5654 J. Am. Chem. Soc. 1986, 108, 5654-5655

# Investigation of a Model Catalytic System in Ultrahigh Vacuum: The Adsorption of Triallylrhodium on the $TiO_2$ (001) Surface

Patricia B. Smith, Steven L. Bernasek,* Jeffrey Schwartz,* and Gregory S. McNulty

*Princeton University, Department of Chemistry*
*Princeton, New Jersey 08544*

*Received February 24, 1986*

Triallylrhodium reacts with OH groups on the surface of (powder) $SiO_2$ to produce a diallylrhodium surface species.[1-4] Upon subsequent reaction with hydrogen, an allylrhodium hydride species is formed which exhibits unusual catalytic activity for hydrogenation of alkenes and arenes. However, covalent bonding in these surface-bound species between the metal complexes and the oxide had not been proven, nor had the ligand role of the oxygens of the oxide support been investigated. This type of characterization for both an oxide-bound diallylrhodium complex and a rhodium hydride derivative species has now been accomplished by using UPS and AES techniques in ultrahigh vacuum.

Experiments were carried out in a standard, ion-pumped UHV chamber equipped with a double-pass CMA (3-keV, 13-$\mu$A current measured at the crystal, 2-eV peak to peak modulation for AES), He(I), (21.2 eV) photons for UPS (pulse counting mode), and a quadrupole mass spectrometer. The $TiO_2$ (001) surface was cut and polished. $TiO_2$ has the tetragonal unit cell structure with $a$ = 4.59 Å, and $c$ = 2.96 Å. The (001) surface facets on annealing to produce a (011) (2×1) structure.[5] This surface was produced following cleaning cycles of $Ar^+$ bombarding (2 keV, 20 mA) and annealing (600 °C); the (011) (2×1) structure was verified with LEED. $Ar^+$ bombardment followed by exposure of the surface to water vapor produced the surface hydroxyl groups necessary for subsequent reaction with triallylrhodium. Exposure of a clean $TiO_2$ (001) surface to 20 310 langmuirs of $H_2O$ (1 langmuir = $1 \times 10^{-6}$ torr·s) (degassed prior to use) is shown in Figure 1B. Note that water adsorption on the (001) face differs from that reported for two other low Miller index surfaces:[6,7] no molecular $H_2O$ adsorption was detected, up to an exposure of $2 \times 10^4$ langmuirs of $H_2O$ to the (001) surface.[8] The Auger spectrum for clean $TiO_2$ indicates the experimental peak-to-peak ratio, O(510)/Ti(382), at 2.3. This ratio and the Rh/C ratio noted below do not directly indicate molecular stoichiometries since the accuracy of such analyses is only 20-50%.[9-10] Consequently, the ratios presented herein can only be regarded qualitatively.

The reaction between triallylrhodium and polycrystalline $TiO_2$ and subsequent treatment with $H_2$ are shown in Scheme I.[2] Since all reactions in UHV are analogous, save for pressures, chemical transformations in UHV are believed to parallel those noted[2] under "normal" conditions. The introduction of triallylrhodium[4] vapor into the UHV chamber (via a Kovar seal to stainless steel tubing connected to the UHV leak valve) was preceded by pumping (15 min) via a glass diffusion pump to remove residual solvent vapor. The hydroxylated surface of $TiO_2$ (001) was exposed to 2420 langmuirs of triallylrhodium to produce an Auger spectrum which suggests a surface composition of 5.2% carbon and 3.4% Rh (calculated accounting for atomic sensitivity factors). The rhodium hydride species was obtained by exposing the diallylrhodium surface species to hydrogen; Figure 1 contains UP spectra of these first examples of chemically active complexes formed by deposition and subsequent chemical modification in an ultrahigh vacuum "clean" experiment.

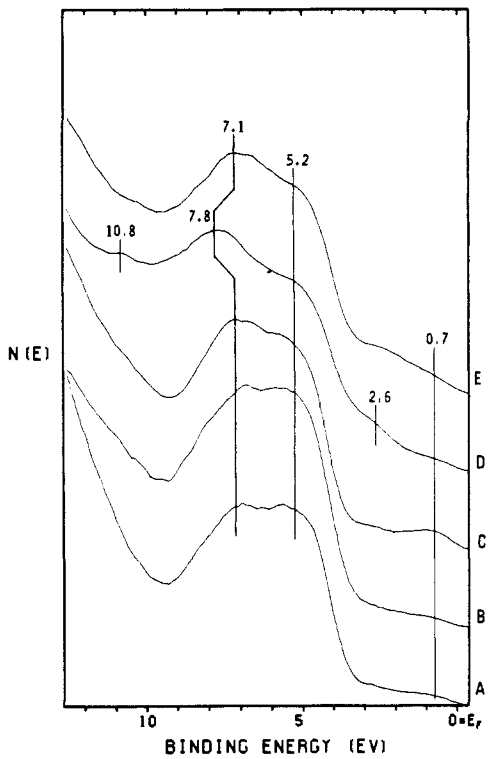
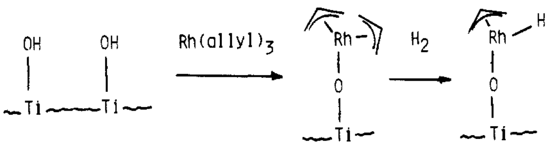


Figure 1. (A) Clean $TiO_2$ (001); (B) 20310 langmuirs of $H_2O$ adsorption on $TiO_2$ (001); (C) $Ar^+$-bombarded clean surface exposed to 205 langmuirs of $H_2O$; (D) surface of (C) exposed to 2420 langmuirs of triallylrhodium; (E) surface of (D) exposed to 3230 langmuirs of $H_2$.

Scheme I



Triallylrhodium adsorption (Figure 1D) induces many changes in the UPS features which indicate covalent bonding to the support. There is a suppression of Ti 3d emission at approximately 0.7 eV below the Fermi level, $E_f$. A new feature appears at 2.6-eV binding energy which we attribute to Rh 4d electrons. There is a new emission at 10.8-eV binding energy which is assigned to electrons from allyl ligand molecular orbitals, consistent with values observed for other allylic complexes.[11] The most dramatic variation observed in the UP spectrum occurs in the O(2p) region. The peak at 7.1 eV in Figure 1C shifts 0.7 eV to higher binding energy following formation of the diallylrhodium surface species. This demonstrates allylrhodium complex covalent attachment to the oxide which decreases the electron density at the bonding oxygen. Spectrum E shows that formation of the hydride surface species causes a shift of the O(2p) band to 7.1 eV, indicating a significant ligand effect for allyl vs. hydride on the oxygen electron density, consistent with XPS observations made for rhodium[12-14] and other metals[15] in several hydride-ligated complexes (for example, Rh($3d_{5/2}$): [$SiO_2$]Rh(allyl)$_2$, 308.9 eV;[12] [$SiO_2$]Rh(allyl)H, 308.0 eV[13]).[16] No significant increase in the UPS emission at

---

(1) Ward, M. D.; Harris, T. V.; Schwartz, J. *J. Chem. Soc., Chem. Commun.* **1980**, 357.

(2) Ward, M. D.; Schwartz, J. *J. Mol. Catal.* **1981**, *11*, 397. Ward, M. D. Ph.D. Thesis, Princeton University, Princeton, NJ, 1981.

(3) Ward, M. D.; Schwartz, J. *J. Am. Chem. Soc.* **1981**, *103*, 5253.

(4) Powell, J.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1966**, 323.

(5) Firment, L. E. *Surf. Sci.* **1982**, *116*, 205.

(6) Henrich, V. E.; Dresselhaus, G.; Zeiger, H. J. *Solid State Commun.* **1977**, *24*, 623.

(7) Lo, W. J.; Chung, Y. W.; Somorjai, G. A. *Surf. Sci.* **1978**, *71*, 199.

(8) Smith, P. B.; Bernasek, S. L., manuscript in preparation.

(9) Grant, J. T. *Appl. Surf. Sci.* **1982**, *13*, 35.

(10) Minni, E. *Appl. Surf. Sci.* **1983**, *15*, 270.

(11) Green, J. C. *Struct. Bonding (Berlin)* **1981**, *43*, 100.

(12) Foley, H. C.; DeCanio, S. J.; Tau, K. D.; Chao, K. J.; Onuferko, J. H.; Dybowski, C.; Gates, B. C. *J. Am. Chem. Soc.* **1983**, *105*, 3074.

(13) Kitajima, N.; Schwartz, J. *J. Mol. Catal.* **1984**, *26*, 165.

(14) Schwartz, J. *Acc. Chem. Res.* **1985**, *18*, 302.

(15) Chatt, J.; Elson, C. M.; Hooper, N. E.; Leigh, G. J. *J. Chem. Soc. Dalton Trans.* **1975**, 2392.

0002-7863/86/1508-5654$01.50/0

the Fermi level was noted in either case, suggesting that metallic rhodium was not formed on either deposition or subsequent hydrogenation procedures. Other changes in the UP spectrum (Figure 1E) are also observed. The emission attributed to allyl ligand electrons at 10.8 eV is greatly reduced, as expected for formation of the hydride complex from the diallylrhodium species. The peak near the Fermi level has broadened as compared with the spectrum for the deposited diallyl species. The feature at 5.2 eV remains unchanged throughout the various chemical changes, and this band is assigned to nonbonding oxygen (2p) electrons.[17]

In the experiments described above, the UPS technique has been used to observe changes in electron density at oxygen effected by the formation of new chemical surface species made according to reaction schemes developed under "normal" conditions. This represents the first use of UHV techniques to directly probe bonding changes in a catalytically active transition-metal complex supported on a single-crystal oxide under conditions which approximate actual catalysis.

**Acknowledgment.** We gratefully acknowledge the National Science Foundation and the Atlantic Richfield Co. for financial support of this research.

---

(16) Reaction to the hydride, rather than merely a reversion back to the TiO$_2$ starting material, was concluded based on the lack of similarities between spectrum C and E, as well as the presence of rhodium indicated in the hydride complex Auger spectrum.

(17) Control experiments involving hydrocarbon adsorption and thermal decomposition[14] of the supported diiallylrhodium species indicate that neither Rh particles nor hydrocarbon fragments are responsible for the features observed in Figure 1.

---

## Triply Convergent Synthesis of (−)-Prostaglandin E$_2$[†]

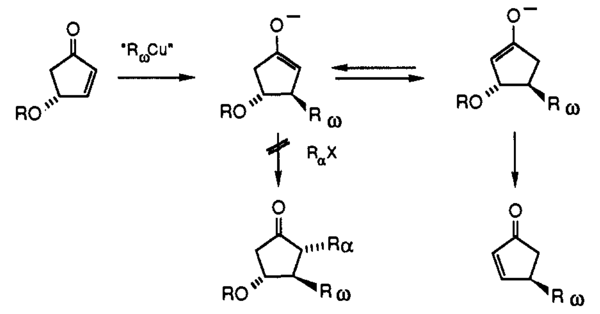
Carl R. Johnson* and Thomas D. Penning

*Department of Chemistry, Wayne State University*
*Detroit, Michigan 48202*

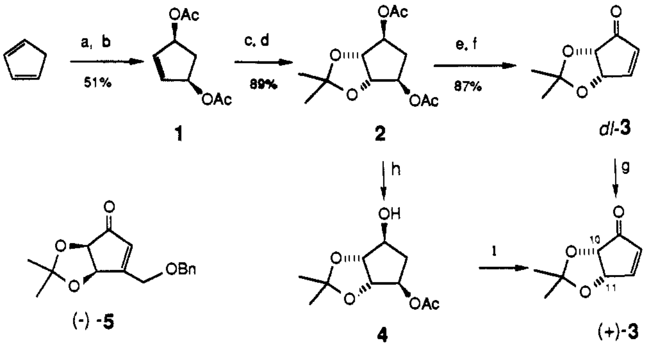
*Received May 19, 1986*

In prostaglandin syntheses, the three-component coupling approach, with its high convergence and potential for flexibility, has attracted considerable attention in recent years.[1] This approach involves the conjugate addition of the ω side chain to a protected 4-hydroxy-2-cyclopentenone, followed by trapping of the enolate with an alkyl halide containing the complete α side chain. A number of groups have reported indirect variations of this approach,[2] but in all the pioneering work the direct alkylation with an alkyl halide has failed,[3] due to enolate equilibration and elimination of the protected 4-hydroxy group (Scheme I). During the course of the work herein described, one solution to this equilibrium/elimination problem appeared; Noyori and coworkers[4a] found that the initially formed enolate (Scheme I) could be trapped at low temperatures as the *O*-(triphenylstannyl) derivative[4b,c] which, in turn, could be directly alkylated with excess R$_\alpha$I.

Scheme I



Scheme II[a]



[a] (a) O$_2$, *hν*, rose bengal, thiourea, MeOH;[6] (b) A$_2$O, pyridine, catalytic DMAP, CH$_2$Cl$_2$; (c) 1 mol % OsO$_4$, Me$_3$NO, THF, acetone; (d) acetone, catalytic TsOH; (e) KOH, MeOH; (f) dicyclohexylcarbodiimide, Me$_2$SO, pyridine, trifluoroacetic acid, benzene; (g) (+)-*N*,*S*-dimethyl-*S*-phenylsulfoximine resolution;[7] (h) electric eel acetylcholinesterase, H$_2$O, 25 °C; (i) CrO$_3$, H$_2$SO$_4$, acetone.

It appeared to us that enone **3** would be an ideal substrate for this three-component coupling process. We postulated that the presence of the α-oxygen functionality constrained in the five-membered ring would supress enolate equilibration (by a combination of charge repulsion and angle strain—double bond exo to 5-membered ring in unfavored enolate) and alkylation would occur regiospecifically to afford the trans vicinally dialkylated product. Reductive removal of the α-oxygen group would yield the PGE structural system.

Enone **3**[5] (mp 37.5–38.5 °C, lit.[5a] 36–38 °C) was synthesized in six steps in 40% overall yield from cyclopentadiene as shown in Scheme II. Optical resolution of **3** was achieved with (+)-*N*,*S*-dimethyl-*S*-phenylsulfoximine[7] to afford (+)-**3**, $[\alpha]^{25}_{D}$ +71.8° (*c* 0.91, CHCl$_3$), and (−)-**3**, $[\alpha]^{25}_{D}$ −70.8° (*c* 0.92, CHCl$_3$). On the basis of a comparative ORD study with (−)-**5** (+ Cotton effect) obtained from (−)-ribose,[8] (+)-**3** (− Cotton effect) was assigned the 10*S*,11*S* (PG numbering) absolute stereochemistry as shown in Scheme II. On the basis of earlier studies on enzymatic differentiation[9a] of the acetates of *meso*-**1**, we examined a number of esterase-catalyzed hydrolyses of *meso*-**2**. Success was variable until our attention was drawn to electric eel acetylcholinesterase by a recent report[9b] on the asymmetric hydrolysis of **1**. Treatment of **2** in aqueous suspension with electric eel acetylcholinesterase

---

[†] Dedicated to Prof. Nelson J. Leonard on the occasion of his seventieth birthday.

(1) For a review, see: Noyori, R.; Suzuki, M. *Angew. Chem., Int. Ed., Engl.* **1984**, *23*, 847.

(2) (a) Suzuki, M.; Yanagisawa, A.; Noyori, R. *Tetrahedron Lett.* **1984**, 1384. (b) Tanaka, T.; Toru, T.; Okamura, N.; Hazato, A.; Sugiura, S.; Manabe, K.; Kurozumi, S.; Suzuki, M.; Kawagishi, T.; Noyori, R. *Ibid.* **1983**, 4103. (c) Suzuki, M.; Kawagishi, T.; Noyori, R. *Ibid.* **1982**, 5563. (d) Suzuki, M.; Kawagishi, T.; Suzuki, T.; Noyori, R. *Ibid.* **1982**, 4057. (e) Donaldson, R. E.; Saddler, J. C.; Byrn, S.; McKenzie, A. T.; Fuchs, P. L. *J. Org. Chem.* **1983**, *48*, 2167. (f) Stork, G.; Isobe, M. *J. Am. Chem. Soc.* **1975**, *97*, 6260.

(3) (a) Davis, R.; Untch, K. G. *J. Org. Chem.* **1979**, *44*, 3755. (b) Patterson, J. W.; Fried, J. H. *Ibid.* **1974**, *39*, 2506.

(4) (a) Suzuki, M.; Yanagisawa, A.; Noyori, R. *J. Am. Chem. Soc.* **1985**, *107*, 3348. (b) Nishiyama, H.; Sakuta, K.; Itoh, K. *Tetrahedron Lett.* **1984**, 223, 2487. (c) See also: Binns, M. R.; Haynes, R. K.; Lambert, D. E.; Schober, P. A. *Tetrahedron Lett.* **1985**, 3385.

(5) (a) Cocu, F. G.; Posternak, T. *Helv. Chim. Acta* **1972**, *55*, 2828, 2838. (b) McDonald, C. E.; Dugger, R. W. *Abstract of Papers*, 186th National Meeting of the American Chemical Society, Washington, DC; American Chemical Society: Washington, DC; ORGN 129.

(6) Kaneko, S.; Sugimoto, A.; Tanaka, S. *Synthesis* **1974**, 876.

(7) (a) Johnson, C. R. *Aldrichimica Acta* **1985**, *18*, 3. (b) Johnson, C. R.; Zeller, J. R. *Tetrahedron* **1984**, *40*, 1225.

(8) Lim, M. I.; Marquez, V. E. *Tetrahedron Lett.* **1983**, 5559.

(9) (a) For example, see: Miura, S.; Kurozumi, S.; Toru, T.; Tanaka, T.; Kobayashi, M.; Matsubara, S.; Ishimoto, S. *Tetrahedron* **1976**, *32*, 1893; Laumen, K.; Schneider, M. *Tetrahedron Lett.* **1984**, 5875. (b) Deardorff, D. R.; Matthews, A. J.; McMeekin, D. S.; Craney, C. L. *Tetrahedron Lett.* **1986**, 1255. We thank Prof. Deardorff for advice concerning the use of this enzyme. (c) Obtained from Sigma Chemical Co.