The First Rotational Isomers of Stable Selenoaldehydes and Their η^1-Tungsten Complexes**

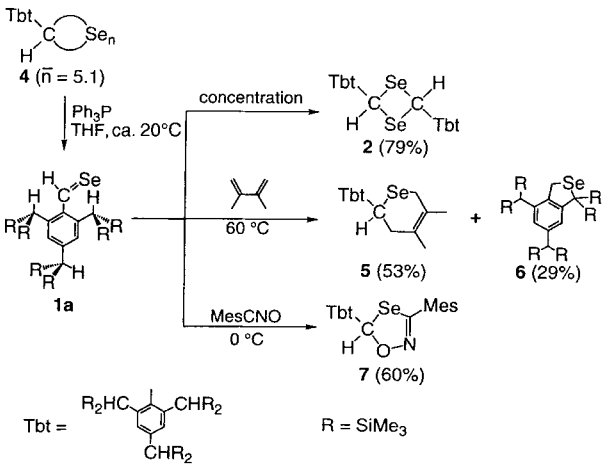
Nobuhiro Takeda, Norihiro Tokitoh, and Renji Okazaki*

In recent decades much attention has been paid to the chemistry of thiocarbonyl[1] and selenocarbonyl[2] compounds. Selenoaldehydes, however, have been very little explored because they are highly reactive and difficult to prepare. Some selenoaldehydes stabilized by mesomeric effects due to heteroatoms such as nitrogen and sulfur[3] or by coordination to transition metals[2, 4, 5] have been isolated. The only known stable, electronically unperturbed selenoaldehyde, 2,4,6-tri-*tert*-butylselenobenzaldehyde, is stabilized kinetically by a bulky substituent.[6] In addition, some transient selenoaldehydes have been reported.[7]

Recently, we succeeded in synthesizing rotational isomers of 2,4,6-tris[bis(trimethylsilyl)methyl]thiobenzaldehydes as stable compounds[8] by the desulfurization of the corresponding cyclic polysulfides TbtCHS$_n$ (n = 5, 8).[9] This synthesis takes advantage of an efficient steric protecting group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl, which we will refer to Tbt. We now report here on 1) the synthesis of stable selenoaldehydes **1a** and **1b** (the rotational isomer of **1a**), 2) an equilibrium among 1,3-diselenetane **2** and the seleoaldehydes **1a** and **1b**, and 3) the synthesis of η^1-selenoaldehyde complexes **3a** and **3b** and the structure of **3a**, the first η^1-selenoaldehyde complex characterized by X-ray crystallography.

Deselenation of cyclic polyselenide TbtCHSe$_n$ **4**[10] with excess triphenylphosphane at room temperature resulted in the formation of the corresponding selenoaldehyde **1a** (greenish yellow solution), which was identified based on its spectroscopic data (δ_H(CHSe) = 16.06, δ_C(CHSe) = 237.6, $^1J_{CH}$(CHSe) = 161.2 Hz, δ_{Se} = 2075, λ_{max} = 792 nm; Scheme 1, Table 1). This deselenation of cyclic polyselenides with a trivalent phosphorous reagent is a novel synthetic approach to selenocarbonyl compounds. The isolation of **1a** was unsuccessful; concentration of the reaction solution resulted in the complete conversion of **1a** into the head-to-tail dimer **2** (79%). Like reactive selenoaldehydes generated in situ,[7] **1a** reacted with 2,3-dimethyl-1,3-butadiene and mesitonitrile oxide to afford the corresponding cycloadducts **5** (53%) and **7**[12] (60%), respectively (Scheme 1). The formation of **5** and **7** indicates that **1a** still has a high reactivity toward these reagents in spite of its severe steric congestion, which prohibits its dimerization in a dilute solution for several hours. This is in sharp contrast to the fact that 2,4,6-tri-*tert*-butylselenobenzaldehyde is too crowded to produce the corresponding cycloadducts.[13]

When a solution of **2** was heated at 45 °C, the formation of **1a** and its isomer **1b** (rotation of the bis(trimethylsilyl)methyl (disyl) group at the 2-position[14]) was evident in the ^{1}H NMR and UV/Vis spectra (**2**:**1a**:**1b** = 1:8:3). In another experiment **1a** was trapped when **2** was treated with 2,3-dimethyl-1,3-butadiene at 60 °C giving the [4 + 2] cycloadduct **5** (81%) (Scheme 2). A few years ago Erker et al. reported a similar formation of monomeric selenobenzophenone from the corresponding 1,3-diselenetane, although the monomer was not isolated.[15] It is interesting that only **5**, which was formed from **1a**, was obtained in spite of the equilibrium among **1a**, **1b**, and **2**; this indicates that the two rotamers have different reactivities. Heating the solution at 100 °C in the absence of the trapping agent resulted in the quantitative formation of benzoselenolane **6**. The formation of **1b**, which was not observed in the deselenation at room temperature, suggests the occurrence of the thermal isomerization **1a** → **1b** in solution at 45 °C. Selenoaldehyde **1b** was isolated from the equilibrium mixture by flash column chromatography on silica gel at −20 °C under nitrogen atmosphere (Table 1). It is noteworthy that in **1b** the signal of the methine proton in one *o*-disyl group is at much lower field (δ = 5.87)



Scheme 1. Synthesis and reactions of selenoaldehyde **1a**.

Table 1. Selected spectroscopic data for compounds **1** and **3**. ^{1}H NMR: 500 MHz, $CDCl_3$, 27 °C, TMS; ^{13}C NMR: 125 MHz, $CDCl_3$, 27 °C, TMS; ^{77}Se NMR: 95 MHz, $CDCl_3$, 27 °C, Me_2Se; UV/Vis: hexane; IR: KBr.

1a: ^{1}H NMR: δ = 0.02 (s, 36H), 0.09 (s, 18H), 1.47 (s, 1H), 3.24 (s, 1H), 3.59 (s, 1H), 6.34 (s, 1H), 6.46 (s, 1H), 16.06 (s, 1H); ^{13}C NMR: δ = 0.4 (q), 0.7 (q), 24.9 (d), 25.4 (d), 33.0 (d), 237.6 (d, ^1J(C,H) = 161.2 Hz, C=Se); the signals of the aromatic C atoms could not be assigned due to overlap with signals from Ph_3P and Ph_3P=Se; ^{77}Se NMR: δ = 2075; UV/Vis: λ_{max} = 792 nm; HRMS (70 eV): *m/z* found: 644.2457, calcd for $C_{28}H_{60}Si_6{}^{80}Se$: 644.2476.

1b: m.p. 195–202 °C (decomp); ^{1}H NMR: δ = 0.00 (s, 18H), 0.06 (s, 18H), 0.08 (s, 18H), 1.48 (s, 1H), 1.75 (s, 1H), 5.87 (s, 1H), 6.37 (2 × s, 2H), 15.51 (s, 1H); ^{13}C NMR: δ = 0.4 (q), 0.5 (q), 1.0 (q), 22.2 (d), 33.4 (d), 35.3 (d), 127.0 (d), 131.0 (d), 141.7 (s), 150.8 (s), 151.7 (s), 152.5 (s), 233.2 (d, ^1J(C, H) = 156.5 Hz, C=Se); ^{77}Se NMR: δ = 1893; UV/Vis: $\lambda_{max}(\varepsilon)$ = 828 nm (38); HRMS (70 eV): *m/z* found: 644.2490, calcd for $C_{28}H_{60}Si_6{}^{80}Se$: 644.2476.

3a: deep blue crystals; m.p. 187–189 °C (decomp); ^{1}H NMR: δ = 0.05 (s, 18H), 0.07 (s, 18H), 0.10 (s, 18H), 1.55 (s, 1H), 3.14 (s, 1H), 3.36 (s, 1H), 6.38 (s, 1H), 6.49 (s, 1H), 13.97 (s, 1H); ^{13}C NMR: δ = 0.4 (q), 0.8 (q), 27.5 (d), 27.7 (d), 34.9 (d), 124.1 (d), 129.0 (d), 141.9 (s), 150.4 (s), 150.8 (s), 154.1 (s), 198.4 (s, ^1J(C,W) = 128.2 Hz, *cis*-CO), 202.1 (s, ^1J(C,W) = 160.2 Hz, *trans*-CO), 227.4 (d, ^1J(C,H) = 162.0 Hz, C=Se); ^{77}Se NMR: δ = 1184; UV/Vis: λ_{max} (ε) = 603 nm (18000); IR: $\tilde{\nu}$ = 2061, 1931, 1908 cm^{-1} (C=O); HRMS (70 eV): *m/z* found: 968.1708, calcd for $C_{33}H_{60}O_5Si_6{}^{80}SeW$: 968.1731.

3b: deep blue crystals; m.p. 171–172 °C (decomp); ^{1}H NMR: δ = 0.04 (s, 18H), 0.08 (s, 18H), 0.11 (s, 18H), 1.52 (s, 1H), 1.80 (s, 1H), 4.69 (s, 1H), 6.37 (s, 1H), 6.40 (s, 1H), 13.33 (s, 1H); ^{13}C NMR: δ = 0.5 (q), 0.8 (q), 1.3 (q), 25.8 (d), 34.3 (d), 35.9 (d), 127.7 (d), 130.9 (d), 142.5 (s), 150.0 (s), 150.8 (s), 152.0 (s), 198.1 (s, ^1J(C,W) = 127.2 Hz, *cis*-CO), 201.9 (s, *trans*-CO), 224.0 (d, ^1J(C,H) = 166.2 Hz, C=Se); ^{77}Se NMR: δ = 1162; UV/Vis: λ_{max} (ε) = 595 nm (21000); IR: $\tilde{\nu}$ = 2066, 1986, 1947, 1929, 1911, 1895 cm^{-1} (C=O).

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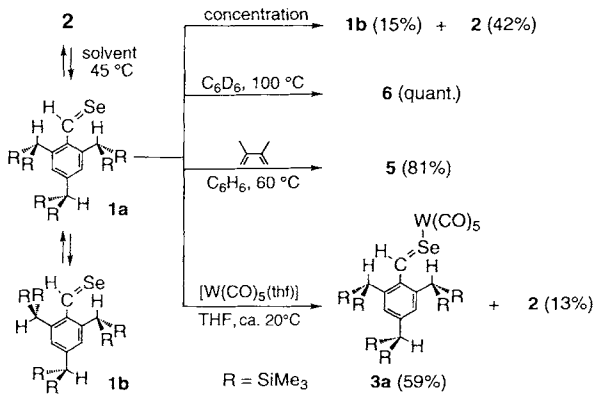


Scheme 2. Synthesis of selenoaldehydes **1a** and **1b** from 1,3-diselenetane **2**.

than that of the other ($\delta = 1.75$). This can be explained by the strong anisotropic effect of the C=Se bond, which is directed toward the methine hydrogen in the former *o*-disyl group in order to avoid steric interactions with the trimethylsilyl groups of the latter *o*-disyl group. In the solid state **1b** is stable even in air, whereas in solution it slowly isomerizes at room temperature to give **1a**, which then dimerizes to afford **2** as a precipitate. The higher stability of **1b** as a monomer indicates that the *o*-disyl groups of **1b** prevent the dimerization of the selenoformyl group more efficiently than those of **1a**; in **1b** one of the *o*-disyl groups is rotated in such a way that the bulky trimethylsilyl groups face the selenoformyl group.

The reaction of **1a**, generated from **2**, with $[W(CO)_5(thf)]$ gave the corresponding η^1-selenoaldehyde tungsten complex **3a** as stable, deep blue crystals (Scheme 2, Table 1). The structure of **3a** was established by X-ray crystallographic analysis (Fig. 1).[16] Although some η^1-selenoaldehyde complexes have

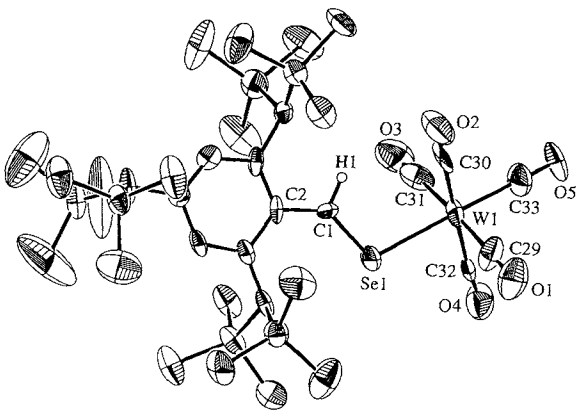
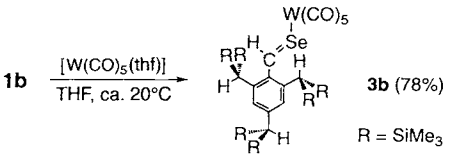


Fig. 1. X-ray crystal structure of **3a** (ORTEP drawing with thermal ellipsoids at 30% probability for non-hydrogen atoms). Selected bond lengths [Å] and angles [°]: C1–Se1 1.783(15), C1–C2 1.44(2), W1–Se1 2.638(2), W1–C29 1.95(2), W1–C30 1.97(2), W1–C31 1.93(2), W1–C32 2.02(2), W1–C33 2.01(2), O1–C29 1.19(2), O2–C30 1.14(2), O3–C31 1.17(2), O4–C32 1.17(2), O5–C33 1.13(2); Se1-C1-C2 136(1), W1-Se1-C1 107.8(4), Se1-W1-C29 87.8(6), Se1-W1-C30 91.4(5), Se1-W1-C31 89.2(6), Se1-W1-C32 89.8(5), Se1-W1-C33 178.9(6).

been synthesized,[4] this is the first to be characterized by X-ray structure analysis. The C–Se bond in **3a** (1.783(15) Å) is significantly shorter than a C–Se single bond (1.970 Å)[17] and the C–Se bond in pentacarbonyl(η^2-selenobenzaldehyde)tungsten (1.864 Å),[4a] and rather close to the length of the C–Se double bond in selenoketones (1,5-dimethyl-3,7-dithiabicyclo[3.3.1]-nonaneselone: 1.774 Å,[18] 4,4′-dimethoxyselenobenzophenone: 1.790 Å[19]). This result indicates weak coordination of the selenoformyl group to the metal in **3a**.

The rotational isomer **1b** was also treated with $[W(CO)_5(thf)]$ to afford the corresponding η^1-selenoaldehyde tungsten complex **3b** [Eq. (a)], which showed satisfactory spectral data



(a)

(Table 1). Complex **3b** is stable in the solid state even in air; however, in solution, it isomerized almost completely to **3a** over several days. This is probably because repulsion between the $[W(CO)_5]$ moiety and the trimethylsilyl groups makes **3b** less stable than **3a**, which does not have such repulsion. It is interesting that as free selenoaldehydes **1b** is isolable but **1a** is not, whereas both complexes **3a** and **3b** are isolable, but **3a** is much more stable than **3b**.

Experimental Procedure

1a, 2: A solution of **4** (26.2 mg, 0.0273 mmol) in THF (10 mL) was added dropwise over 5 min to a solution of Ph_3P (36.7 mg, 0.140 mmol) in THF (5 mL) at room temperature. After stirring for 45 min, the resulting greenish yellow solution containing **1a** was concentrated to dryness under reduced pressure. Distilled hexane (5 mL) was added to the residue and evaporated to remove remaining THF. After hexane (5 mL) was added and evaporated again, a small amount of benzene was added to the pale yellow residue, and insoluble **2** (13.8 mg, 0.0107 mmol, 79%) was removed by filtration. The filtrate was concentrated to dryness, hexane was added to the residue, and insoluble $Ph_3P=Se$ (35.7 mg, 0.105 mmol, 94%) was removed by filtration. The NMR and UV/Vis spectra of **1a** were recorded after the reaction had been performed in $CDCl_3$ and hexane, respectively.

1b: When a suspension of **2** (31.2 mg, 0.0242 mmol) in THF (25 mL) was heated at 45 °C for 17 h under an argon atmosphere, the reaction mixture turned greenish yellow. After evaporation of the solvent, degassed pentane was added to the residue and evaporated to remove the remaining THF. The residue was again dissolved in pentane and insoluble material was filtered off under argon. The filtrate was purified by flash column chromatography (SiO_2, pentane, at −20 °C under nitrogen) to afford **1b** (4.7 mg, 0.0073 mmol, 15%) as a greenish yellow powder. All other fractions were combined and dissolved in hexane, and then insoluble **2** (17.0 mg, 0.0132 mmol, 54%) was recovered by filtration.

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[16] Crystallographic data for **3a**: $C_{33}H_{60}O_5SeSi_6W$, $M = 968.16$, triclinic, space group $P\bar{1}$, $a = 12.859(3)$, $b = 16.680(7)$, $c = 11.748(6)$ Å, $\alpha = 107.67(3)$, $\beta = 97.32(3)$, $\gamma = 95.50(3)^\circ$, $V = 2357(1)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.364$ g cm^{-3}, $\mu = 34.09$ cm^{-1}. The final cycle of full-matrix least-squares refinement was based on 2776 observed reflections [$I < 3.00\sigma(I)$] and 415 variable parameters with R (R_w) = 0.054 (0.032). Further details of the crystal structure investigation may be obtained from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB2 1EZ (UK), on quoting the full journal citation.

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Enantioselective Cycloisomerization of 1,6-Enynes Catalyzed by Chiral Diphosphane–Palladium Complexes

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The cycloisomerization of 1,6-enynes in the presence of Pd^0, acetic acid, and phosphane ligands reported by Trost opened elegant pathways to 1,3- and 1,4-dienes, which are difficult to produce using other methods. 1,3-Dienes with exocyclic double bonds are suitable for Diels–Alder reactions.[1, 2] Of particular interest is the formation of the Alder–ene type 1,4-diene, since the construction of a stereogenic center offers an economical access to optically active five-membered carbo- and heterocycles, which occur abundantly in natural products. To date, only two examples of asymmetric induction have been reported utilizing 1) optically active carboxylic acids in conjunction with Pd^0[3] and 2) chiral phosphanes for the double stereodifferentiation of optically active substrates.[4] We now demonstrate that chiral diphosphane–Pd complexes effectively catalyze this interesting cycloisomerization, furnishing 1,4-dienes in medium to high enantioselectivities.

Although phosphane ligands reduce the rate of the cyclization, they are crucial for smooth conversion and for minimizing side reactions. Pd complexes with (*S,S*)-(*R,R*)-TRAP ligands **4**[5] were found to be particularly effective for the cyclization of **1a** (R = SiMe$_3$) at room temperature [Eq. (a), Table 1]. In-

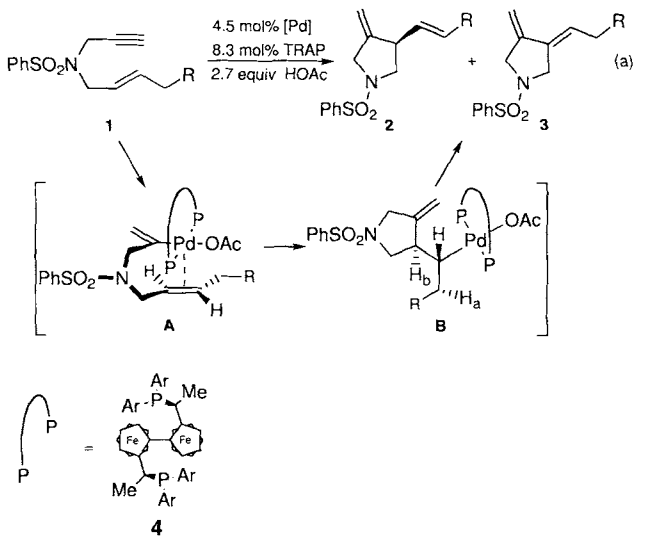

Table 1. Enantioselective cycloisomerization of 1,6-enynes **1a** (R = SiMe$_3$) catalyzed by TRAP–palladium complexes [a].

Entry	TRAP **4** (Ar) [b]	Product **2a** Yield [%] [c]	*ee* [%] [d]	Config. [e]
1	**4a** (C_6H_5)	77	36	(*R*)
2	**4b** (*p*-$CH_3OC_6H_4$)	71	34	(*R*)
3	**4c** (*p*-ClC_6H_4)	66	41	(*R*)
4	**4d** (*p*-FC_6H_4)	70	40	(*R*)
5	**4e** (*p*-$F_3CC_6H_4$)	72	48	(*R*)
		66 [f]	58 [f]	(*R*) [f]
		24 [g]	76 [g]	(*R*) [g]
6	**4f** (*m*-$F_3CC_6H_4$)	61	10	(*R*)
7	**4g** (3,5-$(CF_3)_2C_6H_3$)	60	10	(*R*)
8	**4h** (2-furyl)	76	4	(*R*)

[a] Reactions were carried out in benzene at 40 °C for 5 h; **1a**:[$Pd_2(dba)_3$]·$CHCl_3$:**4**:HOAc = 100:2.25:8.3:180. [b] (*S,S*)-(*R,R*)-configurated TRAPs were used. [c] Yield after purification by chromatography. [d] Determined by HPLC with Chiralcel OJ. [e] Assigned based on elution behavior on chiral HPLC analogous to that of **2e** (Table 2, entry 5). [f] 25 °C for 12 h. [g] 0 °C for 24 h with 2.7 equiv of acetic acid; starting material was recovered.

creasing the electron-withdrawing ability of the ligand P-aryl substituents (**4a**, **4b** < **4c**, **4d** < **4e**) resulted in higher selectivities and also higher reactivities. With **4e** cyclization occurred even at 0 °C (76% *ee*, 24% yield), whereas the reaction with **4a** did not occur at this temperature. On the other hand, ligands **4f–h** did not lead to better results. For the *meta*-substituted TRAPs **4f** and **4g**, steric bulk is assumed to account for these

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