Available online at www.sciencedirect.com

SCIENCE DIRECT®

Tetrahedron Letters 45 (2004) 7863–7865

Tetrahedron Letters

Electrochemistry as a correlation tool candidate with catalytic activities in Ru-catalyzed hydrolytic oxidation of organosilane

Youngim Na,[a] Chongmok Lee,[b,*] Jae Youn Pak,[b] Kuk Hwa Lee[b] and Sukbok Chang[a,*]

[a] *Center for Molecular Design and Synthesis, Department of Chemistry and School of Molecular Science (BK21), Korea Advanced Institute of Science and Technology, Daejeon 305-701, Republic of Korea*
[b] *Department of Chemistry, Ewha Womans University, Seoul 120-705, Republic of Korea*

Received 14 July 2004; revised 23 August 2004; accepted 26 August 2004
Available online 11 September 2004

Abstract—Electrochemical parameters measured from a series of ruthenium complexes are nicely correlated with both structural changes and catalytic activities of those species under the reaction conditions providing a possibility that electrochemistry may offer a facile tool for better understanding of some transition metal-catalyzed reactions.

Introduction of the transition metal catalysis in chemical reactions brought a rapid development of organic transformation in the last few decades.[1] Significant improvement in efficiency, selectivity, and practicability of these transformations has been enabled by precisely tuning the oxidation states and coordination environment of the transition metal complexes. As a consequence, detailed understanding of the catalytic pathways is regarded to be crucial for the development of the next generation catalysts. In connection with this, spectroscopic and crystallographic methods have mainly been employed for mechanistic investigation of the transition metal-catalyzed reactions. Although electrochemical methods would be envisioned to provide highly valuable information on the catalytic processes since catalytic conversions are frequently accompanied with the change of the complexes' structure and metal's oxidation states, practice of the electrochemical approaches for these purposes has not been fully explored.[2] We present herein our initial investigations in the metal-mediated processes by means of electrochemistry. During the course of this work, it is shown that an excellent qualitative correlation between catalysts' activities and electrochemical parameters could be deduced from the electrochemical measurements.

We have recently developed a series of efficient and selective organic transformations[3] with the use of a dimeric ruthenium catalyst, $[RuCl_2(p\text{-cymene})]_2$ (**1**).[4] It was rather surprising that an identical catalyst precursor carries out a diverse range of reactions such as oxidation of alcohols[3a] and silanes,[3b] activation of Si–H[3c] and alkynyl C–H bonds,[3d] and dehydration of aldoximes.[3e,f] It was previously observed by spectroscopic means that dissociation of the dimeric species into monomeric adducts takes place under certain circumstances.[5] In our previous ^{1}H NMR study[3d] quantitative formation of a new monomeric ruthenium complex coordinated with the added base (1:1 ratio) was also observed by addition of pyrrolidine to a solution of **1** in various solvents such as CD_3CN or C_6D_6. Based on the above reports, we believe that the dimeric complex **1** dissociates into its corresponding monomeric adducts coordinated with a polar solvent (*S*), an amine base, or unsaturated π-donor compounds depending on its basicity and reaction conditions. Thus, high catalytic activity of the dimeric ruthenium(arene) complexes seems to be initiated by the formation of the labile bond of Ru–*S*, where *S* represents either an amine base or polar solvents.

Electrochemical measurements using a conventional-size disk electrode (dia 1.6 mm) were carried out *in the*

Keywords: Catalysts; Electrochemistry; Oxidation; Ruthenium and compounds.

* Corresponding authors. Tel.: +82 42 869 2841; fax: +82 42 869 2810 (S.C.); e-mail addresses: cmlee@ewha.ac.kr; sbchang@kaist.ac.kr

0040-4039/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2004.08.154

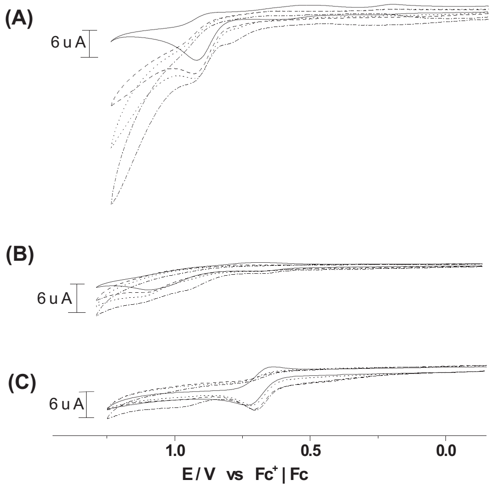
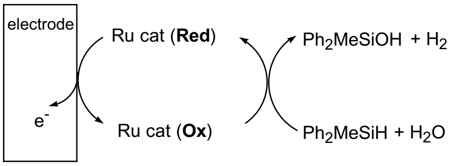


Figure 1. CVs of 1.0 mM of **1** in CH_3CN (A) and CH_2Cl_2 (B), and 1.0 mM of **2** in CH_3CN (C) containing 0.00, 6.25, 12.5, and 25.0 mM Ph_2SiHCH_3 from top to bottom, respectively, and 0.10 M TBAB using a Pt disk (dia 1.6 mm) electrode and a scan rate of 0.10 V/s (twice molar amounts of H_2O with respect to those of Ph_2SiHCH_3 are also included in each case).

presence of reactants as in the real reaction systems with 1/5 concentration scale (Fig. 1).[6]

When the hydrolytic oxidation of organosilanes to silanols was performed using water as an oxidant, it was observed that **1**/CH_3CN system turned out to be the most effective in efficiency and selectivity.[3c] In electrochemical experiments, we adjusted reactants' concentration scale by 1/5 to avoid fouling of measurements due to hydrogen evolution. After the addition of diphenylmethylsilane to the solution of **1**/CH_3CN, the oxidation current was increased at a potential more positive than 0.93 V depending on the amounts of diphenylmethylsilane (Fig. 1A), indicating an electrocatalytic system (Scheme 1). However, such a large increase of the oxidation current was not observed in **1**/CH_2Cl_2 system (Fig. 1B) or $CpRu(NCCH_3)_3^+PF_6^-$ (**2**)/CH_3CN system (Fig. 1C). The difference in current between **1**/CH_3CN and **1**/CH_2Cl_2 system seems to be stemmed from the Lewis basicity of two solvents, that is, the degree of formation of the labile bond of Ru–*S*. To analyze the results we used the oxidation current ratio of Ru-complex with and without Ph_2MeSiH at 1.24 V, i_{cat}/i, as the electrochemical measurement of effectiveness of catalysts in CV experiments. The result of the electrochemical experiments is summarized in Table 1 along with the chemical yield of the hydrolytic oxidation of organosilanes.



Scheme 1.

Table 1. Relationship between catalytic activity of Ru complexes and their current ratio i_{cat}/i in the hydrolytic oxidation reaction of diphenylmethylsilane

$$Ph_2MeSiH + H_2O \xrightarrow[CH_3CN \quad 25\ ^{o}C,\ 10\ min]{Ru\ (2\ mol\ \%)} Ph_2MeSiOH$$

Entry	Ru-catalyst	Yield[a] (%)	i_{cat}/i[b]
1	$[RuCl_2(p\text{-cymene})]_2$	99	6.5
2	$[RuCl_2(benzene)]_2$	94	4.2
3	$RuCl_2(PPh_3)_3$	42	1.9
4	$[CpRu(NCCH_3)_3]PF_6$	20	1.2
5	$[(\eta^5\text{-}Ph_4C_5O)(CO)_2Ru]_2H_2$	13	1.1

[a] Isolated yield.

[b] The anodic current ratio in CV for Ru-complex (1.0 mM)/Ph_2MeSiH (25 mM)/H_2O (50 mM)/TBAP (0.1 M) and Ru-complex (1.0 mM)/TBAP (0.1 M) in CH_3CN, which was measured at 1.24 V (vs Fc^+|Fc) and the scan rate was 0.1 V/s.

Interestingly, in the hydrolytic oxidation reaction, binuclear species, that is, $[RuCl_2(p\text{-cymene})]_2$ or $[RuCl_2(benzene)]_2$ shows higher activity in CH_3CN than mononuclear complexes, that is, $RuCl_2(PPh_3)_3$ or a cationic catalyst $CpRu(NCCH_3)_3^+PF_6^-$.[7] The higher activity observed from the dimeric catalysts can be attributed to the in situ generation of effective mononuclear species bearing relatively a weak Ru–*S* bond that facilitates a subsequent exchange with reactants such as silanes. However, it should be mentioned that this conclusion can be applied only to metal complexes of similar electronic and steric properties. For example, despite the binuclear dimeric structure, $[(\eta^5\text{-}Ph_4C_5O)(CO)_2Ru]_2H_2$ (Shvo complex)[8] gives a poor catalytic activity under the hydrolytic reaction conditions. This may be attributed to the completely distinct electronic nature of the carbonyl ruthenium complex, compared to those of $[RuCl_2(arene)]_2$ types.

With **1** as a catalyst (0.02 equiv), oxidation was completed in 10 min at room temperature to give diphenylmethylsilanol in high yield. The current ratio of **1** in CH_3CN was 6.5 in the presence of the silane. Under the same conditions except the concentration scale, chemical yields and i_{cat}/i of other binuclear and mononuclear ruthenium complexes were obtained. To our surprise, there exists a close correlationship between two parameters of those Ru complexes investigated. While catalysts of good activity give high i_{cat}/i ratio, those of poor efficiency exhibit low values of the ratio. Although more accurate and quantitative correlation factors have to be set up, the present observation that a noticeable relationship exists between catalytic activity and measurable electrochemical parameter would be extended similarly to predict catalytic efficiency in other systems.

In summary, we have shown that electrochemical parameters of ruthenium complexes are effectively correlated with their catalytic activities and structural changes of the species under the reaction conditions. Although there are more factors taken into consideration in transition metal-catalyzed reactions such as coordination sites and ligand properties in addition to the oxidation states of a central metal, this study shows a possibility that electrochemical approaches may lead to better understanding of the pathway in the catalytic reactions.

Acknowledgements

This work was supported by Korea Science & Engineering Foundation (CL, R01-2000-00050).

References and notes

1. *Comprehensive Organometallic Chemistry II*; (a) Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, 1995; (b) *Transition Metals for Organic Synthesis*; Beller, M., Bolm, C., Eds.; Wiley-VCH: Weinheim, 1998; (c) Tsuji, J. *Transition Metal Reagent and Catalysts*; John Wiley & Sons, Ltd: London, 2000.
2. For an example of the use of electrochemistry to investigate the role of halides on Pd-catalyzed additions, see: Amatore, C.; Azzabi, M.; Jutand, A. *J. Am. Chem. Soc.* **1991**, *113*, 8375.
3. (a) Lee, M.; Chang, S. *Tetrahedron Lett.* **2000**, *41*, 7507; (b) Lee, M.; Ko, S.; Chang, S. *J. Am. Chem. Soc.* **2000**, *122*, 12011; (c) Na, Y.; Chang, S. *Org. Lett.* **2000**, *2*, 1887; (d) Chang, S.; Na, Y.; Choi, E.; Kim, S. *Org. Lett.* **2001**, *3*, 2089; (e) Yang, S. H.; Chang, S. *Org. Lett.* **2001**, *3*, 4209; (f) Choi, E.; Lee, C.; Na, Y.; Chang, S. *Org. Lett.* **2002**, *4*, 2369.
4. Bennett, M. A.; Smith, A. K. *J. Chem. Soc., Dalton Trans.* **1974**, 233.
5. For previous studies on this issue, see: (a) Zelonka, R. A.; Baird, M. C. *J. Organomet. Chem.* **1972**, *44*, 383; (b) Luginbühl, W.; Zbinden, P.; Pittet, P. A.; Armbruster, T.; Bürgi, H.-B.; Merbach, A. E.; Ludi, A. *Inorg. Chem.* **1991**, *30*, 2350; (c) McCormick, F. B.; Cox, D. D.; Gleason, W. B. *Organometallics* **1993**, *12*, 610; (d) Takahashi, H.; Kobayashi, K.; Osawa, M. *Anal. Sci.* **2000**, *16*, 777.
6. Bard, A. J.; Faulkner, L. R. *Electrochemical Methods: Fundamentals and Applications*; Wiley: New York, 2001; Chapter 12.
7. Gill, T. P.; Mann, K. R. *Organometallics* **1982**, *1*, 485.
8. Shvo, Y.; Czarkie, D.; Rahamim, Y.; Chodosh, D. F. *J. Am. Chem. Soc.* **1986**, *108*, 7400.