Lewis-base stabilized diiodine adducts with
N-heterocyclic chalcogenamides†Cite this: *Dalton Trans.*, 2013, **42**, 12940Mykyta Tretiakov,^a Yuriy G. Shermolovich,^b Amit Pratap Singh,^a Prinson P. Samuel,^a Herbert W. Roesky,^{*a} Benedikt Niepötter,^a Arne Visscher^a and Dietmar Stalke^{*a}

Oxidation reactions of stable chalcogenamides with iodine are intriguing due to their broad application in various organic syntheses. In the present study we report on the utilization of *N*-heterocyclic carbene and cyclic-alkyl-amino carbenes L^{1-3} : (L^1 : = :C[N(2,6-*i*Pr₂-C₆H₃)CH]₂, L^2 : = :C(CH₂)(CMe₂)(C₆H₁₀)N-2,6-*i*Pr₂-C₆H₃, L^3 : = :C(CH₂)(CMe₂)₂N-2,6-*i*Pr₂-C₆H₃) for the syntheses of chalcogenamides $L^{1-3}=E$ (E = S, Se, Te) **1–4** and zwitterionic adducts $L^{1-3}=E-I-I$ **5–8**. The synthesis of compounds **1–4** involved the addition reaction of ligand L^{1-3} and elemental chalcogen. Treatment of **1–4** with iodine resulted in the formation of adducts **5–8**. Compounds **5–8** are well characterized with various spectroscopic methods and single-crystal X-ray structural analysis.

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Introduction

The reactions of elemental halogens (I₂, Br₂) and interhalogens (IBr, ICl) with organic molecules (L) containing group 16 donor atoms of composition L=E (L = organic framework, E = S, Se, Te) have gained particular interest in recent years. They are used in various fields of research ranging from synthetic chemistry to materials and industrial chemistry.^{1–17} The adduct formation of a donor (group 16 atom) with diiodine (L=E–I–I) stabilizes the lone pair of electrons of the donor by mixing its orbital with the σ^* anti-bonding orbital of I₂.¹⁸ As a result a coordination bond forms and the double bond of the chalcogenone group as well as the iodine–iodine single bond are lengthened. A direct relationship was found to exist between these three bond lengths: if the E–I bond length is short, then the C–E bond length and I–I bond length will be long and the donor functionality is strong. Furthermore the ν_{I-I} frequencies are linearly correlated with the I–I bond lengths. It is also worth mentioning that a zwitterionic structure is formed with the positive charge at the organic framework and the negative charge at the I₂ unit with the result that a lengthening of the C=E double bond is observed. Therefore, chalcogenamides are particularly good donors. Generally, the greater the stabilizing ability of the *N*-alkyl or -aryl groups, the stronger the resulting diiodine complex will be.¹⁹

The motivation for using $L^{1-3}=E$ (L^1 : = :C[N(2,6-*i*Pr₂-C₆H₃)CH]₂, L^2 : = :C(CH₂)(CMe₂)(C₆H₁₀)N-2,6-*i*Pr₂-C₆H₃, L^3 : = :C(CH₂)(CMe₂)₂N-2,6-*i*Pr₂-C₆H₃) compounds as precursors for the reaction with iodine was the possibility of forming an oxidized diiodide E(I)₂ instead of the non-oxidized E–I–I adduct.

Herein, we report on the synthesis and spectroscopic characterization of novel chalcogenamides **1–4** as well as the synthesis, structural, and spectroscopic characterization of novel zwitterionic iodine compounds **5–8** with the *N*-heterocyclic thioamides $L^1=S$ (**1**), $L^2=S$ (**2**), selenoamide $L^3=Se$ (**3**), and telluroamide $L^3=Te$ (**4**).

Results and discussion

The *N*-heterocyclic carbene ligands L^{1-3} are treated with elemental chalcogens (S, Se, Te) to form carbon–chalcogen double bonds (Scheme 1). The rate of reaction of carbenes with chalcogens increases in the order Se < Te < S in accordance with the increase of the chalcogen solubility. All the prepared chalcogenamides can be extracted with hot hexane and recrystallized from THF. Chalcogenamides **1–4** are further treated with diiodine in a molar ratio of 1 : 1 in toluene at room temperature to give the diiodine adducts **5–8** (Scheme 2). The present research is devoted to the comparison of the structural data between diiodine adducts of thio- (**1**, **2**), seleno- (**3**) and telluro- (**4**) amides.

The reactions of elemental sulfur with L^1 as well as L^2 are complete after 12 hours at room temperature to give **1** and **2**, respectively, as colorless pure compounds in moderate yields. Selenoamide **3** as well as telluroamide **4** were prepared under a nitrogen atmosphere in moderate yields by the reaction

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Scheme 1 Synthesis of compounds 1–4.

between L^3 and grey selenium and tellurium, respectively, in a molar ratio of 1 : 1.3 in THF at room temperature. The diiodine adducts 5–8 were obtained in good yields by reacting diiodine with 1–4, respectively, in a molar ratio of 1 : 1 in toluene under a nitrogen atmosphere. Compounds 5–8 are stable under nitrogen for more than 3 months.

The ^{13}C NMR measurements showed distinct differences in the chemical shifts between free carbenes L^{1-3} and chalcogenamides $L^{1-3}=E$ ($E = \text{S}, \text{Se}, \text{Te}$). The ‘carbene’ carbon resonance is shifted more than 50 ppm upfield on converting the ligand L to a respective chalcogenamide. For instance, in the ^{13}C NMR spectra, the difference in ‘carbene’ carbon resonance between L^1 (220.6 ppm) and 1 (167 ppm) is 53.6 ppm, and between L^2 (309.4 ppm) and 2 (213.6 ppm) is 95.8 ppm. Comparable chemical shifts are observed for the ‘carbene’ carbon atoms of compounds 3 (219.8 ppm) and 4 (215.4 ppm) while the corresponding resonance in L^3 is 304.2 ppm.

The ^1H NMR chemical shift of the $\text{CH}(\text{CH}_3)_2$ proton in compound 5 is shifted upfield to 2.65 ppm when compared with that of 1 (2.75 ppm). In the case of compound 6, the chemical shift of the characteristic $\text{N}-\text{C}(\text{Me}_2)\text{CH}_2$ protons is shifted to low field (2.67 ppm) when compared with that of 2 (2.27 ppm).

The ‘carbene’ carbon atom in compound 7 shows the resonance at 231.7 ppm which is more than 10 ppm downfield compared with that of 3 (219.8 ppm). However, the ^{77}Se NMR resonance for selenoamide 3 (492.43 ppm) and the corresponding diiodine adduct 7 (491.26 ppm) are nearly the same. Compound 8 has a very weak solubility in most of the organic solvents, and therefore the ^{13}C NMR spectrum as well as the ^{125}Te NMR spectrum were silent.

All the chalcogenamides are stable in open air. All the diiodine adducts of chalcogenamides are stable under a nitrogen atmosphere.

In order to establish unambiguously the structural features of compounds 5–8, single crystal X-ray structural analyses were carried out. Suitable single crystals of 5–8 were obtained from saturated toluene solutions.

Compound 5 crystallizes in the monoclinic crystal system with space group $C2/c$, and compound 6 crystallizes in the triclinic crystal system with space group $P\bar{1}$ (Table 1). The molecular structures of compounds 5 and 6 are shown in Fig. 1 and 2, respectively. No significant differences in bond lengths and angles were observed in compounds 5 and 6. The $\text{I}(1)-\text{S}(1)$ and $\text{I}(1)-\text{I}(2)$ bond lengths for compound 5 are 2.6981(7) Å and 2.8662(6) Å, respectively, while the $\text{S}(1)-\text{I}(1)-\text{I}(2)$ bond angle is 176.805(13)°. The $\text{I}(1)-\text{S}(1)$ and $\text{I}(1)-\text{I}(2)$ bond lengths for compound 6 are 2.8121(7) Å and 2.8282(6) Å, respectively, while the $\text{S}(1)-\text{I}(1)-\text{I}(2)$ bond angle is 173.783(10)° which is close to that in 5. Both iodine atoms $\text{I}(1)$ and $\text{I}(2)$ in compounds 5 and 6 are not perpendicular to the $\text{C}-\text{S}$ bond ($\text{C}(1)-\text{S}(1)-\text{I}(1) = 101.47(7)^\circ$ (5), $118.08(6)^\circ$ (6)). In compound 5 the $\text{C}-\text{S}$ bond length is 1.706(2) Å, which is nearly the same as that in 6 (1.6961(16) Å). It is clear from the above discussion that the difference in the organic framework does not have a considerable influence on the structural features of the $\text{C}=\text{S}-\text{I}-\text{I}$ part of the molecules.

Scheme 2 Synthesis of compounds 5–8.

Table 1 Crystal and structure refinement parameters for compounds 5–8

Parameters	5	6	7	8
CCDC No.	933418	933419	933420	933421
Empirical formula	C ₃₄ H ₄₄ I ₂ N ₂ S	C ₂₃ H ₃₅ I ₂ NS	C ₂₀ H ₃₁ I ₂ NSe	C ₂₀ H ₃₁ I ₂ NTe
Formula weight	766.57	611.38	618.22	666.86
Temperature	100(2) K	100(2) K	100(2) K	100(2) K
Wavelength	0.56086 Å	0.56086 Å	0.56086 Å	0.56086 Å
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	<i>C2/c</i>	<i>P1</i>	<i>P1</i>	<i>P2₁/n</i>
Unit cell dimensions	<i>a</i> = 37.684(3) Å <i>b</i> = 11.414(2) Å <i>c</i> = 16.103(2) Å α = 90.00° β = 100.24(2)° γ = 90.00°	<i>a</i> = 9.520(2) Å <i>b</i> = 11.141(2) Å <i>c</i> = 12.138(2) Å α = 91.69(2)° β = 100.62(2)° γ = 103.70(2)°	<i>a</i> = 9.8690(10) Å <i>b</i> = 9.876(2) Å <i>c</i> = 11.9680(10) Å α = 92.040(10)° β = 100.33(2)° γ = 93.280(10)°	<i>a</i> = 11.108(2) Å <i>b</i> = 16.440(2) Å <i>c</i> = 12.754(2) Å α = 90.00° β = 99.76(2)° γ = 90.00°
Volume	6816.0(16) Å ³	1225.7(4) Å ³	1144.4(3) Å ³	2295.4(6) Å ³
<i>Z</i>	8	2	2	4
Density (calculated)	1.494 Mg m ^{−3}	1.657 Mg m ^{−3}	1.794 Mg m ^{−3}	1.930 Mg m ^{−3}
Absorption coefficient	1.027 mm ^{−1}	1.412 mm ^{−1}	2.303 mm ^{−1}	2.116 mm ^{−1}
<i>F</i> (000)	3072	604	596	1264
Crystal size	0.178 × 0.133 × 0.063 mm ³	0.118 × 0.102 × 0.088 mm ³	0.128 × 0.061 × 0.047 mm ³	0.090 × 0.085 × 0.058 mm ³
Theta range for data collection	0.867 to 23.633°	1.351 to 25.679°	1.366 to 21.395°	1.609 to 24.813°
Index ranges	−53 ≤ <i>h</i> ≤ 53, −16 ≤ <i>k</i> ≤ 16, −22 ≤ <i>l</i> ≤ 22	−14 ≤ <i>h</i> ≤ 14, −17 ≤ <i>k</i> ≤ 17, −18 ≤ <i>l</i> ≤ 18	−12 ≤ <i>h</i> ≤ 12, −12 ≤ <i>k</i> ≤ 12, −15 ≤ <i>l</i> ≤ 15	−16 ≤ <i>h</i> ≤ 16, −24 ≤ <i>k</i> ≤ 24, −19 ≤ <i>l</i> ≤ 19
Reflections collected	103 802	50 088	33 744	108 910
Independent reflections	10 410 [<i>R</i> (int) = 0.0635]	9450 [<i>R</i> (int) = 0.0454]	5274 [<i>R</i> (int) = 0.0361]	8016 [<i>R</i> (int) = 0.0922]
Completeness to theta = 19.665°	100.0%	100.0%	100.0%	100.0%
Absorption correction	Semi-empirical from equivalents	Analytical	Semi-empirical	Analytical
Max. and min. transmission	0.7449 and 0.6452	1.0000 and 0.8996	0.8618 and 0.8043	0.8140 and 0.7503
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	10 410/0/361	9450/0/250	5274/0/225	8016/3/230
Goodness-of-fit on <i>F</i> ²	1.027	1.054	1.031	1.064
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0304, w <i>R</i> ₂ = 0.0654	<i>R</i> ₁ = 0.0255, w <i>R</i> ₂ = 0.0527	<i>R</i> ₁ = 0.0194, w <i>R</i> ₂ = 0.0390	<i>R</i> ₁ = 0.0313, w <i>R</i> ₂ = 0.0458
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0397, w <i>R</i> ₂ = 0.0687	<i>R</i> ₁ = 0.0357, w <i>R</i> ₂ = 0.0552	<i>R</i> ₁ = 0.0247, w <i>R</i> ₂ = 0.0407	<i>R</i> ₁ = 0.0484, w <i>R</i> ₂ = 0.0492
Extinction coefficient	n/a	n/a	n/a	0.00047(6)
Largest diff. peak and hole	1.439 and −0.997 e Å ^{−3}	1.162 and −0.947 e Å ^{−3}	0.769 and −0.746 e Å ^{−3}	0.829 and −0.748 e Å ^{−3}

Fig. 1 Solid state structure of $L^1=S-I-I$ (**5**). Hydrogen atoms are omitted for clarity. Anisotropic displacement parameters are depicted at the 50% probability level. Selected bond lengths (Å) and angles (°): I(1)–S(1) 2.6981(7), I(1)–I(2) 2.8662(6), S(1)–C(1) 1.706(2), N(1)–C(1) 1.358(3); S(1)–I(1)–I(2) 176.805(13), C(1)–S(1)–I(1) 101.47(7), C(1)–N(1)–C(2) 109.53(16), C(1)–N(2)–C(3) 109.61(16).

Fig. 2 Solid state structure of $L^2=S-I-I$ (**6**). Hydrogen atoms are omitted for clarity. Anisotropic displacement parameters are depicted at the 50% probability level. Selected bond lengths (Å) and angles (°): I(1)–S(1) 2.8121(7), I(1)–I(2) 2.8282(6), S(1)–C(1) 1.6961(16), N(1)–C(1) 1.324(2); S(1)–I(1)–I(2) 173.783(10), C(1)–S(1)–I(1) 118.08(6), C(1)–N(1)–C(12) 122.47(13).

Compound **7** crystallizes in the triclinic space group $P\bar{1}$ and compound **8** in the monoclinic space group $P2_1/n$ (Table 1). The molecular structure of compounds **7** and **8** are shown in Fig. 3 and 4, respectively. Notable differences in the corresponding bond lengths and angles in compounds **7** and **8** were observed. The Se(1)–I(1) and I(1)–I(2) bond lengths in compound **7** are 2.8192(6) Å and 2.8943(5) Å, respectively, while the Se(1)–I(1)–I(2) bond angle is 171.456(8)°. The Te(1)–I(1) and I(1)–I(2) bond lengths for compound **8** are 2.8244(4) Å and 3.0964(4) Å, respectively, while the Te(1)–I(1)–I(2) bond angle (177.431(8)°) is more obtuse than the corresponding bond angle in compound **7** (Se(1)–I(1)–I(2) = 171.456(8)°). The I(1)–I(2) bonds in compounds **7** and **8** are not perpendicular to the

Fig. 3 Solid state structure of $L^3=Se-I-I$ (**7**). Hydrogen atoms are omitted for clarity. Anisotropic displacement parameters are depicted at the 50% probability level. Selected bond lengths (Å) and angles (°): I(1)–Se(1) 2.8192(6), I(1)–I(2) 2.8943(5), Se(1)–C(1) 1.854(2), N(1)–C(1) 1.315(3); Se(1)–I(1)–I(2) 171.456(8), C(1)–Se(1)–I(1) 111.89(6), C(1)–N(1)–C(4) 124.08(17), C(1)–N(2)–C(3) 109.61(16).

Fig. 4 Solid state structure of $L^3=Te-I-I$ (**8**). Hydrogen atoms are omitted for clarity. Anisotropic displacement parameters are depicted at the 50% probability level. Selected bond lengths (Å) and angles (°): I(1)–Te(1) 2.8244(4), I(1)–I(2) 3.0964(4), Te(1)–C(1) 2.100(2), N(1)–C(1) 1.305(3); Te(1)–I(1)–I(2) 177.431(8), C(1)–Te(1)–I(1) 105.71(6), C(1)–N(1)–C(9) 124.2(2).

C–Se and C–Te bonds, but have angles of 111.89° and 105.71(6)°, respectively. In compound **7** the C–Se bond length is 1.854(2) Å, which is about 0.25 Å shorter than the C–Te found in **8** (2.100(2) Å) due to the difference in the atomic radii between selenium and tellurium. The structural differences in C=E–I–I (E = Se, Te) bonds and angles are dictated by the difference of the atomic radii of chalcogens.

From the above discussed structural details the bonding situation in compounds **5–8** can be explained as follows. The bond formation between chalcogenamide and iodine occurs through donation of electron density from the chalcogen atom to the iodine unit. This results in a partial positive charge at the chalcogen atom and some negative charge in the iodine

part (Scheme 2). The involvement of the nitrogen lone pair in a C=N double bond causes a positive charge on the nitrogen with partial compensation of the electron density of the chalcogen atom resulting in a final weak zwitterionic structure with the positive nitrogen atom and the negative I-I part. As a result of this electronic delocalization, the C-N and C-E bond lengths show a partial double bond character. The C-N bond lengths in compounds **5–8** are very close to the C=N double bond distance which indicates that the positive charge density is mainly located on the nitrogen atom. This is further evidenced by the almost planar geometry around the nitrogen atom in compounds **5–8**. In **5**, the C-N bond distance is 1.358(3) Å which is longer than the corresponding bond lengths in **6** (1.324(2) Å), **7** (1.315(3) Å) and **8** (1.305(3) Å). This is due to the two nitrogen atoms which are present in compound **5**, and both of them participate in the charge delocalization whereas in the latter compounds only one nitrogen atom is present.

Experimental section

All manipulations were performed in a dry and oxygen free atmosphere (N₂) using standard Schlenk-line techniques and inside an MBraun MB 150-GI glove box maintained at or below 1 ppm of O₂ and H₂O. All solvents were dried by an MBraun solvent purification system prior to use. *N*-Heterocyclic carbene **L**¹: and cyclic-alkyl-amino carbene **L**^{2,3}: were synthesized using reported procedures.^{20,21} Sulfur was sublimed before using, and grey selenium, tellurium and iodine were purchased and used as received. The ¹H, ¹³C, ⁷⁷Se, and ¹²⁷Te NMR spectra were recorded on a Bruker Avance DRX instrument (300 or 500 MHz). The chemical shifts δ are given in ppm with tetramethylsilane as an external standard. Elemental analyses were performed at the Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen.

Synthesis of **L**¹=S (**1**)

Compound **1** was synthesized from the reaction of *N*-heterocyclic carbene **L**¹: (3.00 g, 7.72 mmol) in THF with elemental sulfur (0.37 g, 11.58 mmol) at room temperature in open air. The mixture was stirred overnight. The solvent was removed in vacuum. The residue was extracted with hot hexane (2 × 50 mL), filtered and dried to yield colorless pure **1** (yield 2.23 g, 69%). Mp 298 °C (dec.). Elemental analysis (%) calcd for C₂₇H₃₆N₂S (420.59): C, 73.22; H, 6.93; N, 4.38. Found: C, 73.43; H, 7.02; N, 4.25. ¹H NMR (200 MHz, CDCl₃, TMS, 25 °C): δ 7.60–7.29 (m, 6H, CH_{ar}), 6.84 (s, 2H, CH-N), 2.75 (sept, 4H, CH), 1.31 (d, *J* = 6.8 Hz, 12 H, CH₃), 1.21 (d, *J* = 6.8 Hz, 12 H, CH₃) ppm. ¹³C NMR (126 MHz, CDCl₃, TMS, 25 °C): δ 167.0, 146.5, 133.8, 130.1, 124.2, 119.0, 28.9, 24.2, 23.4 ppm. EI-MS: *m/z* 420.2 (M⁺) (100%).

Synthesis of **L**²=S (**2**)

Compound **2** was synthesized from the reaction of **L**²: (2.00 g, 7 mmol) in THF with elemental sulfur (0.29 g, 9.1 mmol) at room temperature under a nitrogen atmosphere. The mixture

was stirred overnight. The dark red solution was evaporated to dryness. The residue was extracted with boiling hexane (2 × 50 mL), filtered and dried to yield light yellow pure **2** (yield 1.27 g, 58%). Mp 138 °C (dec.). Elemental analysis (%) calcd for C₂₇H₃₆N₂S (357.60): C, 77.25; H, 9.87; N, 3.92. Found: C, 77.43; H, 9.42; N, 4.05. ¹H NMR (200 MHz, THF-d₈, TMS, 25 °C): δ 7.30–7.11 (m, 3H, CH_{ar}), 2.82 (sept, 2H, Ar-CH(CH₃)₂), 2.27 (s, 2H, CH₂), 2.16–1.00 (m, 10 H, CH₂), 1.29 (s, 6 H, CH₃), 1.25 (d, *J* = 6.9 Hz, 6 H, CH₃), 1.17 (d, *J* = 6.9 Hz, 6 H, CH₃) ppm. ¹³C NMR (126 MHz, THF-d₈, TMS, 25 °C): δ 213.6, 148.2, 138.5, 129.3, 124.5, 96.4, 69.7, 55.5, 39.6, 32.9, 30.0, 27.3, 26.4, 23.5 ppm. EI-MS: *m/z* 357.2 (M⁺) (100%).

Synthesis of **L**³=Se (**3**)

Compound **3** was synthesized by the reaction of **L**³: (1.00 g, 3.5 mmol) in THF with grey selenium (0.36 g, 4.55 mmol) at room temperature under a nitrogen atmosphere. The mixture was stirred for 4 days. The dark solution was evaporated to dryness. The residue was extracted with boiling hexane (2 × 40 mL), filtered and dried to yield light yellow colorless pure **3** (yield 0.84 g, 66%). Mp 150 °C. Elemental analysis (%) calcd for C₂₀H₃₁NSe (364.43): C, 65.92; H, 8.57; N, 3.84. Found: C, 66.78; H, 8.60; N, 3.85. ¹H NMR (200 MHz, THF-d₈, TMS, 25 °C): δ 7.34–7.23 (m, 3H, CH_{ar}), 2.80 (sept, 2H, Ar-CH(CH₃)₂), 2.27 (s, 2H, CH₂), 1.46 (s, 6 H, CH₃), 1.31 (s, 6 H, CH₃), 1.27 (d, *J* = 5.7 Hz, 6 H, CH₃), 1.24 (d, *J* = 5.7 Hz, 6 H, CH₃) ppm. ¹³C NMR (126 MHz, THF-d₈, TMS, 25 °C): δ 219.8, 147.6, 135.4, 129.5, 125.3, 72.6, 54.0, 51.4, 32.3, 30.1, 29.1, 27.3, 23.9 ppm. ⁷⁷Se NMR (95 MHz, THF-d₈, TMS, 25 °C): δ 492.43 ppm. EI-MS: *m/z* 365 (M⁺) (100%).

Synthesis of **L**³=Te (**4**)

Compound **4** was synthesized by the reaction of **L**³: (1.00 g, 3.5 mmol) in THF with tellurium (0.58 g, 4.55 mmol) at room temperature under a nitrogen atmosphere. The mixture was stirred for 2 days until the color of the solution turned dark. The solution was evaporated to dryness. The residue was extracted with boiling hexane (2 × 40 mL), filtered and dried to yield orange pure **4** (yield 0.90 g, 62%). Mp 162 °C. Elemental analysis (%) calcd for C₂₀H₃₁NTe (413.07): C, 58.15; H, 7.56; N, 3.39. Found: C, 58.98; H, 7.84; N, 3.36. ¹H NMR (500 MHz, toluene-d₈, TMS, 25 °C): δ 7.13–7.03 (m, 3H, CH_{ar}), 2.76 (sept, 2H, Ar-CH(CH₃)₂), 1.77 (s, 2H, CH₂), 1.48 (d, *J* = 11 Hz, 6 H, CH₃), 1.41 (s, 6 H, CH₃), 1.18 (d, *J* = 11 Hz, 6 H, CH₃), 0.98 (s, 6 H, CH₃) ppm. ¹³C NMR (126 MHz, toluene-d₈, TMS, 25 °C): δ 215.4, 146.3, 136.9, 129.1, 125.2, 75.8, 58.7, 49.6, 33.1, 29.7, 28.3, 27.9, 24.1 ppm. ¹²⁵Te NMR (95 MHz, toluene-d₈, TMS, 25 °C): δ 472.04 ppm. EI-MS: *m/z* 415 (M⁺) (100%).

Synthesis of **L**¹=S-I-I (**5**)

For the synthesis of compound **5** a mixture of crystalline iodine (0.097 g, 0.38 mmol) and **L**¹=S (**1**) (0.16 g, 0.38 mmol) was dissolved in toluene (20 mL) at room temperature. The color of the solution turned dark immediately. The solution was stirred for 3 days and then filtered and the filtrate was evaporated to dryness. The residue was dissolved in toluene

(10 mL) and stored at $-32\text{ }^{\circ}\text{C}$ for 3 days in a freezer to give brown crystals of **5** suitable for single crystal X-ray structural analysis (yield 0.25 g, 99%). Mp $180\text{ }^{\circ}\text{C}$ (dec.). ^1H NMR (200 MHz, THF- d_8 , TMS, $25\text{ }^{\circ}\text{C}$): δ 7.50–7.33 (m, 8H, CH_{ar} + $\text{CH}-\text{N}$), 2.65 (sept, 4H, $\text{Ar}-\text{CH}(\text{CH}_3)_2$), 1.38 (d, $J = 6.8\text{ Hz}$, 12 H, CH_3), 1.20 (d, $J = 6.8\text{ Hz}$, 12 H, CH_3) ppm. ^{13}C NMR (126 MHz, THF- d_8 , TMS, $25\text{ }^{\circ}\text{C}$): δ 157.0, 146.8, 133.7, 131.6, 125.2, 124.1, 30.0, 23.9 ppm. EI-MS: m/z 420 ($\text{M}^+ - 2\text{I}$) (100%).

Synthesis of $\text{L}^2=\text{S}-\text{I}-\text{I}$ (**6**)

For the synthesis of compound **6**, crystalline iodine (0.21 g, 0.84 mmol) was added to a solution of $\text{L}^2=\text{S}$ (**2**) (0.3 g, 0.84 mmol) in toluene (15 mL) at room temperature. The color of the solution turned dark red immediately. The solution was stirred for 1 day and then filtered and the filtrate was evaporated to dryness. The residue was dissolved in 10 mL of toluene and stored at $-32\text{ }^{\circ}\text{C}$ for 3 days in a freezer to give dark brown crystals of **6** suitable for single crystal X-ray structural analysis (yield 0.15 g, 29%). Mp $146\text{ }^{\circ}\text{C}$ (dec.). ^1H NMR (200 MHz, THF- d_8 , TMS, $25\text{ }^{\circ}\text{C}$): δ 7.26 (m, 3H, CH_{ar}), 2.81 (sept, 2H, $\text{Ar}-\text{CH}(\text{CH}_3)_2$), 2.67 (s, 2 H, CH_2), 1.83–1.45 (m, 10 H, CH_2), 1.32 (s, 6 H, CH_3), 1.26 (d, 6 H, CH_3), 1.18 (d, 6 H, CH_3) ppm. ^{13}C NMR (126 MHz, THF- d_8 , TMS, $25\text{ }^{\circ}\text{C}$): δ 209.4, 145.4, 138.4, 128.9, 124.4, 85.3, 73.0, 53.8, 35.2, 30.5, 29.1, 26.8, 26.4, 22.5 ppm. EI-MS: m/z 357.3 ($\text{M}^+ - 2\text{I}$) (100%).

Synthesis of $\text{L}^3=\text{Se}-\text{I}-\text{I}$ (**7**)

For the synthesis of compound **7**, crystalline iodine (0.58 g, 2.30 mmol) was added to a solution of $\text{L}^3=\text{Se}$ (**3**) (0.84 g, 2.3 mmol) in toluene (20 mL) at room temperature. The color of the solution turned immediately dark. The solution was stirred for 2 days and then the precipitate was filtered and dried. The product was dissolved in toluene (10 mL) and stored at $-32\text{ }^{\circ}\text{C}$ for 3 days to give dark brown crystals of **7** suitable for single crystal X-ray structural analysis (yield 1.10 g, 77%). Mp $232\text{ }^{\circ}\text{C}$ (dec.). ^1H NMR (200 MHz, THF- d_8 , TMS, $25\text{ }^{\circ}\text{C}$): δ 7.56–7.35 (m, 3H, CH_{ar}), 2.73 (sept, 2H, $\text{Ar}-\text{CH}(\text{CH}_3)_2$), 2.40 (s, 2 H, CH_2), 1.70 (s, 6 H, CH_3), 1.30 (m, 18 H, CH_3) ppm. ^{13}C NMR (126 MHz, THF- d_8 , TMS, $25\text{ }^{\circ}\text{C}$): δ 231.7, 146.7, 133.1, 131.1, 126.5, 77.2, 55.0, 51.9, 30.6, 30.5, 30.2, 27.0, 25.3 ppm. ^{77}Se NMR (95 MHz, THF- d_8 , TMS, $25\text{ }^{\circ}\text{C}$): δ 491.26 ppm. EI-MS: m/z 365 ($\text{M}^+ - 2\text{I}$) (100%).

Synthesis of $\text{L}^3=\text{Te}-\text{I}-\text{I}$ (**8**)

For the synthesis of compound **8**, crystalline iodine (0.46 g, 1.81 mmol) was added to a solution of $\text{L}^3=\text{Te}$ (**4**) (0.75 g, 1.81 mmol) in toluene (20 mL) at room temperature. The color of the solution turned dark and a precipitate was formed immediately. The solution was stirred for 2 days, and the precipitate was filtered and dried *in vacuo*. The saturated solution of **8** in DMSO was stored at room temperature for 3 days to give black crystals of **8** suitable for single crystal X-ray structural analysis (yield 1.20 g, 99%). Mp $206\text{ }^{\circ}\text{C}$ (dec.). ^1H NMR (300 MHz, DMSO- d_6 , TMS, $25\text{ }^{\circ}\text{C}$): δ 7.50 (m, 3H, CH_{ar}), 2.64 (sept, 2H, $\text{Ar}-\text{CH}(\text{CH}_3)_2$), 2.10 (s, 2 H, CH_2), 1.67 (s, 6 H, CH_3),

1.44 (s, 6 H, CH_3), 1.32 (d, $J = 6.6\text{ Hz}$, 6 H, CH_3), 1.26 (d, $J = 6.6\text{ Hz}$, 6 H, CH_3) ppm. EI-MS: m/z 415 ($\text{M}^+ - 2\text{I}$) (100%).

Crystal structure determination

Suitable single crystals for X-ray structural analysis of **5**, **6**, **7**, and **8** were mounted at low temperature in inert oil under an argon atmosphere by applying the X-Temp2 device.²² The data were collected on a Bruker D8 three circle diffractometer equipped with a SMART APEX II CCD detector and an INCOA-TEC Ag microfocus source with INCOATEC Quazar mirror optics.²³ The data were integrated with SAINT²⁴ and a semi-empirical (for **5**, **7**) and an analytical (for **6**, **8**) absorption correction with SADABS²⁵ were applied. The structure was solved by direct methods (SHELXS-97) and refined against all data by full-matrix least-squares methods on F^2 (SHELXL-97).²⁶ All non-hydrogen-atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions using a riding model with their U_{iso} values constrained to $1.5U_{\text{eq}}$ of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times for all other carbon atoms. The disordered parts were refined using distance restraints and restraints for the anisotropic displacement parameters.

Conclusions

The synthesis and reactivity of compounds with heavier group 16 elements is a rapidly growing field in chemistry because of their extensive use in various applications. In the present study we show that an *N*-heterocyclic carbene L^1 : as well as cyclic-alkyl-amino carbenes L^{2-3} : react with chalcogens to form air stable chalcogenamides **1–4**. All the chalcogenamides regardless of the organic framework or chalcogen are able to form diiodine adducts with the general formula $\text{L}=\text{E}-\text{I}-\text{I}$. These experiments show the easy access to this class of compounds. Compounds **5–8** are well-characterized with various spectroscopic methods and single-crystal X-ray analyses. These compounds might prove to be promising candidates for the synthesis of iodine containing compounds, which are sensitive to elemental iodine. The formation of an oxidized $\text{E}(\text{I})_2$ compound which we were aiming at was not observed due to the low oxidation potential of iodine.

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