

Syntheses, Structures, and Reactions of the First Rotational Isomers of Stable Selenobenzaldehydes, 2,4,6-Tris[bis(trimethylsilyl)methyl]selenobenzaldehydes, and Their η^1 -Tungsten Complexes

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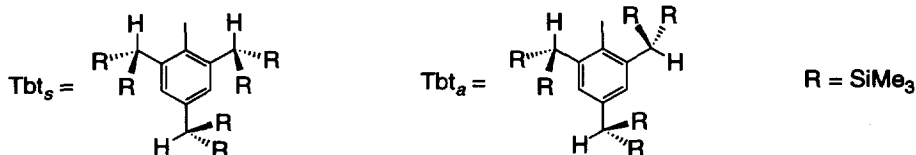
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Abstract: Deselenation of a cyclic polyselenide mixture, $\text{Tbt}_n\text{CHSe}_n$ **5**, resulted in the formation of Tbt_nCHSe **3a**, which gave its head-to-tail dimer **12** upon concentration of the reaction solution although it was stable in a dilute solution. Thermolysis of **12** gave an equilibrium mixture of **12**, **3a**, and its rotational isomer Tbt_nCHSe **3b**, and **3b** was isolated as a solid stable even in air. Reaction of **3a** and **3b** with $\text{W(CO)}_5 \cdot \text{THF}$ gave the corresponding η^1 -selenoaldehyde tungsten complexes **4a** and **4b**, respectively. Some reactions of **4a** were carried out to give products accompanied by decomplexation.
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INTRODUCTION

Carbonyl compounds play a very important role in organic chemistry. In contrast, the chemistry of thio- and selenocarbonyl compounds, which are sulfur and selenium analogs of carbonyl compounds, has been relatively less explored because they are highly reactive and usually undergo oligomerization or polymerization. In the past decades the synthesis of many stable thiocarbonyl compounds has been realized by taking advantage of the steric protection due to bulky substituents, and their chemistry has been extensively studied.¹ However, the study of selenocarbonyl compounds has been limited² because of their instability resulting from the small overlap between the 2p-orbitals of carbon and the 4p-orbitals of selenium. Selenoaldehydes are particularly reactive because they have a hydrogen atom which cannot act either as an electronically stabilizing substituent or as a sterically protecting group. Therefore, the chemistry of selenoaldehydes has scarcely been investigated. Some electronically stabilized selenoaldehydes have been isolated by taking advantage of mesomeric effects due to heteroatoms such as nitrogen and sulfur³ or coordination to the transition metals.^{2,4,5} As for electronically unperturbed selenoaldehydes, the only stable selenoaldehyde, 2,4,6-tri-*tert*-butylselenobenzaldehyde (**1**),⁶ has been isolated by kinetic stabilization due to a bulky substituent, although some selenoaldehydes have been reported as a transient species.⁷

Recently, we have succeeded in the synthesis of stable thiobenzaldehydes, TbtCHS (**2a** and **2b**; Tbt : 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl),⁸ via desulfurization of the corresponding cyclic polysulfides, TbtCHS_n ($n=5$ or 8),⁹ by taking advantage of the Tbt group which is an efficient steric protecting group.¹⁰ As shown below, the two *o*-bis(trimethylsilyl)methyl (disyl) groups of **2a** are symmetrical with regard to the thioformyl group (denoted as Tbt_s in this paper), while those of **2b** are asymmetric (denoted as Tbt_a in this paper). These rotational isomers due to rotation of the disyl group undergo thermal interconversion and the kinetic studies on the conversion of **2a** to **2b** revealed that **2a** is thermodynamically more stable than **2b**. Competitive reactions



between them showed that **2b** is kinetically more stable than **2a**. We became interested in the synthesis of isomeric selenobenzaldehydes bearing Tbt₁ and Tbt₂ groups, and preliminarily reported the syntheses and some reactions of the first rotational isomers of 2,4,6-tris[bis(trimethylsilyl)methyl]selenobenzaldehyde (**3a** and **3b**) and their η^1 -tungsten complexes (**4a** and **4b**).¹¹ In this paper, we report a detailed account of the syntheses, structures and reactions of selenobenzaldehydes **3a** and **3b** and their η^1 -tungsten complexes **4a** and **4b**.

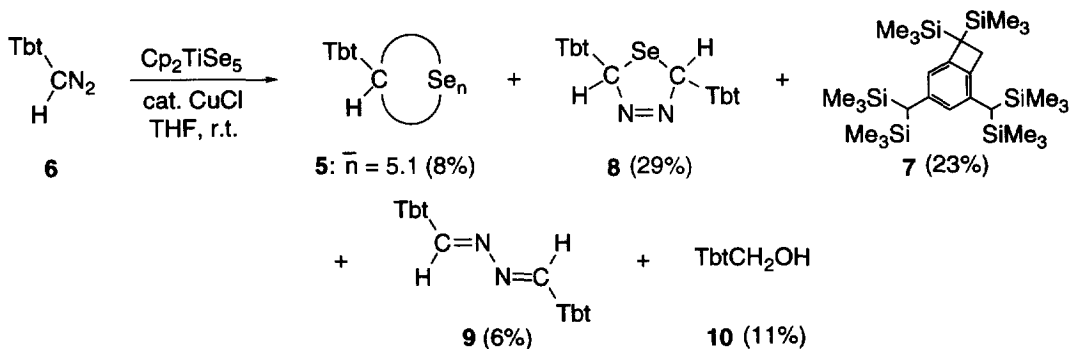
RESULTS AND DISCUSSION

Synthesis of a Mixture of Cyclic Polyselenides **5**

Few studies on cyclic polyselenides have been reported,¹² although many cyclic polysulfides have been synthesized in view of their unique physical and chemical properties as well as their biological activities.¹³ As for cyclic polyselenides containing one carbon atom in the polyselenide ring, only [(Ph₃P)₂N][Se₅C(Se)COMe] having a CSe₅ ring has been reported.^{12c}

Since the cyclic polysulfide, TbtCHS₈, is readily synthesized by the thermal reaction of Tbt-substituted diazomethane **6** with elemental sulfur,⁹ we first attempted the synthesis of a cyclic polyselenide bearing a Tbt group by this method. Diazomethane **6** was added dropwise to a refluxing benzene suspension of elemental selenium to afford only benzocyclobutene **7**, which was undoubtedly formed by an intramolecular C-H insertion of a carbene, TbtCH:, generated from **6** toward the *o*-disyl group. Because the insolubility of elemental selenium was considered to be responsible for the absence of products containing selenium in this reaction, we decided to use titanocene pentaselenide Cp₂TiSe₅¹⁴ instead of elemental selenium as a relatively soluble selenium source.

When diazomethane **6** was treated with Cp₂TiSe₅ in THF at room temperature in the presence of a catalytic amount of cuprous chloride, a mixture of cyclic polyselenides, TbtCHSe_n (**5**; *n* = 5.1), was obtained as an inseparable mixture together with selenadiazoline **8**, benzocyclobutene **7**, azine **9**, and alcohol **10**. The average number of selenium (*n*) in **5** was determined by elemental analysis.

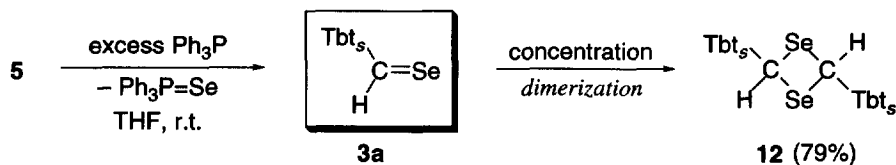


When the cyclic polyselenide mixture **5**, which was separated from compounds bearing two or more Tbt groups by gel permeation liquid chromatography (GLPC), was subjected to GLPC again, surprisingly, a small amount of a mixture of cyclic polyselenides bearing two and three Tbt groups, (-Se_n-(Tbt)CH-Se_m)_x (*x* = 2 or 3), **11** was obtained. The mixture **11** was also chromatographed (GLPC) to give the monomeric cyclic polyselenides, TbtCHSe_n, together with **11**. These results suggest an equilibrium between TbtCHSe_n and **11** in solution. The cyclic polyselenide mixture **5** is referred to as TbtCHSe_n in this paper for convenience, although **5** is considered to be the equilibrium mixture.

Desulfurization of TbtCHS₈ using three equivalents of triphenylphosphine resulted in the convergence of the number of sulfur to give pentathiane, TbtCHS₅.⁹ On the other hand, reaction of **5** with an equivalent of triphenylphosphine did not give a cyclic polyselenide with a definite number of selenium, but yielded **5** (17%) and a complex mixture of compounds bearing two and three Tbt groups. Further heating of **5** at 110 °C effected no change in the products, judging from ¹H NMR.

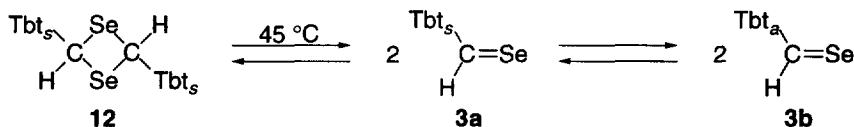
Syntheses of Stable Selenoaldehydes **3a** and **3b**

As in the case of the synthesis of the thioaldehydes **2a**, **b**,⁸ deselenation of the cyclic polyselenide mixture **5** with an excess amount of triphenylphosphine at room temperature resulted in the formation of the corresponding selenoaldehyde **3a** (greenish-yellow solution). The structure of **3a** was confirmed by its



spectroscopic data, which will be discussed later in detail. Since **5** is considered to have a Tbt_s form as in the case of TbtCHS₈,⁹ the formation of Tbt_sCHSe (**3a**) alone without Tbt_aCHSe (**3b**) in this reaction is probably due to the absence of the rotational isomerization of the Tbt_s form to the Tbt_a form throughout this reaction at room temperature. This deselenation of cyclic polyselenides with a trivalent phosphorus reagent is noteworthy as a novel synthetic approach to selenocarbonyl compounds. When the reaction mixture was allowed to stand at room temperature, 1,3-diselenetane **12**,¹⁵ a head-to-tail dimerization product of **3a**, was gradually formed as insoluble precipitates. Since concentration of this mixture led to the complete conversion of **3a** into **12** (79%), the isolation of **3a** was unsuccessful.

Heating of **12** in a THF or C₆D₆ solution at 45 °C gave a greenish-yellow solution, the ¹H NMR spectrum of which indicated the formation of selenoaldehyde **3a** and its rotamer **3b** in the ratio of **12** : **3a** : **3b** = 1 : 8 : 3.



The formation of **3b**, which was not observed in the deselenation of **5** at room temperature, suggests the occurrence of the thermal isomerization of **3a** to **3b** in solution at 45 °C. When the equilibrium mixture was concentrated and separated by flash column chromatography on silica gel at -20 °C under nitrogen atmosphere, **3b** was isolated as a stable monomeric selenoaldehyde in 15% yield, although **3a** dimerized to form **12** (42%). Selenoaldehyde **3b** showed satisfactory spectral data, which will be discussed later in detail. Erker *et al.* recently reported a similar formation of monomeric selenobenzophenone from the corresponding 1,3-diselenetane, although the monomer was not isolated.¹⁶ In the solid state **3b** is stable even in open air, while in solution it slowly isomerizes at room temperature to give **3a**, which then dimerizes to yield **12** as precipitates. The higher stability of **3b** than **3a** as a monomer is explained by the more efficient steric protection of the selenoformyl group by the Tbt_a group, where one of the *o*-disyl groups is rotated in such a way that the bulky trimethylsilyl groups face the selenoformyl group.

Structures of Rotational Isomers of Selenoaldehydes **3a** and **3b** in Solution

The spectral data of **3a** and **3b** are shown in Table 1 together with those of Mes*CHSe (1: Mes* = 2,4,6-tri-*tert*-butylphenyl).

Comparison of the spectral data for selenoaldehydes **1**, **3a**, and **3b** shows a tendency similar to that observed for Mes*CHS (**13**), Tbt_sCHS (**2a**), and Tbt_aCHS (**2b**).⁸ In the order of **1**, **3a**, and **3b**, the selenoformyl signals in the ¹H, ¹³C, and ⁷⁷Se NMR spectra shift to a higher field and λ_{max} identified as an n-π* transition in the UV/vis spectra becomes red-shifted. The coupling constant between the selenoformyl proton and its carbon-13, ¹J_{CH}, which is proportional to the s-character of the C-H bond, is larger for **3a** than for **3b**. These comparisons suggest that the conjugation between the selenoformyl group and the benzene ring in these three selenoaldehydes becomes larger in the order of **1**, **3a**, and **3b** in solution. A similar tendency was observed for thiobenzaldehydes **13**, **2a**, and **2b** from their NMR spectra and X-ray structural analysis.⁸

Table 1. The Spectral Data of Selenoaldehydes **1**, **3a**, and **3b** and Their Complexes **4a** and **4b**

		RCH=Se			RCH=Se·W(CO) ₅	
		1 ¹⁷ R=Mes*	3a R=Tbt ₃	3b R=Tbt ₂	4a R=Tbt ₃	4b R=Tbt ₂
δ _H	(CH=Se) (<i>o</i> -methine)	17.38	16.06	15.51	13.97	13.33
δ _C	(CH=Se) (cis-CO) (trans-CO)	258.2	3.24, 3.59 237.6	1.75, 5.87 233.2	3.14, 3.36 227.4 198.4	1.80, 4.69 224.0 198.1
δ _{Se}		2398	2075	1893	1184	1162
¹ J _{CH/Hz}	(CH=Se)		161.2	156.5	162.0	166.2
¹ J _{Cw/Hz}	(cis-CO) (trans-CO)				128.2 160.2	127.2
UV-vis/nm		722 (ε 42) 758 (ε 39)	792 (ε 50)	828 (ε 38)	603 (ε 18000)	595 (ε 21000)

It is noteworthy that the methine proton in one *o*-disyl group of **3b** resonates at a much lower field (δ = 5.87) than that in another *o*-disyl group of **3b** does (δ = 1.75). This lower-field shift can be explained by the strong anisotropic effect of the C=Se double bond which is directed toward the methine hydrogen in the former *o*-disyl group. An analogous lower-field shift was also observed for **2b**.⁸

The conformations of the isomeric selenoaldehydes **3a** and **3b** in solution were confirmed by difference ¹H{¹H} nuclear Overhauser effect (NOE) experiments (Figure 1) as in the case of thioaldehydes **2a** and **2b**.⁸

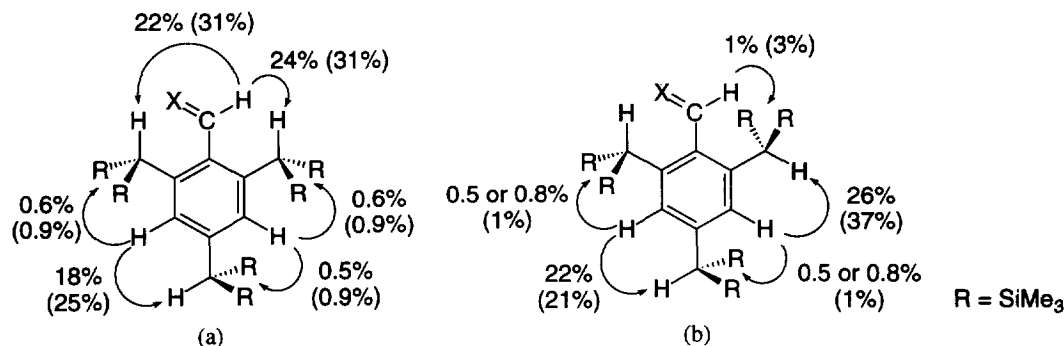


Figure 1. Schematic representation of the observed NOEs (270 MHz, CDCl₃, 25 °C): (a) **3a** (X = Se) and **4a** (X = Se·W(CO)₅; the values are in parentheses) and (b) **3b** (X = Se) and **4b** (X = Se·W(CO)₅; the values are in parentheses).

The equilibrium mixture of **3a**, **3b** and **12** was used for the NOE experiments of **3a**. As shown in Figure 1, irradiation of the aromatic protons (δ = 6.34, 6.46) of **3a**, which are equivalent on the time scale of the NOE experiments, resulted in the enhancement at the methyl protons of the trimethylsilyl groups (δ = 0.02, 0.09) and the methine proton of the *p*-disyl group (δ = 1.47). When the selenoformyl proton (δ = 16.06) of **3a** was irradiated, the NOEs were observed at the methine protons of the *o*-disyl groups (δ = 3.24, 3.59). These difference NOEs observed for **3a** strongly suggest that the molecular structure of **3a** in solution is a Tbt₃ form. The selenoformyl group of **3a** is considered to rotate freely, because the free rotation of the thioformyl group of **2a** has been suggested by the NOE experiments at -60 °C.⁸

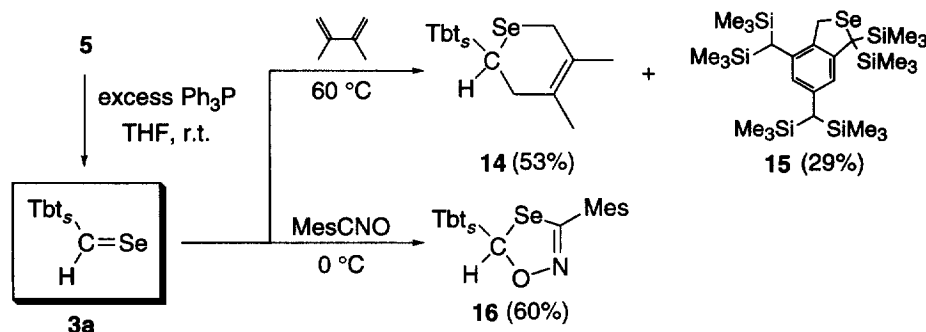
Irradiation of the aromatic protons (δ = 6.37) in **3b** causes NOEs at the methine protons of *p*- (δ = 1.48) and one *o*-disyl group (δ = 1.75) and the methyl protons of *p*- and *o*-trimethylsilyl groups (δ = 0.00, 0.08). The

selenoformyl proton ($\delta = 15.51$) was irradiated to enhance only the signal of the methyl protons of the *o*-trimethylsilyl groups ($\delta = 0.06$). The observed difference NOEs for **3b** and the absence of enhancement of NOEs between the selenoformyl proton and the methine protons of the *o*-disyl groups in **3b** strongly suggest that, in solution, **3b** has a Tbt_o group and the selenium atom of the selenoformyl group is placed toward the methine proton of the *o*-disyl group in the most stable conformation.

Thus, it has been revealed that selenoaldehydes **3a** and **3b** have structures similar to those of the corresponding thioaldehydes **2a** and **2b**,⁸ respectively.

Reactions of Stable Selenoaldehydes **3a** and **3b**

As in the case of reactive selenoaldehydes generated in situ,⁷ the stable selenoaldehyde **3a** generated by the deselenation of **5** reacted with 2,3-dimethyl-1,3-butadiene and mesitronitrile oxide to afford the corresponding cycloadducts **14**¹⁵ (53%) and **16**¹⁵ (60%), respectively. The formation of **14** and **16** indicates that **3a** still has a

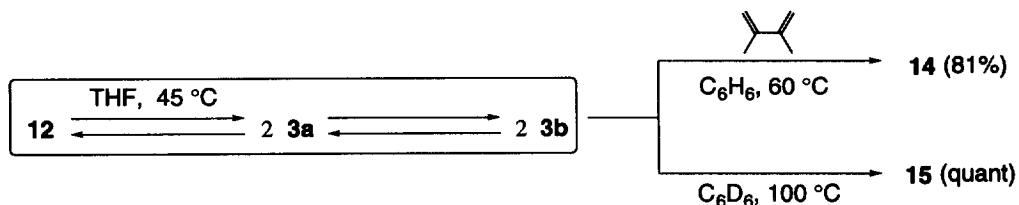


high reactivity toward these reagents in spite of its severe steric congestion which retards its dimerization in dilute solution for several hours. In sharp contrast to these results, 2,4,6-tri-*tert*-butylselenobenzaldehyde (**1**) is too crowded to react with 2,3-dimethyl-1,3-butadiene.¹⁸ Furthermore, in the reaction of **1** with mesitronitrile oxide, the corresponding [2+3] adduct can not exist as a stable compound in solution at room temperature because of the presence of two overcrowded substituents, leading to decomposition to Mes*CHO and MesNCSe.¹⁸

As for the formation of **15** in the reaction with 2,3-dimethyl-1,3-butadiene, a similar intramolecular cyclization has been reported in the thermolysis of 2,4,6-tri-*tert*-butylselenobenzaldehyde (**1**),⁶ 2,4,6-tri-*tert*-butylthiobenzaldehyde (**13**),¹⁷ and thioaldehyde **2a**.⁸ A radical mechanism has been proposed for the intramolecular cyclization in the thermolysis of **13** on the basis of a kinetic study which showed a second or third order rate profile with regard to **13**.¹⁷ The formation of **15** is considered to be explained similarly in terms of such a radical mechanism.

Oxaselenazole **16** gradually decomposed to give the corresponding aldehyde, TbtCHO and MesNCSe in solution at room temperature. A similar reaction has been reported in the thermolysis of an oxathiazole.¹⁹

Reaction of the equilibrium mixture of **3a**, **3b**, and **12** with 2,3-dimethyl-1,3-butadiene at 60 °C resulted in the production of [4 + 2] cycloadduct **14** (81%). It is interesting that only **14**, which was formed from **3a**, was obtained in spite of the equilibrium among **3a**, **3b**, and **12**, indicating the difference in reactivities between the

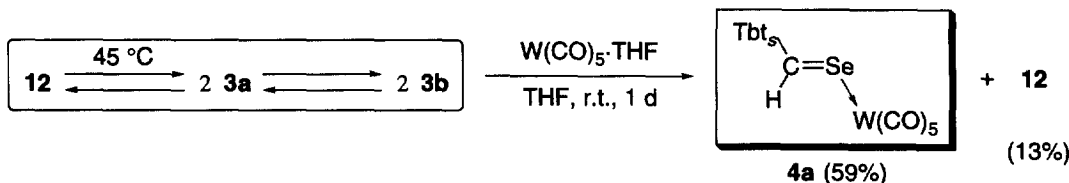


two rotamers. Heating the solution at 100 °C in the absence of the trapping agent resulted in a quantitative formation of benzoselenolane **15**.

Synthesis of η^1 -Selenoaldehyde Tungsten Complexes **4a** and **4b**

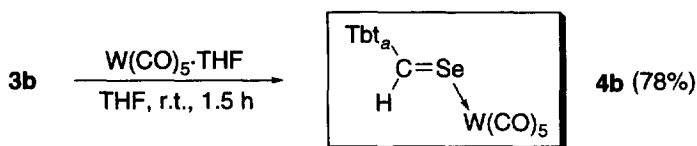
Since selenoketone complexes are usually synthesized by reaction of selenocarbonyl compounds with some transition metal carbonyl complexes,^{2,4e,20} attempts at the synthesis of the selenoaldehyde complexes were carried out using reactions of the selenoaldehydes **3a**, **b** with $W(CO)_5 \cdot THF$.

When an equilibrium mixture of selenoaldehydes **3a**, **b** and diselenetane **12** was allowed to react with $W(CO)_5 \cdot THF$ at room temperature for 1 day, only the corresponding η^1 -selenoaldehyde tungsten complex bearing Tbt_s group **4a** (59%) was obtained as stable deep-blue crystals. The lack of the corresponding selenoaldehyde tungsten complex bearing Tbt_a group **4b** suggests that an equilibrium between **4a** and **4b** lies to



the side of **4a**. The structure of **4a** was established by the spectral data and X-ray crystallographic analysis which will be discussed later. The complex **4a** was stable in solution at room temperature for several hours even in air.

Treatment of the isolated rotational isomer of selenoaldehyde **3b** with $W(CO)_5 \cdot THF$ afforded the corresponding η^1 -selenoaldehyde tungsten complex **4b** in 78% yield, which showed satisfactory spectral data. The structure of **4b** was definitively confirmed by X-ray crystallographic analysis (*vide infra*).



The complex **4b** was stable in the solid state even in air, although in solution it isomerized almost completely to **4a** at room temperature over several days. This is probably because the repulsion between the $W(CO)_5$ moiety and the trimethylsilyl groups makes **4b** less stable than **4a** which does not suffer from such repulsion. This also explains why **4b** was not formed in the reaction of the equilibrium mixture with $W(CO)_5 \cdot THF$ as mentioned above.

Structures of Rotational Isomers of η^1 -Selenoaldehydes Tungsten Complexes **4a** and **4b** in Solution

The 1H , ^{13}C , and ^{77}Se NMR spectra of **4a** and **4b** (Table 1) showed the signals due to the selenoformyl group at lower fields than those reported for pentacarbonyl(η^2 -selenobenzaldehyde)tungsten ($\delta_H = 8.2$, $\delta_C = 74.0$, $\delta_{Se} = 210.5$),^{4a,c} but almost similar to those of η^1 -complexes (*p*- $CH_3C_6H_4CH=Se \cdot W(CO)_5$: $\delta_H = 14.2$;^{4c} $Ph_2C=Se \cdot W(CO)_5$: $\delta_C = 240.0$, $\delta_{Se} = 143.1$).²¹ In the UV/vis spectra, absorption maxima were observed at ca. 600 nm ($\log \epsilon = \text{ca. } 4.3$) which are similar to that for a η^1 -complex, $PhCH=Se \cdot W(CO)_5$ (597 nm).^{4a,c} These transitions are most likely assigned as LMCT (ligand to metal charge-transfer) spectra where a CT band is fully allowed and intense. This is in sharp contrast to forbidden and weak $n-\pi^*$ transitions which are observed in selenoaldehydes. These results indicate that **4a** and **4b** are η^1 -complexes. The up-field shift of the selenoformyl

carbon by the complexation is relatively small in contrast to the large up-field shift in the ^{77}Se NMR, suggesting small perturbation to the selenoformyl carbon atom in support of η^1 -complexation in **4a** and **4b**.

In the ^1H NMR of **4b**, the signal of the methine proton in one *o*-disyl group ($\delta = 4.69$) was observed at extremely lower field than the other *o*-methine proton ($\delta = 1.80$) as in the case of the corresponding free selenoaldehyde **3b**. This phenomenon can be explained in terms of the anisotropic effect of the $\text{C}=\text{Se}$ double bond, which suggests that the $\text{C}=\text{Se}$ bond in **4b** still has a substantial double bond character.

The larger $^1J_{\text{CW}}$ value between the trans-carbonyl and tungsten center (160 Hz) than that between the cis-carbonyl and tungsten (128 Hz) in **4a** suggests the weak coordination of the selenoformyl group to the tungsten.

The conformations of the complexes **4a** and **4b** in solution were confirmed by the difference NOE experiments as in the cases of selenoaldehydes **3a** and **3b**. The results of the NOE experiments were similar to those of **3a** and **3b** (Figure 1); the complex **4a** has a Tbt_s group while **4b** bears a Tbt_a group where the hydrogen atom of the selenoformyl group directs toward the two trimethylsilyl groups of the rotated *o*-disyl group.

X-ray Crystallographic Analysis of η^1 -Selenoaldehyde Tungsten Complexes 4a and 4b

The structures of the η^1 -selenoaldehyde complexes **4a** and **4b** were definitively determined by X-ray crystallographic analysis. These are the first examples of X-ray crystallographic analysis of η^1 -selenoaldehyde complexes, although, as mentioned above, some η^1 -selenoaldehyde metal complexes have been synthesized.⁴ The ORTEP drawings of **4a** and **4b** are shown in Figure 2, and their selected bond lengths and angles are summarized in Tables 2 and 3, respectively.

The ORTEP drawings clearly indicate that the complexes **4a** and **4b** are η^1 - σ complexes where the lone pair of the selenium coordinates to the tungsten center. It was confirmed that, in the crystals, the Tbt groups in **4a** and **4b** are Tbt_s and Tbt_a , respectively. In **4b**, the hydrogen atom of the selenoformyl group is located

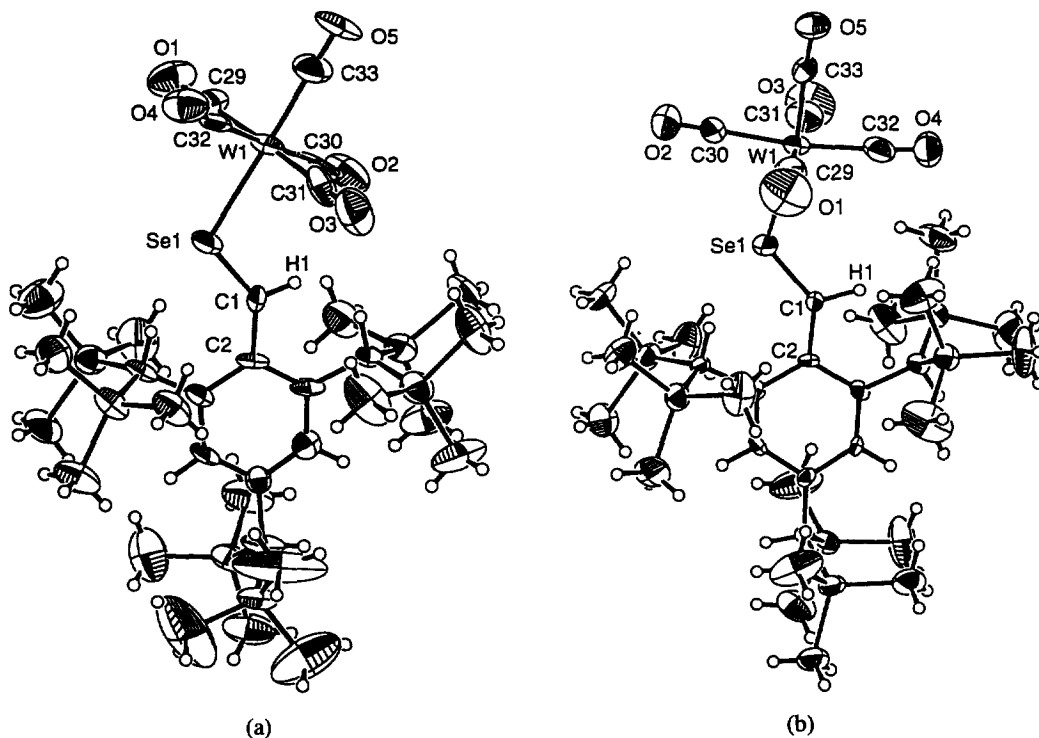


Figure 2. ORTEP drawings of **4a** (a) and **4b** (b) with thermal ellipsoid plots (30% probability for nonhydrogen atoms).

Table 2. Selected Bond Lengths (Å) of Complexes **4a** and **4b**

	4a	4b		4a	4b
C1–Se1	1.783(15)	1.781(13)	W1–C33	2.01(2)	1.95(2)
C1–C2	1.44(2)	1.45(2)	C29–O1	1.19(2)	1.20(2)
Se1–W1	2.638(2)	2.617(2)	C30–O2	1.14(2)	1.12(2)
W1–C29	1.95(2)	1.93(2)	C31–O3	1.17(2)	1.15(2)
W1–C30	1.97(2)	2.02(2)	C32–O4	1.17(2)	1.17(2)
W1–C31	1.93(2)	1.98(2)	C33–O5	1.13(2)	1.17(2)
W1–C32	2.02(2)	1.98(2)			

Table 3. Selected Bond Angles (deg) of Complexes **4a** and **4b**

	4a	4b		4a	4b
C2–C1–Se1	136(1)	131(1)	Se1–W1–C31	89.2(6)	91.1(7)
C1–Se1–W1	107.8(4)	119.6(4)	Se1–W1–C32	89.8(5)	104.8(5)
Se1–W1–C29	87.8(6)	87.5(7)	Se1–W1–C33	178.9(6)	169.8(5)
Se1–W1–C30	91.4(5)	82.1(5)			

between the two trimethylsilyl groups of the rotated *o*-disyl group. This positioning minimizes the repulsion between the selenium atom and these trimethylsilyl groups.

The C–Se bond lengths in **4a** (1.783 Å) and **4b** (1.781 Å) are significantly shorter than the average of C–Se single bond lengths (1.970 Å)²² and the C–Se bond length in pentacarbonyl(η^2 -selenobenzaldehyde)tungsten (1.864 Å),^{4a} and are rather close to the C–Se double bond length in selenoketones (1,5-dimethyl-3,7-dithiabicyclo[3.3.1]nonaneselone: 1.774 Å;²³ 4,4'-dimethoxyselenobenzophenone: 1.790 Å²⁴) and the C–Se bond length of a η^1 -selenoketone complex, pentacarbonyl(1,1,3,3-tetramethylindaneselone)tungsten (1.792 Å).²⁵ This result indicates weak coordination of the selenoformyl group to the metal in **4a** and **4b**.

In the case of **4a**, the Se1–W1–C33 moiety is almost linear (179°), and the Se1–W1 bond is nearly perpendicular to the W1–C29, W1–C30, W1–C31, and W1–C32 bonds. On the other hand, in the case of **4b**, the Se1–W1–C33 unit is slightly bent (170°), and the bond angles of Se1–W1–C30 (82°) and Se1–W1–C32 (105°) are largely deviated from the ideal right angle. This distortion of the SeW(CO)₅ moiety in **4b** is probably due to repulsion between the W(CO)₅ moiety and the two trimethylsilyl groups of the inverted *o*-disyl group.

In both cases, the selenoformyl π -planes are nearly coplanar with the benzene rings (6.4° for **4a**, 11.6° for **4b**), and the torsion angles of C2–C1–Se1–W1 (177° for **4a**, 174° for **4b**) indicate that these four atoms are located on the same plane. In contrast, in the case of the Tbt-substituted thioaldehydes, Tbt₃CHS **2a** and Tbt₂CHS **2b**, the thioformyl π -plane of **2a** is not coplanar with the benzene ring (48.7°), although, in **2b**, these two planes are almost coplanar (10.6°).⁸

Reactions of η^1 -Selenoaldehyde Tungsten Complexes **4a** and **4b**

Thermolysis of **4a** resulted in the formation of a compound without metal coordination, benzoselenolane **15**, which is identical with the product obtained by the thermolysis of free selenoaldehyde **3**, suggesting that the decomplexation into **3a** preceded the intramolecular cyclization in this reaction. Reaction of **4a** with 2,3-dimethyl-1,3-butadiene also gave a cycloadduct **14** without metal coordination in 60% yield.



In contrast to these results, treatment of η^1 -selenobenzaldehyde metal complexes with conjugated dienes reportedly gives the corresponding metal-coordinated cycloadducts resulting from reactions across the C=Se

double bond.²⁶ This difference in the reactivity is probably due to severe steric repulsion between the $W(CO)_5$ moiety and Tbt group in **4a** which results in very weak coordination to the metal.

CONCLUSIONS

We succeeded in the synthesis of the rotational isomers of Tbt-substituted selenoaldehydes **3a** and **3b** and their η^1 -tungsten complexes **4a** and **4b**. It is interesting that **3b** is isolable as a free selenoaldehyde but **3a** is not, whereas both **4a** and **4b** are isolable as tungsten complexes though **4a** is much more stable than **4b**. This seemingly strange phenomenon is due to the fact that **3a** and **4a** with a Tbt₃ group are kinetically less stable but thermodynamically more stable than **3b** and **4b** bearing a Tbt₂ group.

Isomeric selenoaldehydes **3a** and **3b** were found to be formed by thermolysis of 1,3-diselenetane **12** under very mild conditions. Since selenoaldehyde **3a** is still highly reactive toward 2,3-dimethyl-1,3-butadiene and mesitronitrile oxide in spite of its severe steric congestion, **3a** is considered to be suitable for investigation of the reactivities of the selenoformyl group.

These findings in the present work indicate that the reactivity of isolable selenoaldehydes **3a** and **3b** is essentially the same as that of transient selenoaldehydes. Also, the availability of these selenoaldehydes has enabled us to study some new reactions such as the reaction with mesitronitrile oxide, the reversible dimerization, and the direct formation of transition metal complexes from selenoaldehydes which were impossible in the case of transient selenoaldehydes and the stable selenoaldehyde **1** bearing a too bulky substituent.

The spectroscopic data, X-ray crystallographic analysis, and reactions for **4a** and **4b** suggested that the selenoaldehyde ligand weakly coordinates to the tungsten center and the complexes **4a** and **4b** still have a substantial C=Se double bond character. Since reactions of **4a** gave products accompanied by metal decomposition, **4a** is expected to be very useful as a selenoaldehyde precursor.

EXPERIMENTAL

General Procedure

All melting points were uncorrected. All solvents used in reactions were purified by the reported methods.²⁷ THF was purified by distillation from sodium diphenylketyl before use. All reactions were carried out under an argon atmosphere. Preparative gel permeation liquid chromatography (GPLC) was performed on an LC-908 or an LC-908-C60 instrument with JAI gel 1H+2H columns or JAI gel 1H-40+2H-40 columns (Japan Analytical Industry) and chloroform as solvent, unless otherwise noted. Dry column chromatography (DCC), preparative thin-layer chromatography (PTLC), and flash column chromatography (FCC) were performed with ICN silica DCC 60A, Merck Kieselgel 60 PF254 (Art. No. 7747), and Merck Silica Gel 60, respectively. The ¹H NMR (500 or 270 MHz) and ¹³C NMR (125 or 68 MHz) spectra were measured in CDCl₃ or 1,1,2,2-tetrachloroethane-d₂ with a Bruker AM-500, JEOL α -500, or JEOL EX-270 spectrometer using CHCl₃ or 1,1,2,2-tetrachloroethane as an internal standard. The ⁷⁷Se NMR (95 or 51 MHz) spectra were measured in CDCl₃ or 1,1,2,2-tetrachloroethane-d₂ with a JEOL α -500 or JEOL EX-270 spectrometer using diphenyl diselenide as an external standard. High-resolution mass spectral data were obtained on a JEOL SX-102 mass spectrometer. The electronic spectra were recorded on a JASCO Ubsct-50 UV/vis spectrometer. Infrared spectra were obtained on a Horiba FT-200 or JASCO FT/IR-300E spectrophotometer. Elemental analyses were performed by the Microanalytical Laboratory of the Department of Chemistry, Faculty of Science, The University of Tokyo.

Reaction of Diazomethane **6** with Cp_2TiSe_5 Catalyzed by CuCl

To a THF suspension (30 ml) of Cp_2TiSe_5 ¹⁴ (1.11 g, 1.94 mmol) and CuCl (18.6 mg, 0.188 mmol) was added dropwise a THF solution (45 ml) of **6** (prepared from 724 mg, 0.965 mmol of the corresponding tosylhydrazone, TbtCHNNHTs; Ts = *p*-MeC₆H₄SO₂-)⁹ at room temperature over 1.5 h, and the reaction mixture was stirred for additional 2 h. After removal of the solvent under reduced pressure, hexane was added to the

residue and evaporated to remove remaining THF. Hexane was added again to the mixture, insoluble Cp_2TiSe_5 (955 mg, 1.67 mmol, 86%) was filtered off through Celite. After evaporation of the filtrate, the residue was separated by FCC (hexane, then CH_2Cl_2). The orange fraction was subjected to GLPC (toluene as solvent) to afford a mixture of Tbt-substituted cyclic polyselenides **5** (75.6 mg, 0.0809 mmol, 8%). Other fractions except for **5** were purified by GLPC, PTLC (hexane) and DCC (hexane : CH_2Cl_2 = 3 : 1) to give 3,5-bis[bis(trimethylsilyl)methyl]-1,1-bis(trimethylsilyl)benzocyclobutene (**7**)⁹ (127 mg, 0.224 mmol, 23%), an unseparable mixture of 2,5-bis[2,4,6-tris[bis(trimethylsilyl)methyl]phenyl]-1,3,4-selenadiazoline (**8**) and 2,4,6-tris[bis(trimethylsilyl)methyl]benzaldehyde azine (**9**)⁹ (201 mg, **8** : **9** = 8 : 2, **8**: ca. 0.14 mmol, ca. 29%; **9**: ca. 0.027 mmol, ca. 6%), and 2,4,6-tris[bis(trimethylsilyl)methyl]benzylalcohol (**10**) (61.2 mg, 11%). **5**: orange solid. Anal. Calcd for $\text{C}_{28}\text{H}_{60}\text{Se}_5\text{Si}_6$: C, 34.74; H, 6.25; Se, 41.60. Found C, 34.71; H, 6.55; Se, 41.41. **8**: white crystals; mp >300 °C; ^1H NMR (500 MHz, CDCl_3) δ 0.02 (s, 36H), 0.06 (s, 36H), 0.10 (s, 36H), 1.35 (s, 2H), 1.54 (s, 4H), 6.36 (s, 2H), 6.44 (s, 2H), 7.85 (s, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 0.7 (q), 0.8 (q), 1.2 (q), 24.6 (d \times 2), 30.2 (d), 100.6 (d), 122.9 (d), 125.9 (s), 126.9 (d), 143.0 (s), 144.0 (s \times 2). Anal. Calcd for $\text{C}_{56}\text{H}_{120}\text{N}_2\text{SeSi}_{12}\cdot 2\text{H}_2\text{O}$: C, 52.81; H, 9.50; N, 2.19; Se, 6.20. Found C, 52.67; H, 9.65; N, 2.35; Se, 5.96. **10**: white crystals; mp 223–225 °C; ^1H NMR (500 MHz, CDCl_3) δ 0.02 (s, 36H), 0.03 (s, 18H), 0.87 (s, 1H), 1.31 (s, 1H), 1.91 (s, 1H), 2.01 (s, 1H), 4.51 (s, 2H), 6.29 (s, 1H), 6.42 (s, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 0.4 (q), 0.7 (q), 23.8 (d \times 2), 30.2 (d), 59.3 (t), 122.0 (d), 126.8 (d), 129.9 (s), 142.7 (s), 143.6 (s), 143.9 (s). Anal. Calcd for $\text{C}_{28}\text{H}_{62}\text{OSi}_6$: C, 57.65; H, 10.71. Found: C, 57.43; H, 10.70.

Reaction of a Mixture of Polyselenides 5 with One Equivalent of Ph_3P

To an orange solution of **5** (17.8 mg, 0.0183 mmol) in THF (5 ml) was added dropwise a THF solution (3 ml) of Ph_3P (4.9 mg, 0.019 mmol) at –78 °C over 5 min. After stirring for 10 min at the same temperature, the reaction mixture was warmed to room temperature. After evaporation of the solvent, the residue was chromatographed (GLPC) to give the starting material **5** (3.1 mg, 0.0032 mmol, 17%), a mixture of compounds having two Tbt groups (3.9 mg), and a mixture of compounds having more than two Tbt groups (7.1 mg) together with a quantitative production of $\text{Ph}_3\text{P}=\text{Se}$ (6.7 mg, 0.019 mmol).

Thermolysis of a Mixture of Polyselenides 5

In a 5 ϕ NMR tube was placed a C_6D_6 solution (0.8 ml) of **5** (9.2 mg, 0.0095 mmol), and after five freeze-pump-thaw cycles, the tube was evacuated and sealed. The solution was heated at 70 °C for 1 h to cause no change in the ^1H NMR spectrum. Even after heating at 80 °C for 8 h and then at 110 °C for 7 h, no change in the ^1H NMR spectrum was observed.

Reaction of a Mixture of Polyselenides 5 with an Excess of Ph_3P

To a THF solution (5 ml) of Ph_3P (36.7 mg, 0.140 mmol, 5.1 eq. to **5**) was added dropwise an orange solution of **5** (26.2 mg, 0.0273 mmol) in THF (5 ml) at room temperature for 5 min. After stirring for 45 min, the resulting greenish yellow solution containing 2,4,6-tris[bis(trimethylsilyl)methyl]selenobenzaldehyde (**3a**) was evaporated 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 2,4-bis[2,4,6-tris[bis(trimethylsilyl)methyl]-phenyl]-1,3-diselenetane (**12**) (13.8 mg, 0.0107 mmol, 79%) was filtered off. After evaporation of the filtrate, hexane was added to the mixture and insoluble $\text{Ph}_3\text{P}=\text{Se}$ (35.7 mg, 0.105 mmol, 383 % from **5**) was filtered off. The filtrate was chromatographed (GLPC) to afford Ph_3P (8.2 mg, 0.0313 mmol, 115% from **5**). In this reaction, all the procedure before addition of benzene to the reaction mixture was performed under argon using the solvent distilled under nitrogen or argon. **12**: white crystals; mp 227–230 °C (decomp); ^1H NMR (270 MHz, CDCl_3) δ 0.03 (s, 72H), 0.17 (s, 36H), 1.28 (s, 2H), 2.57 (s, 2H), 3.76 (s, 2H), 6.27 (s, 2H), 6.45 (s, 2H), 6.52 (s, 2H, TbtHC). High-resolution FAB-MS m/z calcd for $\text{C}_{56}\text{H}_{121}^{80}\text{Se}_2\text{Si}_{12}$: 1289.5030; found: 1289.5243 ($[\text{M}+\text{H}]^+$). Anal. Calcd for $\text{C}_{56}\text{H}_{120}\text{SeSi}_{12}\cdot 2\text{H}_2\text{O}$: C, 50.78; H, 9.44; Se, 11.92. Found: C, 50.33; H, 9.24; Se, 12.23. The ^1H , ^{13}C , and ^{77}Se NMR and UV spectra of **3a** were measured by performing the above

experiment in a solution of CDCl_3 or hexane. The values of ϵ were determined by assuming quantitative generation of **3a** from **5**. **3a**: ^1H NMR (500 MHz, CDCl_3) 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 (125 MHz, CDCl_3) δ 0.4 (q), 0.7 (q), 24.9 (d), 25.4 (d), 33.0 (d), 237.6 (d, $^1J_{\text{CH}} = 161.2$ Hz, $\text{C}=\text{Se}$); the signals for aromatic carbons could not be assigned due to the overlap with the signals of Ph_3P and $\text{Ph}_3\text{P}=\text{Se}$; ^{77}Se NMR (95 MHz, CDCl_3) δ 2075; UV/vis (hexane) λ_{max} 400 (ϵ ca. 6000), 792 (ϵ ca. 50) nm. High-resolution EI-MS m/z calcd for $\text{C}_{28}\text{H}_{60}^{80}\text{SeSi}_6$: 644.2476; found: 644.2457.

Measurement of the Ratio among Selenoaldehydes 3a, 3b, and Diselenetane 12 in an Equilibrium Mixture

In a 5 ϕ NMR tube was placed a CDCl_3 solution (ca. 0.6 ml) of **12** (7.2×10^{-4} mmol l^{-1}) prepared from **12** (4.2 mg, 0.033 mmol) and CDCl_3 (4.5 ml). After five freeze-pump-thaw cycles, the tube was evacuated and sealed. The solution was heated at 45 °C on a thermostat (LAUDA K6) until the ratio among **3a**, **3b**, and **12** became constant while the temperature was being monitored by a digital thermometer CT-500P (Custom Co.) with the calibration error being ± 0.1 °C. The ratio among **3a**, **3b**, and **12** was determined by observation of the signals of TbtCH (**3a**: 16.06 ppm, **3b**: 15.51 ppm, **12**: 6.52 ppm) on the ^1H NMR spectra.

Isolation of Selenoaldehyde 3b by Thermolysis of Diselenetane 12

A THF suspension (25 ml) of **12** (31.2 mg, 0.0242 mmol) was warmed at 45 °C for 17 h and the resulting greenish yellow solution containing selenoaldehyde **3a**, its rotational isomer **3b**, and **12** was evaporated at 0 °C. Pentane was added to the mixture and evaporated to remove remaining THF. Pentane was added to the residue again and insoluble **12** was filtered off as white precipitates. The filtrate was separated by low temperature FCC (−30 °C, pentane) under nitrogen. An orange yellow fraction was evaporated at room temperature and a small amount of pentane was added to the residue. After filtration of **12** generated from remaining **3a**, the filtrate was evaporated to afford 2,4,6-tris[bis(trimethylsilyl)methyl]selenobenzaldehyde (**3b**) (4.7 mg, 0.0073 mmol, 15%). Up to here, all the procedures were performed under nitrogen or argon atmosphere using the solvents distilled under nitrogen or argon. All the fractions except for **3b** were collected and pentane was added to the mixture. Insoluble **12** (17.0 mg, 0.0132 mmol, 54%) was filtered off. **3b**: orange yellow powder; mp 195–202 °C (decomp); ^1H NMR (500 MHz, CDCl_3) 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 (s, 2H), 15.51 (s, 1H); ^{13}C NMR (125 MHz, CDCl_3) 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, $^1J_{\text{CH}} = 156.5$ Hz, $\text{C}=\text{Se}$); ^{77}Se NMR (95 MHz, CDCl_3) δ 1893; UV/vis (hexane) λ_{max} 405 (ϵ 7500), 828 (ϵ 38) nm. High-resolution EI-MS m/z calcd for $\text{C}_{28}\text{H}_{60}^{80}\text{SeSi}_6$: 644.2476; found: 644.2490.

Reaction of Selenoaldehyde 3a with 2,3-Dimethyl-1,3-butadiene

In a dry Pyrex 10 ϕ glass tube was placed a THF solution (3.5 ml) of **5** (27.7 mg, 0.0286 mmol), and a THF solution (1 ml) of Ph_3P (35.3 mg, 0.135 mmol) was added dropwise to the orange solution of **5** at room temperature. A large excess of 2,3-dimethyl-1,3-butadiene (0.15 ml, 1.326 mmol) was added to the resulting greenish yellow solution of **3a**. After three freeze-pump-thaw cycles, the tube was evacuated and sealed. When the mixture was heated at 60 °C for 14.5 h, the solution turned pale yellow. After removal of the solvent, hexane was added and evaporated to remove remaining THF. Hexane was added again and insoluble $\text{Ph}_3\text{P}=\text{Se}$ (32.0 mg, 0.0938 mmol, 361% from **5**) was filtered off. The filtrate was evaporated to dryness and the mixture was separated by PTLT (hexane) and GLPC to afford the corresponding [2+4] cycloadducts, 3,6-dihydro-4,5-dimethyl-2-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-2H-selenapyran (**14**) (9.9 mg, 0.0136 mmol, 53%), 4,6-bis[bis(trimethylsilyl)methyl]-1,1-bis(trimethylsilyl)-2-benzoselenolane (**15**) (4.9 mg, 0.00761 mmol, 29%), and Ph_3P (7.5 mg, 0.0286 mmol, 110% from **5**). **14**: white crystals; mp 218–219 °C (decomp); ^1H NMR (500 MHz, CDCl_3 , 60 °C) δ 0.04 (s, 9H), 0.05 (s, 18H), 0.06 (s, 9H), 0.09 (s, 9H), 0.10 (s, 9H), 1.29 (s, 1H), 1.72 (s, 3H), 1.82 (dd, 1H, $^2J = 16.7$ Hz, $^3J = 12.7$ Hz), 1.83 (s, 3H), 2.04 (dd, 1H, $^2J = 16.7$ Hz, $^3J = 3.1$ Hz), 2.57 (br s, 1H), 2.99 (br s, 1H), 3.03 (d, 1H, $^2J = 14.7$ Hz), 3.38 (d, 1H, $^2J = 14.7$ Hz), 4.59

(dd, 1H, $^3J = 12.7, 3.1$ Hz), 6.33 (br s, 2H); ^{13}C NMR (125 MHz, CDCl_3 , 60 °C) δ 0.8 (q), 1.6 (q), 1.8 (q), 20.0 (q), 20.6 (q), 24.9 (t), 25.0 (dx2), 30.0 (d), 35.7 (d, $^1J_{\text{CSe}} = 53.7$ Hz), 40.2 (t), 123.7 (br d), 124.7 (s), 127.5 (br d), 130.2 (s), 130.6 (s), 140.9 (s), 142.9 (s), 145.0 (s); ^{77}Se NMR (51 MHz, CDCl_3 , 60 °C) δ 224.1. High-resolution EI-MS m/z calcd for $\text{C}_{34}\text{H}_{70}^{80}\text{SeSi}_6$: 726.3258; found: 726.3298. Anal. Calcd for $\text{C}_{34}\text{H}_{70}\text{SeSi}_6$: C, 56.22; H, 9.71; Se, 10.87. Found C, 56.38; H, 9.55; Se, 10.71. **15**: white crystals; mp 184–186 °C (decomp); ^1H NMR (500 MHz, $\text{Cl}_2\text{CDCDCl}_2$, 100 °C) δ 0.05 (s, 18H), 0.06 (s, 18H), 0.13 (s, 18H), 1.37 (s, 1H), 1.53 (s, 1H), 4.01 (s, 2H, $^2J_{\text{HSe}} = 13.3$ Hz), 6.34 (s, 1H), 6.38 (s, 1H); ^{13}C NMR (125 MHz, $\text{Cl}_2\text{CDCDCl}_2$, 100 °C) δ 1.3 (q), 2.1 (q), 2.2 (q), 28.3 (d), 31.0 (t), 31.7 (d), 40.7 (s), 122.7 (br d), 126.4 (br d), 136.5 (s), 142.7 (s), 143.2 (s), 149.1 (s); ^{77}Se NMR (51 MHz, $\text{Cl}_2\text{CDCDCl}_2$, 100 °C) δ 210.7. High-resolution EI-MS m/z calcd for $\text{C}_{28}\text{H}_{60}^{80}\text{SeSi}_6$: 644.2476; found 644.2435. Anal. Calcd for $\text{C}_{28}\text{H}_{60}\text{SeSi}_6 \cdot 1/2\text{H}_2\text{O}$: C, 51.48; H, 9.26; Se, 12.09. Found C, 51.23; H, 9.21; Se, 11.43.

Reaction of Selenoaldehyde **3a** with Mesitonitrile Oxide

To a THF solution (5 ml) of Ph_3P (34.1 mg, 0.130 mmol) was added dropwise a THF solution (10 ml) of **5** (27.7 mg, 0.0286 mmol) at 0 °C over 5 min. After stirring at 0 °C for 15 min and at room temperature for 25 min, a THF solution (2 ml) of mesitonitrile oxide (22.6 mg, 0.140 mmol) was added at 0 °C to the resulting greenish yellow solution containing selenoaldehyde **3a**. The mixture was stirred for 40 min at 0 °C and the solvent was evaporated under reduced pressure at 0 °C. The residue was separated by GPLC (toluene as solvent) to afford a mixture of 3-mesityl-5-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-1,4,2-oxaselenazole (**16**), TbtCHO^9 and MesNCSe (16.5 mg, **16** : TbtCHO : MesNCSe = 5 : 1 : 1; **16**: ca. 0.017 mmol, ca. 60%; TbtCHO : ca. 0.0035 mmol, ca. 12%). Further purification of the other fractions by GPLC gave $\text{Ph}_3\text{P}=\text{O}$ (4.3 mg, 0.0155 mmol, 54% from **5**) and $\text{Ph}_3\text{P}=\text{Se}$ (25.3 mg, 0.0741 mmol, 257% from **5**). It was impossible to obtain pure **16**, because **16** gradually decomposed in solution to the corresponding aldehyde TbtCHO and MesNCSe at room temperature. **16**: white crystals; ^1H NMR (500 MHz, CDCl_3) δ 0.05 (s, 36H), 0.06 (s, 18H), 1.35 (s, 1H), 2.21 (br s, 1H), 2.29 (s, 3H), 2.40 (s, 6H), 2.52 (br s, 1H), 6.33 (s, 1H), 6.45 (s, 1H), 6.90 (s, 2H), 8.07 (s, 1H); ^{13}C NMR (68 MHz, CDCl_3 , 0 °C) δ 0.5 (q), 0.7 (q), 0.9 (q), 1.0 (q), 19.8 (q), 21.2 (q), 25.3 (dx2), 30.1 (d), 93.9 (d), 120.2 (s), 122.7 (s), 126.8 (s), 127.2 (d), 128.4 (d), 136.3 (s), 139.3 (s), 144.0 (s), 145.0 (s), 145.7 (s), 158.5 (s); ^{77}Se NMR (51 MHz, CDCl_3 , 0 °C) δ 507.0. High-resolution FAB-MS m/z calcd for $\text{C}_{38}\text{H}_{72}\text{ON}^{80}\text{SeSi}_6$: 806.3395; found: 806.3409 ($[\text{M}+\text{H}]^+$).

Reaction of the Equilibrium Mixture of **3a**, **3b**, and **12** with 2,3-Dimethyl-1,3-butadiene

In a dry Pyrex 10 ϕ glass tube was placed a benzene suspension (4 ml) of **12** (13.3 mg, 0.0103 mmol) and 2,3-dimethyl-1,3-butadiene (0.15 ml, 1.326 mmol). After five freeze-pump-thaw cycles, the tube was evacuated and sealed. After heating at 60 °C for 13 h, the reaction mixture was evaporated and the residue was separated by PTLT (hexane) to afford **14** (12.1 mg, 0.0167 mmol, 81%) and a trace amount of **15**.

Thermal Reaction of the Equilibrium Mixture of **3a**, **3b**, and **12**

In a 5 ϕ NMR tube was placed a C_6D_6 suspension (1 ml) of **12** (5.2 mg, 0.0040 mmol). After five freeze-pump-thaw cycles, the tube was evacuated and sealed. When the suspension was heated at 60 °C for 3 h, the formation of selenoaldehydes **3a** and **3b** was observed by the ^1H NMR spectrum. The mixture was gradually warmed to 100 °C while the reaction was being monitored by ^1H NMR spectroscopy, and further heating at 100 °C for 89 h resulted in a quantitative formation of benzoselenolane **15**.

Reaction of the Equilibrium Mixture of **3a**, **3b**, and **12** with $\text{W}(\text{CO})_5\cdot\text{THF}$

A THF suspension (25 ml) of **12** (32.2 mg, 0.0250 mmol) was heated at 45 °C for 17 h, and to the resulting mixture of selenoaldehydes **3a** and **3b** and diselenetane **12** was added at room temperature a THF solution of $\text{W}(\text{CO})_5\cdot\text{THF}$ (0.0199 M, 3.8 ml, 0.0756 mmol), prepared by photoreaction of $\text{W}(\text{CO})_6$ in THF.²⁸ After stirring at room temperature for 24 h, the solvent was evaporated. Hexane was added to the mixture and evaporated to remove remaining THF. The residue was separated by FCC [1) hexane, 2) CHCl_3] to afford

pentacarbonyl{2,4,6-tris[bis(trimethylsilyl)methyl]selenobenzaldehyde}tungsten (**4a**) (28.7 mg, 0.0297 mmol, 59%). All the fractions except for **4a** were collected and hexane was added to the mixture. White precipitates were filtered off and extracted by CHCl_3 . The extract was evaporated to afford **12** (4.3 mg, 0.0033 mmol, 13%). **4a**: deep blue crystals; mp 187–189 °C (decomp); ^1H NMR (500 MHz, CDCl_3) 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 (125 MHz, CDCl_3) 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, $^1J_{\text{CW}} = 128.2$ Hz, cis- CO), 202.1 (s, $^1J_{\text{CW}} = 160.2$ Hz, trans- CO), 227.4 (d, $^1J_{\text{CH}} = 162.0$ Hz, $\text{C}=\text{Se}$); ^{77}Se NMR (95 MHz, CDCl_3) δ 1184; UV/vis (hexane) λ_{max} 381 (ϵ 19000), 434 (ϵ 5000), 603 (ϵ 18000) nm; IR (KBr) 2061, 1931, 1908 cm^{-1} ($\text{C}=\text{O}$ stretch). High-resolution FAB-MS m/z calcd for $\text{C}_{33}\text{H}_{60}\text{O}_5^{80}\text{SeSi}_6\text{W}$: 968.1731; found: 968.1708. Anal. Calcd for $\text{C}_{33}\text{H}_{60}\text{O}_5\text{SeSi}_6\text{W}$: C, 40.94; H, 6.25; Se, 8.16. Found: C, 41.03; H, 6.21; Se, 8.02.

Reaction of Selenoaldehyde **3b** with $\text{W}(\text{CO})_5\cdot\text{THF}$

To a THF solution (3 ml) of **3b** (4.6 mg, 0.00714 mmol) was added a THF solution of $\text{W}(\text{CO})_5\cdot\text{THF}$ (0.0199 M, 0.54 ml, 0.0107 mmol) at 0 °C. The solution was stirred at 0 °C for 30 min and warmed to room temperature. After stirring for 1 h, a THF solution of $\text{W}(\text{CO})_5\cdot\text{THF}$ (0.0199 M, 0.54 ml, 0.0107 mmol) was added to the mixture again. The reaction mixture was stirred for 30 min, and the solvent was evaporated under argon atmosphere. Hexane was added to the mixture and the solvent was evaporated to remove remaining THF. The residue was separated by FCC [1) hexane, 2) CHCl_3] to afford pentacarbonyl{2,4,6-tris[bis(trimethylsilyl)methyl]selenobenzaldehyde}tungsten (**4b**) (5.4 mg, 0.0056 mmol, 78%). **4b**: deep blue crystals; mp 171–172 °C (decomp); ^1H NMR (500 MHz, CDCl_3) 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 (125 MHz, CDCl_3) 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, $^1J_{\text{CW}} = 127.2$ Hz, cis- CO), 201.9 (s, trans- CO), 224.0 (d, $^1J_{\text{CH}} = 166.2$ Hz, $\text{C}=\text{Se}$); ^{77}Se NMR (95 MHz, CDCl_3) δ 1162; UV/vis (hexane) λ_{max} 381 (ϵ 21000), 445 (ϵ 5600), 595 (ϵ 21000) nm; IR (KBr) 2066, 1986, 1947, 1929, 1911, 1895 cm^{-1} ($\text{C}=\text{O}$ stretch). High-resolution FAB-MS m/z calcd for $\text{C}_{33}\text{H}_{60}\text{O}_5^{80}\text{SeSi}_6\text{W}$: 968.1731; found: 968.1714.

Isomerization of Selenoaldehyde Tungsten Complex **4b** to Its Rotational Isomer **4a**

In a 5 ϕ NMR tube was placed a C_6D_6 solution (0.6 ml) of **4b** (5.6 mg, 0.0058 mmol). After five freeze-pump-thaw cycles, the tube was evacuated and sealed. After standing at ca. 20 °C for 24 h, the formation of **4a** was observed by ^1H NMR. When the mixture was allowed to stand at ca. 20 °C for 120 h, a complete conversion of **4b** to **4a** was confirmed by ^1H NMR.

X-ray Data Collection for Selenoaldehyde Tungsten Complexes **4a**, **b**

Crystallographic data for **4a**: $\text{C}_{33}\text{H}_{60}\text{O}_5\text{SeSi}_6\text{W}$, $M = 968.16$, crystal size (mm) $0.5 \times 0.3 \times 0.1$, triclinic, space group $P\bar{1}$, $a = 12.859(3)$ Å, $b = 16.680(7)$ Å, $c = 11.748(6)$ Å, $\alpha = 107.67(3)^\circ$, $\beta = 97.32(3)^\circ$, $\gamma = 95.50(3)^\circ$, $V = 2357(1)$ Å³, $Z = 2$, $\rho = 1.364$ g cm^{-3} , $\mu = 34.09$ cm^{-1} , $R = 0.054$ ($R_w = 0.032$), and **4b**: $\text{C}_{33}\text{H}_{60}\text{O}_5\text{SeSi}_6\text{W}$, $M = 968.16$, crystal size (mm) $0.3 \times 0.3 \times 0.3$, triclinic, space group $C2/c$, $a = 34.523(3)$ Å, $b = 12.290(3)$ Å, $c = 24.585(3)$ Å, $\beta = 112.073(9)^\circ$, $V = 9667(2)$ Å³, $Z = 8$, $\rho = 1.330$ g cm^{-3} , $\mu = 33.25$ cm^{-1} , $R = 0.053$ ($R_w = 0.037$). The intensity data for **4a** and **4b** were collected on a Rigaku AFC5R diffractometer with graphite monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.71069$ Å). The structures of **4a** and **4b** were solved by direct methods with SHELXS-86²⁹ and refined by the full matrix least-squares method. All the non-hydrogen atoms were refined anisotropically. The final cycles of the least square refinement were based on 2776 [for **4a**] and 3044 [for **4b**] observed reflections [$I > 3\sigma(I)$] and 415 [for **4a** and **4b**] variable parameters.

Thermal Reaction of Selenoaldehyde Tungsten Complex **4a**

In a 5 ϕ NMR tube was placed a C_6D_6 solution (0.6 ml) of **4a** (14.7 mg, 0.0152 mmol). After five freeze-pump-thaw cycles, the tube was evacuated and sealed. When the solution was heated at 60 °C for 6 h, only the

starting material **4a** was observed by the ^1H NMR spectrum and isomerization of **4a** to its rotamer **4b** was not confirmed. Further heating at 80 °C for 63 h, however, resulted in the disappearance of **4a**. After CHCl_3 was added to the mixture, inorganic compounds were removed by filtration through Celite. The solvent was removed under reduced pressure, and the residue was separated by PTLC (hexane) to afford benzoselenolane **15** (5.7 mg, 0.0089 mmol, 58%).

Reaction of Selenoaldehyde Tungsten Complex 4a with 2,3-Dimethyl-1,3-butadiene

In a 5 ϕ NMR tube was placed a C_6D_6 solution (0.6 ml) of **4a** (15.6 mg, 0.0161 mmol) and 2,3-dimethyl-1,3-butadiene (0.1 ml, 0.866 mmol). After five freeze-pump-thaw cycles, the tube was evacuated and sealed. After heating at 60 °C for 3 h, the ^1H NMR spectrum of the reaction mixture showed a slow decrease of the starting material **4a**. Further heating at 70 °C for 28 h resulted in the disappearance of **4a**, and the solvent was evaporated from the reaction mixture. The residue was separated by PTLC (hexane : CH_2Cl_2 = 5 : 1) to afford **14** (7.0 mg, 0.0096 mmol, 60%).

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15. The Tbt group of **12**, **14**, and **16** is considered to be the Tbt₂ form like for almost all other compounds containing the Tbt group on an sp³ carbon,⁸⁻¹⁰ because of the absence of the signals for its rotamer in the NMR spectra, although experimental confirmation of the structures was not performed.
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