

mers. (Scheme 2). The predominant isomer was separated by chromatography on SiO_2 and its ^1H NMR showed the presence of trans-double bond ($J = 15$ Hz). This aldehyde was further reduced to the previously known trans-allylic alcohol with $[\alpha]_D^{17} = 33.8^\circ$ (CHCl_3 , $c = 2.28$)⁸.

This isomerization prompted us to prepare several derivatives and examine the ratio of E/Z isomers of the corresponding aldehydes 6-8. The results are exhibited in Table 1. When we used CH_3I instead of HgO/HgCl_2 in order to circumvent the metallic effect, we could obtain exclusively thermodynamically stable trans-aldehyde. Currently we are looking for the reactions which can furnish the exclusive generation of E isomers.

References and Notes

1. S. Kusumoto, S. Tsuji, and T. Shiba, *Bull. Chem. Soc. Japan*, **47**, 2690 (1974).
2. E. J. Corey, D. A. Clark, G. Goto, A. Marfat, C. Mioskowski, B. Samuelsson, and S. Hammarstrom, *J. Am.*

Chem. Soc., **102**, 1436 (1980).

3. B. Schonenberger, W. Summermatter, and C. Ganter, *Helv. Chim. Acta*, **65**, 2333 (1982).
4. J. Jurczak, S. Pikul, and T. Bauer, *Tetrahedron*, **42**, 447 (1986) and references cited therein.
5. S. Hanessian, A. Bargiotti, and M. Larue, *Tetrahedron Lett.*, 737 (1978) and mp of the elimination product was identical with this reference value. mp 62-63°C.
6. E. J. Corey and J. I. Shulman, *Tetrahedron Lett.*, 3655 (1968).
7. (a) R. S. Tipson and A. Cohen, *Carbohydr. Res.*, **1**, 338 (1965). (b) H. R. Schuler and K. N. Slessor, *Can. J. Chem.*, **55**, 3280 (1977). (c) S.-Y. Chen and M. M. Joullie, *J. Org. Chem.*, **49**, 1769 (1984).
8. The trans allyl alcohol was prepared according to the method reported by N. Minami, S. S. Ko and Y. Kishi (*J. Am. Chem. Soc.* **104**, 1109 (1982)) and also it was further converted to aldehyde by Swern oxidation in order to confirm Z-5.

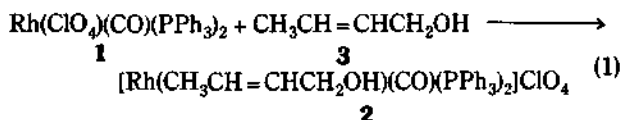
Synthesis of Cationic Rhodium(I) Complex of But-2-en-1-ol

Chong Shik Chin* and Jeonghan Park

Department of Chemistry, Sogang University, C.P.O Box 1142, Seoul 121. Received August 6, 1987

Reactions of $\text{Rh}(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2$ (**1**) with unsaturated nitriles,¹ aldehydes² and esters³ (L) produce four coordinated cationic rhodium(I) complexes, $[\text{Rh}(\text{L})(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$ which are catalytically active for isomerization, oligomerization and hydrogenation of L. Complex **1**⁴ and $[\text{Rh}(\text{CO})(\text{PPh}_3)_3]\text{ClO}_4$ ⁵ catalyze various reactions of unsaturated alcohols. Accordingly, we launched an investigation into the rhodium complexes presented in the reaction mixtures of **1** and unsaturated alcohols, and we now wish to report a new cationic rhodium(I) complex, $[\text{Rh}(\text{CH}_3\text{CH}=\text{CHCH}_2\text{OH})(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$ (**2**) where $\text{CH}_3\text{CH}=\text{CHCH}_2\text{OH}$ (**3**) is coordinated through the oxygen atom but not through the olefinic group. To our knowledge, no metal complexes of unsaturated alcohols coordinated through the oxygen atom have been reported before while some metal complexes of unsaturated alcohols coordinated through the olefinic group have been reported.^{6,7}

Addition of **3** (mixture of *cis* and *trans* isomers) into the benzene solution of **1** immediately results in precipitation of yellow micro-crystals of **2** (eq. 1). Attempts to prepare the similar complexes of the other unsaturated alcohols (prop-2-en-1-ol, 2-methylprop-2-en-1-ol, but-3-en-1-ol, but-2-en-2-ol, 3-methylbut-2-en-1-ol) have not been successful thus far



whereas the reaction of 3-phenylprop-2-en-1-ol with **1** produces a rhodium (I) complex of an unsaturated aldehyde, $[\text{Rh}$

Table 1. Spectral and Conductivity Data for $[\text{Rh}(\text{CH}_3\text{CH}=\text{CHCH}_2\text{OH})(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$ (**2**)

compound	electronic absorption, nm (ϵ) ^a		
2 ^b	350 (3820)		
compound	infrared absorption, cm^{-1} ^c		
	$\nu(\text{O-H})$	$\nu(\text{C=C})$	$\nu(\text{C=O})$
$\text{CH}_3\text{CH}=\text{CHCH}_2\text{OH}$ ^b	3325	1675	
2 ^b	3205	1667	1994
compound	proton NMR, ppm ^d		
$\text{CH}_3\text{CH}=\text{CHCH}_2\text{OH}$ ^b	1.70(m, CH_3), 2.31 (s, OH), ^e 4.09 (m, CH_2), 5.70 (m, $\text{CH}=\text{CH}$)		
2 ^b	1.60 (m, CH_3), 3.51 (s, OH), ^f 3.29 (m, CH_2), 5.20 (m, $\text{CH}=\text{CH}$), 7.50 (m, $\text{P}(\text{C}_6\text{H}_5)_3$)		
compound	molar conductivity, $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ ^g		
$(n\text{-Bu})_4\text{NClO}_4$	34		
2 ^b	33		

^aIn CH_2Cl_2 . ^b*cis* and *trans* isomers. ^cIn Nujol. ^dIn CDCl_3 under nitrogen at 25°C at 60 MHz. Chemical shifts are relative to Me_4Si . ^eOne drop of $\text{CH}_3\text{CH}=\text{CHCH}_2\text{OH}$ in 0.4 ml of CDCl_3 . chemical shift varies depending on the concentration of $\text{CH}_3\text{CH}=\text{CHCH}_2\text{OH}$ / 7.5×10^{-5} mole of **2** in 0.4 ml of CDCl_3 . Chemical shift varies depending on the concentration of **2**. ^f $[(n\text{-Bu})_4\text{NClO}_4] = [\text{Rh}] = 4.4 \times 10^{-4}$ M in CH_2Cl_2 at 25°C.

$(\text{C}_6\text{H}_5\text{CH}=\text{CHCHO})(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$ apparently *via* dehydrogenation of 3-phenylprop-2-en-1-ol.⁴

Spectral and conductivity data (Table 1) unambiguously indicate that complex **2** is a four coordinated cationic rho-

dium(I) complex and **3** in **2** is coordinated only through the oxygen atom (i.e., not through the olefinic group) to rhodium. It is known that the perchlorato group is readily replaced by CH_3OH to give a cationic complex, $[\text{Rh}(\text{CH}_3\text{OH})(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$.⁸

Coordination of $\text{CH}_3\text{CH}=\text{CHCH}_2\text{OH}$. It is well-established that the four coordinated rhodium(I) complexes, $\text{RhA}(\text{CO})(\text{PPh}_3)_2$ (A = monodentate ligand) show an absorption band in the region of 350-400 nm (ϵ , 2,600-4,300) which shifts with respect to the ligating atom of A.⁹ It is also known that $\text{RhA}(\text{CO})(\text{PPh}_3)_2$ show an absorption band at 350-360 nm when A is the ligand that coordinates to rhodium through the oxygen atom such as, OCIO_3 , OReO_3 , OCO_2H , OH , ONO ,⁹ $\text{RCH}=\text{CHCHO}$,² and $\text{RCH}=\text{CHCO}_2\text{R}$.³ Accordingly, the electronic absorption spectral data in Table 1 suggest that complex **2** is a four coordinated rhodium(I) complex and **3** is coordinated only through the oxygen atom in **2**.

A significant decrease in $\nu(\text{O-H})$ and a slight decrease in $\nu(\text{C}=\text{C})$ of **3** upon coordination to $\text{Rh}(\text{CO})(\text{PPh}_3)_2^+$ (Table 1) also support the oxygen-bonded **3** in **2**. It is well-known that $\nu(\text{O-H})$ of alcohols are shifted to lower frequencies and $\nu(\text{C}=\text{C})$ of olefins show considerable shifts to lower frequencies upon coordination to metal.¹⁰ A strong and broad band at $\approx 1100\text{ cm}^{-1}$ observed for **2** is attributable to the tetrahedral (Td) anion ClO_4^- , which supports that **2** is a 1:1 electrolyte as confirmed by the conductance measurements (see Table 1).

The absence of the spin coupling between ^{103}Rh and the olefinic protons of **3** in **2** suggests that the coordination of **3** does not occur through the olefinic group (see Table 1). No significant changes in the chemical shifts of the protons of **3** have been measured upon coordination to $\text{Rh}(\text{CO})(\text{PPh}_3)_2^+$ as observed for the related complexes, $[\text{RhL}(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$ where L are unsaturated nitriles,¹ unsaturated aldehydes² and unsaturated esters³ coordinated through the nitrogen and oxygen atom, respectively.

Synthesis of $[\text{Rh}(\text{CH}_3\text{CH}=\text{CHCH}_2\text{OH})(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$. Addition of **3** ($\approx 0.5\text{ mmol}$) into the benzene solution

(15 ml) of **1** (0.15 g, 0.2 mmol) under N_2 at 25°C immediately resulted in precipitation of yellow micro-crystals that were collected by filtration, washed with benzene (5 ml) and hexane (50 ml), and dried under vacuum. The yield was 0.13g (80% based on **2**). Anal. Calcd for $\text{C}_{41}\text{H}_{38}\text{ClO}_6\text{P}_2\text{Rh}$: C, 59.54; H, 4.63; Cl, 4.29; P, 7.49. Found; C, 60.70; H, 4.73; Cl, 4.37; P, 7.64. Elemental analyses were carried out in Spang Microanalytical Lab. Eagle Harbor, MI, U.S.A.

It remains uncertain why complex **2** can be prepared while related complexes of other unsaturated alcohols can not be prepared by the same method.

Acknowledgement. We wish to thank the Korea Science and Engineering Foundation and the Ministry of Education for the support of this study.

References

1. H.-K. Park, I. B. Kim, and C. S. Chin, *J. Organomet. Chem.*, **326**, 431 (1987) and references therein.
2. K. J. Yang, I. B. Kim, and C. S. Chin, *Tran. Met. Chem.*, **12**, 45 (1987), and references therein.
3. H. M. Jeong and C. S. Chin, *Bull. Korean Chem. Soc.*, **7**, 468 (1986).
4. J. Park and C. S. Chin, *Bull. Korean Chem. Soc.*, **8**, 324 (1987).
5. J. Park and C. S. Chin, *Chem. Commun.*, 1213 (1987).
6. L. Erickson and D. C. Brower, *Inorg. Chem.*, **21**, 838 (1982).
7. R. Aneja, B. T. Golding, and C. Pierpont, *J. Chem. Soc. Dalton Trans.*, 219 (1984).
8. J. Peone, Jr. and L. Vaska, *Angew. Chem. Int. Ed.*, **10**, 511 (1971).
9. R. Brady, B. R. Flynn, G. L. Geoffroy, H. B. Gray, J. Peone, Jr. and L. Vaska, *Inorg. Chem.*, **15**, 1485 (1976).
10. K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds" 3rd Ed., Wiley, 1978, p. 230, 383.