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Note

Reactions of β-diketiminates with selenium and tellurium halides

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Abstract

The complexes [nacnac$TeCl_4$] and nacnac$SeCl^+Cl^-$ (nacnac = $[\{N(C_6H_3{}^iPr_22,6)C(Me)\}_2CH]^-$) have been prepared in good yields and characterized in the solid state by X-ray crystallography. The crystals of both compounds show C–H activation of the ligand backbone. In the case of tellurium, no LiCl displacement or nitrogen chelation is observed and an ionic $TeCl_4$ complex is isolated. By contrast, under similar reaction conditions, the reaction with $SeCl_4$, affords a cationic Se(II) complex with loss of four chlorines and rearrangement of the chloride atom to the nacnac ligand.
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Keywords: Selenium; Tellurium; β-Diketiminato; C–H activation

1. Introduction

Despite the wealth of research and structural characterization of metallic β-diketiminato complexes [1], the elements of tellurium and selenium appear to have been neglected. The recent reports of novel group 15 β-diketiminato complexes [2] has prompted us to report our results from the investigation of nacnacLi (nacnac = $[\{N(C_6H_3{}^iPr_22,6)C(Me)\}_2CH]^-$) with $TeCl_4$ and $SeCl_4$. We were interested in exploring the nacnac compounds of these elements, given the relatively few Se–N and Te–N compounds that are structurally characterized [3]. Previous attempts at synthesizing the electron rich p-block β-diketiminato complexes has yielded compounds that avoid the usual *N*,*N*′-chelation through reacting at the γ carbon (Fig. 1) [4].

2. Experimental

Solvents used were dried over sodium or potassium and degassed before use. All manipulations were performed under anaerobic conditions using standard Schlenk techniques. DippnacnacH and the corresponding lithium salt were prepared according to published procedures [5]. All other reagents were purchased from Aldrich and used as received.

2.1. Preparation of **1**

A thf solution of DippnacnacLi (0.5 g, 1.2 mmol) was added rapidly by cannula to a stirred thf solution of $TeCl_4$ (0.33 g, 1.2 mmol) at −78 °C. The resultant yellow colored reaction mixture was immediately removed from the dry-ice bath and allowed to reach ambient temperature. Stirring was maintained for a further 12 h, after which time the deep green colored solution was filtered, thf removed *in vacuo* and the foamy green solid extracted into toluene. Concentration of the toluene solution and storage at 25 °C for 1 day afforded **1** as large yellow cubic crystals in 22% yield, pure powder yield = 58%. M.p. 128–130 °C turns green, 160–161 °C melts, ^1H NMR (d^6 C_6D_6, 25 °C): δ (ppm) 0.63, 0.79, (doublets, $^1J_{H-H} = 6.3$ Hz, ^{i}Pr–Me) 0.88, 1.01, (2 doublets, $^1J_{H-H} = 6.6$ Hz, ^{i}Pr–Me), 1.28 (s, 3H, CH_3, backbone), 1.81 (m, CH_{2-} Te, $^1J_{H-H}$ 20.10) 2.67, 3.23, (^{i}Pr C–*H* Dipp, multiplet, $^1J_{H-H} =$ 6.9 Hz), 4.61 (s, CH– backbone), 4.92 (br, s, N–H), 6.72 (aromatic-H, Dipp, overlapping doublets, $^1J_{H-H} =$ 7.5 Hz), 6.84 (triplet, H-Dipp, $^1J_{H-H} = 7.5$ Hz); ^{13}C

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NMR ($CDCl_3$, 25 °C): δ (ppm) 21.7, 22.8, 23.4, 23.6, 23.8, (C–^{i}Pr), 24.9 (Me-nacnac backbone), 28.7, 29.0 (CH–^{i}Pr), 96.8 ($\underline{C}$H-backbone), 124.3, 124.7, 125.0, 125.5, 128.5, 129.26, 130.58 (aromatic ^{13}C), 146.5 (N-$\underline{C}$(Me)CC), 161.9 ($\underline{C}$–NH-Dipp), 170.1 (Te–C), IR (Nujol Mull, v cm^{-1}); 3200 (shoulder, N–H stretch), 1716 (w), 1705(w), 1364 (w), 1067 (m), 911.7 (s)

2.2. Preparation of 2

To a stirred thf solution of $SeCl_4$ (0.22 g, 1.2 mmol) at −78 °C, a thf solution of nacnacLi (0.5 g, 1.2 mmol), was slowly added. An immediate color change was observed and a dark red colored solution resulted. The reaction mixture was brought to ambient temperature and stirred overnight. Removal of the thf under vacuum afforded an orange colored solid that was readily soluble in toluene. Overnight storage of the toluene solution at room temperature afforded yellow crystals of **2**, along with a small quantity of red monoclinic elemental selenium [6]. The yellow crystalline material was separated from red crystalline Se by hand in the dry box and used for further characterization. Yield: 54.1%, M.p. = 124–123 °C, ^{1}H NMR (d^6 C_6D_6, 25 °C): δ (ppm) 0.95, 0.88, 1.13, 1.14, (4 doublets, $^1J_{H-H} = 6.6$ Hz, ^{i}Pr–Me), 1.38 (s, 3H, CH_3, backbone), 1.99 (s, CH_2), 2.36, 3.02, (^{i}Pr C–H Dipp, multiplet, $^1J_{H-H} = 6.9$ Hz), 4.59 (br, s), 4.86, (s, N–H), 6.75 (ortho, H, aromatic, $^1J_{H-H} = 6.2$ Hz), 6.92 (triplet, meta H Dipp, $^1J_{H-H} = 6.2$ Hz); ^{13}C NMR ($CDCl_3$, 25 °C): δ (ppm) 21.3, 22.0, 22.9, 23.1 (C–^{i}Pr), 28.1 (Me-nacnac backbone), 28.8, 30.1 (C–H, ^{i}Pr) 111.4 (CH– backbone), 131.7, 136.0, 137.2, 137.8, 143.9, 144.8 (aromatic ^{13}C), 158.5, (N$\underline{C}$(Me)C) 166.1 (C–NH-Dipp), Se–C, not observed, IR (Nujol Mull, v cm^{-1}), 3268 (m, N–H), 2253 (m), 1262 (w), 906.9 (w), 752.5 (s), 726.6 (s), 651.1(m)

3. Results and discussion

The reaction between tellurium tetrachloride and one equivalent of nacnacLi afforded a dark green solution and yellow crystals of **1**, Scheme 1, crystalline yield = 26%. A reproducible yield of 58% can be obtained in pure powder form. [Nacnac$TeCl_4$] is highly air and moisture sensitive but stable in an inert atmosphere at ambient temperature and in solution for weeks.

The molecular structure of **1** is displayed in Fig. 2.

Compound **1** crystallizes in the monoclinic space group, $P21/c$, crystal data is shown in Table 1. The coordination sphere of the tellurium center can be described as trigonal bipyramidal with the lone pair presumably occupying the vacant coordination site. In a similar manner as was seen with nacnac antimony complexes and other reactive species, for example, Ca^{2+} [2b,7], C–H activation of the ligand backbone is observed. Surprisingly there is no LiCl elimination and no nitrogen–tellurium interaction. A distance of 4.052(1) Å separates the nitrogen and tellurium

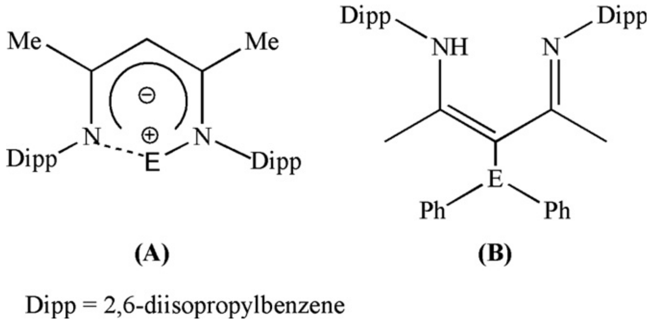


Fig. 1. (A) = usual N-chelation of β-diketiminato ligands to metals and metalloids and in (B), attachment at the γ carbon has been more common in reactions with group 15 elements [4].

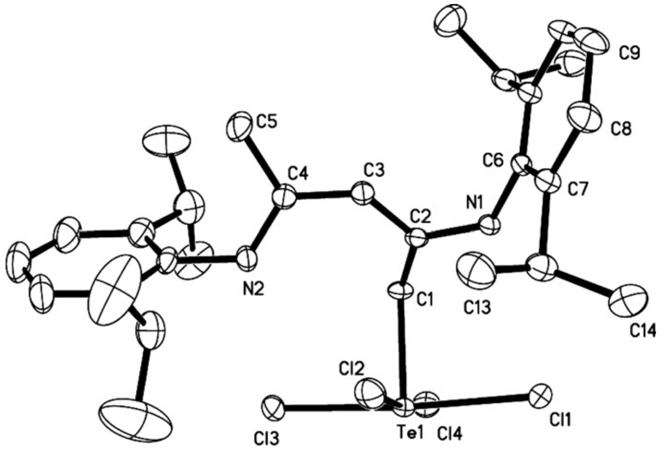
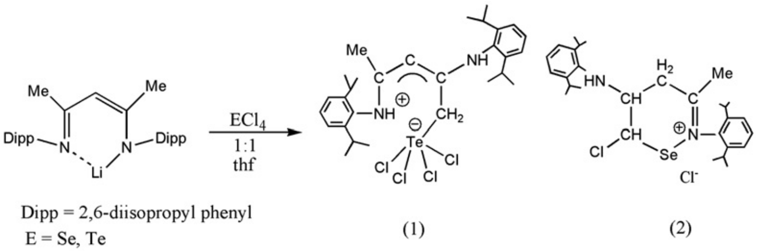


Fig. 2. ORTEP of compound **1**, thermal ellipsoids at 30% probability, hydrogen atoms and two molecules of toluene omitted for clarity.



Scheme 1. Synthesis of compounds **1** and **2**.

Table 1
Crystal data for compounds **1** and **2**

Compound name	**1**	**2**
Chemical formula	$C_{43}H_{56}Cl_4N_2Te$	$C_{36}H_{48}Cl_2N_2Se$
Formula weight	870.30	658.62
Crystal system	Monoclinic	Triclinic
Space group	$P21/c$	$P\bar{1}$
T (K)	91(2)	91(2)
a (Å)	11.607(2)	11.011(2)
b (Å)	18.005(4)	12.537(2)
c (Å)	21.187(4)	13.281(3)
α (°)	90	87.918(4)
β (°)	93.601(4)	83.931(4)
γ (°)	90	81.721(4)
V (Å ^{3})	4419.0(15)	1803.66
Z	4	2
Reflections collected	19618	14918
Independent reflections	7964	6462
Data/restraints/ parameter ratio	7964/18/461	6462/1/378
Unique data (R_{int})	0.0456	0.0604
D_{calc} (mg/m^3)	1.308	1.213
Absorption coefficient (mm^{-1})	0.945	1.214
F(000)	1792	692
Crystal size (mm)	0.08 × 0.06 × 0.05	0.03 × 0.04 × 0.05
θ Range for collection (°)	2.09–25.25	1.54–25.25
R indices (all data)	$R_1 = 0.0714$, $wR_2 = 0.1315$	$R_1 = 0.0840$, $wR_2 = 0.1210$
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0427$, $wR_2 = 0.1065$	$R_1 = 0.0449$, $wR_2 = 0.1021$
Largest difference in peak and hole (e Å^{-3})	0.792 and −0.820	0.501 and −0.348

atoms, which is longer than the van der Waals interaction of these elements (Te–N, van der Waals radii = 3.70 Å) [8].

Typically, five coordination Te (IV) complexes are square pyramidal with a short bond to the apical atom [9]. An example of such coordination is observed in [Te(ttp)Cl_2] (TTP = tetra-*p*-tolyl porphyrin) [10]. The short bond lengths, 1.394(6) and 1.387(6) Å (Fig. 3) in the carbon backbone of the nacnac ligand, lead us to believe that there is delocalization over carbons **2**–**4**. Ionic tellurium complexes are not unusual [11] and an ionic system in which the cation and anion are connected in the same molecule has been observed in tetrachloro[(3-allyl-2-methyl-oxazolin-5-yl)methyl]-tellurium [11c]. The exact mechanism for the formation of compound **1** is unclear despite numerous attempts to isolate intermediates. The reaction proceeds rapidly in toluene or thf and despite no loss of a chloride ion from the tellurium center in the solid state analysis, a white precipitate of LiCl is observed alongside a small quantity of elemental tellurium, thereby indicating that reduction of some $TeCl_4$ occurs.

By contrast, the analogous reaction involving nacnacLi with $SeCl_4$ leads to reduction of selenium and affords yellow crystalline **2**, (Fig. 4), in good yield alongside a side product of red monoclinic elemental selenium [6]. The crystal structure of the cation was determined by X-ray diffraction analysis, crystal data is given in Table 1.

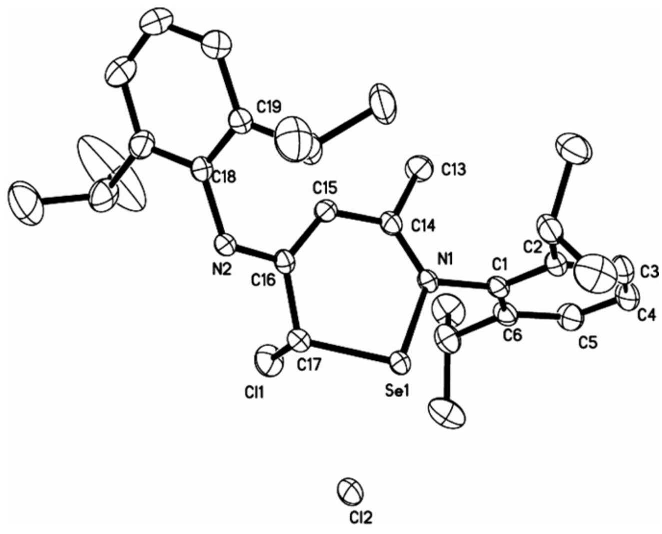


Fig. 4. ORTEP of compound **2**, thermal ellipsoids at 30% probability, hydrogen atoms omitted for clarity.

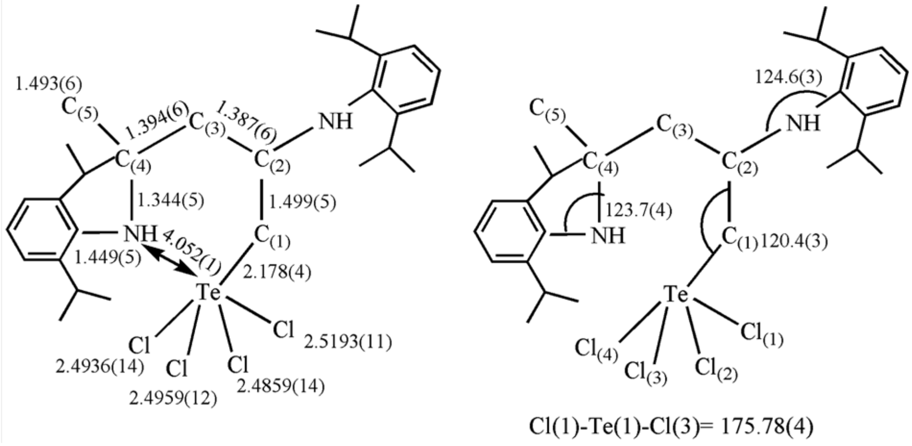


Fig. 3. Bond lengths (Å) and angles (°) of compound **1**.

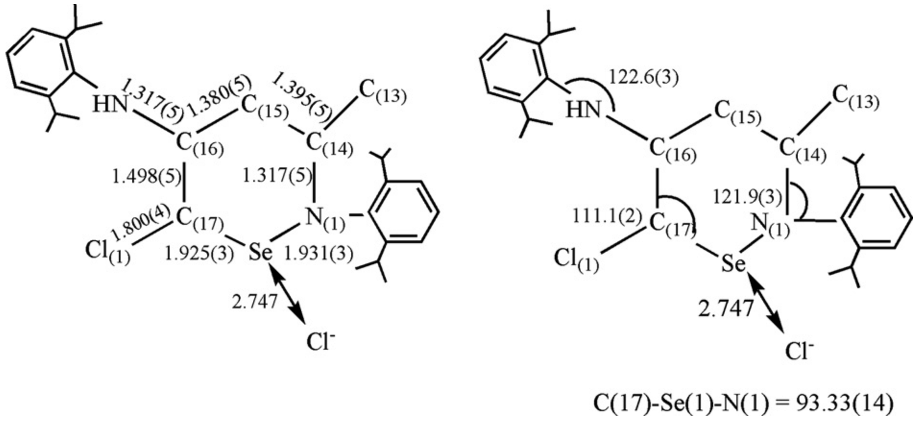


Fig. 5. Bond lengths (Å) and angles (°) of compound **2**.

The solid-state analysis reveals an interaction of 2.747 Å between the Se cation and the Cl anion. The Se–N distance of 1.931(3) Å is longer than a nominal Se–N single bond, these generally fall within the range of 1.8245–1.846 Å (cov. radii = 1.865 Å) [3a,12]. Furthermore, the 93.33(14)° angle separating C(17)–Se(1)–N(1) is more acute than in previously reported two coordinated N–Se systems [13], but greater than the value of 88.4(3)° in the selenium nitrogen heterocyle reported by Ragogna et al. [3a]. These deviations can be attributed to the steric hindrance associated with the bulky ligand (see Fig. 5).

The rearrangement of the Cl^- ion is unusual, but presumably occurs because of the loss of delocalization over the ligand backbone, thus making the ∝ carbon more prone to nucleophilic attack.

4. Conclusions

In summary, the first β-diketiminato complexes of Se and Te have been prepared. Both show ligand rearrangement *via* C–H activation and in the case of selenium a Se (II) center. The structures are interesting given the few Se–N, Te–N compounds characterized and the long-standing interest in selenium and tellurium nitrides.

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Appendix A. Supplementary information

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 615765 for compound **1**, CCDC No. 615764 for compound **2**. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK; fax (int code): +44 1223 336 033 or email: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.08.026.

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