

which complements transient infrared absorption,^{21,10} to other organometallic systems.

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Selenoaldehydes: Preparation and Dienophilic Reactivity

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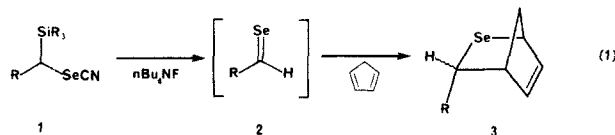
Selenoaldehydes have been elusive compounds by virtue of their high reactivity and difficulty of preparation.² Only a handful of literature reports discuss this rare class of compounds. The simplest of the selenoaldehydes, selenoformaldehyde, has been reported as a bridging ligand in binuclear osmium³ and manganese⁴ complexes and as a simple ligand in mononuclear rhodium complexes.⁵ Recently, selenoformaldehyde in trace quantities has been detected in the gas phase by near-infrared and infrared spectroscopy, following flash pyrolysis of its trimer,⁶ and by microwave⁷ and photoelectron⁸ spectroscopy of pyrolysis mixtures of dimethylselenide. No report, however, describing the specific preparation or characterization of selenoformaldehyde in condensed phases has appeared. Selenoacetaldehyde has been characterized in the gas phase by microwave spectroscopy following pyrolysis of its trimer,⁹ but it and other simple alkyl or aryl selenoaldehydes have been reported only as trimers or polymers in condensed phases.¹⁰ Selenoketene also has been observed in the gas phase by microwave spectroscopy following pyrolysis of 1,2,3-selenodiazole.¹¹ Two reports describe the isolation of several electron-rich selenoaldehydes,¹² though these derivatives are more accurately characterized as vinylogous selenoformamides. In this paper we report the preparation of simple alkyl and aryl selenoaldehydes, including selenoformaldehyde, and

Table I

compound	R	endo:exo	% yield
3a	H		66
3b	Me	2.3:1	83
3c	Et	4.3:1	78
3d	Pr	3.4:1	76
3e	Ph	2.6:1	81
3f	PhCH ₂	3.5:1	89
3g	<i>t</i> -Bu	9.0:1	39

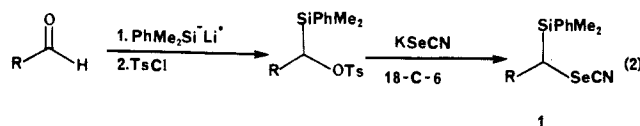
describe the intermolecular cycloadditions of these selenoaldehydes with cyclopentadiene.

Selenoaldehyde formation occurs efficiently and under mild conditions by the fluoride-induced elimination of cyanide from α -silyl selenocyanates **1**, as illustrated in eq 1. The seleno-



aldehydes **2** are generated slowly at 0 °C by syringe pump addition of Bu₄NF/THF to the α -silyl selenocyanates in the presence of 2 equiv of cyclopentadiene and readily undergo the Diels-Alder reaction to form the bicyclic adducts **3**.¹³ Representative examples are provided in Table I.^{14,15} The yields of bicyclic adducts are quite high (66–89%) except for the selenopivaldehyde analogue (39%), indicating efficient selenoaldehyde generation and cycloaddition. The slow generation and in situ trapping prevent accumulation of the reactive selenoaldehydes, suppressing trimerization or polymerization.

The α -silyl selenocyanate precursors are prepared quite readily by addition of the appropriate aldehyde to PhMe₂SiLi¹⁶ in THF at -78 °C, trapping of the α -silyl alkoxide with *p*-toluenesulfonyl chloride, and displacement of the *p*-toluenesulfonate with KSeCN, as shown in eq 2. Yields for this sequence are high, ranging from



70% to 90%. It is possible to execute this sequence in one reaction vessel, though yields are generally higher when the α -silyl tosylates are isolated and purified. This sequence converts simple aldehydes to selenoaldehydes in three steps with one purification, and proceeds in overall yields of 62–80%. The α -silyl selenocyanates are stable molecules and can be purified readily by flash chromatography on silica gel.

The Diels-Alder reaction of substituted selenoaldehydes with cyclopentadiene gave mixtures of exo and endo stereoisomers, with the endo isomer predominating in all cases. The mixtures were inseparable by GC or HPLC except for **3e**. Exo and endo isomer ratios were determined by NMR integration.

These Diels-Alder reactions closely parallel the analogous reaction of thioaldehydes with cyclopentadiene, in which endo:exo ratios range from 3.5:1 to 7:1.¹⁷ The structures of these Diels-

(13) A typical experimental procedure for selenoaldehyde cycloaddition is described as follows. Preparation of **3f**: To a vigorously stirred solution of 115 mg (0.334 mmol) of 1-(phenyldimethylsilyl)-2-phenylethyl selenocyanate and 44 mg (0.67 mmol) of cyclopentadiene in 8 mL of CH₂Cl₂ under N₂ at 0 °C was added an 8-mL solution (0.401 mmol) of *n*-Bu₄NF in THF over a 1-h period via syringe pump. The reaction mixture was subsequently warmed to room temperature, then diluted to 50 mL with pentane, filtered through activated, neutral aluminum oxide, and concentrated at reduced pressure. Flash chromatography on activated, neutral aluminum oxide (25:1:1, pentane/Et₂O/CH₂Cl₂) provided 74.0 mg (89.2%) of a 3.5:1 mixture of endo and exo cycloadducts **3f** as a colorless oil.

(14) All adducts and precursors gave satisfactory NMR, IR, and mass spectral data.

(15) Selenoformaldehyde was prepared from Me₂SiCH₂SeCN, obtained by potassium selenocyanate displacement of Me₂SiCH₂Cl in the presence of catalytic 18-crown-6 in refluxing THF.

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Alder adducts were determined by ^{13}C and ^1H NMR studies, including decoupling and nuclear Overhauser enhancement experiments. The NMR spectra of the selenoaldehyde adducts are quite similar to the corresponding thioaldehyde adducts,¹⁷ with some resonances shifted downfield and slight variations in coupling constants. As in the case of the substituted thioaldehyde adducts, the stereochemistry of the adducts was established on the basis of NOE studies. For instance, in the predominant (endo) isomer of the benzyl substituted adduct **3f**, the following pertinent enhancements were observed: the C-3 proton (12%) upon irradiation of the syn C-7 proton; the C-4 (bridgehead) proton resonance (10%) and the C-5 vinylic proton resonance (8%) upon irradiation of the C-8 (benzylic) methylene resonance. In the minor (exo) isomer, enhancement of the syn C-7 proton resonance (8%) was observed upon irradiation of the C-8 benzylic methylene proton resonance and enhancement of the C-5 vinylic proton resonance (7%) was observed upon irradiation of the C-3 endo proton resonance. These experiments firmly establish the identity of the predominant isomer as the endo Diels-Alder adduct.

The ability to generate selenoaldehydes efficiently and selectively by this method will facilitate further investigation of their structures, spectroscopic properties, and reactivity with other organic molecules and will permit application of these new reactions in synthetic and mechanistic chemistry.

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Supplementary Material Available: ^1H and ^{13}C NMR data for compounds **3a-g** and general experimental procedures for the synthesis of α -silyl selenocyanates from aldehydes (8 pages). Ordering information is given on any current masthead page.

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Direct SIMS Observation of Methylidyne, Methylene, and Methyl Intermediates on a Ni(111) Methanation Catalyst

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Methylidyne, methylene, and methyl fragments have been proposed to be key intermediates in the methanation of CO and H_2 over Group VIII (groups 8-10) metals,^{1-5,15} but the direct experimental observation of these species has proven difficult to achieve.^{1,2,5} Methylidyne and methylene fragments adsorbed on Fe(110) have been observed by electron energy loss spectrometry (EELS) immediately after Fischer-Tropsch synthesis at 1 atm,¹

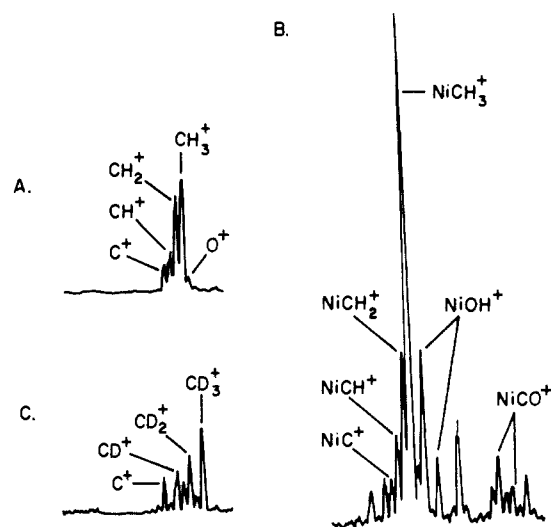


Figure 1. SIMS spectra of (A) low mass region, (B) Ni^+ region after $\text{CO} + \text{H}_2$ methanation, and (C) low mass region after $\text{CO} + \text{D}_2$ methanation.

Table I. SIMS Data for CH_x^+ and NiCH_x^+ Molecular Cluster Ions

ion	intensity	ion	intensity
C^+	0.19	NiC^+	0.09
CH^+	0.34	NiCH^+	0.17
CH_2^+	0.81	NiCH_2^+	0.34
CH_3^+	1.0	NiCH_3^+	1.0
O^+	0.12	NiO^+	0.11

but on Ru(001) only methylidyne was detected by EELS after hydrogenation of a predeposited carbide under vacuum conditions.² Only methyl fragments have been previously observed by X-ray photoelectron spectroscopy (XPS) after CH_3Cl decomposition on Ni or Co surfaces between 170 and 200 K.⁶ Here we present static secondary ion mass spectrometry (SIMS) and XPS data on a Ni(111) single crystal immediately after $\text{CO} + \text{H}_2$ reaction at 50-100 torr, 550 K, which show the formation of all three of the intermediates methyne, methylene, and methyl.

Experiments were conducted in a reactor-transfer system capable of shuttling a sample from an ambient pressure reactor to an ultrahigh vacuum (UHV) chamber where SIMS and XPS can be used to probe the sample surface composition.⁷ After cleaning the Ni crystal in the UHV chamber it was transferred to the batch reactor where a CO/H_2 (1:4) mixture was allowed to react at 473-573 K, 50-100 torr, for 30-60 min. The gas mixture was then analyzed by gas chromatography which showed the formation of CH_4 and CO_2 . An activation energy value of ~ 23.6 kcal/mol and a sample turnover frequency (TOF) of 5.1×10^{-3} molecules $\text{CH}_4/\text{site s}$ at 510 K were determined which are similar values to those obtained on previously studied Ni catalysts.^{8,9} Within 5 min after stopping the reaction, the crystal was transferred into the vacuum chamber and analyzed by XPS and SIMS, the latter using a 3-KeV Ar^+ ion beam at < 5 nA current. Care was taken to cool the crystal to ~ 298 K before evacuating the reactor to keep surface intermediates from desorbing.

Separate SIMS spectra were obtained in the NiCH_x^+ and CH_x^+ mass regions where $x = 0-3$, and typical data are shown in Figure 1A,B. The type of observed ions and their relative intensities are given in Table I. Both regions indicate that the molecular ion intensity decreases with decreasing values of x . The ionization potentials (IP) for the CH_x fragments decrease by 1.3 eV as x increases from 0 to 3.¹⁰ Correction for these differences using

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