Alder adducts were determined by ^{13}C and ^{1}H 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: ^{1}H 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] 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 CO + H_2 reaction at 50–100 torr, 550 K, which show the formation of all three of the intermediates methyne, methylene, and methyl.

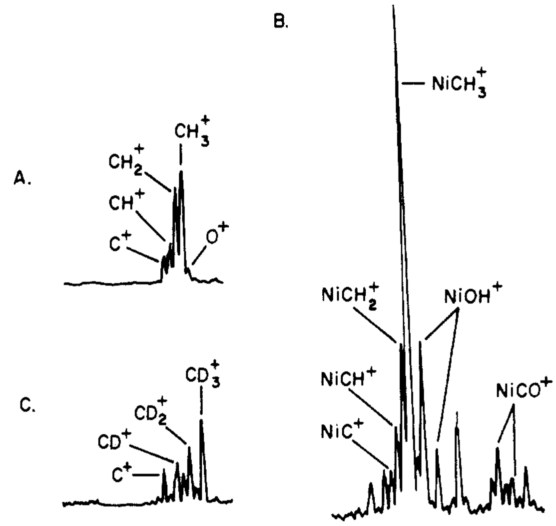

Figure 1. SIMS spectra af (A) low mass region, (B) Ni^+ region after CO + H_2 methanation, and (C) low mass region after CO + D_2 methanation.

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^{+3}	0.11

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 CH_4/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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the known exponential dependence of ion yield ion IP indicates that the concentration of the neutral intermediates is nearly equal.[11] Note also that there is a small isobaric $FeOH^+$ interference arising from the sample holder which contributes to the $NiCH_3^+$ intensity. As far as we know, CH_x distributions similar to those reported above have not been previously observed on Ni crystals exposed to CO + H_2 reaction conditions. An indirect observation by Happel et al. using labeling studies is the only other study which indicates that the concentrations of CH, CH_2, and CH_3 are within an order of magnitude of each other on a Ni/SiO_2 catalyst.[3]

To prove that the CH_x^+ species form from the reactant gases, a deuterium labeling study was performed under similar reaction conditions. The SIMS analysis, as shown in Figure 1C, indicates that C^+, CD^+, CD_2^+ are now the principal molecular ions. The intensity pattern follows that seen for the CH_x^+ ions. A similar experiment conducted with ^{13}CO yielded the expected $Ni^{13}CH_x^+$ cluster ions, without $Ni^{12}C^+$ cluster ions, indicating that the carbon in these species arises from the presence of the reactant gases and not from adventitious sources.

It is possible that the CH^+ and CH_2^+ ions are produced by CH_3^+ fragmentation during Ar^+ ion bombardment or by a number of complex gas-phase recombination processes. If all three ions are being generated from a single precursor, they each should exhibit identical dependencies as the temperature of the target is increased. Our experiments show that the CH_2^+ ion decreases in intensity when the target temperature reaches ~411 K, the CH_3^+ ion remains constant until ~443 K, and the CH^+ ion signal does not decrease until 483–503 K. One would expect that CH is more tightly bound to the metal than CH_2 or CH_3 fragments since it has the highest possible metal coordination. The C^+ ion loses very little intensity over the temperature range of 340–523 K, indicating it arises primarily from graphitic carbon deposited during the methanation reaction.

X-ray photoelectron spectra were utilized to characterize the carbon present on the surface after the methanation reaction. These spectra show the presence of graphitic carbon with a binding energy of 285.0 eV as well as partially hydrogenated carbide at 283.8 eV, in agreement with data and assignments given by Bonzel and Krebs.[12] All binding energies are referenced to the Ni Fermi level which places the Ni $2p_{3/2}$ level at 853.7 eV. The carbon coverage was estimated to be the equivalent of about $^1/_2$ monolayer, although our results as yet do not yield morphological information. There is also a linear increase in total (graphitic plus carbidic) carbon coverage with reaction temperature between 480 and 580 K.

For the reasons discussed above, we believe that the SIMS results suggest that CH_x fragments have similar stabilities on the Ni(111) surface. The data argue against a model in which the rate-determining step for methanantion is the formation of CH species directly from active carbon.[13] If these surface concentrations are similar to within an order of magnitude, a mechanism involving the sequential hydrogenation of surface carbon similar to that originally proposed by Fischer and Tropsch seems most plausible.[14]

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$HOs_3(CO)_{10}(C_2H_5)$: An Alkyl Complex with Observable α, β, and Reductive Elimination Processes[‡]

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An alkyl moiety complexed to an array of metal atoms is a key putative intermediate in hydrocarbon transformations catalyzed by metal surfaces.[1] There is a need for molecular polynuclear complexes with alkyl ligands to serve as models for such intermediates, particularly in terms of providing relative probabilities for competing reaction pathways.[2] We wish to report the synthesis of a metal cluster compound containing a prototypical alkyl group and the observation of concomitant α, β, and reductive elimination reactions (see Scheme I).

The ethyl compound **3** is prepared in two steps from the vinyl compound **1**.[3] Thus, the ^1H NMR hydride signal of **1** (δ –19.4) in THF is replaced by that due to **2** (δ –15.95) following the addition of ca. 2 equiv of $LiHBEt_3$ (1 M in THF) at room temperature. Metathesis with R_4NBr (R = Me,Et) in aqueous THF (1:2) allows isolation of $R_4N[2]$ as an air-sensitive orange-brown solid in ca. 90% yield.[4] Protonation of this salt at low temperature (–70 °C, CD_2Cl_2, $HBF_4{\cdot}Et_2O$) yields **3** (hydride at δ –14.88),[5] which is isolated as a bright yellow solid in 70% yield after pentane extraction of the dry residue at low temperature.

A single ^1H NMR pattern is observed for the methylene protons on C_α in **3**, but its high field postion (δ –4.71) suggests that the two protons are equilibrating between two quite different sites, one a normal C–H bond and the other an "agostic"[6] three-center, two-electron C··H··Os bond. This picture is substantiated by the position of the methylene proton signal for **3**-α-*d*(from **2** + DBF_4), which occurs at δ –5.78 at 20 °C and shifts to δ –6.29 at –72 °C, due to the energetic preference of H over D for the bridging site.[7] These effects were observed previously for the methyl complex $HOs_3(CO)_{10}(CH_3)$,[8] and an analogous structure is therefore indicated for **3**.[9]

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(4) $[Et_4N]$-**2**: ^1H NMR (CD_2Cl_2, 360 MHz) δ 7.00 (q of d, 1 H), 2.41 (d, 3 H, $J(CH{-}CH_3)$ = 7.5 Hz), –15.95 (d, 1 H, $J(CH{-}H)$ = 2.8 Hz); Et_4N cation resonances at 3.21 (q, 8 H) and 1.35 (t, 12 H, J = 7 Hz). $[Me_4N]$-**2** Anal. Calcd for $C_{16}H_{17}NO_{10}Os_3$: C, 20.15; H, 1.80; N, 1.47; Os, 59.82. Found: C, 20.41; H, 1.85; N, 1.32; Os, 59.62. IR (KBr) ν(CO) 2090 (w), 2069 (m), 2048 (m), 2009 (vs), 1980 (s, sh), 1931 (s) cm^{-1}. IR(CH_2Cl_2) ν(CO) 2074 (w), 2048 (w), 2016 (vs), 1981 (s), 1937 (m) cm^{-1}.

(5) ^1H NMR (CD_2Cl_2, 360 MHz, –10 °C) δ 1.89 (t, 3 H), –4.71 (q, 2 H, $J(CH_2{-}CH_3)$ = 5.8 Hz), –14.88 (s (b), 1 H).

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