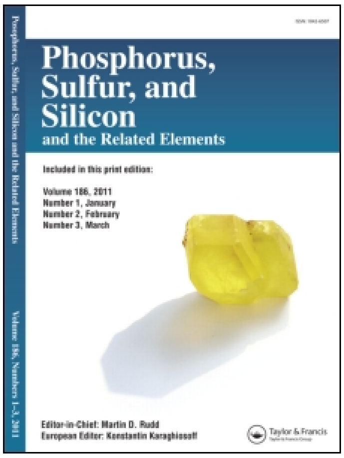

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THE FIRST ROTATIONAL ISOMERS OF STABLE SELENOBENZALDEHYDES AND THEIR η^1- TUNGSTEN COMPLEXES

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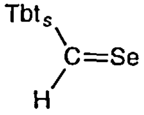
The first rotational isomers of stable selenoaldehydes are synthesized by deselenation of cyclic polyselenides having an efficient steric protection group, 2, 4, 6-tris[bis(trimetylsilyl)methyl]phenyl (Tbt). Reactions of these selenoaldehydes with $W(CO)_5\cdot THF$ gives the corresponding η^1-selenoaldehyde tungsten complexes, the structures of which are established by X-ray crystallography.

Keywords: selenoaldehyde; η^1-tungsten complex; rotational isomer; steric protection; X-ray crystallography

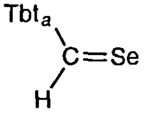
INTRODUCTION

Recently, many stable thiocarbonyl compounds have been synthesized by taking advantage of steric protection due to bulky substituents, and their chemistry has been extensively studied. However, the study of selenocarbonyl compounds has been limited because of their instability. Selenoaldehydes are particularly reactive because they have a hydrogen atom which cannot act either as an electronically stabilizing substituent or as a sterically protection group. Therefore, the chemistry of selenoaldehydes has scarcely been investigated.

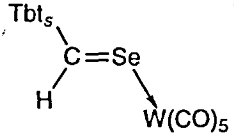
In this paper, we report the syntheses, structures, and reactions of the first rotational isomers of stable selenoaldehydes, 2, 4, 6-tris[bis(trimetylsilyl)methyl]selenobenzaldehydes (**1a**, **1b**), and their η^1-tungsten complexes (**2a**, **2b**).[1]



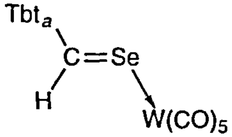
1a



1b

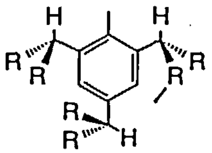


2a

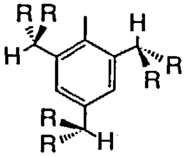


2b

Tbt$_s$ =



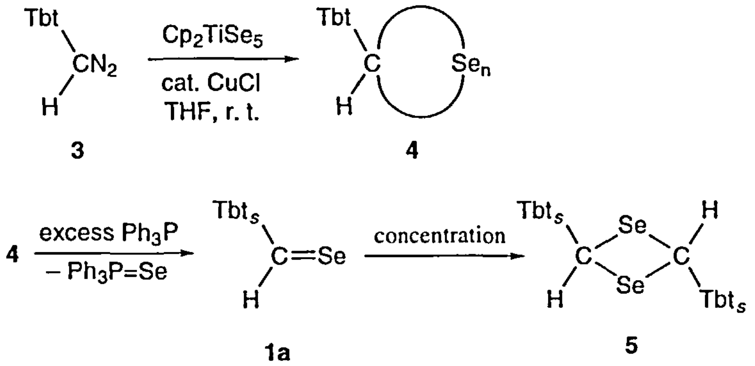
Tbt$_a$ =



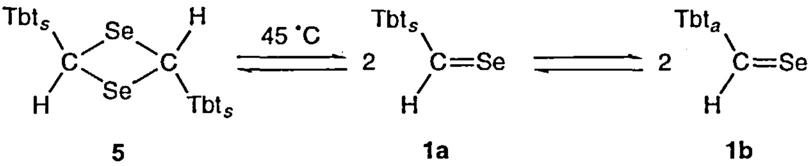
R = SiMe$_3$

RESULTS AND DISCUSSION

The reaction of diazomethane **3** with titanocene pentaselenide Cp_2TiSe_5 [2] in the presence of a catalytic amount of CuCl afforded a mixture of cyclic polyselenides, $TbtCHSe_n$ (**4**; n=5.1, 8%) along with some byproducts. When the polyselenides **4** were deselenized with triphenylphosphine in THF, a greenish-yellow solution of selenoaldehyde **1a** was obtained. This deselenation reaction of cyclic polyselenides represents a new synthetic method for a selenoaldehyde.

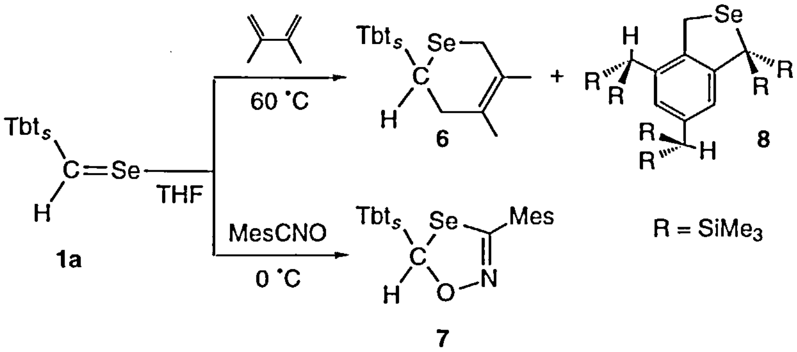


The concentration of the solution of **1a** resulted in the formation of the corresponding dimer **5** (79%), but heating of **5** in solution at 45 °C gave a greenish-yellow solution, the ^1H NMR spectrum of which indicated the formation of selenoaldehyde **1a** and its rotamer **1b** in the ratio of **5**:**1a**:**1b**=1:8:3. Concentration of the equilibrium mixture followed by separation by flash colum chromatography resulted in the isolation of **1b** (15%), although **1a** dimerized to form **5** (42%).



The conformations of **1a** and **1b** were confirmed by difference $^1H\{^1H\}$ nuclear Overhauser effect (NOE) experiments.

The selenoaldehyde **1a** synthesized by deselenation of **4** reacted with 2, 3-dimethyl-1, 3-butadiene and mesitonitrile oxide to afford the corresponding cycloadducts **6** (53%) (along with **8**, 29%) and **7** (60%), respectively.



Reaction of an equilibrium mixture of **1a**, **1b**, and **5** with $W(CO)_5$·THF afforded η^1-selenoaldehyde tungsten complex **2a** (59%) bearing Tbt$_s$ group, whereas treatment of the isolated **1b** with $W(CO)_5$·THF gave the corresponding tungsten complex **2b** (78%) bearing Tbt$_a$ group. Both **2a** and **2b** are stable deep-blue crystals and their structures were determined by X-ray crystallography. These are the first examples of X-ray crystallographic analysis of η^1-selenoaldehyde complexes.

Thermolysis (in benzene, 80°C) of **2a** resulted in the formation of a compound without metal coordination, benzoselenane **8** (58%), suggesting that the decomplexation into **1a** preceded the intramolecular cyclization. Reaction of **2a** with 2, 3-dimethyl-1, 3-butadiene in benzene at 70 °C also gave the cycloadduct **6** (60%). This is in sharp contrast with a reported fact that treatment of η^1-selenoaldehyde metal complexes with conjugated dienes gives the corresponding metal-coordinated cycloadducts resulting from reactions across the C=Se double bond.

References

[1] N. Takeda, N. Tokitoh, and R. Okazaki, *Angew. Chem., Int. Ed. Engl.* 35, 660 (1996); *Tetrahedron* 53, 12167 (1997).
[2] A. Shaver and J. M. McCall, *Organometallics* 3, 1823 (1984).