ease of opening the chelate ring because of (a) size, (b) bulkiness, and (c) a strong acyl-trans effect. Chelate opening may be important also in the CO insertion step.[19]

Chlorobenzene oxidative addition to **1** is also more facile compared to phenylphosphine palladium complexes. High electron density at the metal is undoubtedly one reason, but the low affinity of **1** for CO, leaving in solution a higher concentration of an unsaturated complex, may also be important. Clearly a number of factors may be involved in making **1** an efficient, unique catalyst.[20] This, as well as potential use of **1** and related complexes in other catalytic reactions, is under active investigation.

Acknowledgment. We thank the Minerva Foundation, Munich, Germany, and the Yeda Fund, Israel, for supporting this work. Thanks are also due to Prof. K. Tani for information on the preparation of dippp.

---

[18] Alcoholysis of acylpalladium complexes containing monodentate phosphines requires heating[7,17] and appears to be much slower than that of **3**.

[19] The ligand dppp was recently observed to have an accelerating effect on the carbomethoxylation of the reactive aryl trifluoromethanesulfonates: Dolle, R. E.; Schmidt, S. J.; Kruse, L. I. *J. Chem. Soc., Chem. Commun.* **1987**, 904.

[20] The second dippp ligand may also play a role in the catalysis. Significantly lower yields are obtained when either **2** or **3** is utilized as catalyst.

Direct Observation of β-Hydride Elimination Reactions on Metal Surfaces

Francisco Zaera

Department of Chemistry
University of California, Riverside
Riverside, California 92521

Received July 3, 1989
. *Revised Manuscript Received September 14, 1989*

In this communication we report direct evidence for a β-hydride elimination mechanism in hydrocarbon decomposition over metal surfaces. This pathway is perhaps the most common of the decomposition reactions in transition-metal alkyls containing β-hydrogens; there are many examples for such a mechanism in the organometallic literature.[1] β-Elimination has also been indirectly invoked when explaining mechanisms for hydrocarbon conversion over transition-metal catalysts.[2,3] However, due to the difficulty in forming alkyl moieties on metal surfaces, the direct detection of such processes has so far eluded surface scientists. We here present thermal programmed desorption (TPD) spectra from partly deuterated fragments chemisorbed on Pt(111) which unequivocally show that ethyl moieties decompose on those surfaces by β-hydrogen elimination to form adsorbed ethylene.

The experiments were performed in an ultrahigh-vacuum chamber equipped with surface-sensitive instrumentation, as described in detail elsewhere.[4] Ethyl groups were formed on the platinum surface by saturation with ethyl iodide at liquid nitrogen temperatures followed by annealing above 170 K. Using X-ray photoelectron (XPS) and reflection-absorption infrared (RAIRS) spectroscopies, we have previously shown that this procedure conduces to the breaking of the C-I bond with the concurrent formation of ethyl moieties,[5,6] and Lloyd et al. have recently used high-resolution electron energy loss spectroscopy (HREELS) to demonstrate that ethyl groups are stable on Pt(111) below 230 K.[7]

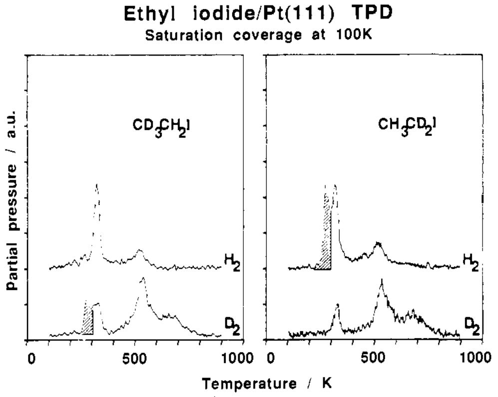


Figure 1. H_2 and D_2 thermal programmed desorption (TPD) spectra from saturation coverages of CD_3CH_2I (left) and CH_3CD_2I (right) on Pt(111). The peaks corresponding to the first decomposition step (a β-hydride elimination) are highlighted.

Adsorbed ethyl decomposes thermally above 230 K to yield a new intermediate with C_2H_4 stoichiometry. This conversion has been studied by XPS,[5] HREELS,[7] and TPD.[5,7] Hydrogen (H_2) thermal desorption from CH_3CH_2I displays several peaks, the first at 275 K which corresponds to one-fifth of the total area under the spectrum (one out of five hydrogen atoms in CH_3CH_2I).[5] Here we have used partly deuterated ethyl iodide compounds in order to determine the origin of that first desorption feature. Figure 1 shows TPD spectra for H_2 and D_2 desorption from both adsorbed CD_3CH_2I and CH_3CD_2I. It is clear from the data that in the case of CD_3CH_2I the first desorption peak is composed almost exclusively of deuterium gas, while for CH_3CD_2I this feature is only seen in the H_2 trace (shadowed areas in the figure). These results clearly indicate that the hydrogen atom extracted in the first decomposition step of ethyl chemisorbed on Pt(111) comes from the β position. Additional TPD, XPS, and HREELS data has been used to determine that chemisorbed ethylene forms as a result of ethyl decomposition, corroborating the proposed β-hydride elimination mechanism.[5,7] Adsorbed ethylene then reacts to form ethylidyne by going through a vinyl intermediate.[5,8] This reaction starts at temperatures as low as 260 K, but its rate peaks around 305 K in TPD experiments.[9]

This is, to the best of our knowledge, the first study showing that a β-hydride elimination mechanism is operative in the decomposition of chemisorbed alkyls, in an analogous fashion to well-known chemistry for organometallic compounds. A particularly interesting example has been given recently by Brown et al., in which an ethyldiplatinum(I) complex was synthesized by starting from ethyl iodide and $Pt_2(\mu\text{-}Ph_2PCH_2PPh_2)_3$.[10] This compound undergoes β-H elimination at temperatures between 60 and 100 °C to yield ethylene and ethane. Ethane formation was also seen in our system.[5] Establishing the viability of the β-H elimination pathway on surfaces has clear implications in determining the mechanism for catalytic H-D exchange and hydrogenolysis of alkanes.[2,3] In particular, ethane H-D exchange on Pt(111) yields d_1- and d_6-substituted molecules predominantly. This product distribution can be explained by a mechanism involving ethyl groups as a common intermediate, which then reacts further by following two competitive pathways.[11,12] An additional intermediate with C_2H_4 stoichiometry is required to explain the high yield of fully deuterated ethane.[12] Previous data suggested

---

[1] Davidson, P. J.; Lappert, M. F.; Pearce, R. *Chem. Rev.* **1976**, *76*, 219.

[2] Kemball, C. *Catal. Rev.* **1971**, *5*, 33.

[3] Clarke, J. K. A.; Rooney, J. J. *Adv. Catal.* **1976**, *25*, 125.

[4] Zaera, F. *J. Vac. Sci. Technol.* **1989**, *A7*, 640.

[5] Zaera, F. *Surf. Sci.* **1989**, *219*, 453.

[6] Zaera, F.; Hoffmann, H.; Griffiths, P. R. *Vacuum*, submitted.

[7] Lloyd, K. G.; Roop, B.; Campion, A.; White, J. M. *Surf. Sci.* **1989**, *214*, 227.

[8] Zaera, F. *J. Am. Chem. Soc.* **1989**, *111*, 4240.

[9] Zaera, F.; Fischer, D. A.; Carr, R. G.; Kollin, E. B.; Gland, J. L. In *Molecular Phenomena at Electrode Surfaces*; Soriaga, M. P., Ed.; ACS Symposium Series 378; American Chemical Society: Washington, DC, 1988.

[10] Brown, M. P.; Yavari, A. *J. Chem. Soc., Dalton Trans.* **1985**, 2421.

[11] Zaera, F.; Somorjai, G. A. *J. Phys. Chem.* **1985**, *89*, 3211.

[12] Miyahara, K. *J. Res. Inst. Catal., Hokkaido Univ.* **1956**, *4*, 143.

0002-7863/89/1511-8744$01.50/0

it to be ethylidene fragments ($Pt_n{=}CHCH_3$),[11] but our present results argue for the formation of chemisorbed ethylene instead. More research is needed to clarify this point.

Registry No. Pt, 7440-06-4; CH_3CH_2I, 75-03-6; ethyl, 2025-56-1.

Cycloisomerization of α,ω-Diynes to Macrocycles

Barry M. Trost,* Seijiro Matsubara, and Joseph J. Caringi

Department of Chemistry, Stanford University
Stanford, California 94305

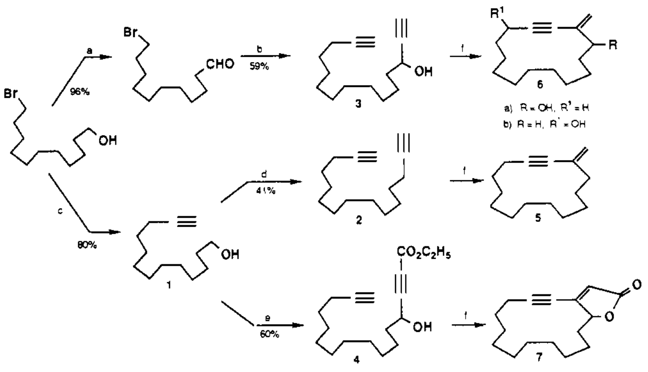
Received June 19, 1989

Cyclic acetylenes have attracted considerable interest recently with the discovery of the potent antitumor properties of neocarzinostatin and calichemicin/esperamicin.[2] In exploring new synthetic strategies, we have attempted to develop reactions in which the sum of the reactants corresponds precisely to the desired product to enhance chemical efficiency. In terms of a cyclization, such a process is an isomerization.[3,4] We record a successful realization of this goal directed toward cycloalkynes as outlined in eq 1 in which remarkable chemoselectivity is observed.[5]

(1)

Scheme I exemplifies the ease with which suitable substrates **2**–**4** can be synthesized. Displacements of alkyl halides with acetylide anion require the use of a dipolar aprotic solvent admixed with THF. HMPA or DMPU (1,3-dimethylhexahydro-2-pyrimidone) proved efficacious.[6] In the synthesis of **3**, both acetylenes were introduced in a single operation, wherein addition of the first equivalent of the acetylide in THF at −78 °C occurred at the carbonyl group and subsequent addition of HMPA and a second equivalent of the acetylide effected displacement of the bromide.

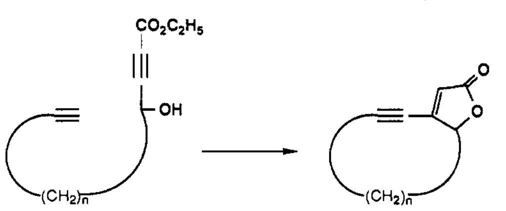
Scheme I. Synthesis and Cyclization of Diyne Substrates Exemplified[a]



[a] (a) $(COCl)_2$, DMSO, $(C_2H_5)_3N$, CH_2Cl_2. (b) (i) TMSC≡CLi, THF, −78 °C, then add HMPA, −78 °C to room temperature; (ii) TBAF, THF, H_2O, room temperature. (c) (i) TMSC≡CLi, THF, DMPU, −78 °C to room temperature (see text), then H_2SO_4, H_2O, THF; (ii) TBAF, THF, H_2O, room temperature. (d) (i) Br_2, dppe, CH_2Cl_2, 0 °C to room temperature; (ii) TMSC≡CLi, THF, DMPU, −78 °C to room temperature; (iii) TBAF, THF, H_2O, room temperature. (e) (i) $(COCl)_2$, DMSO, $(C_2H_5)_3N$, CH_2Cl_2; (ii) $LiC{\equiv}CCO_2C_2H_5$, THF, −78 °C. (f) See text.

If both acetylenes are terminal, the issue of chemoselectivity arises. To evade this issue initially, a benzene solution of the symmetrical diyne **2** was added slowly to 10 mol % of palladium acetate and 20 mol % of TDMPP [tris(2,6-dimethoxyphenyl)phosphine] in benzene at reflux. This reaction produced a 41% yield[7] of the monocyclic 14-membered-ring compound **5**.[8] The enyne moiety is characterized by both the ^1H (δ 5.16, d, $J = 2.3$ Hz, 1 H and 5.11, t, $J = 1.1$ Hz, 1 H for $=CH_2$; 2.34, t, $J = 6.2$ Hz, 2 H for $=CCH_2$; 2.12, t, $J = 7.3$ Hz, 2 H for $\equiv CCH_2$) and ^{13}C (δ 132.5 and 119.4 for $C{=}CH_2$; 90.7 and 81.3 for C≡C) NMR spectra. *Repeating this protocol with the unsymmetrical diyne **3** remarkably led to a single macrocycle in 46% yield.* Assignment as **6a**[8] rather than **6b** arises from the ^1H NMR spectrum, in which the signal for the propargylic methylene group remains (δ 2.38, ddd, $J = 16.3$, 6.9, 4.1 Hz and 2.33, ddd, $J = 16.3$, 7.0, 4.0 Hz) and the single allylic hydrogen appears at δ 4.08 (q, $J = 6.0$ Hz)[9] with small couplings to the terminal methylene hydrogens ($J = 1.2$ and 0.8 Hz) established by spin-decoupling experiments. This remarkably chemoselective cyclization appears to generate the thermodynamically more stable product, as predicted by MM2 calculations, which indicate that **6a** is about 1.9 kcal/mol more stable than **6b**.

Replacing the terminal hydrogen of the acceptor acetylene with an electron-withdrawing group enhances the efficiency of the cyclization. The tetrolic ester substrate **4** constitutes a particularly intriguing case to examine compatibility with functional groups since a tandem annulation can result in direct formation of a bicyclic lactone. Indeed, subjecting diyne **4** to the above cyclization conditions produced macrocycle **7**[8] in 66% yield. Utilizing 5 mol % of $[(o\text{-tol})_3P]_2Pd(OAc)_2$ as an alternative catalyst, and approximately an amount of 5 Å molecular sieves equivalent in weight to substrate at 0.02 M in substrate in refluxing benzene, gave a 59% yield of the macrocycle **7**[8]. This novel bicycloannulation was extended to the 13-membered (**8**, $n = 9$, 58%)[8] and 16-membered (**8**, $n = 12$, 38%)[8] macrocycles (eq 2) by employing the latter conditions. The power of this strategy is revealed by the fact that even a 10-membered ring (**8**, $n = 6$)[8] can be produced, albeit in only 16% yield.[10]



8

(2)

---

(1) Hensens, O. D.; Dewey, R. S.; Liesch, J. M.; Napier, M. A.; Reamer, R. A.; Smith, J. L.; Albers-Schonberg, G.; Goldberg, I. H. *Biochem. Biophys. Res. Commun.* **1983**, *113*, 538. Edo, K.; Mizugaki, M.; Koide, Y.; Seto, H.; Furihata, K.; Otake, N.; Ishida, N. *Tetrahedron Lett.* **1985**, *26*, 331. Meyers, A. G.; Proteau, P. J.; Handed, T. M. *J. Am. Chem. Soc.* **1988**, *110*, 7212.

(2) Lee, M. D.; Dunne, T. S.; Siegel, M. M.; Chang, C. C.; Morton, G. O.; Borders, D. B. *J. Am. Chem. Soc.* **1987**, *109*, 3464. Lee, M. D.; Dunne, T. S.; Chang, C. C.; Ellestad, G. A.; Siegel, M. M.; Morton, G. O.; McGahren, W. J.; Borders, D. B. *J. Am. Chem. Soc.* **1987**, *109*, 3466. Golik, J.; Clardy, J.; Dubay, G.; Groenewold, G.; Kawaguchi, H.; Konishi, M.; Krishnan, B.; Ohkuma, H.; Saithoh, K.; Doyle, T. W. *J. Am. Chem. Soc.* **1987**, *109*, 3461. Golik, J.; Dubay, G.; Groenewold, G.; Kawaguchi, J.; Konishi, M.; Krishnan, B.; Ohkuma, H.; Saithoh, K.; Doyle, T. W. *J. Am. Chem. Soc.* **1987**, *109*, 3462.

(3) The intramolecular Diels–Alder and Alder ene reactions are excellent illustrations. See: Taber, D. F. *Intramolecular Diels–Alder and Alder Ene Reactions*; Springer-Verlag: Berlin, 1984.

(4) (a) For metal-catalyzed examples, see: Trost, B. M.; Lee, D. C. *J. Org. Chem.* **1989**, *54*, 2271 and earlier references therein. Trost, B. M.; Tour, J. M. *J. Am. Chem. Soc.* **1988**, *110*, 5231 and earlier references therein. Trost, B. M.; Hane, J. T.; Metz, P. *Tetrahedron Lett.* **1986**, *27*, 5695 and earlier references therein. (b) For cyclizations involving palladium-catalyzed carbametalations of acetylenes as the ring-forming step, see: Zhang, Y.; Negishi, E. *J. Am. Chem. Soc.* **1989**, *111*, 3454. Burns, B.; Grigg, R.; Sridharan, V.; Worakun, T. *Tetrahedron Lett.* **1988**, *29*, 4325. Chatani, N.; Takeyasu, T.; Horiuchi, N.; Hanafusa, T. *J. Org. Chem.* **1988**, *53*, 3539. Trost, B. M.; Lee, D. C. *J. Am. Chem. Soc.* **1988**, *110*, 7255. (c) For an example of a simple base-catalyzed cycloisomerization to produce a cycloalkyne, see: Deslongchamps, P.; Roy, B. L. *Can. J. Chem.* **1986**, *64*, 2068.

(5) For intermolecular Pd-catalyzed acetylene coupling, see: Trost, B. M.; Chan, C.; Ruhter, G. *J. Am. Chem. Soc.* **1987**, *109*, 3486.

(6) Cf.: Smith, W. N.; Beumet, O. F., Jr. *Synthesis* **1974**, 441.

(7) We believe the yield reflects mechanical losses upon workup due to the volatility of the compound.

(8) Satisfactory characterization was obtained.

(9) Coupling to the hydroxyl proton with coupling equal to that with the adjacent methylene group. A broad triplet results when OH exchange is rapid.

0002-7863/89/1511-8745$01.50/0