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Methylaluminum complexes based on tridentate 2,6-bis(mercaptoalkyl)pyridine SNS-ligands

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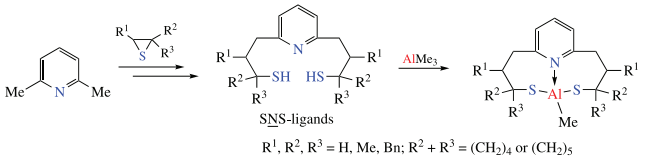
New SNS-ligands were obtained by consequent ring-opening of substituted thiiranes by lithiated 2,6-lutidine, monofunctionalized SN-ligands having been isolated as the intermediate compounds. The molecular structure of ligand 2,6-Py(CH$_2$CH$_2$CBn$_2$SH)$_2$ was elucidated by XRD analysis. The reaction of AlMe$_3$ with SNS-ligands afforded monomeric methyl aluminum complexes which have been tested in ring-opening polymerization of ε-caprolactone in bulk.



Keywords: organoaluminum compounds, thiiranes, SNS-polydentate ligands, methyl aluminum complexes, ring-opening of thiiranes, ring-opening polymerization of lactones.

Polydentate ligands are useful tools in modern organometallic and inorganic chemistry[1] for stabilization of reactive species or complexes with unusual bonding. Rational ligand design (variation of the nature of donor atoms and tuning ligand backbone by changing steric and electronic properties) even allows one to govern the type of the complex formed.[2] Interestingly, majority of polydentate ligands includes O- and N-compounds, whereas S-analogues[3,4] have been studied in significantly less extent. The aim of this work was the synthesis and investigation of coordination properties of novel SNS-ligands (N atom bonded to the metal by dative bond is underlined; S atoms are bonded covalently) with organoaluminum moiety. Interest to aluminum derivatives was caused by potential application in catalysis. In contrast to O-polydentate ligands, synthesis of polydentate sulfur-containing ligands represents a significant challenge due to special reactivity of SH-groups (high acidity and nucleophilicity) and limited range of available reagents to introduce SH-group.

Based on high reactivity of small heterocycles as well as on application of oxiranes[5,6] and aziridines[7–9] in reactions with C-nucleophiles, we would propose that relative thiiranes may be used as convenient reagents in reactions with organolithium compounds for the synthesis of SNS-polydentate[10,11] ligands. To the best of our knowledge, only few examples of such reactions have been documented including stabilized organometallics, *i.e.* allyllithium,[12] allylmagnesium bromide[13] or 2-pyridylmethyllithium.[14] In contrast, attack of simple alkyl and aryl lithium reagents at thiiranes affects desulfurization yielding alkenes as main products.[15]

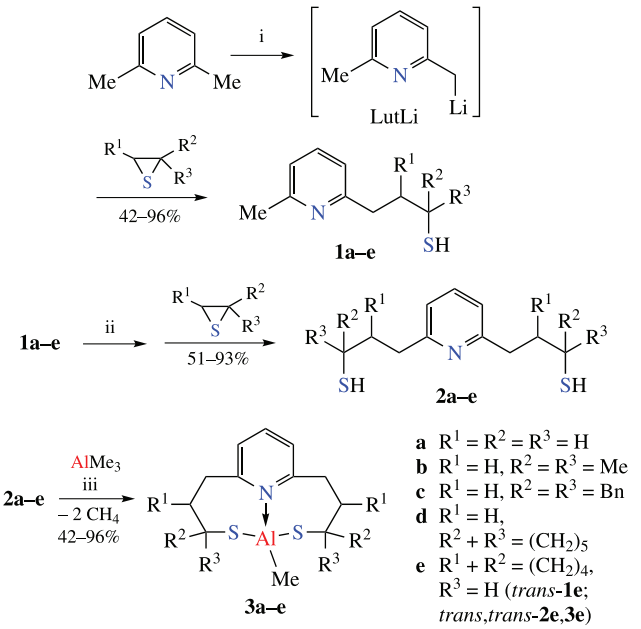
In this work, a representable series of substituted thiiranes was used; we varied the substituents at one or both C atoms of the thiirane cycle. The products, substituted SNS-ligands, with elongated methylenic 'arms' (CH$_2$CH$_2$ *vs.* usual CH$_2$) are prospective for complexation with heavier metals.

In general, thiiranes are available compounds.[16–22] In this work several new substituted 2,2-thiiranes were obtained by simple treatment of oxiranes with KSCN in water[23] or in water/EtOH[24] thus providing good yields of the target compounds (for details, see Online Supplementary Materials).

The target SNS-tridentate ligands were obtained in two-stage synthesis with isolation of intermediate compounds **1a–e**, which themselves may be regarded as SN-bidentate ligands (Scheme 1). Ring-opening of thiiranes proceeded regioselectively through attack of lutidinyllithium (LutLi) intermediate at the least hindered carbon atom. The moderate yields may be accounted for the peculiarities of their purification (distillation, chromatography or high solubility in crystallization). The two-stage synthesis of SNS-ligands **2a–e** with isolation of intermediate SN-compounds **1a–e** is explained by the governed type of interaction and simplicity of product isolation procedure. Ligands **2a–d** are characterized by one set of signals in ^{13}C NMR spectra (C_{2v} symmetry). Due to S$_N$2 mechanism of ring-opening of thiirane cycle, ligand **1e** was obtained as *trans*-isomer (*rac*-); ligand **2e** was formed as *trans*,*trans*-isomer [mixture of two diastereomers, with (*R**,*S**/*S**,*R**)/(*R**,*S**/*R**,*S**) C atoms configurations]. These ligands may be regarded as analogues of pincer compounds,[25–30] which have found wide application in catalysis.

Molecular structure of ligand **2c** was investigated by single crystal XRD analysis (Figure 1; see also Online Supplementary Materials, Table S1).[†] It should be noted that structures of 2,6-bis(mercaptoalkyl)pyridines have not been described

[†] *Crystal data for* **2c**. C$_{39}$H$_{41}$NS$_2$ (M = 587.85), orthorhombic, space group *Pbcn* at 120(2) K: a = 6.4574(6), b = 17.4109(16) and c = 28.481(3) Å, V = 3202.1(5) Å^3, Z = 4, d_{calc} = 1.219 g cm^{-3}, μ(MoKα) = 0.195 mm^{-1}, F(000) = 1256. Total of 2848 reflections were collected (3504 independent reflections, R_{int} = 0.0506) and used in the



Scheme 1 *Reagents and conditions*: i, BuLi (1 equiv.), THF or Et_2O, –50 °C, then thiiranes; ii, BuLi (2 equiv.), THF or Et_2O, –50 °C, then thiiranes; iii, $AlMe_3$, PhMe, –50 °C to room temperature, overnight.

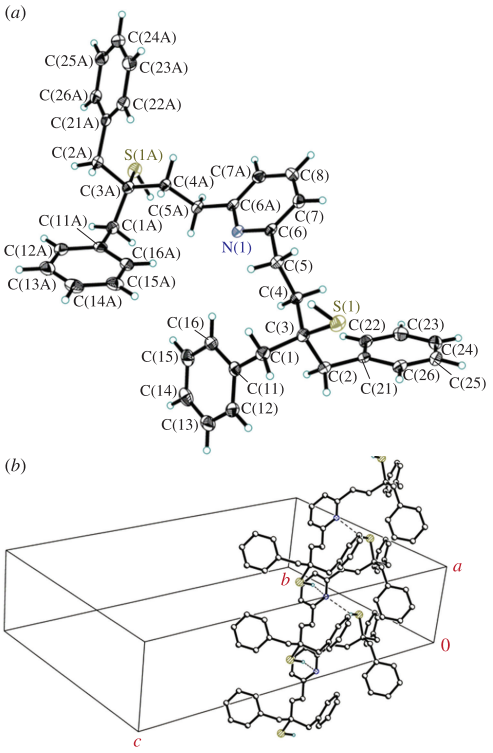


Figure 1 X-ray structure data for compound **2c**: (*a*) molecular structure, displacement ellipsoids are shown at 50% probability level; (*b*) fragment of packing in crystal, hydrogen bonds are shown by dashed lines. Selected bond lengths (Å) and angles (°): S(1)–H(1), 1.25(2); H(1)···N(1), 2.97(2); S(1)···N(1), 4.0935(5); S(1)–H(1)···N(1) 149.1(13).

to date; only the structures of related salts such as 2,6-Py(CH_2C(Ad)SH)$_2\cdot$HCl, 2,6-Py(CH_2C(Ad)SH)$_2\cdot HNO_3$ (Ad = 2-adamantyl)[31] with short 'arms' have been described. In compound **2c**, the formation of intermolecular hydrogen S–H···N bonds is observed, which may be characterized as moderate in terms of strength;[32] this bonding results to the appearance of chains in the crystal.

Methylaluminum complexes **3a–e** were obtained under mild conditions using simple alkyl protonolysis approach (thiodemethylation reaction) upon treatment of $AlMe_3$ with SNS-ligands **2a–e** (see Scheme 1); gaseous methane was the single by-product, so the yields of the products were high.

Structures of complexes **3a–e** were established on the basis of their multinuclear (^{1}H, ^{13}C, ^{27}Al) NMR spectroscopy. In the ^{1}H NMR spectra, the signal of AlMe group is observed at δ (–0.21)–(–0.12) ppm. Interestingly, the signals of Py ring are shifted upfield in comparison with free ligands **2a–e** (Δ 0.2–0.4 ppm). The chelated complexes with seven-membered *N–C–*CH_2*–*CHR^1*–*CR^2R^3*–S–Al* fused cycles were formed with fixed chelate rings conformations; this results in decreasing of ligand framework flexibility with reduction of symmetry. Thus, the protons for –CH_2CH_2– groups in complexes **3a–d** are diastereotopic due to cyclic complex structure. Moreover, substituents R^2 and R^3 are also diastereotopic as seen from ^{1}H as well as ^{13}C NMR spectra, indicating the diminishing of complex symmetry (from C_{2v} to C_s) upon alumocycle formation. In the ^{13}C NMR spectra, there is only one set of signals for carbon N–CH_2–CH_2–*C*–Al framework, indicating monomeric structure; however, rapid interconversion monomer–dimer is also possible. The data on ^{27}Al NMR spectra[33] obtained for complexes **3b** (δ 153 ppm), **3c** (δ 154 ppm) and **3e** (δ 156 ppm) indicate SNSC-coordination of Al atom and common geometry (monomeric tetrahedral structure, T-4) for all members of this Al series. Complex **3e** was obtained as a 2 : 1 diastereomeric mixture of C_1 [two sets of signals in ^{13}C NMR spectrum; (*R*,S*/S*,R**) configurations of C atoms] and C_2 [one set of signals in ^{13}C NMR spectrum; (*R*,S*/R*,S**)] symmetry.

Catalytic activity of complexes **3c**,**d** was tested in ring-opening polymerization of ε-caprolactone (CL) using benzyl alcohol as co-initiator (100 °C, 12 h, [CL]/[Al]/[BnOH] = = 300 : 1 : 1) (see Online Supplementary Materials, Table S2). It was established that the polymerization proceeds with high control (M_n up to 21000 Da; M_w/M_n is less than 1.3) in bulk, whereas in toluene solution the conversion is decreased significantly. Introduction of sterically voluminous substituents into ligand (such as cyclohexane moiety in **3d**) results in diminishing the rate of polymerization.

In conclusion, a convenient synthetic strategy for preparation of new pyridine SN- and SNS-polydentate ligands based on regioselective ring-opening of thiiranes was developed. These SNS-ligands were used for the synthesis of monomeric methylaluminum complexes by simple protonolysis approach. The obtained methylaluminum complexes based on SNS-ligands seem to be promising initiators of ring-opening polymerization of lactones in bulk, giving polyesters with controlled characteristics. Investigations of application of these polydentate ligands for stabilization of derivatives of other metals and metalloids as well as their application are underway in our laboratory.

Crystal data were collected at the Centre of Joint Equipment of IGIC RAS.

refinement, which converged to wR_2 0.0859, GOOF 1.027 for all independent reflections [R_1 = 0.0364 was calculated for 3504 reflections with $I > 2\sigma(I)$].

The X-ray diffraction analysis was carried out on a Bruker Smart Apex II diffractometer (graphite monochromatized MoKα radiation, λ = 0.71073 Å) using ω-scan mode. Absorption correction based on measurements of equivalent reflections (SADABS) was applied. The structure was solved by direct methods and refined by full matrix least-squares on F^2 (Shelxtl) with anisotropic thermal parameters for all non-hydrogen atoms. All H atoms were found from difference Fourier synthesis and refined isotropically.

CCDC 2088271 contains the supplementary crystallogaphic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2021.11.026.

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