, *40*, 5668–5674.
- (16) a) Scheiper, C.; Naglav, D.; Bläser, D.; Wölper, C.; Schulz, S. *Z. Anorg. Allg. Chem.* **2015**, *641*, 871–875; b) Gondzik, S.; Bläser, D.; Wölper, C.; Schulz, S. *J. Organomet. Chem.* **2015**, *783*, 92–95; c) Scheiper, C.; Wölper, C.; Bläser, D.; Roll, J.; Schulz, S. *Z. Naturforsch.* **2014**, *69b*, 1365–1374; d) Schulz, S.; Bayram, M.; Bläser, D.; Wölper, C. *Organometallics* **2014**, *33*, 2080–2087; e) Scheiper, C.; Ditrach, D.; Wölper, C.; Bläser, D.; Roll, J.; Schulz, S. *Eur. J. Inorg. Chem.* **2014**, 2230–2240; f) Gutschank, B.; Schulz, S.; Bläser, D.; Wölper, C. *J. Chem. Soc., Dalton Trans.* **2014**, *43*, 2907–2914; g) Gutschank, B.; Bayram, M.; Schulz, S.; Bläser, D.; Wölper, C. *Eur. J. Inorg. Chem.* **2013**, 5495–5502; h) Scheiper, C.; Schulz, S.; Wölper, C.; Bläser, D.; Roll, J. *Z. Anorg. Allg. Chem.* **2013**, *639*, 1153–1159; i) Gutschank, B.; Schulz, S.; Marcinkowski, M.; Jansen, G.; Bandmann, H.; Bläser, D.; Wölper, C. *Angew. Chem.* **2012**, *124*, 11051–11055, *Angew. Chem. Int. Ed.* **2012**, *51*, 10893–10897; j) Bendt, G.; Schulz, S.; Spielmann, J.; Schmidt, S.; Bläser, D.; Wölper, C. *Eur. J. Inorg. Chem.* **2012**, 3725–3731; k) Schmidt, S.; Gutschank, B.; Schulz, S.; Bläser, D.; Boese, R.; Wölper, C. *Eur. J. Inorg. Chem.* **2011**, 4464–4470; l) Schmidt, S.; Schulz, S.; Bläser, D.; Boese, R.; Bolte, M. *Organometallics* **2010**, *29*, 6097–6103; m) Gutschank, B.; Schulz, S.; Bläser, D.; Boese, R.; Wölper, C. *Organometallics* **2010**, *29*, 6133–6136; n) Schulz, S.; Eisenmann, T.; Schmidt, S.; Bläser, D.; Westphal, U.; Boese, R. *Chem. Commun.* **2010**, *46*, 7226–7228; o) Gutschank, B.; Schulz, S.; Westphal, U.; Bläser, D.; Boese, R. *Organometallics* **2010**, *29*, 2093–2097.
- (17) Warrens, C. P.; Woollins J. D.; Witt M.; Roesky H. W. *Inorg. Syntheses* **1989**, *25*, 43–47.
- (18) Blom, R.; Boersma, J.; Budzelaar, P. H. M.; Fischer, B.; Haaland, A.; Volden, H. V.; Weidlein, W. *Acta Chem. Stand. A* **1986**, *40*, 113–120.
- (19) Mena, M.; Royo, P.; Serrano, R. *Organometallics* **1989**, *8*, 476–482.
- (20) Llinás, G. H.; Mena, M.; Palacios, F.; Royo, P.; Serrano, R. *J. Organomet. Chem.* **1988**, *340*, 37–40.
- (21) SHELXS-97, Sheldrick, G. M. *Acta Crystallogr. Sect. A* **1990**, *46*, 467–473.
- (22) SHELXL-97, Program for Crystal Structure Refinement, Sheldrick, G. M.; Universität Göttingen, 1997. See also: Sheldrick, G. M. *Acta Crystallogr. Sect. A* **2008**, *64*, 112–128.
- (23) Pyykkö, P.; Atsumi, M. *Chem. Eur. J.* **2009**, *15*, 186–197.
- (24) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441–451.
- (25) A search for C–S(···N)···N···M with the number of atoms bonded to S set to three yielded 24 hits which included 144 S–N bonds. The bond lengths range from 1.569 Å to 1.687 Å with a mean value of 1.631(17) Å. Cambridge Structural Database, Version 5.36, see also: Allen, F. H. *Acta Cryst.* **2002**, *B58*, 380–388.
- (26) Schmidt, S.; Schäper, R. Schulz, S.; Bläser, D.; Wölper, C. *Organometallics* **2011**, *30*, 1073–1078; Schulz, S.; Schmidt, S.; Bläser, D.; Wölper, C. *Eur. J. Inorg. Chem.* **2011**, *27*, 4157–4160; Schulz, S.; Schmidt, S.; Bläser, D.; Wölper, C. *Z. Anorg. Allg. Chem.* **2012**, *638*, 1705–1710.
- (27) Walfort, B.; Bertermann, R.; Stalke, D. *Chem.-Eur. J.* **2001**, *7*, 1424–1430.
- (28) a) Wrackmeyer, B.; Klaus, U.; Milius, W. *Inorg. Chim. Acta* **1996**, *250*, 327; b) Edelmann, F. T.; Knösel, F.; Pauer, F.; Stalke, D.; Bauer, W. *J. Organomet. Chem.* **1991**, *438*, 1–10; c) Meyer, J. T. E.; Schultz, T.; Pandey, S. K.; Stalke, D. *Inorg. Chem.* **2010**, *49*, 2743–2749; d) Chivers, T.; Edwards, M.; Hilts, R. W.; Parvez M.; Vollmerhaus, R. *Chem. Commun.* **1993**, 1483–1485.

Table 1. ^1H and ^{13}C NMR chemical shifts of **1** - **5** and **9** (C_6D_6 , 300 MHz, 25 ° C) and **6** - **8** ($\text{THF}-d_6$, 300 MHz, 25 ° C) in ppm.

Compound	MMe		NSiMe ₃		SMe		Cp*	
	^1H	^{13}C	^1H	^{13}C	^1H	^{13}C	^1H	^{13}C
1	-0.30	-5.27	0.23	1.99	2.83	48.09	–	–
2	–	–	0.21, 0.42, 0.44, 0.57	0.89, 2.10, 2.34, 3.01	–	–	–	–
3	0.63	13.30	0.24	2.68	1.94	48.80	2.05	65.25, 123.26
4	0.28	12.50	0.19	2.40	2.02	46.14	2.09	50.90, 119.85
5	0.05	12.39	0.18	2.40	2.06	53.28	2.06	67.83, 118.83
6	–	–	0.25	1.19	2.78	12.68	2.08	44.64, 125.38
7	–	–	0.24	1.94	2.70	13.39	2.17	48.31, 125.91
8	–	–	0.24	1.97	2.67	13.08	2.22	48.15, 123.70
9	–	–	0.34	2.64	2.24	53.49	–	–

Table 2. Selected bond lengths [$\text{\AA}$] and angles [$^\circ$] of **3**, **4**, **5** and **9**.

	3	4	5	9
M-N	2.1420(11), 2.1586(10)	2.2656(16), 2.2780(16)	2.2417(16), 2.2588(15)	2.1800(17), 2.0390(18)
M'-N	–	–	–	2.0906(18)
S-N	1.6220(11), 1.6227(10)	1.6214(17), 1.6253(16)	1.6254(16), 1.6284(16)	1.6202(8), 1.6039(8)
M-Me	2.1440(13), 2.1537(13)	2.270(2), 2.2801(19)	2.250(2), 2.2641(19)	–
M-Cp*[^a]	2.0871	2.2332	2.2160	–
S-C	1.8018(14)	1.802(9)	1.797(2)	1.8027(10)
N-S-N	97.99(5)	98.75(8)	98.10(8)	103.94(4)
N-M-N	69.41(4)	65.68(6)	66.19(5)	73.94(6), 103.21(7)
M-N-M	–	–	–	76.79(7)
N-M-Me	84.86(5), 85.71(5), 129.19(5), 133.16(5)	85.04(7), 86.11(7), 128.32(7), 133.68(7)	84.70(6), 85.69(7), 28.15(7), 133.75(6)	–
Me-M-Me	81.23(5)	85.29(7)	85.42(7)	–
Cp*-M-Me	108.01, 109.82	106.33, 106.85	107.18, 107.79	–
Cp*-M-N	118.73, 120.96	119.72, 124.59	118.76, 123.76	–

^[a] Cp* refers to the centroid of the C₅-ring of the Cp* ligand. Since the centroid's position is constrained to the positions of the C atoms no standard uncertainty can be given.

Reactions of equimolar amounts of Me_2Zn and $\text{S}(\text{NSiMe}_3)_2$ yielded the expected S-methyl diimidosulfinate $[\text{MeZnN}(\text{SiMe}_3)\text{S}(\text{Me})\text{NSiMe}_3]_2$ **1**, while the analogous reaction with Cp^*_2Zn gave the unexpected complex $\{\text{Me}_3\text{SiNS}[\text{N}(\text{SiMe}_3)\text{SNSiMe}_3]\text{N}(\text{SiMe}_3)\text{Zn}\}_2$ **2**. Insertion reactions of $\text{S}(\text{NSiMe}_3)_2$ with Cp^*MMe_3 yielded $\text{Cp}^*(\text{Me})_2\text{M}[\text{Me}_3\text{SiNS}(\text{Me})\text{NSiMe}_3]$ ($\text{M} = \text{Ti}$ **3**, Zr **4**, Hf **5**), while the corresponding Cl-substituted derivatives $\text{Cp}^*(\text{Cl})_2\text{M}[\text{Me}_3\text{SiNS}(\text{Me})\text{NSiMe}_3]$ ($\text{M} = \text{Ti}$ **6**, Zr **7**, Hf **8**) were obtained from salt elimination reactions of Li S-methyl diimidosulfinate $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{S}(\text{Me})\text{Li}(\text{thf})_2$ **9** with Cp^*MCl_3 .

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