Correlation of Electrochemical Characteristics and Catalytic Activity of $Rh_2(OAc)_4$ in the Presence of Various Phosphines

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Received June 9, 2008

Dirhodium complexes have been received great attention due to the catalytic utilization in C-H insertion, cyclopropanation, allylic oxidations, and oxidative Mannich reaction[1] as well as the biological activity of dirhodium complexes.[2] To improve the activity of dirhodium complexes in the catalytic reactions or biological reactions, a variety of ligands can be employed not only at the axial position but also at the bridging position of dirhodium complexes. Since ligands at either bridging or axial positions vary the electronic and steric properties of dirhodium complexes, investigations on appropriate ligands through the electrochemical analysis have been demanded. The electrochemical analysis of dirhodium complexes bearing electronically different ligands has been reported to account for the different catalytic activity of dirhodium complexes.[3] As one of the symbolic examples, Doyle's Rh(II)-catalyzed allylic oxidation shows that replacing four acetate ligands ($Rh_2(OAc)_4$) to four caprolactamate ligands ($Rh_2(cap)_4$) at the bridging position lowers the oxidation potential of the dirhodium complex spawning successful catalytic allylic oxidations.[4]

In contrast to quite a few reports on dirhodium complexes involving various bridging ligands, it is infrequent to conduct electrochemical studies of $Rh_2(OAc)_4$ with axial ligands to understand the catalytic behavior of $Rh_2(OAc)_4L_n$ in organic reactions. Recently, we have reported $Rh_2(OAc)_4NHC$ (NHC = N-heterocyclic carbene) catalyzed allylic oxidation, where the NHC ligand is located at the axial position and affects the catalytic activity of the dirhodium complex. Based on the electrochemical data of $Rh_2(OAc)_4$ and $Rh_2(OAc)_4NHC$, the different catalytic activity in the allylic oxidation was interpreted as the electron donating effect of the NHC ligand.[5] By employing a good σ-donor, NHC ligand at the axial position of $Rh_2(OAc)_4$, the reversible oxidation of Rh_2^{4+} and its reduction become facile, accelerating the yield of the allylic oxidation. As continuation of this work, in this account, we report the electrochemical study of $Rh_2(OAc)_4$ with a variety of phosphine ligands (L = P(Ph-pOMe)$_3$, PPh$_3$, P(Ph-pCF$_3$)$_3$) and pursue the correlation between the catalytic activity and the electrochemical properties of dirhodium complexes involving phosphine ligands at the axial position of the dirhodium complex.

Cyclic voltammograms of $Rh_2(OAc)_4$, shown in Figure 1a, were obtained in the solution containing 100 equivalents of the phosphine ligand, L (L = P(Ph-pOMe)$_3$, PPh$_3$, P(Ph-pCF$_3$)$_3$) with nBu$_4$NClO$_4$ (TBAP) as a supporting electrolyte

in tetrahydrofuran (THF). In the presence of 100 equivalents of phosphine, both axial positions of $Rh_2(OAc)_4$ are expected to be coordinated by phosphine ligands, forming $Rh_2(OAc)_4L_2$ and excluding either the complex with one phosphine ligand coordinated at one of axial positions ($Rh_2(OAc)_4L$) or no phosphine ligand coordinated $Rh_2(OAc)_4$. Phosphines are well known to coordinate to the metal ion, changing the electronic and steric properties of metal complexes. With regard to the electronic effect of phosphine, phosphine can act as a σ-donor and π^*-acceptor to the metal ion depending on substituents of phosphine.[6,7] Phosphines possessing electron donating groups provide electron density toward the metal ion, forming the electron rich metal complex. Phosphines with electron withdrawing groups might pull electron density from the metal ion, resulting in the low electron density around the metal ion. Accordingly, in the solutions of $Rh_2(OAc)_4$ with P(Ph-pOMe)$_3$, phosphines are presumabley coordinated at the axial positions of $Rh_2(OAc)_4$, affording electron rich dirhodium complexes. $Rh_2(OAc)_4$ with P(Ph-pCF$_3$)$_3$ is expected to be the electron deficient complex due to the electron withdrawing ability of CF$_3$. The electronic property of PPh$_3$ is considered to be between those of P(Ph-pOMe)$_3$ and P(Ph-pCF$_3$)$_3$.

Cyclic voltammogram of $Rh_2(OAc)_4$ obtained in the electrolyte solution with no phosphine ligand shows a quasireversible redox potential wave with peak potential of E_{pa} = 1.10 V and E_{pc} = 0.95 V. The quasireversible redox potential waves of $Rh_2(OAc)_4$ in the solution containing high concentration of P(Ph-pOMe)$_3$ and PPh$_3$ appear in a range of 0.8 to 1.2 V with noticeable peak potential shifts. As listed in Figure 1b, the anodic and cathodic peak potentials vary depending on the electronic property of phosphine ligands. The anodic peak potential of $Rh_2(OAc)_4$ with P(Ph-pOMe)$_3$ is E_{pa} = 1.00 V. In comparison to the anodic peak potential of $Rh_2(OAc)_4$ in the absence of phosphine in the solution, the peak potential of $Rh_2(OAc)_4$ with P(Ph-pOMe)$_3$ was cathodically shifted, which verified the strong electron donating ability of the P(Ph-pOMe)$_3$ ligand in the complex. The electron rich phosphine is known to behave as a strong σ-donor and weak π^*-acceptor upon the coordination to the metal ion. Similar electronic effect of electron rich phosphine ligands on the metal complex was previously demonstrated.[6,7] In the case of another phosphine ligand, PPh$_3$, due to the σ-donor ability of PPh$_3$, the anodic peak potential of $Rh_2(OAc)_4$ in the solution containing high
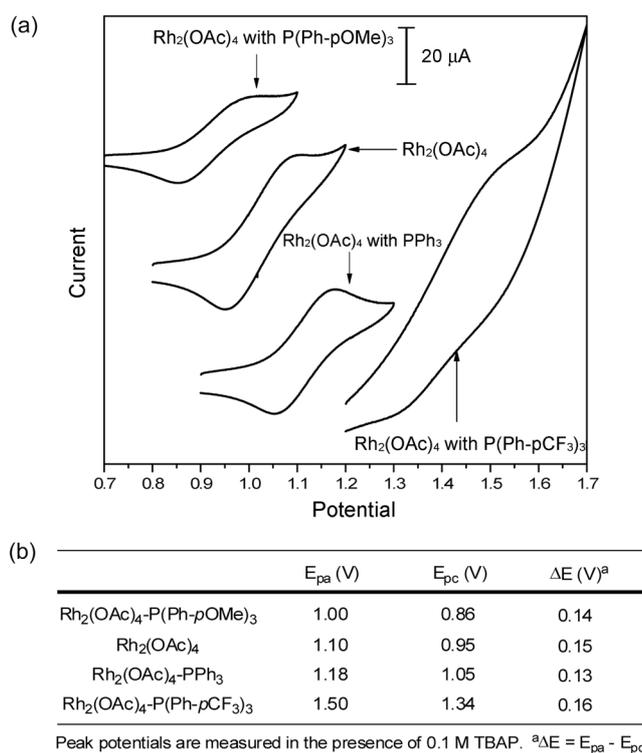
Notes

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(a)

(b)

	E_{pa} (V)	E_{pc} (V)	ΔE (V)[a]
$Rh_2(OAc)_4$-P(Ph-pOMe)$_3$	1.00	0.86	0.14
$Rh_2(OAc)_4$	1.10	0.95	0.15
$Rh_2(OAc)_4$-PPh$_3$	1.18	1.05	0.13
$Rh_2(OAc)_4$-P(Ph-pCF$_3$)$_3$	1.50	1.34	0.16

Peak potentials are measured in the presence of 0.1 M TBAP. [a]$\Delta E = E_{pa} - E_{pc}$

Figure 1. (a) Cyclic voltammograms of $Rh_2(OAc)_4$ with 100 equivalent of L (L = P(Ph-pOMe)$_3$, no phosphine, PPh$_3$, P(Ph-pCF$_3$)$_3$) obtained in THF solution with TBAP (0.1 M) at a scan rate of 100 mV/s. (b) Peak potentials (E_{pa}, E_{pc}) of $Rh_2(OAc)_4$ with 100 equivalent of L (L = P(Ph-pOMe)$_3$, no phosphine, PPh$_3$, P(Ph-pCF$_3$)$_3$) in THF solution containing TBAP as a supporting electrolyte.

concentration of PPh$_3$ is also expected to be lower than that of $Rh_2(OAc)_4$. However, the anodic peak potential of $Rh_2(OAc)_4$ in the solution containing PPh$_3$ was observed at 1.18V, that was 0.08 V anodically shifted than that of $Rh_2(OAc)_4$, which was attributed to the strong π^*-accepting ability of the phosphine ligand.

Cyclic voltammogram of $Rh_2(OAc)_4$ in the solution containing high concentration of electron deficient P(Ph-pCF$_3$)$_3$ ligand was obtained in the far anodically shifted potential region, with the oxidation peak potential at *ca.* 1.50 V. Presumably, the electrochemical oxidation of $Rh_2(OAc)_4$ possessing P(Ph-pCF$_3$)$_3$ is harder than other complexes since the coordination of electron deficient phosphine ligands to $Rh_2(OAc)_4$ makes the dirhodium complex difficult to be oxidized. $Rh_2(OAc)_4$ with electron deficient P(Ph-pCF$_3$)$_3$ also underwent the oxidation irreversibly. The irreversible redox behavior of $Rh_2(OAc)_4$ solution containing P(Ph-pCF$_3$)$_3$ is attributed to the low stability of the cationic radicals stemming from the oxidation of $Rh_2(OAc)_4$-P(Ph-pCF$_3$)$_3$.

The reversibility of potential waves of dirhodium complexes seems to be correlated with the electron density of the rhodium ion with electron rich phosphine ligands around it. The separations between the anodic and the cathodic peak of $Rh_2(OAc)_4$ containing P(Ph-pOMe)$_3$ and PPh$_3$ are ca. 0.14 V and 0.13 V, respectively, which are smaller than that of $Rh_2(OAc)_4$ without phosphine ligand. Based on above data, the reversible oxidation/reduction of dirhodium complexes

becomes more facile in the presence of PPh$_3$ and P(Ph-pOMe)$_3$. The reversible oxidation/reduction is closely associated with the generation of catalytically competent Rh_2^{5+} and regeneration of Rh_2^{4+} during catalytic cycle. Dirhodium complexes with PPh$_3$ and P(Ph-pOMe)$_3$ exhibiting the low oxidation potential or the reversibility are presumed to display higher catalytic activity than dirhodium complexes without phosphine and with P(Ph-pCF$_3$)$_3$.

Subsequent to the electrochemical studies of $Rh_2(OAc)_4$ with phosphine ligands, the allylic oxidation of 1-phenylcyclohexene **1** was carried out using these dirhodium complexes as catalysts. Initially, in the absence of phosphine ligand, compound **1** was exposed to the mixture of 2 mol% of $Rh_2(OAc)_4$, 500 mol% of *tert*-Butylhydroperoxide (TBHP) in dichloromethane at 40 °C. The desired product was formed in 26% yield. In light of electrochemical studies of $Rh_2(OAc)_4$ with phosphines, we envision that the dirhodium complex involving electron rich phosphine ligands facilitates the reversible oxidation of Rh_2^{4+} and the reduction of Rh_2^{5+}, enhancing the yield of the allylic oxidation. In accordance with the electrochemical data, the combination of $Rh_2(OAc)_4$ and P(Ph-pOMe)$_3$ showing both the increased reversible behavior and the lowest oxidation peak potential provided the oxidation product **2** in 31% yield under the conditions of 2 mol% of $Rh_2(OAc)_4$ and 2 mol% of P(Ph-pOMe)$_3$ (entry 2, Table 1). In contrast to the electrochemical studies using 100 equivalents of phosphine ligands with resepect to $Rh_2(OAc)_4$, 1 equivalent of phosphine was utilized in the catalytic reaction, allowing one of axial positions of $Rh_2(OAc)_4$ to participate in the allylic oxidation through the coordination of the substrate. The $Rh_2(OAc)_4$ containing PPh$_3$ catalyzed allylic oxidation to afford the product **2** in 32% yield (entry 3 in Table 1), highest yield for the reaction. Even if the redox potential wave $Rh_2(OAc)_4$ with PPh$_3$ is shifted to the anodic direction compared to that of $Rh_2(OAc)_4$ without PPh$_3$ ligand, the reversibility of the redox behavior of dirhodium complex ($Rh_2^{4+} \leftrightarrow Rh_2^{5+}$) is expressed by the redox peak separation (ΔE_p) in the cyclic voltammograms. The redox peak separation is smallest ($\Delta E_p = 0.13$ V) for $Rh_2(OAc)_4$ in the presence of PPh$_3$ among the tested phosphine ligands. The best reversibility of $Rh_2(OAc)_4$-PPh$_3$ is related to the highest comparable catalytic activity, although the oxidation peak potential of $Rh_2(OAc)_4$ with PPh$_3$ is higher than that of

Table 1. Allylic oxidation of compound **1** catalyzed by $Rh_2(OAc)_4$ with various phosphine ligands

Entry	Ligand	Yield
1	no ligand	26%
2	P(Ph-pOMe)$_3$	31%
3	PPh$_3$	32%
4	P(Ph-pCF$_3$)$_3$	19%
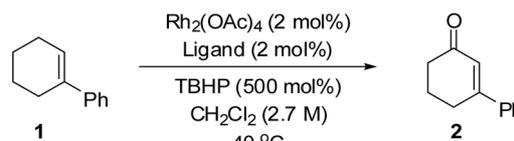
Rh$_2$(OAc)$_4$-P(Ph-pOMe)$_3$. The catalytic system involving electron deficient phosphine P(Ph-pCF$_3$)$_3$, showing the irreversible redox potential wave, afforded product **2** in the lowest yield 19% (entry 4, Table 1). Overall, the electrochemical data of dirhodium complexes possessing various phosphine ligands can be correlated with the catalytic activity in the allylic oxidation. In the presence of P(Ph-pOMe)$_3$ and PPh$_3$, Rh$_2$(OAc)$_4$ catalyzed allylic oxidation generated desired products in higher yield than Rh$_2$(OAc)$_4$ catalyzed reaction conditions without ligands and with electron poor ligand P(Ph-pCF$_3$)$_3$.

In summation, the electrochemical properties of Rh$_2$(OAc)$_4$ involving electronically different phosphines, P(Ph-pOMe)$_3$, PPh$_3$, P(Ph-pCF$_3$)$_3$, assuming the axial substitution of phosphines on Rh$_2$(OAc)$_4$, were investigated *via* cyclic voltammetry. The electrochemical data of each dirhodium complex were compared to the catalytic activity, showing that the rhodium complex with PPh$_3$ provided the highest yield in the allylic oxidation. Introducing electronically different ligands to the axial position of dirhodium complexes induced the modest changes in the electrochemical reversibility of the dirhodium complex, oxidation potentials and chemical yield in the allylic oxidation. Hence, this account has shown the possibility of the cyclic voltammetry of metal complexes as a tool to speculate the catalytic activity of metal complexes in the organic reactions.

Experimental

Anhydrous solvents were transferred by an oven dried syringe. Flasks were flame-dried and cooled under a stream of nitrogen. Dichloromethane was distilled from calcium hydride. THF was distilled from benzophenone ketyl. Electrochemical data were recorded on a potentiostat/galvanostat (PARC (Princeton Applied Research), model 263) with Electrochemistry Power Suite Module and Cyclic voltammetry software. The three-electrode cell consisting of Pt disc (the working electrode, 2 nm dia.), Ag wire (the pseudo reference electrode), and Pt wire (the auxiliary electrode) was employed. Rh$_2$(OAc)$_4$ (5×10^{-4} M) was dissolved in THF solution containing 0.1 M TBAP. The resulting solutions were subject to cyclic voltammetry experiments at a scan rate of 100 mV/s. Compound **2**[4b] exhibited spectral properties consistent with previous literature reports.

Representative procedure for the allylic oxidation. To a stirred mixture of Rh$_2$(OAc)$_4$ (10 mg, 0.024 mmol), PPh$_3$ (8 mg, 0.024 mmol) crashed potassium carbonate (83 mg, 0.6 mmol) and 1-phenyl cyclohexene (190 mg, 1.2 mmol) in dichloromethane (4.4 mL) was added a solution of TBHP (1.1 mL, 5.0-6.0 M in decane solution) slowly at 40 °C. The resulting mixture was stirred overnight. The solvent was removed with a rotary evaporator to produce a residue which was purified by column chromatography on a silica gel eluting with hexane and ethyl acetate (v/v, 10:1).

References

1. (a) Doyle, M. P.; McKervey, M. A.; Ye, T. *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds*; John Wiley: New York, 1998. (b) Doyle, M. P.; Forbes, D. C. *Chem. Rev.* **1998**, *98*, 911. (c) Doyle, M. P.; Protopopova, M. N. *Tetrahedron* **1998**, *54*, 7919. (d) Dörwald, F. Z. In *Metal Carbenes in Organic Synthesis*; Wiley-VCH: Weinheim, Germany, 1999; pp 171-232. (e) Davies, H. M. L. *Eur. J. Org. Chem.* **1999**, 2459. (f) Doyle, M. P.; Ren, T. In *Progress in Inorganic Chemistry*; Karlin, K. D., Ed.; John Wiley: New York, 2001; pp 113-168. (g) Forbes, D. C.; McMills, M. C. *Curr. Org. Chem.* **2001**, *5*, 1091. (h) Davies, H. M. L.; Beckwith, R. E. J. *Chem. Rev.* **2003**, *103*, 2861. (i) Evans, P. A. *Modern Rhodium-Catalyzed Organic Reactions*; Wiley-VCH: Weinheim, Germany, 2005.

2. (a) Hughes, R. G.; Bear, J. L.; Kimball, A. P. *Proc. Am. Assoc. Cancer Res.* **1972**, *13*, 120. (b) Erck, A.; Rainen, L.; Whileyman, J.; Chang, I.; Kimball, A. P.; Bear, J. L. *Proc. Soc. Exp. Biol. Med.* **1974**, *145*, 1278. (c) Bear, J. L.; Gray, H. B.; Rainen, Jr. L.; Chang, I. M.; Howard, R.; Serio, G.; Kimball, A. P. *Cancer Chemother. Rep.* **1975**, *59*, 611. (d) Asara, J. M.; Hess, J. S.; Lozada, E.; Dunbar, K. R.; Allison, J. *J. Am. Chem. Soc.* **2000**, *122*, 8. (e) Howard, R. A.; Kimball, A. P.; Bear, J. L. *Cancer Res.* **1979**, *39*, 2568. (f) Aoki, K.; Yamazaki, H. *J. Chem. Soc., Chem. Commun.* **1980**, 186. (g) Dale, L. D.; Dyson, T. M.; Tocher, D. A.; Tocher, J. H.; Edwards, D. L. *Anti-Cancer Drug Des.* **1989**, *4*, 295. (h) Catalan, K. V.; Hess, J. S.; Maloney, M. M.; Mindiola, D. J.; Ward, D. L.; Dunbar, K. R. *Inorg. Chem.* **1999**, *38*, 3904. (i) Asara, J. M.; Hess, J. S.; Lozada, E.; Dunbar, K. R.; Allison, J. *J. Am. Chem. Soc.* **2000**, *122*, 8.

3. (a) Das, K.; Kadish, K. M.; Bear, J. L. *Inorg. Chem.* **1978**, *17*, 930. (b) Kawamura, T.; Fukamachi, K.; Hayashida, S. *J. Chem. Soc. Chem. Comm.* **1979**, 945. (c) Kawamura, T.; Fukamachi, K.; Sowa, T.; Hayashida, S.; Yonezawa, T. *J. Am. Chem. Soc.* **1981**, *103*, 364. (d) Zhu, T. P.; Ahsan, M. Q.; Malinski, T.; Kadish, K. M.; Bear, J. L. *Inorg. Chem.* **1984**, *23*, 3. (e) Chavan, M. Y.; Zhu, T. P.; Lin, X. Q.; Ahsan, M. Q.; Bear, J. L.; Kadish, K. M. *Inorg. Chem.* **1984**, *23*, 4538. (f) Best, S. P.; Chandley, P.; Clark, R. J. H.; McCarthy, S. *J. Chem. Soc. Dalton Trans.* **1989**, 581. (g) Kawamura, T.; Katayama, H.; Nishikawa, H.; Yamabe, T. *J. Am. Chem. Soc.* **1989**, *11*, 8156. (h) Bear, J. L.; Yao, C.-L.; Lifsey, R. S.; Korp, J. D.; Kadish, K. M. *Inorg. Chem.* **1991**, *30*, 336. (i) Sargent, A. L.; Rollog, M. E.; Eagle, C. T. *Theor. Chem. Acc.* **1997**, *97*, 283. (j) Hirva, P.; Esteban, J.; Lloret, J.; Lahueta, P.; Pérez-Prieto, J. *Inorg. Chem.* **2007**, *46*, 2619. (k) Aguirre, J. D.; Lutterman, D. A.; Angeles-Boza, A. M.; Dunbar, K. R.; Turro, C. *Inorg. Chem.* **2007**, *46*, 7494.

4. (a) Padwa, A.; Austin, D. J.; Price, A. T.; Semones, M. A.; Doyle, M. P.; Protopopova, M. N.; Winchester, W. R.; Tran, A. *J. Am. Chem. Soc.* **1993**, *115*, 8669. (b) Catino, A. J.; Forslund, R. E.; Doyle, M. P. *J. Am. Chem. Soc.* **2004**, *126*, 13622. (c) Catino, A. J.; Nichols, J. M.; Nettles, B. J.; Doyle, M. P. *J. Am. Chem. Soc.* **2006**, *128*, 5648. (d) Doyle, M. P. *J. Org. Chem.* **2006**, *71*, 9253.

5. Na, S. J.; Lee, B. Y.; Bui, N.-N.; Mho, S.-I.; Jang, H.-Y. *J. Organomet. Chem.* **2007**, *692*, 5523.

6. Richel, A.; Demonceau, A.; Noels, A. F. *Tetrahedron Lett.* **2006**, *47*, 2077.

7. Ahmad, J.; Bothata-Nareetsile, F.; Becker, C. A. L. *Can. J. Chem.* **2003**, *81*, 982.