Ni^{II}(TPA) as an efficient catalyst for alkane hydroxylation with *m*-CPBA†

Takayuki Nagataki, Yoshimitsu Tachi and Shinobu Itoh*

Received (in Cambridge, UK) 13th June 2006, Accepted 1st August 2006
First published as an Advance Article on the web 16th August 2006
DOI: 10.1039/b608311k

A simple Ni^{II}(TPA) complex [TPA = tris(2-pyridylmethyl) amine] has been demonstrated to act as an efficient turnover catalyst for alkane hydroxylation with *m*-CPBA (*m*-chloroperbenzoic acid), in which contribution of a NiO^+ (nickel-oxo) type active oxygen species is suggested.

Selective hydroxylation of alkanes (saturated hydrocarbons) is an important but still very difficult chemical transformation process. A great deal of effort has long been made to develop efficient catalysts for the alkane hydroxylation in synthetic organic chemistry and industrial chemistry.[1–9] The catalytic alkane hydroxylation reaction is also worthy to be investigated in detail in connection with the catalytic mechanisms of monooxygenase metalloenzymes. So far, much attention has been paid to heme and non-heme iron complexes due to their high catalytic activity and biological relevance.[10–18] Catalytic activities of some Mn, Co, Cu, and Ru complexes in the alkane hydroxylation have also been examined.[8,19–22]

Nickel complexes have also attracted much recent attention in active oxygen chemistry. So far, dinuclear nickel–active oxygen complexes such as bis(μ-oxo)dinickel(III), bis(μ-superoxo) dinickel(II), bis(μ-alkylperoxo)dinickel(II), and (*trans*-μ-1,2-peroxo)dinickel(II) complexes as well as a mononuclear nickel(II)-superoxo complex have been characterised by X-ray crystallographic analysis and/or several spectroscopic techniques.[23–26] On the other hand, Schröder, Schwarz and co-workers have systematically investigated the gas-phase reactions of the first-row metal-oxo species MO^+ with methane, where they demonstrated that NiO^+ was the most preferable oxidant with respect to the efficiency and the alcohol product selectivity.[27] The mechanistic aspect of the gas phase reaction has also been investigated in detail by DFT calculations to support the experimental results.[28] Nonetheless, little has been accomplished in nickel chemistry as far as the *catalytic alkane hydroxylation* is concerned.[29]

We herein demonstrate that a simple Ni^{II}(TPA) complex [TPA: tris(2-pyridylmethyl)amine] is a very efficient turnover catalyst for alkane hydroxylation with *m*-CPBA (*m*-chloroperbenzoic acid). The complex is robust enough to achieve high catalytic turnover and shows a high alcohol-selectivity. Mechanistic study based on the product analysis has suggested possible contribution of a NiO^+ (nickel-oxo) type active oxygen species.

The Ni^{II}(TPA) complex containing acetate and water molecules as the co-ligands, $[Ni^{II}(TPA)(OAc)(H_2O)]BPh_4$ (**1**), was obtained by treating the ligand with an equimolar amount of $Ni^{II}(OAc)\cdot 4H_2O$ followed by anion exchange reaction with $NaBPh_4$ in methanol. The complex exhibits a slightly distorted octahedral geometry with the N_4O_2 donor set as shown in Fig. 1. The complex is paramagnetic (S = 1) as demonstrated by the ^1H NMR resonances spread over a chemical shift range of 0 ∼ 50 ppm (see Fig. S5†).[30]

Catalytic activity of **1** was then examined in the oxygenation reaction of alkanes with *m*-CPBA as summarized in Table 1. In the case of cyclohexane as the substrate (entry 1), the oxygenation reaction took place very efficiently to give cyclohexanol as the major product together with a small amount of cyclohexanone as the minor product, where alcohol selectivity (alcohol/ketone; A/K)

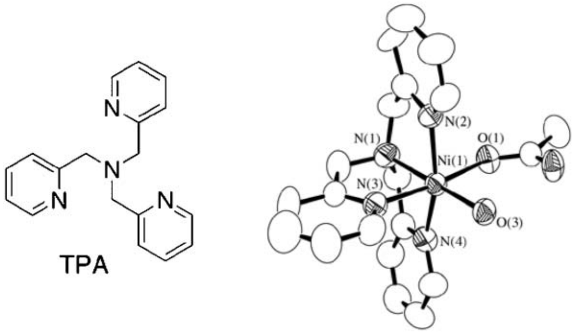

Fig. 1 The ligand structure of TPA and an ORTEP drawing of nickel(II) complex **1** showing 50% probability thermal ellipsoid. The counter anion (BPh_4^-) and hydrogen atoms are omitted for clarity.

Table 1 Oxygenation of alkanes with *m*-CPBA catalysed by **1**[a]

Entry	Substrate	Products	TON[b]	A/K
1	Cyclohexane	Cyclohexanol	587	8.5
		Cyclohexanone[d]	69	
2	Cyclooctane	Cyclooctanol	626	12.5
		Cyclooctanone	50	
3	Adamantane[c]	1-Adamantanol	258	
		2-Adamantanol	53	5.9
		2-Adamantanone	9	
4	Ethylbenzene	1-Phenylethanol	225	7.3
		Acetophenone	31	

[a] Reaction conditions: [**1**] = 0.33 mM, [*m*-CPBA] = 0.33 M, [Substrate] = 2.5 M in CH_2Cl_2–CH_3CN (3 : 1) at room temperature for 1 h under Ar. [b] Determined by GLC. [c] Reaction conditions: [**1**] = 0.17 mM, [*m*-CPBA] = 83 mM, [Substrate] = 0.33 M. [d] A trace amount of ε-caprolactone was obtained as an over-oxidation product of cyclohexanone by *m*-CPBA.

Department of Chemistry, Graduate School of Science, Osaka City University, 3-3-138 Sugimoto, Sumiyoshi-ku, Osaka, 558-8585, Japan.
E-mail: shinobu@sci.osaka-cu.ac.jp; Fax: +81-6-6605-2564;
Tel: +81-6-6605-2564

† Electronic supplementary information (ESI) available: Details of the synthetic procedures, the product analysis and the X-ray structural determinations. See DOI: 10.1039/b608311k

was 8.5. The total turnover number (TON = moles of product/moles of catalyst) of the catalyst reached 656 within 1 h, and the oxidant efficiency (moles of product/moles of *m*-CPBA consumed) was 71%. Similar results were obtained in the case of cyclooctane (entry 2). Furthermore, an appreciable amount of kinetic deuterium isotope effect (k_H/k_D = 2.8) was obtained, when perdeuterated substrate cyclohexane-d_{12} was employed.† On the other hand, other oxidants such as *t*-BuOOH and H_2O_2 were not effective at all in the present system.

Oxidation of adamantane with *m*-CPBA also proceeded efficiently with a high TON (320 within 1 h) to give the corresponding alcohols together with a small amount of ketone (entry 3). In this case, a high regioselectivity between the tertiary (3°) and the secondary (2°) carbons was obtained (3°/2° = 12.5; the value was derived from the amount of 1-adamantanol divided by the amounts of 2-adamantanol and 2-adamantanone and multiplied by 3 to correct for the higher number of the secondary C–H bonds). In the case of ethylbenzene (entry 4), the benzylic position was selectively oxidized.

Although the active-oxygen species involved in the present alkane hydroxylation process has yet to be elucidated, the large A/K ratio and the significantly high 3°/2° regioselectivity in the adamantane oxidation as well as the appreciable amount of KIE strongly suggest that the reaction involves a highly reactive metal-based oxidant such as (L)NiO^+.[5]

In order to evaluate the catalytic efficiency of **1**, the oxygenation reaction of cyclohexane with *m*-CPBA was also examined by using other divalent transition-metal complexes such as $[Co^{II}(TPA)(OAc)]BPh_4$ (**2**), $[Fe^{II}_2(TPA)_2(\mu\text{-}OAc)_2](BPh_4)_2$ (**3**)[31] and $[Mn^{II}_2(TPA)_2(\mu\text{-}OAc)_2](BPh_4)_2$ (**4**)[32] under the same experimental conditions (Table 2). All these complexes contain TPA as the supporting ligand, acetate (OAc^-) as the anionic co-ligand and BPh_4^- as the uncoordinating counter anion. The complexes also exhibit a six-coordinate octahedral geometry with the N_4O_2 donor set at the metal center, although complexes **3** and **4** form the dimeric structure bridged by two *μ*-acetate ligands (Chart 1, Fig. S1–S4†). Notably, the total TON value was highest in nickel(II) complex **1**, whereas a high A/K selectivity was also obtained with cobalt(II) complex **2** despite its TON being relatively lower. It should also be noted that both the TON value and the A/K selectivity of iron(II) complex **3** were lower than those of **1**, and those values of manganese(II) complex **4** were hopeless.

In Table 3 are presented the efficiency *ϕ* and the product blanching ratios for the gas phase reactions of methane with the series of MO^+ under ion cyclotron resonance (ICR) conditions reported by Schröder and Schwarz.[27] As clearly seen, the methanol (alcohol product) selectivity of NiO^+ and CoO^+ is very high (100%), whereas that of FeO^+ is much lower (41%). Moreover, in the case of MnO^+, methyl radical was obtained as the major product, but little amount of methanol was produced. On the other hand, efficiency of CoO^+ (0.5) is significantly lower than that of others (20 ∼ 40). Overall, the nickel-oxo (NiO^+) species is the most desirable oxidant from the viewpoints of efficiency and alcohol-selectivity in the gas phase reaction. It should also be emphasized that the tendencies of reactivity (TON) and alcohol-selectivity (A/K) of **1** ∼ **4** in the cyclohexane oxygenation in solution (Table 2) apparently resemble those of efficiency and alcohol-selectivity of MO^+ in the gas phase reaction (Table 3). This strongly suggests that the active oxygen species involved in both reactions are very similar, that is, MO^+-type oxidants.

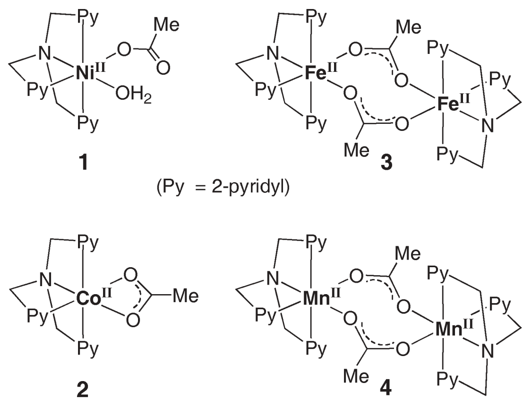

Chart 1

Table 3 Efficiencies *ϕ* (%) and product branching ratios (%) for the reactions of MO^+ with methane under ion cyclotron resonance (ICR) conditions[a]

MO^+	*ϕ*	$MOH^+ + CH_3^{\bullet}$	$MCH_2^+ + H_2O$	$M^+ + CH_3OH$
NiO^+	20			100
CoO^+	0.5			100
FeO^+	20	57	2	41
MnO^+	40	100		<1

[a] Data are taken from ref. 27.

Table 2 Oxygenation of cyclohexane catalysed by **1–4**[a]

Catalyst	TON[b] cyclohexanol	TON[b] cyclohexanone[c]	Total	A/K
1 (Ni)	587	69	656	8.5
2 (Co)	300	16	316	18.8
3 (Fe)	396	62	458	6.4
4 (Mn)	99	55	154	1.8

[a] Reaction conditions; $[M^{2+}]$ = 0.33 mM, all other reaction conditions are the same as those described in Table 1. [b] Determined by GLC based on the metal ion concentration. [c] A trace amount of ε-caprolactone was obtained as an over-oxidation product of cyclohexanone by *m*-CPBA.

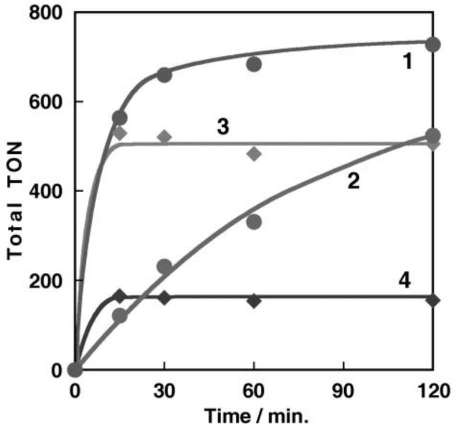

Fig. 2 Time courses of the total TON for the oxidation of cyclohexane with *m*-CPBA catalyzed by 1, 2, 3 and 4 in CH_2Cl_2–CH_3CN at room temperature.

The time courses of the total TON of **1** ∼ **4** in the cyclohexane oxidation are shown in Fig. 2, which clearly indicate that the catalytic activity of the iron(II) and manganese(II) catalysts (**3** and **4**) is completely lost at the early stage of the reaction (within 15 min), whereas the catalytic reaction gradually proceeds even after 60 min in the case of nickel(II) and cobalt(II) complexes (**1** and **2**). The lower product selectivity of the iron and manganese catalysts would produce free radical species as in the case of the gas phase reaction (Table 3), which may destroy the catalysts, depressing the catalytic activity.

In summary, the nickel(II)–TPA complex **1** has been demonstrated for the first time to act as a very efficient turnover catalyst for the alkane hydroxylation with *m*-CPBA, where a high alcohol-selectivity is achieved. Mechanistic details as well as the ligand effects on the catalytic efficiency of nickel(II) complexes are now under investigation.

This work was financially supported in part by Grants-in-Aid for Scientific Research (No. 17350086) from the Ministry of Education, Culture, Sports, Science and Technology, Japan. The authors also thank Professor Yoshizawa of Kyushu University for his valuable suggestions.‡

Notes and references

‡ X-ray diffraction data were collected by a Rigaku RAXIS-RAPID imaging plate two-dimensional area detector using graphite-monochromated MoKα radiation (λ = 0.71069 Å) to $2\theta_{\max}$ of 55.0°. The crystal structures were solved by a direct method and refined by the full-matrix least-squares using SIR92. Crystal data for **1**: $C_{44}H_{43}N_4O_3NiB$, M = 745.36, orthorhombic, space group $Pca2_1$ (No. 29), a = 31.474(7) Å, b = 14.028(4) Å, c = 9.3475(18) Å, V = 4127.2(16) Å^3, Z = 4, D_{calcd} = 1.199 g cm^{-3}, T = 173 K, μ(MoKα) = 0.5123 mm^{-1}, Total data = 37384, Unique data = 9070 (R_{int} = 0.036), Observed data [$I > 1\sigma(I)$] = 5347, R = 0.063, R_w = 0.096, GOF = 1.007. CCDC 611580. Crystal data for **2**: $C_{44}H_{41}N_4O_2CoB$, M = 727.58, triclinic, space group P-1 (No. 2), a = 11.103(6) Å, b = 13.010(7) Å, c = 13.255(10) Å, α = 97.54(2)°, β = 104.24(2)°, γ = 90.660(18)°, V = 1838.0(20) Å^3, Z = 2, D_{calcd} = 1.315 g cm^{-3}, T = 173 K, μ(MoKα) = 0.5107 mm^{-1}, Total data = 17939, Unique data = 8149 (R_{int} = 0.049), Observed data [$I > 1\sigma(I)$] = 5215, R = 0.036, R_w = 0.048, GOF = 1.007. CCDC 611581. Crystal data for **3**: $C_{88}H_{82}N_8O_4Fe_2B_2$, M = 1448.98, triclinic, space group P-1 (No. 2), a = 10.919(11) Å, b = 12.417(10) Å, c = 13.935(10) Å, α = 105.00(3)°, β = 95.42(3)°, γ = 92.60(3)°, V = 1812.0(26) Å^3, Z = 1, D_{calcd} = 1.328 g cm^{-3}, T = 173 K, μ(MoKα) = 0.4600 mm^{-1}, Total data = 17001, Unique data = 7848 (R_{int} = 0.052), Observed data [$I > 2\sigma(I)$] = 5763, R = 0.046, R_w = 0.054, GOF = 1.018. CCDC 611582. Crystal data for **4**: $C_{88}H_{82}N_8O_4Mn_2B_2$, M = 1447.16, triclinic, space group P-1 (No. 2), a = 10.865(7) Å, b = 12.502(10) Å, c = 14.047(8) Å, α = 105.04(2)°, β = 95.394(20)°, γ = 91.88(3)°, V = 1831.4(21) Å^3, Z = 1, D_{calcd} = 1.312 g cm^{-3}, T = 173 K, μ(MoKα) = 0.4041 mm^{-1}, Total data = 18142, Unique data = 8276 (R_{int} = 0.037), Observed data [$I > 1\sigma(I)$] = 5998, R = 0.037, R_w = 0.041, GOF = 1.011. CCDC 611583. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b608311k.

1 D. H. R. Barton and D. Doller, *Acc. Chem. Res.*, 1992, **25**, 504.
2 D. T. Sawyer, A. Sobkowiak and T. Matsushita, *Acc. Chem. Res.*, 1996, **29**, 409.
3 M. Fontecave, S. Ménage and C. Duboc-Toia, *Coord. Chem. Rev.*, 1998, **178–180**, 1555.
4 A. E. Shilov and A. A. Shteinman, *Acc. Chem. Res.*, 1999, **32**, 763.
5 M. Costas, K. Chen and L. Que, Jr., *Coord. Chem. Rev.*, 2000, **200–202**, 517.
6 P. Stavropoulos, R. Çelenligil-Çetin and A. E. Tapper, *Acc. Chem. Res.*, 2001, **34**, 745.
7 K. Chen, M. Costas and L. Que, Jr., *J. Chem. Soc., Dalton Trans.*, 2002, 672.
8 T. Punniyamurthy, S. Velusamy and J. Iqbal, *Chem. Rev.*, 2005, **105**, 2329.
9 *Metal-Oxo and Metal-Peroxo Species in Catalytic Oxidations*, ed. B. Meunier, Springer, Berlin, 2000.
10 A. Nanthakumar and H. M. Goff, *J. Am. Chem. Soc.*, 1990, **112**, 4047.
11 T. Higuchi, K. Shimada, N. Maruyama and M. Hirobe, *J. Am. Chem. Soc.*, 1993, **115**, 7551.
12 (*a*) M. H. Lim, Y. J. Lee, Y. M. Goh, W. Nam and C. Kim, *Bull. Chem. Soc. Jpn.*, 1999, **72**, 707; (*b*) W. Nam, M. H. Lim, S. K. Moon and C. Kim, *J. Am. Chem. Soc.*, 2000, **122**, 10805.
13 R. H. Fish, M. S. Konings, K. J. Oberhausen, R. H. Fong, W. M. Yu, G. Christou, J. B. Vincent, D. K. Coggin and R. M. Buchanan, *Inorg. Chem.*, 1991, **30**, 3002.
14 H.-C. Tung, C. Kang and D. T. Sawyer, *J. Am. Chem. Soc.*, 1992, **114**, 3445.
15 N. Kitajima, M. Ito, H. Fukui and Y. Moro-oka, *J. Chem. Soc., Chem. Commun.*, 1991, 102.
16 (*a*) S. Ménage, J. M. Vincent, C. Lambeaux, G. Chottard, A. Grand and M. Fontecave, *Inorg. Chem.*, 1993, **32**, 4766; (*b*) S. Ménage, J. M. Vincent, C. Lambeaux and M. Fontecave, *J. Chem. Soc., Dalton Trans.*, 1994, 2081.
17 (*a*) R. A. Leising, J. Kim, M. A. Pérez and L. Que, Jr., *J. Am. Chem. Soc.*, 1993, **115**, 9524; (*b*) G. Roelfes, M. Lubben, R. Hage, L. Que, Jr. and B. L. Feringa, *Chem.–Eur. J.*, 2000, **6**, 2152; (*c*) K. Chen and L. Que, Jr., *J. Am. Chem. Soc.*, 2001, **123**, 6327; (*d*) J. Kaizer, E. J. Klinker, N. Y. Oh, J.-U. Rohde, W. J. Song, A. Stubna, J. Kim, E. Münck, W. Nam and L. Que, Jr., *J. Am. Chem. Soc.*, 2004, **126**, 472.
18 M. Kodera, H. Shimakoshi and K. Kano, *Chem. Commun.*, 1996, 1737.
19 B. R. Cook, T. J. Reinert and K. S. Suslick, *J. Am. Chem. Soc.*, 1986, **108**, 7281.
20 (*a*) W. Nam, I. Kim, Y. Kim and C. Kim, *Chem. Commun.*, 2001, 1262; (*b*) W. Nam, J. Y. Ryu, I. Kim and C. Kim, *Tetrahedron Lett.*, 2002, **43**, 5487.
21 (*a*) H. Ohtake, T. Higuchi and M. Hirobe, *J. Am. Chem. Soc.*, 1992, **114**, 10660; (*b*) K. Jitsukawa, Y. Oka, S. Yamaguchi and H. Masuda, *Inorg. Chem.*, 2004, **43**, 8119.
22 C. Shimokawa, J. Teraoka, Y. Tachi and S. Itoh, *J. Inorg. Biochem.*, 2006, **100**, 1118.
23 S. Itoh, H. Bandoh, M. Nakagawa, S. Nagatomo, T. Kitagawa, K. D. Karlin and S. Fukuzumi, *J. Am. Chem. Soc.*, 2001, **123**, 11168.
24 S. Hikichi, M. Yoshizawa, Y. Sasakura, H. Komatsuzaki, Y. Moro-oka and M. Akita, *Chem.–Eur. J.*, 2001, **7**, 5012.
25 (*a*) K. Shiren, S. Ogo, S. Fujinami, H. Hayashi, M. Suzuki, A. Uehara, Y. Watanabe and Y. Moro-oka, *J. Am. Chem. Soc.*, 2000, **122**, 254; (*b*) J. Cho, H. Furutachi, S. Fujinami and M. Suzuki, *Angew. Chem., Int. Ed.*, 2004, **43**, 3300.
26 (*a*) B. S. Mandimutsira, J. L. Yamarik, T. C. Brunold, W. Gu, S. P. Cramer and C. G. Riordan, *J. Am. Chem. Soc.*, 2001, **123**, 9194; (*b*) M. T. Kieber-Emmons, R. Schenker, G. P. A. Yap, T. C. Brunold and C. G. Riordan, *Angew. Chem., Int. Ed.*, 2004, **43**, 6716; (*c*) K. Fujita, R. Schenker, W. Gu, T. C. Brunold, S. P. Cramer and C. G. Riordan, *Inorg. Chem.*, 2004, **43**, 3324.
27 D. Schröder and H. Schwarz, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1973.
28 Y. Shiota and K. Yoshizawa, *J. Am. Chem. Soc.*, 2000, **122**, 12317.
29 Aliphatic ligand oxygenation reactions have been reported: (*a*) E. Kimura, A. Sakonaka, R. Machida and M. Kodama, *J. Am. Chem. Soc.*, 1982, **104**, 4255; (*b*) D. Chen and A. E. Martell, *J. Am. Chem. Soc.*, 1990, **112**, 9411; (*c*) K. Haas, H. Dialer, H. Piotrowski, J. Schapp and W. Beck, *Angew. Chem., Int. Ed.*, 2002, **41**, 1879; see also ref. 23.
30 E. Szajna, P. Dobrowolski, A. L. Fuller, A. M. Arif and L. M. Berreau, *Inorg. Chem.*, 2004, **43**, 3988.
31 Prepared by the reported procedures: S. Ménage, Y. Zang, M. P. Hendrich and L. Que, Jr., *J. Am. Chem. Soc.*, 1992, **114**, 7786.
32 The di(μ-acetate)dimanganese(II) with two TCNQ$^-$ molecules as the counter anions was reported: H. Oshio, E. Ino, I. Mogi and T. Ito, *Inorg. Chem.*, 1993, **32**, 5697.