

# Surface Organometallic Chemistry on Oxides: The First Well-Defined Selenium(IV) Derivative Grafted onto Silica

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Treatment of (EtO)<sub>2</sub>SeO with Aerosil silica dehydroxylated at 500 °C results in the formation of a unique surface derivative [≡SiO–Se(O)OEt] (**1**), which has been fully characterized by elemental analysis, IR, labelling reaction and solid-state

NMR spectroscopy. This is the first example of a silica-supported selenium(IV) derivative.  
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## Introduction

Glyoxal and glyoxylic acid are important pharmaceutical intermediates ( $1.2 \times 10^5$  t·y<sup>−1</sup>).<sup>[1–2]</sup> They are generally manufactured from ethylene glycol or from acetaldehyde, by use of different oxidizing agents such as air or nitric acid, respectively.<sup>[3]</sup> In both processes there is a high amount of residue, which causes waste disposal problems. Moreover, the separation of the products becomes expensive. A possible solution is the use of a highly selective oxidizing agent. For at least 80 years, selenium dioxide and selenous and selenic acids have been known to oxidize acetaldehyde to glyoxal and glyoxylic acid.<sup>[4–6]</sup> However, they had to be used as stoichiometric oxidants, and precipitated as metallic selenium. Nevertheless, several studies confirm that all selenium derivatives can easily be reoxidized by any oxidant, such as *t*BuO<sub>2</sub>H,<sup>[7]</sup> H<sub>2</sub>O<sub>2</sub><sup>[8]</sup> and O<sub>2</sub>,<sup>[9]</sup> thus allowing selenium derivatives to be used in catalytic amounts, so their use as oxidizing agents attracted more interest. Moreover, one way to facilitate the separation of the reaction products and the oxidant, and also to reduce the risks due to the toxicity of selenium, is to link the oxidizing agent to a support.<sup>[10]</sup> Nicolaou's group has recently synthesized several natural products by means of a novel cycloaddition technique in which a prenylated phenol group is immobilized on a polystyrene-based selenyl bromide derivatized resin.<sup>[11]</sup> Another approach would be to graft selenium derivatives onto inorganic supports, such as silica.

In this work we report the synthesis, characterization and reactivity of the first silica-supported selenium oxide [≡SiOSe(O)OEt] (**1**). In order to determine the coordination sphere of Se in **1**, a systematic study on the oxidation

of acetaldehyde with SeO<sub>2</sub>, H<sub>2</sub>SeO<sub>3</sub> and PhSeO<sub>2</sub>H was performed first.

## Results and Discussion

The aim of this study was to develop a supported oxidant capable of replacing nitric acid for performing the oxidation reaction of acetaldehyde to glyoxal. It is known that several selenium derivatives can perform this oxidation. It was also important to determine which one of them could provide the best selectivity for glyoxal under stoichiometric reaction conditions. So several selenium derivatives were tested under homogeneous conditions in order to determine the influence of the coordination sphere around the selenium atom on this oxidation reaction and to reproduce a similar coordination sphere around Se grafted onto silica.

### Molecular Homogeneous Oxidation of Acetaldehyde

We first reproduced Corey's results: the oxidation of acetaldehyde to glyoxal and glyoxylic acid in the presence of SeO<sub>2</sub>, at 90 °C for 12 h, in acetic acid.<sup>[5]</sup>

The observed level of consumption of acetaldehyde reached 90%. As the yields of glyoxal (33%), glyoxylic acid (13%) and formic and oxalic acids (< 1%) did not account for the material balance, acetic acid had presumably also been formed. To confirm this hypothesis, the reaction was performed under the same experimental conditions, but now with propionic acid as solvent. In this case, the degree of conversion of acetaldehyde was the same (90%) and the yields of glyoxal (48–50%), glyoxylic acid (10–20%), formic acid (0–3%) and acetic acid (20%) gave the correct ma-

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terial balance. Whatever the solvent, metallic selenium is formed and precipitates (Figure 1).

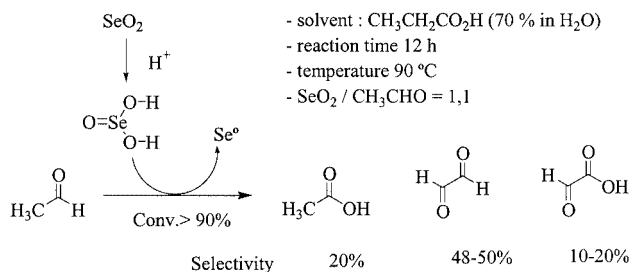


Figure 1. Distribution of oxidation products of acetaldehyde with  $\text{SeO}_2$  in propionic acid

The degree of conversion of acetaldehyde and the selectivities for the products described are dependent on the reaction temperature, as depicted in Figure 2 (top). There is still formation of acetic acid, but whereas its selectivity decreases with temperature, its yield remains roughly constant (about 20%; Figure 2, bottom). From 25 up to 90 °C the total selectivity for glyoxal and glyoxylic acid together varies from 44 to 70%. However, the ratio of the selectivity for glyoxal to the selectivity for glyoxylic acid varies from 0.5 to 2.5, due to the fact that the yield of glyoxal increases from 8 to 45% whereas the yield of glyoxylic acid remains constant (Figure 2, bottom). As the level of conversion of acetaldehyde increases with temperature, this indicates that the limiting factor is the activation energy of the oxidation of acetaldehyde to glyoxal, and not the nature of the oxidant.

The oxidation of acetaldehyde was also performed with benzeneseleninic acid [ $\text{PhSe}(\text{O})(\text{OH})$ ] and benzeneseleninic peracid [ $\text{PhSe}(\text{O})(\text{OOH})$ ], generated in situ by addition of  $\text{H}_2\text{O}_2$ , both of which are known to be highly reactive oxidants.<sup>[8,12]</sup> Whatever the experimental conditions, mostly acetic acid is formed, in up to 50% yield, while less than 20% of glyoxal is obtained. No metallic selenium was observed and the reduced product  $\text{PhSe}-\text{SePh}$  was identified by  $^{77}\text{Se}$  NMR [ $\delta_{\text{Se}}(\text{C}_6\text{D}_6) = 460$  ppm].<sup>[13]</sup>

The nature of the coordination sphere around the selenium atom seems to play a crucial role in the oxidation reaction studied. When the selenium atom is bonded to three oxygen atoms, there is increased formation of glyoxal than when it is bonded to two oxygen atoms and one carbon atom.

### Surface Organometallic Chemistry

Reactions between organometallic complexes ( $\text{MX}_n$ ;  $\text{X} = \text{R}, \text{OR}, \text{NR}_2, \text{Cl}, \dots$ ;  $\text{M} = \text{transition metal or main group element}$ ) and a silica surface in most cases give organometallic fragments  $\sigma$ -bonded to the surface through one, two or three oxygen–metal bonds.<sup>[14–16]</sup> This kind of bonding can stabilize well-defined and highly electrophilic fragments capable of performing several kinds of catalytic reactions,<sup>[16]</sup> and in particular oxidation reactions.<sup>[17–25]</sup>

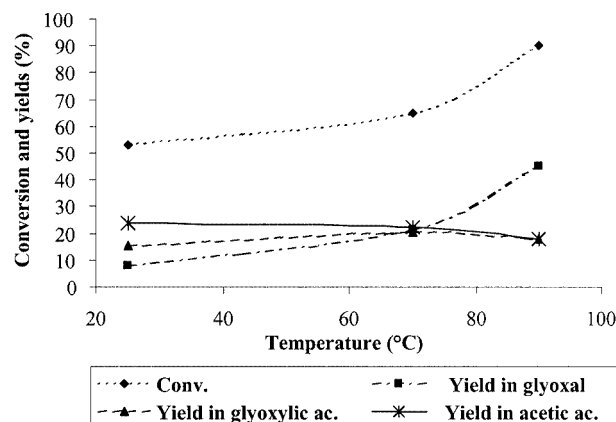
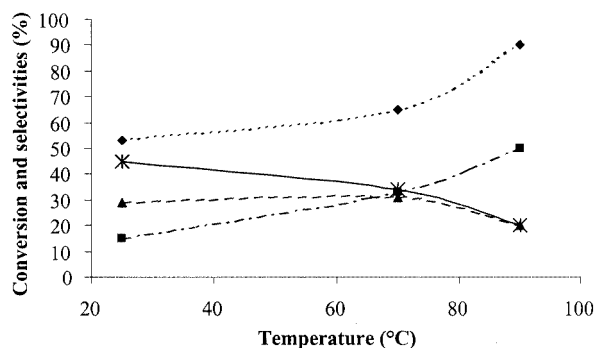


Figure 2. Variation of the conversion and selectivities (top) and conversion and yields (bottom) versus temperature in the oxidation reaction of acetaldehyde with  $\text{SeO}_2$ ; reaction time 12 h

One possible route to the surface species  $\text{M}_1$  or  $\text{M}_2$  (Figure 3), presenting the required coordination sphere around the selenium atom for the oxidation of acetaldehyde to glyoxal, might be through reaction between  $\text{Cl}_2\text{SeO}$  or  $(\text{EtO})_2\text{SeO}$  and silica.

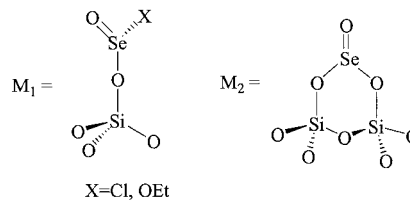


Figure 3. Target selenium species grafted on silica

### Silica Surface

The support used is a Degussa flame Aerosil® silica, dehydroxylated at increasing temperatures ( $T$  [°C]), that we shall call  $\text{SiO}_{2-(T)}$ . The specific surface areas were  $200 \text{ m}^2 \cdot \text{g}^{-1}$  for  $\text{SiO}_{2-(500)}$ . The silanol group content, determined by quantitative solid-state  $^1\text{H}$  NMR and by treatment with  $\text{CH}_3\text{Li}$ , is  $1.2 \text{ OH} \cdot \text{nm}^{-2}$  for  $\text{SiO}_{2-(500)}$ .<sup>[26–29]</sup>

## Surface Chemistry of Selenium on Silica

**a) Reaction between Selenium Oxychloride  $\text{Cl}_2\text{Se}=\text{O}$  and  $\text{SiO}_{2-(500)}$** 

The reaction between  $\text{Cl}_2\text{Se}=\text{O}$ <sup>[30–31]</sup> and  $\text{SiO}_{2-(500)}$  at room temperature was monitored by Fourier-Transform infrared (FTIR) spectroscopy and by quantitative analysis of the products. During the reaction the colour of the silica changed from white to yellow/orange. At first, the infrared spectra showed the nearly complete disappearance of the free silanol groups ( $\equiv\text{Si}-\text{OH}$ ) as judged by the decrease in the intensity of the band at  $3747\text{ cm}^{-1}$ . At the same time, a broad band attributable to hydrogen-bonded silanol appeared at  $3300\text{ cm}^{-1}$ . After the pellet had been kept under dynamic vacuum at  $25^\circ$  for 36 h, however, the intensity of the band at  $3747\text{ cm}^{-1}$  had mostly returned, and elemental analysis indicated selenium loading lower than 1% and a chlorine/selenium molar ratio of up to 10. These results indicated that the selenium oxychloride reacts, like thionyl chloride, with an  $\equiv\text{Si}-\text{OH}$  group to form an  $\equiv\text{Si}-\text{Cl}$  function, with no grafting reaction being observed.<sup>[32]</sup>

**b) Reaction between Diethyl Selenite  $(\text{EtO})_2\text{SeO}$  and  $\text{SiO}_{2-(500)}$** 

The reaction between  $(\text{EtO})_2\text{SeO}$  and  $\text{SiO}_{2-(500)}$  was also monitored at room temperature by Fourier-Transform infrared (FTIR) spectroscopy and by quantitative analysis of the products. During the reaction the colour of the silica changed from white to deep yellow. After the addition of  $(\text{EtO})_2\text{SeO}$  (300 Torr) to  $\text{SiO}_{2-(500)}$ , the pellet was again kept under dynamic vacuum at  $25^\circ$  for 12 h in order to eliminate volatile materials. The infrared spectra showed the nearly complete disappearance of the free silanol groups ( $\equiv\text{Si}-\text{OH}$ ), as judged by the decrease in the intensity of the band at  $3747\text{ cm}^{-1}$ . At the same time, besides a broad band attributable to hydrogen-bonded silanol at  $3300\text{ cm}^{-1}$ , new bands attributable to the ethoxy ligand vibrations appeared in the  $\nu(\text{C}-\text{H})$  stretching ( $2982, 2938, 2903\text{ cm}^{-1}$ ) and deformation  $\delta(\text{C}-\text{H})$  ( $1488, 1447, 1389$  and  $1364\text{ cm}^{-1}$ ) regions (Figure 4).

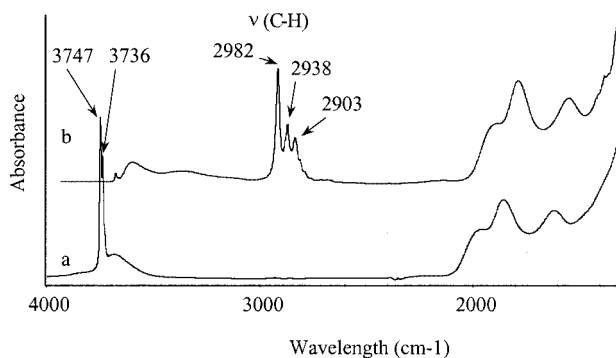


Figure 4. IR spectra of (a) partially labelled  $\text{Si}^{18}\text{O}_{2-(500)}$ , (b) after treatment with  $(\text{EtO})_2\text{SeO}$ , (c) after 6 h under vacuum ( $10^{-5}$  Torr) at room temperature in the expanded  $4000\text{--}2500\text{-cm}^{-1}$  region

The low-frequency region ( $1020\text{--}850\text{ cm}^{-1}$ ) shows new bands at  $934$  (broad) and  $874$  (sharp)  $\text{cm}^{-1}$ . A reaction between  $(\text{EtO})_2\text{SeO}$  and partially  $^{18}\text{O}$ -labelled surface hydroxy group (Figure 5) resulted in a shift of the  $934\text{-cm}^{-1}$  band to  $917\text{ cm}^{-1}$ . On this basis and by comparison with shifts of similar magnitude in the IR spectra of silica-supported  $^{18}\text{O}$ -labelled molybdenum,<sup>[33]</sup> and titanium<sup>[34–35]</sup> species, the vibration at  $934\text{ cm}^{-1}$  is attributed to  $\nu(\text{Si}-\text{OSe})$ .

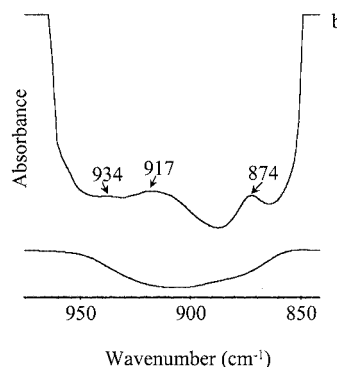
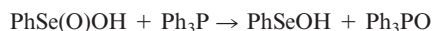


Figure 5. IR spectra of (a) partially labelled  $\text{Si}^{18}\text{O}_{2-(500)}$ , (b) after treatment with  $(\text{EtO})_2\text{SeO}$ , (c) after 6 h under vacuum ( $10^{-5}$  Torr) in the expanded  $1000\text{--}850\text{-cm}^{-1}$  region

The band at  $874\text{ cm}^{-1}$  could be attributed to the  $\nu(\text{Se}=\text{O})$  vibration.<sup>[30]</sup> From the literature,<sup>[13,36]</sup> it is known that the  $\text{Se}=\text{O}$  bond in  $\text{PhSeO}_2\text{H}$  can be reduced in the presence of  $\text{Ph}_3\text{P}$  to form  $\text{Ph}_3\text{PO}$  by the following reaction.



In order to confirm the presence of the  $\text{Se}=\text{O}$  bond in **1**, the reaction between **1** and a solution of triphenylphosphane in  $\text{C}_6\text{D}_6$  was performed and monitored by  $^{31}\text{P}$  NMR spectroscopy. After 2 h at  $60^\circ\text{C}$ , the  $^{31}\text{P}$  NMR spectrum presented, besides the resonance at  $\delta = -5$  ppm due to free  $\text{Ph}_3\text{P}$ , two new peaks, at  $\delta = +24$  ppm, due to  $\text{Ph}_3\text{PO}$ , and at  $\delta = +35$  ppm, attributed to  $\text{Ph}_3\text{PSe}$  (see below). The oxidation of  $\text{Ph}_3\text{P}$  to  $\text{Ph}_3\text{PO}$  was support for the continued presence of the  $\text{Se}=\text{O}$  bond in the grafted selenium species **1**.

The solid-state  $^{13}\text{C}$  MAS NMR spectrum of **1** contained two resonances at  $\delta = 17$  and  $57$  ppm, attributed to the  $\text{CH}_3$  and  $\text{CH}_2$  of an ethoxy group, respectively.

Se elemental analysis of the solid sample indicated that for two different samples the loading in Se was 3.84 and 3.72%, corresponding to an  $\text{Se}/\text{OH}$  group ratio of ca. 1.2, and C elemental analysis (C 1.45%) gave a molar ratio of  $\text{C}/\text{Se} = 2.5$ .

In conclusion, these data are consistent with the formation of an Se-surface compound, the Se atom being linked to three different ligands: an ethoxy, an oxo and a siloxy group from the surface [ $\equiv\text{SiOSe}(\text{O})\text{OEt}$ ] (**1**).

**Thermal Stability of 1**

The excess of carbon in the elemental analysis and the presence in the infrared spectrum (Figure 4) of a broad band attributable to hydrogen-bonded silanol at  $3300\text{ cm}^{-1}$

are probably due to physisorbed EtOH, which cannot be totally eliminated at room temperature even after 72 h under dynamic vacuum. On warming the sample at 60 °C or 100 °C, to eliminate the excess of ethanol, we observed a change in the colour of the pellet, which became orange (60 °C) to deep orange (100 °C) and the elemental analysis indicated a decrease in the % value of Se from 3.8 to 0.8. At the same time, small, red needles of metallic selenium appeared in the cold part of the glass equipment. Note that the formation of  $\text{Ph}_3\text{PSe}$  was observed during the reaction between **1** and  $\text{PPh}_3$ , suggesting that there was selenium leaching at 60 °C (see above).

An increase in the temperature caused changes of the species **1** towards metallic Se and traces of  $\equiv\text{SiOEt}$ , characterized by solid-state  $^{13}\text{C}$  MAS NMR (resonance at  $\delta = 16$  and 60 ppm attributed to the  $\text{CH}_3$  and  $\text{CH}_2$ , respectively, of an ethoxy group of  $\equiv\text{Si}-\text{OCH}_2\text{CH}_3$ ).<sup>[25]</sup>

## Reactivity of **1** towards Acetaldehyde

### a) Surface Chemistry of Acetaldehyde on Silica

The reaction between acetaldehyde and silica  $\text{SiO}_{2-(500)}$  was monitored in situ by infrared spectroscopy. It was observed that, as with  $\text{SiO}_{2-(300)}$ , there was formation of crotonaldehyde species by surface aldolization of adsorbed acetaldehyde.<sup>[37]</sup> In contrast, this reaction was not observed with  $\text{SiO}_{2-(800)}$ .<sup>[38]</sup>



### b) Surface Chemistry of Acetaldehyde on **1**

The reaction between acetaldehyde and silica modified with selenium derivative **1** was also monitored in situ by infrared spectroscopy (Figure 6, a and b). At first, comparison of the infrared spectra indicated that there was no more acetaldehyde (no band at 2804 and 1730  $\text{cm}^{-1}$ ), and no formation of crotonaldehyde species (no bands at 3042 and 1642  $\text{cm}^{-1}$ ) (Figure 6, b). No free silanol groups were generated, and a new, broad band at 3368  $\text{cm}^{-1}$  could be attributed to a hydrogen-bonded OH group. The pattern due to the EtO group, at 2982, 2938 and 2903  $\text{cm}^{-1}$ , was unchanged, suggesting that the ethoxy group was still present (Figure 6, a). The new weak band at 2881  $\text{cm}^{-1}$  (versus 2804  $\text{cm}^{-1}$  for free acetaldehyde) could be due to aldehydic C–H stretching for an aldehyde with an electronegative group in the  $\alpha$ -position.<sup>[39]</sup> The vibration at 1725  $\text{cm}^{-1}$  could be attributable to glyoxal, which shows only one carbonyl adsorption peak with no shift from the normal absorption position of monoaldehyde absorptions.<sup>[39]</sup>

At the same time, in the 950–850- $\text{cm}^{-1}$  region, the band at 873  $\text{cm}^{-1}$  attributed to  $\nu(\text{Se}=\text{O})$  had disappeared whereas the bands at 935 and 917  $\text{cm}^{-1}$ , attributed to  $\nu(\text{Si}-^{16}\text{OSe})$  and  $\nu(\text{Si}-^{18}\text{OSe})$ , respectively, were still present (Figure 7).

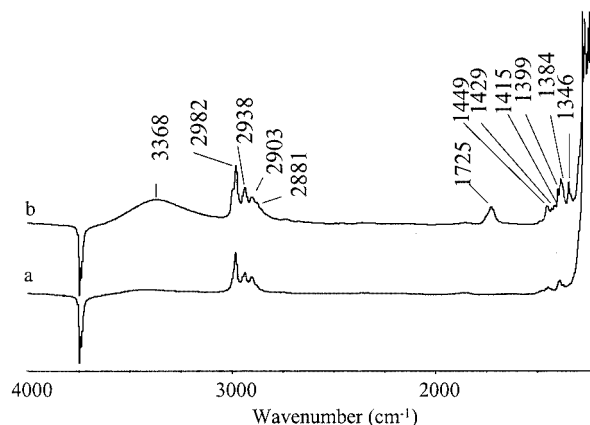


Figure 6. IR spectra of (a) difference spectrum of partially labelled  $\text{Si}^{18}\text{O}_{2-(500)}$  after treatment with  $(\text{EtO})_2\text{SeO}$  and the spectrum of starting silica, (b) difference spectrum of **1** after treatment with acetaldehyde (at 25 °C and evacuation at  $10^{-5}$  Torr) and the spectrum of starting silica in the expanded 4000–1200- $\text{cm}^{-1}$  region

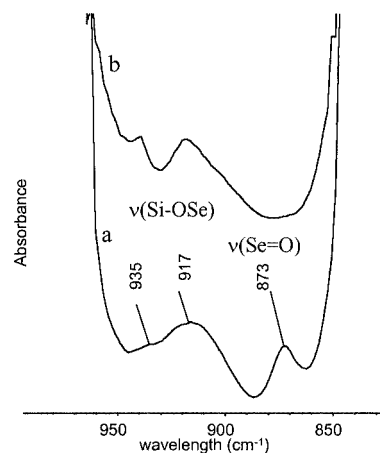


Figure 7. IR spectra of (a) difference spectrum of partially labelled  $\text{Si}^{18}\text{O}_{2-(500)}$  after treatment with  $(\text{EtO})_2\text{SeO}$  and the spectrum of starting silica, (b) difference spectrum of **1** after reaction with acetaldehyde (at 25 °C and evacuation at  $10^{-5}$  Torr) and the spectrum of starting silica in the expanded 1000–850- $\text{cm}^{-1}$  region

All these data seemed to indicate that the stoichiometric reaction between acetaldehyde and surface species **1**, resulted firstly in the exchange of the ethoxy ligand by vinyl alcohol, with concomitant formation of ethanol, and secondly in the formation of the selenate(II) ester of the enol species **2**, stopping at this stage in the absence of protic solvent (Figure 8).

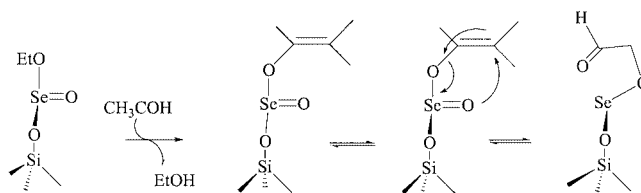


Figure 8. Proposed reaction between acetaldehyde and **1**



## Conclusion

The reaction between  $(\text{EtO})_2\text{SeO}$  and silica resulted in the formation of a unique surface species  $(\equiv\text{SiO})\text{Se}(\text{O})\text{OEt}$  (**1**), which has been fully characterized. Preliminary results from the reaction between acetaldehyde and **1** seemed to indicate that there was formation of ethanol and the selenate(II) ester of the enol derivative on the surface (**2**). However, the use of **1** as an oxidative reagent is limited, due to its low thermal stability and easy leaching of selenium in the presence of protic solvent.

## Experimental Section

**General:** All chemicals were purchased from Aldrich. Cyclohexane was distilled under argon from Na/K alloy, degassed and stored under argon in the presence of Na.  $\text{C}_6\text{D}_6$  (SDS, 99.6%) was degassed by three “freeze-pump-thaw” cycles and dried with freshly regenerated 3-Å molecular sieves. All operations were performed in the strict absence of oxygen and water, under purified argon with use of vacuum-line techniques. Elemental analyses were performed by the Central Analysis Service of the CNRS at Solaize. Solid-state NMR spectra were recorded with a Bruker DSX-300 machine equipped with a standard 4-mm double-bearing probe head and operating at 75.47 and 300.18 MHz for  $^{13}\text{C}$  and  $^1\text{H}$ , respectively. Chemical shifts are given with respect to TMS, with adamantane as an external reference ( $\delta = 37.7$  ppm for the highest chemical shift). Solution NMR spectra were recorded with Bruker AC 300 MHz ( $^1\text{H}$ ,  $^{13}\text{C}$ ) and DRX 500 MHz ( $^{77}\text{Se}$ ) spectrometers. Chemical shifts are reported in ppm and referenced to residual solvent resonances ( $\text{C}_6\text{D}_6$ :  $\delta = 7.15$  ppm for  $^1\text{H}$ ;  $\delta = 128$  ppm for  $^{13}\text{C}$ ), or external standards ( $^{77}\text{Se}$ ,  $\text{Me}_2\text{Se}$ ).<sup>[40]</sup> Infrared spectra were recorded under vacuum with a Nicolet 550 FT spectrometer in an infrared cell equipped with ZnSe windows. The conversion and selectivities were determined by HPLC. Two columns were necessary. For the detection of acetaldehyde, glyoxal and glyoxylic acid (as oxime derivatives),<sup>[41]</sup> an Interchim N7 column (symmetry C18, 5  $\mu\text{m}$ ;  $l = 25$  cm,  $d = 4.6$  mm; eluent: acetonitrile/water/sulfuric acid, 35:65:0.1 (v/v); flow rate: 1 mL/min; detection: UV 235 nm) thermostatted at 42 °C was used. *o*-Toluic acid was used as an internal reference. For the quantification of other acids (acetic, formic and oxalic ...) a Waters Phenomex column was used ( $l = 30$  cm,  $d = 3/8''$ ; eluent: 0.05 N sulfuric acid; flow rate: 0.5 mL/min; detection: UV 210 nm). Mass spectrometry was performed with an MAT 95 XL Thermoquest-Finnigan instrument (chemical ionization,  $\text{NH}_3$ ). The mass was calculated by use of  $^{80}\text{Se}$  (49.8%). The silica support (Aerosil® Degussa, 200  $\text{m}^2\cdot\text{g}^{-1}$ ) was compacted into a disk (30 mg) for infrared studies or was hydrated, dried (80 °C) and crushed to prepare large quantities (1–2 g) for NMR studies and elemental analysis. Before the reaction, the silica was calcinated at 400 °C in air for 4 h to remove hydrocarbon impurities and dehydroxylated at the desired temperature (500 °C) under high vacuum ( $10^{-5}$  Torr) for 12 h (referred to as  $\text{SiO}_{2-(500)}$ ).  $\text{Si}^{18}\text{O}_2$  was prepared by calcination in air at 500 °C for 4 h, followed by partial dehydroxylation at 500 °C for 10 h.  $^{18}\text{O}$ -enrichment of the surface hydroxy groups was achieved by exposing the silica to  $\text{H}_2^{18}\text{O}$  vapour at room temperature for 12 h, followed by dehydroxylation under dynamic vacuum at 500 °C for 10 h.

**General Procedure for the Oxidation of Acetaldehyde with  $\text{SeO}_2$  or  $\text{H}_2\text{SeO}_3$ :** A mixture of  $\text{SeO}_2$  (39 mmol) and  $\text{CH}_3\text{CHO}$  (35 mmol) in propionic acid (70% in water, 10 mL) was stirred under argon at

90 °C for 12 h in a Schlenk tube fitted with a condenser. After filtration of metallic selenium, which had precipitated during the reaction, the reaction mixture was analysed by HPLC.

**General Procedure for the Oxidation of Acetaldehyde with  $\text{PhSeO}_2\text{H}$  or  $\text{PhSeO}_2\text{H} + \text{H}_2\text{O}_2$  (1:1, mol/mol):** A mixture of  $\text{PhSeO}_2\text{H}$  (39 mmol) and  $\text{CH}_3\text{CHO}$  (35 mmol) in propionic acid (70% in water, 10 mL) was stirred under argon at 90 °C for 12 h in a Schlenk tube fitted with a condenser [with  $\text{PhSeO}_2\text{H}$  in the presence of  $\text{H}_2\text{O}_2$  (1:1, mol/mol) the reaction time was 20 min]. A white precipitate was filtered off and identified as  $\text{PhSe-SePh}$  by  $^{77}\text{Se}$  NMR [ $\delta_{\text{Se}}$  ( $\text{C}_6\text{D}_6$ ) = 460 ppm].<sup>[13]</sup> No metallic selenium was observed. The reaction mixture was then analysed by HPLC.

**Synthesis of Diethoxy Selenite  $(\text{EtO})_2\text{SeO}$ :**<sup>[30–31]</sup> A mixture of  $\text{SeO}_2$  (3.4 g, 31 mmol) and  $\text{EtOH}$  (20 mL, 348 mmol) in cyclohexane (35 mL) was stirred at reflux under argon for 16 h, in a Schlenk tube fitted with a Dean–Stark condenser. After filtration of metallic selenium and evaporation of the solvent,  $(\text{EtO})_2\text{SeO}$  was distilled (76 °C/15 mbar) as a pale yellow liquid (4.2 g, 74%).  $\text{C}_4\text{H}_{10}\text{O}_3\text{Se}$  (185.1): calcd. C 25.8, H 5.4, Se 43.0; found C 24.6, H 5.4, Se 42.6. IR (vapour):  $\tilde{\nu} = 874$   $\nu(\text{Se=O})$ , 659  $\nu(\text{Se-O})$   $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta = 3.85$  ( $\text{CH}_2$ , ABX<sub>3</sub> system), 1.1 ( $\text{CH}_3$ , t,  $J_{\text{HH}} = 7$  Hz) ppm.  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta = 57.4$  ( $\text{OCH}_2$ ), 16.8 ( $\text{CH}_3$ ) ppm.  $^{77}\text{Se}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta = 1339.8$  ppm. MS (CI):  $m/z$  (%) = 187 (50) [ $\text{M} + \text{H}$  ( $^{80}\text{Se}$ )]<sup>+</sup>.

**Reaction between Diethyl Selenite  $(\text{EtO})_2\text{SeO}$  and  $\text{SiO}_{2-(500)}$ :** For in situ infrared experiments, silica (30 mg) was pressed into an 18-mm self-supporting disk, placed in a sealed glass high-vacuum reactor fitted with ZnSe windows, and partially dehydroxylated under vacuum (500 °C, 12 h).  $(\text{EtO})_2\text{SeO}$  (300 Torr) was then introduced at room temperature onto the silica disk, which was maintained at liquid nitrogen temperature. The infrared cell was isolated. The silica disk was warmed to room temperature and kept at this temperature for 1 h. The pellet turned from white to yellow/orange. The cell was attached to a high vacuum line and the excess of  $(\text{EtO})_2\text{SeO}$  was removed by reverse distillation in a liquid nitrogen cooled tube. The pellet was then kept under dynamic vacuum ( $10^{-5}$  Torr, 12 h at 25 °C) in order to eliminate volatile materials. For NMR and elemental analysis samples, the same procedure as above was used with 2 g of  $\text{SiO}_{2-(500)}$  in a Schlenk tube attached to a high vacuum line. Elemental analysis: Se (3.84%) and C (1.45%). Solid-state  $^{13}\text{C}$  MAS NMR:  $\delta = 17$  and 57 ppm.

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