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]

Acknowledgment. We are grateful to Dr. D. W. Goodman for information concerning the gas analysis system and for other helpful discussions. This research was supported by the National Science Foundation, Air Force Office of Scientific Research, and the Office of Naval Research.

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(11) Norskov, J. K.; Lundqvist, B. I. *Phys. Rev. B* **1979**, *19*, 5661.

(12) Krebs, H. J.; Bonzel, H. P. *Surf. Sci.* **1980**, *99*, 570.

(13) Hayes, R. E.; Thomas, W. J.; Hayes, K. E. *Appl. Catal.* **1983**, *6*, 53.

(14) Fischer, F.; Tropsch, H. *Brennst.-Chem.* **1926**, *7*, 97; *Chem. Ber.* **1926**, *59*, 830.

(15) In this paper the periodic group notation in parenthesis is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block element comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

$HOs_3(CO)_{10}(C_2H_5)$: 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]

[‡] Dedicated to the memory of Earl L. Muetterties.

(1) (a) Muetterties, E. L.; Stein, J. *Chem. Rev.* **1979**, *79*, 479. (b) Brady, R. C.; Pettit, R. *J. Am. Chem. Soc.* **1980**, *102*, 6181; **1981**, *103*, 1287. (c) Bell, A. T. *Catal. Rev.-Sci. Eng.* **1981**, *23*, 1981. (d) Biloen, P.; Sachtler, W. M. H. *Adv. Catal.* **1981**, *30*, 165. (e) For a contrasting view, see: Zaera, F.; Somorjai, G. A. *J. Am. Chem. Soc.* **1984**, *106*, 2288.

(2) Studies on binuclear alkyl complexes that address mechanistic issues include the following: (a) Chisholm, M. H.; Huffman, J. C.; Tatz, R. J. *J. Am. Chem. Soc.* **1983**, *105*, 2075. (b) Azam, K. A.; Brown, M. P.; Cooper, S. J.; Puddephatt, R. J. *Organometallics* **1982**, *1*, 1183. (c) Schore, N. E.; Ilenda, C. S.; White, M. A.; Bryndza, H. E.; Matturro, M. G.; Bergman, R. G. *J. Am. Chem. Soc.* **1984**, *106*, 7451. (d) Nutton, A.; Vazquez de Miguel, A.; Isobe, K.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1983**, 166.

(3) Nucleophilic attack occurs at the β-carbon of the vinyl moiety rather than at an osmium atom. See: (a) Churchill, M. R.; DeBoer, B. G.; Shapley, J. R.; Keister, J. B. *J. Am. Chem. Soc.* **1976**, *98*, 2357. (b) Deeming, A. J.; Hasso, S. *J. Organomet. Chem.* **1976**, *112*, C39. (c) Deeming, A. J.; Manning, P. J. *J. Organomet. Chem.* **1984**, *265*, 87.

(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).

(6) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395.

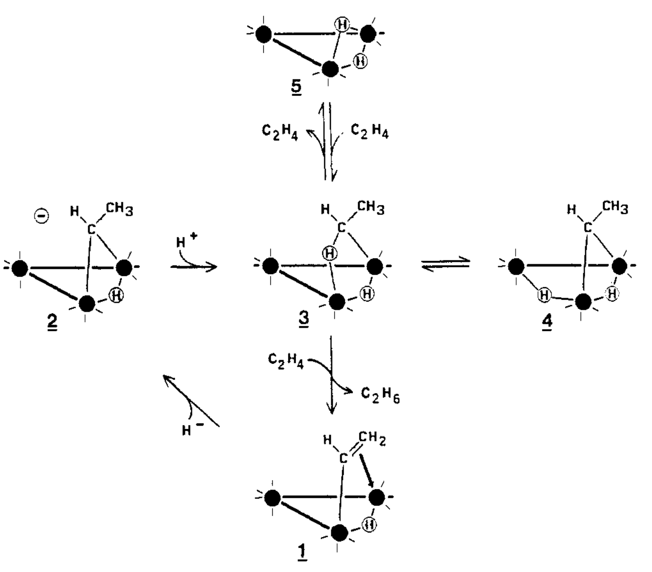
(7) The energy difference between the D- and H-bridged forms can be determined from equations analogous to those derived for the methyl complex[8a] and within experimental error the value is the same (130 ± cal/mol) for both compounds.

(8) (a) Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1978**, *100*, 7726. (b) Calvert, R. B.; Shapley, J. R.; Schultz, A. J.; Williams, J. M.; Suib, S. L.; Stucky, G. D. *J. Am. Chem. Soc.* **1978**, *100*, 6240.

(9) The equilibrium isotope effects taken to characterize this type of bridging methyl group have been substantiated in the case of a diiron complex with a crystal structure: Dawkins, G. M.; Green, M.; Orpen, A. G.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1982**, 41.

0002-7863/86/1508-1316$01.50/0

Scheme I



When the temperature of a solution of **3** is raised above −20 °C, the ^1H NMR signals due to **3** decrease in intensity while four new signals appear and increase in intensity (δ 6.76 (q, 1 H), 2.49 (d, 3 H, J = 7.0 Hz), −14.26 (s, 1 H), −20.43 (s, 1 H). These signals arise from the ethylidene tautomer **4**, formed by elimination of a C_α–H bond of **3**. This process is first order in **3** with a rate constant at −10 °C of 1.6 ± 0.1 × 10^{-4} s^{-1}. The equilibrium constant $K = [4]/[3] = 7.3 \pm 0.7$ is temperature independent over the range −10 to 16 °C. This value compares with $K = 3.5 \pm 0.1$ (CD_2Cl_2, 32 °C) for the analogous methyl/methylene system.[8b]

Upon raising the sample temperature to ca. 19 °C, a C_β–H elimination process becomes observable as ethylene and **5** form. The appearance of **5** is first order with a rate constant of 5.9 ± 0.3 × 10^{-4} s^{-1} at 19 °C. At this temperature the rate of α-elimination is approximately 100-fold greater.[10] The overall β-elimination process is actually reversible,[11] since upon treatment of **5** with a large excess of ethylene (ca. 5 atm) approximately 10% of **3** + **4** is observable after ca. 3 h. However, over the same time period formation of **1** together with an equivalent of ethane also occurs.[12] Thus, ethylene coordination to **3** induces reductive elimination of ethane at a rate which is comparable with the formation of **3** from **5**. Reductive elimination of ethane from **3** is induced also by excess styrene (with formation of $HOs_3(CO)_{10}(\mu\text{-}CH{=}CHPh)$) or more readily by stronger nucleophiles L = PPh_2Me or t-BuNC (with formation of $Os_3(CO)_{10}L_2$). This ligand dependence controls the competition between ethane and ethylene elimination. For example, with L = t-BuNC added to the **3** + **4** mixture at 25 C, a L:Os_3 ratio of 2:1 leads to a C_2H_6:C_2H_4 ratio of 3:1 in the gas produced, but if the L:Os_3 ratio is increased to 10:1, the C_2H_6:C_2H_4 ratio becomes 18:1.

Although the methylene hydrogens in **3** should be diasterotopic, they appear equivalent by ^1H NMR even at −90 °C. Examination of the ^{13}C NMR spectrum of **3** down to −90 °C shows averaged spectra indicative of a time-averaged plane of symmetry perpendicular to the osmium triangle.[13] We propose that equilibration of the methylene hydrogens occurs by breaking the C··H··Os bond on one side of the cluster and then forming a new C··H··Os bond on the other side.[14] This process,[15] which apparently has $\Delta G^* \leq 5$ kcal/mol, presumably proceeds via a symmetric unsaturated intermediate, electronically analogous to the dihydride complex **5**. This symmetric species, in which *neither* C–H bond interacts with the osmium, may be highly significant for the β-elimination process. Although the ground-state structure of **3** involves an α-C–H bond in a donor interaction with the metal center, interaction of a β-C–H bond must develop in order for β elimination to occur.[16] We are unable to say whether this involves two metal centers or just one.[2a,b]

In summary, for this cluster–alkyl system the familiar β-elimination process is thermodynamically favored, at least when driven by ethylene dissociation. However, the kinetically favored α-elimination process generates a relatively high concentration of the alkylidene form. This serves to "protect" the alkyl by inhibiting destructive pathways. This property could be important also for alkyl reactions on metals, if, for example, migration onto CH_2 or CO moieties must compete with elimination of alkene or alkane. Furthermore, an analogous ethyl → ethylidene conversion is likely to be involved in the conversion of ethylene to ethylidyne observed on many metal surfaces.[17]

Acknowledgment. This work was supported by National Science Foundation Grant CHE 84-07233. Instruments supported by the Grants NSF CHE 79-16100 and NIH GM-27029 were utilized for NMR and mass spectra, respectively.

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[10] The fact that the D atom in **3**-*d* stays in the α position rules out rapid equilibration with an ethylene complex, assuming facile rotation in the latter.

[11] This is consistent with previous observations that $H_2Os_3(CO)_{10}$ is an olefin isomerization catalyst: (a) Keister, J. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1976**, *98*, 1056; (b) Deeming, A. J.; Hasso, S. *J. Organomet. Chem.* **1976**, *114*, 313.

[12] Keister, J. B.; Shapley, J. R. *J. Organomet. Chem.* **1975**, *85*, C29.

[13] The ^{13}C NMR spectrum (90 MHz, CD_2Cl_2, −90 °C) (from ca. 50% ^{13}CO-enriched $Os_3(CO)_{12}$) shows carbonyl signals at δ 183.6 (s, 0.5 C; d, 0.5 C, ^2J(C–C) = 35 Hz), 182.3 (s, 0.5 C; d, 0.5 C, ^2J(C–C) = 35 Hz), 176.6 (s, 2 C), 176.0 (s, 2 C), 172.3 (s, 2 C), 170.7 (d, 2 C, ^2J(C–H) = 11 Hz).

[14] The complexes $[ReW(\mu\text{-}CH_2R)(\mu\text{-}Me_2PCH_2PMe_2)(CO)_7]$ (R = C_6H_4Me, Me) have a C_α··H··W bridge that is fixed; the two methylene hydrogens do not exchange: Jeffery, J. C.; Orpen, A. G.; Robinson, W. T.; Stone, F. G. A.; Went, M. J. *J. Chem. Soc., Chem. Commun.* **1984**, 396.

[15] This process is related conceptually to the σ,π-interconversion of the bridging vinyl group in $HOs_3(CO)_{10}(\mu\text{-}CH{=}CH_2)$: Shapley, J. R.; Richter, S. I.; Tachikawa, M.; Keister, J. B. *J. Organomet. Chem.* **1975**, *94*, C43.

[16] (a) Brookhart, M.; Green, M. L. H.; Pardy, R. B. A. *J. Chem. Soc., Chem. Commun.* **1983**, 691. (b) Cracknell, R. B.; Orpen, A. G.; Spencer, J. L. *J. Chem. Soc., Chem. Commun.* **1984**, 326.

[17] Beebe, T. P., Jr.; Albert, M. R.; Yates, J. T., Jr. *J. Catal.* **1985**, *96*, 1. This paper also provides an excellent summary of prior work on the ethylidyne species.

Does Lysozyme Follow the Lysozyme Pathway? An Alternative Based on Dynamic, Structural, and Stereoelectronic Considerations[†]

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In this paper we present a pathway (Scheme I) for the hydrolysis of oligoglycosides by the enzyme lysozyme that differs from the accepted mechanism (Scheme II).[1-4] The new pathway, suggested by results of a 55-ps molecular dynamics simulation of a lysozyme complex with hexakis(N-acetylglucosamine), $(GlcNAc)_6$, is consistent with the available experimental data and with stereoelectronic considerations. A fundamental feature of the modified pathway is that an *endo*cyclic bond is broken in the initial step, in contrast to the *exo*cyclic bond cleavage in the accepted mechanism.

The molecular dynamics simulation employed an initial structure with $(GlcNAc)_6$ built into the active site by use of the coordinates of a lysozyme–$(GlcNAc)_3$ complex and of the native enzyme; details are given separately.[5] Minor reorientation of

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[1] Walsh, C. "Enzymatic Reaction Mechanisms"; W. H. Freeman: San Francisco, 1979.

[2] Blake, C. C. F.; Mair, G. A.; North, A. C. T.; Phillips, D. C.; Sarma, V. R. *Proc. R. Soc. London, Ser. B* **1967**, *167*, 365.

[3] Vernon, C. A. *Proc. R. Soc. London, Ser. B* **1967**, *167*, 378.

[4] Imoto, T.; Johnson, L. M.; North, A. C. T.; Phillips, D. C.; Rupley, J. A. "The Enzymes"; Academic: New York, 1972; Vol. 7, p 665.

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