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Preparation of Telluro- and Selenoalumoxanes under Mild Conditions

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Supporting Information

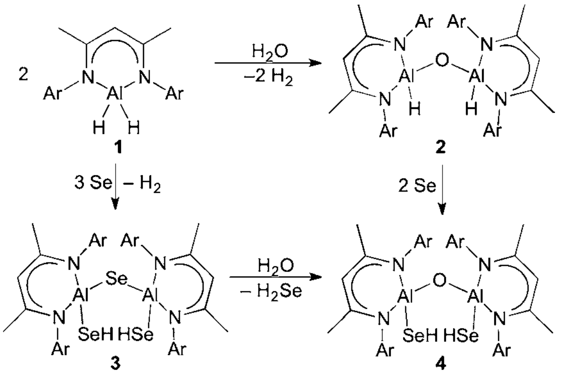
ABSTRACT: Syntheses of the heavy chalcogen-containing alumoxanes $[^{Me}LAl(SeH)]_2(\mu\text{-}O)$ (**4**) and $(^{Me}LAl)_2(\mu\text{-}Te)(\mu\text{-}O)$ (**7**) were accomplished by the reaction of $(^{Me}LAlH)_2(\mu\text{-}O)$ (**2**; $^{Me}L = HC[(CMe)N(2,4,6\text{-}Me_3C_6H_2)]_2^-$) with either red selenium or metallic tellurium. The aluminum hydrogenselenide $[^{Me}LAl(SeH)]_2(\mu\text{-}Se)$ (**3**) was also prepared from the reaction of red selenium and $^{Me}LAlH_2$ (**1**). All compounds were characterized by spectroscopic methods and X-ray diffraction studies. Density functional theory calculations were performed on **4** and **7**.

Alumoxanes are important catalysts and cocatalysts in the polymerization of a broad variety of organic molecules,[1] and their chemistry has been under investigation in the last few decades.[2] Nonetheless, structurally modified alumoxanes remain a synthetic challenge, mainly because of the difficulty in stabilizing them in low aggregation and crystalline forms. Indeed, tailor-made alumoxanes, particularly those bearing chalcogen atoms, are unknown to date. Albeit, the presence of both hard and soft donor atoms bound to aluminum can lead to a change in the properties of the metal center and, thus, to an overall modification of their chemical behavior. In this regard, the chemistry of aluminum compounds containing heavy chalcogens has been comparatively less studied than that of compounds containing Al−O bonds. To a certain extent, this is due to the thermodynamic stability of the latter and to the use of highly toxic and sometimes thermally unstable reagents in the preparation of heavier congeners.

We recently reported on the use of the sterically modified aluminum hydride $^{Me}LAlH_2$ (**1**; $^{Me}L = HC[(CMe)N(2,4,6\text{-}Me_3C_6H_2)]_2^-$) and the alumoxane hydride $[\{^{Me}LAl(H)\}_2(\mu\text{-}O)]$ (**2**) in the preparation of functionalized alumoxanes.[3] As an extension of this research, we focused our attention on the heavier and less studied group 16 congeners. Herein we report on the synthesis of the unprecedented alumoxane hydrogenselenide $[\{^{Me}LAl(SeH)\}_2(\mu\text{-}O)]$ (**4**) and the cyclic alumoxane telluride $[\{^{Me}LAl\}_2(\mu\text{-}Te)(\mu\text{-}O)]$ (**7**), along with reactivity of **1** toward selenium.

The reaction of **1** with 1.5 equiv of red selenium in toluene at ambient temperature gave $[\{^{Me}LAl(SeH)\}_2(\mu\text{-}Se)]$ (**3**) in 87% yield (Scheme 1). No evidence was found to suggest formation of the mononuclear aluminum hydrogenselenide $[^{Me}LAl(SeH)_2]$, in contrast to the observed behavior for the analogous compound containing the bulkier β-diketiminate ligand ($^{iPr}L = HC[(CMe)N(2,6\text{-}iPr_2C_6H_3)]_2^-$).[4] Compound **3** reacts in a simple and rapid exchange process with 1 equiv of water to produce the alumoxane **4**, which represents the first example of an alumoxane bearing hydrogenselenide groups. Alternatively, **4** can be obtained from the reaction of **2** and red selenium in toluene at low temperature in 80% yield (Scheme 1).

Scheme 1. Preparation of Compounds 3 and 4



The IR spectra of **3** and **4** show Se−H valence vibrations at 2308 and 2310 cm^{-1}, respectively. The ^1H NMR signals corresponding to the AlSe−H moieties in these compounds appear at δ −2.67 (**3**) and −3.45 (**4**). The ^{77}Se NMR spectrum for **4** shows one broad signal at δ −419, while the corresponding spectrum for **3** exhibits two broad signals due to the μ-selenium (δ −414) and SeH groups (δ −339). A tendency similar to that in **3** is observed for the SeH groups (δ −341) in the related compound $[\{^{iPr}LAl(SeH)\}_2(\mu\text{-}Se)]$[4] although not for the μ-selenium atom (δ −535). This suggests that ^{77}Se NMR chemical shifts of these compounds are considerably influenced by both the structural changes on the ligand and the nature of the bridging atom.

The electron impact mass spectrometry (MS-EI) spectra of **3** and **4** did not exhibit the $[M]^+$ peaks, although the fragments at m/z 521 ($[^{Me}LAl(Se)SeH]^+$) and m/z 441 ($[^{Me}LAlSeH]^+$) were

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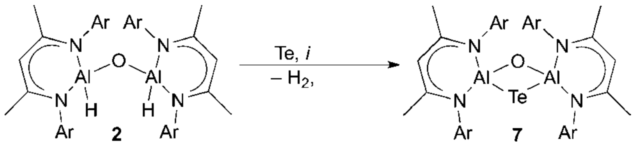
detected for **3**, while for **4** it was only possible to observe the peak corresponding to the $[^{Me}LAl{-}O{-}Al^{Me}L]^+$ fragment at *m*/*z* 737. Compound **3** is unstable in solution and undergoes cyclization reactions, leading to the cyclic four-membered compound $[\{^{Me}LAl(\mu\text{-}Se)\}_2]$ (**5**; Figure S1 in the Supporting Information, SI). This facile cyclization process prevented us from obtaining suitable crystals of **3** for X-ray diffraction studies.

On the basis of the results of the chalcogen insertion reaction into the Al−H bonds of **1** and **2**, the synthesis of the functionalized alumoxane $[\{^{Me}LAl(TeH)\}_2(\mu\text{-}O)]$ was intended by reacting compound **2** and elemental tellurium. Although compound **2** reacts readily with red selenium to yield **4**, the reaction with elemental tellurium does not proceed at ambient temperature. However, the addition of nBu_3P or heating (80 °C) promotes the reaction between **2** and metallic tellurium, leading to the unprecedented alumoxane **7** as the only product in 84% yield (Scheme 2). The ^1H NMR spectrum of **7** shows the characteristic signals corresponding to the ligand, and its formation was confirmed by the $[M]^+$ peak at *m*/*z* 866 in the MS-EI spectrum. Compound **7** is extremely moisture-sensitive and reacts readily with 2 equiv of water to yield $[\{^{Me}LAl(OH)\}_2(\mu\text{-}O)]$ and elemental tellurium as the only isolable products.

Scheme 2. Preparation of 7 (i = cationic nBu_3P or heat)



Yellow single crystals of **4** and deep-green crystals of **7** were grown from their saturated toluene solutions at −30 °C within several days. Furthermore, a saturated toluene solution of **3** gave colorless crystals of the cyclic compound **5**, which contains about 5% of impurity in the form of $[\{^{Me}LAl\}_2(\mu\text{-}Se)(\mu\text{-}Se_2)]$ (**6**). Compound **5** crystallizes in the triclinic space group $P\bar{1}$ with half of the molecule in the asymmetric unit (Figure S1 in the SI), while compound **4** crystallizes in the orthorhombic space group *Pccn*, with half of the molecule and one molecule of toluene in the asymmetric unit (Figure 1). Compound **7** crystallizes in the triclinic space group *P*1, with one molecule in the asymmetric unit (Figure 2). In all three compounds, the aluminum atom possesses a distorted tetrahedral geometry and is coordinated to two nitrogen atoms from the ligand. The remaining two coordination sites are occupied by two selenium atoms (**5**), selenium and oxygen atoms (**4**), or tellurium and oxygen atoms (**7**).

Furthermore, the Al−O−Al angle in **4** [141.7(2)°] is within the range of the previously reported alumoxanes $[\{^{Me}LAl(SH)\}_2(\mu\text{-}O)]$ [155.2(2)°] and $[^{Me}LAl(OH)]_2(\mu\text{-}O)$ [136.8(1)°],[3] which, in turn, are more obtuse than those observed for $[\{^{iPr}LAl(OH)\}_2(\mu\text{-}O)]$ (112.4°)[5] but significantly smaller than those reported for $[(tBu)_2Al(3,5\text{-}Me_2py)]_2(\mu\text{-}O)$ (180°; $3,5\text{-}Me_2py$ = 3,5-dimethylpyridine)[6] and $\{(tBu)_2Al[NH(Me)CH_2CH_2NMe_2]\}_2(\mu\text{-}O)$ (180°).[7]

The Al−O distances in **4** [1.693(1) Å] are comparable with those observed for $[\{^{Me}LAl(SH)\}_2(\mu\text{-}O)]$ (1.691 and 1.701 Å), $[\{^{Me}LAl(OH)\}_2(\mu\text{-}O)]$ [1.691(2) and 1.701(2) Å],[3] and $[\{^{iPr}LAl(OH)\}_2(\mu\text{-}O)]$ (1.698 and 1.694 Å).[5] The Al−Se bond length in **4** [2.370(1) Å] is comparable to those in $[\{^{iPr}LAl(SeH)\}_2(\mu\text{-}Se)]$ [2.375(2) and 2.371(2) Å] and slightly longer than those observed for the mononuclear compound $^{iPr}LAl(SeH)_2$ [2.331(3) and 2.340(3) Å].[4]

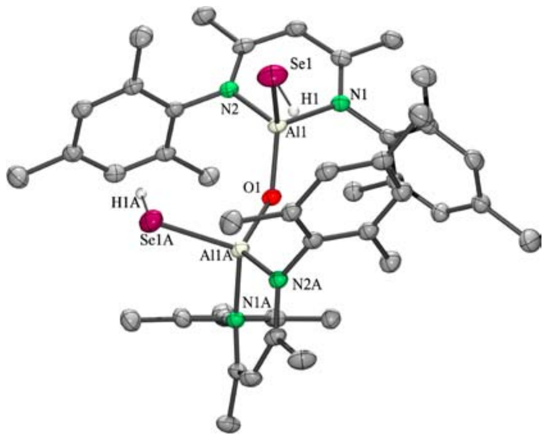


Figure 1. Molecular structure of **4**·2toluene (50% probability). Hydrogen atoms (except SeH) and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): Al1−O1 1.693(1), Al1−Se1 2.370(1), Al1−N1 1.897(2), Al1−N2 1.903(2), Se−H 1.14(4); Al1−O1−Al1a 141.7(2), O1−Al1−Se1 112.7(2).

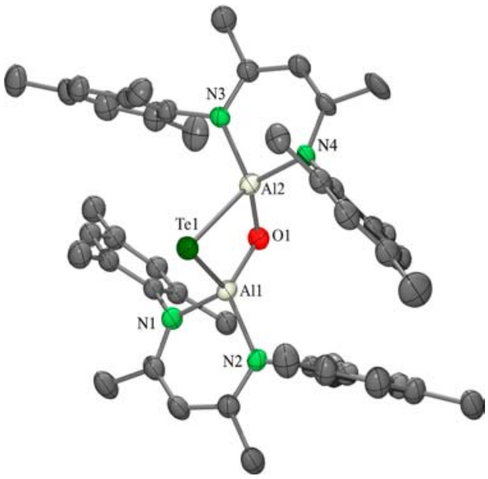


Figure 2. Molecular structure of **7** (50% probability). Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): Al1−O1 1.588(3), Al2−O1 1.735(3), Al1−Te1 2.629(1), Al2−Te1 2.712(1), Al1···Al2 2.717(1); Al1−O1−Al2 109.3(2), Al1−Te1−Al2 60.8(1).

The Al_2OTe ring in **7** is planar, and the presence of two different group 16 bridging atoms has clear consequences on its geometry. The Al−O bond distances for **7** [1.588(3) and 1.735(3) Å] are shorter than those observed for $[\{(^{iPr}LAl)(\mu\text{-}O)\}_2]$ (1.759 and 1.763 Å),[9] which is to some extent compensated for by the presence of two long Al−Te bonds [2.629(1) and 2.712(1) Å], thus lowering the ring strain. These Al−Te bonds are longer than those observed for $[\{(^{iPr}LAl)(\mu\text{-}Te)\}_2]$ (2.574 and 2.581 Å)[9] and $[RAl(\mu\text{-}Te)]_2$ [R = $N(SiMe_3)C(Ph)C(SiMe_3)_2$; 2.561 and 2.576 Å].[10] The Al−O−Al and Al−Te−Al angles also reflect the presence of oxygen and tellurium as bridging atoms in the four-membered ring. Whereas the Al−Te−Al angle in **7** [61.0(1)°] is significantly smaller that that in $[\{(^{iPr}LAl)(\mu\text{-}Te)\}_2]$ (82.1°),[9] the Al−O−Al angle is more obtuse [109.3(2)°] than that observed for $[\{(^{iPr}LAl)(\mu\text{-}O)\}_2]$ (89.1°).[8] The Al−O−Al angle in $[\{(^{iPr}LAl)\text{-}$

$(\mu\text{-O})\}_2]$ is unusually acute because of both the size of the bridging atoms and the high steric requirement of the $^{\mathrm{iPr}}$L ligand. In our case, the lower steric bulk of $^{\mathrm{Me}}$L may also play a role in the shortening of the Al−O bond lengths, thus resulting in a more obtuse Al−O−Al angle, which, in turn, relieves the ring strain to some extent.

In order to gain further insight into the bonding properties of the inorganic cores in **4** and **7**, the local and integrated properties[15] of the electron density in these compounds were calculated together with those in the related compounds $[\{^{\mathrm{Me}}\mathrm{LAl(EH)}\}_2(\mu\text{-O})]$ (E = O, S, Te).[16] A comparison of the data obtained from the calculated structure of $[\{^{\mathrm{Me}}\mathrm{LAl(TeH)}\}_2(\mu\text{-O})]$ and that of **7** allowed a better understanding of the influence of the ring strain on the electronic properties of the latter.

From the molecular graphs of **4** and **7** (Figures S4 and S5 in SI), it is possible to observe the set of bond paths corresponding to the Se−Al−O−Al−Se fragment and the $\mathrm{Al_2OTe}$ ring. In both cases, several C−H···O, C−H···E (E = Te, Se), and C−H···π interactions were observed, which help to stabilize the structure. On the basis of the properties of the bond critical points,[17,18] it is possible to determine the ionic order in the Al−E bonds: Al−O ≫ Al−Te(cyclic) > Al−S > Al−Se > Al−Te(acyclic) (Table S4 in the SI).

The atomic charges (q) in the E−Al−O−Al−E fragment of these compounds show tendencies related to the chalcogen atom E, as well as to the cyclic or acyclic nature of the compounds (Table S5 in the SI). The positive atomic charge of the aluminum atom decreases with an increase of the atomic number of E, as opposed to an increase of the negative charge of the bridging oxygen atom. On the other hand, the q(Te) in $[\{^{\mathrm{Me}}\mathrm{LAl(TeH)}\}_2(\mu\text{-O})]$ corresponds to −0.57, while that for the cyclic tellurium alumoxane **7** corresponds to −1.3, more than twice the value of that in the former. This can be rationalized in terms of the difference in the connectivity of the tellurium atoms in these compounds, specifically to the electronic demand that the two aluminum atoms in **7** exert on the tellurium atom.

In summary, a facile method was developed for preparation of the molecular hydrogenselenide **3** and the unique alumoxanes **4** and **7**. Furthermore, **3** and **4** can by useful synthons for the preparation of unusual heterobimetallic ring systems.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic procedure details for compounds **4**, **5**, and **7** (Table S1), details on the refinement of **5** (Table S2), space group assignment for **7** (Table S3), CIF format files for **4**, **5**, and **7**, detailed experimental procedures for compounds **3**, **4**, and **7** (Figures S1−S5), further details of the DFT computational studies (Tables S4 and S5), and the full ref 14. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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